B.Tech Thesis

On

Recovery of liquid fuels from cellulosic feedstock

Submitted by

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(Roll No: 108CH042)

In partial fulfillment of the requirements for the degree in

Bachelor of Technology in Chemical Engineering

Under the guidance of

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CERTIFICATE

This is to certify that the work in this report entitled **"Recovery of liquid fuels from cellulosic feedstock"** submitted by **Bijayani Biswal (108CH042)** in partial fulfillment of the requirements of the prescribed curriculum for Bachelor of Technology in Chemical Engineering Session 2008-2012 in the Department of Chemical Engineering, National Institute of Technology Rourkela, is an authentic work carried out by her under my supervision and guidance. To the best of my knowledge the matter embodied in the report is her bonafide work.

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ACKNOWLEDGEMENT

CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

TGA	Thermo-gravimetric Analysis
PID	Proportional-integral-derivative
ASTM	American Society for Testing and Materials
SEM	Scanning Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
GCV	Gross Calorific Value
IEA	International Energy Agency
GHG	Green House Gases
BtL	Biomass to Liquid
MWP	Mixed Waste Paper
LDPE	Low Density Polyethylene

ABSTRACT

Biomass has been identified as an ideal resource for partly substituting the fossil fuels. Cellulosic biomass including paper, wood, fibrous plant materials etc., being abundant and low in cost, offers a potential solution for bio-fuels production. Waste paper cups (cellulosic feedstock) are piling up very rapidly on earth's surface and urgently needs attention. Pyrolysis is one of the latest technologies which have the potential to provide valuable liquid and gaseous fuels from these biomass sources. Hence pyrolysis of paper cups is done and the bio oil and solid char were analyzed. Physical and Chemical analysis was done for the pyrolytic oil. The functional groups were obtained by FTIR and the compounds present were given by GC-MS data. The bio-oil was compared with standard fuels. The reaction kinetics of pyrolysis process is also studied.

Keywords: *Pyrolysis, Cellulosic feedstock, Paper Cup, Bio-Oil, FT-IR, GC-MS, Kinetic Study*

1. INTRODUCTION

1.1 Fuel Consumption Statistics

Urbanization is an important determinant of both the quantity and the type of fuel used in developing countries. In general, urbanization leads to higher energy consumption, also accompanied with increased income levels. Hence there is a shift from traditional to commercial fuels. Several other factors that contribute to this trend include decline in access to biomass fuels, inconvenience of transportation and storage of biomass fuels, and improvement in availability of commercial fuels in urban areas [1].

The twentieth century evidenced a rapid twentyfold increase in the use of fossil fuels. Coal fueled the industrial revolution in the 18th and 19th century. With the advent of the automobile, airplanes and the spreading use of electricity, oil became the dominant fuel during the twentieth century. From 1965 to 2008, the consumption of fossil fuels has continued to grow and their share of the energy supply has increased. From 2003 to 2008, coal was the fastest growing fossil fuel [2].

Table 1: India's Consumption by fuel, million tones oil equivalent [3]

Consumption by fuel, million tones oil equivalent. Source: BP Statistical Review of World Energy	Oil	Natural gas	Coal	Nuclear energy	Hydro electric	Total
2007	128.53	36.05	212.86	4.03	27.70	409.16
2008	143.6	37.2	230.90	3.40	26.00	441.10
2009	148.50	46.70	245.80	3.80	24.00	468.90

Table 1 gives an overview of the consumption of different types of fuels in India over a period of 3 years starting from 2007 to 2009. It's clearly evident that fossil fuels consumption is continuously growing. Fossil fuels account for 94% of the total fuel consumption in 2009.

Figure 2 shows a pie chart representing the total energy consumption in India in the year 2009. According to the International Energy Agency (IEA), hydrocarbons occupy majority of

1

India's energy use. Coal and oil, together represent about two-thirds of total energy use. Natural gas now accounts for a seven percent share, which is expected to grow with the discovery of new gas deposits. Combustible renewables and waste account for one forth of Indian energy use. This includes traditional biomass sources such as firewood and cow dung, which are used by more than 800 million Indian households for cooking. Other renewables like wind, geothermal, solar, and hydroelectricity represent a 2 % share of the Indian fuel mix. Nuclear holds only one percent share [4].
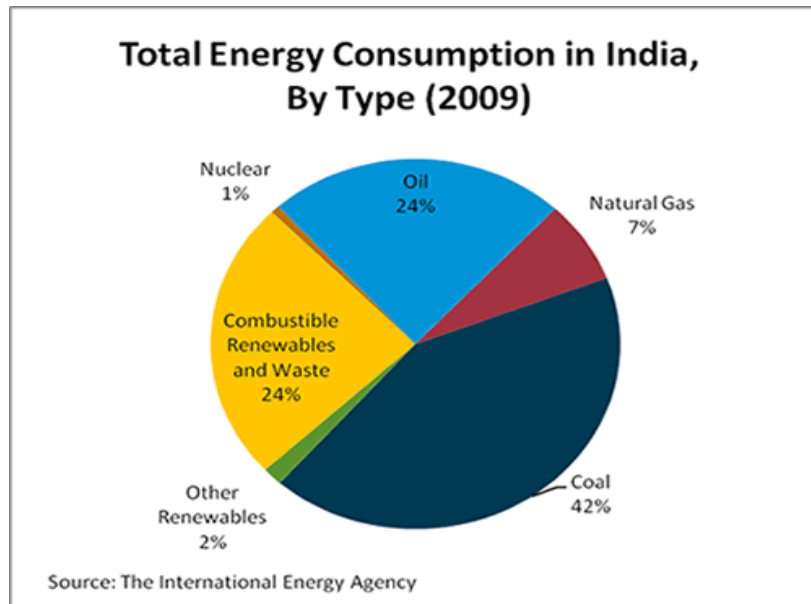
Figure 1: Total energy consumption in India (2009)[4]

1.2. Biomass Energy

It's high time now to realize that all non- carbon emitting resources are required to become the energy sources in this crucial state of fossil fuels crisis. In such case one kind of renewable energy, biomass can achieve zero emission of CO_2 and can also help in sustainable development.

Biomass refers to plant-derived organic matter generated through photosynthesis and other biological processes. It mainly includes trees and grasses, agricultural residues, forest residues, animal wastes and industrial wastes. It is a cost-effective energy source with the potential to greatly reduce greenhouse gas emissions. It can directly be converted to energy or liquid & gaseous fuels such as ethanol, methanol, methane, and hydrogen [5].

1.3. Biofuels

Bio-fuels obtained from the biomass seem to be a potential alternative source of energy and may supplement the traditional petroleum–based transportation fuel. This sector has witnessed a continuous growth and development over the last few years. The fluctuations in oil prices and production levels have heightened the need for further development of the sector [6].

Biofuel production possesses a solution to waste management as well, by converting waste into usable form of energy. In addition to three distinct perspectives of biofuels in the international context viz. energy security, GHG mitigation & business opportunities, the fourth dimension of augmentation of rural income & employment generation assumes importance particularly for developing countries like India [7].

The major issues concerning the technology development challenges include the utilization of multiple feedstock and optimization of process parameters, exploitation of by – products generated during the conversion processes, environmental & social impacts and economic feasibility.

1.4. Potential & Scope of Biofuels in India

It may be possible to bring 10 – 20% under cultivation of plants that can yield biomass for energy, out of the 107 million hectares of wasteland available. As per estimates of the International Energy Agency, farmers could supply the world with about 10% of its gasoline by 2025. Edible oils are used as biodiesel in Europe, USA and other countries, whereas for countries like India which are already short of edible oils, use of non-edible oils only seems to be a suitable option. In countries like Brazil, USA and Canada where food gains like corn and wheat are being diverted for ethanol production, India cannot afford this option owing to limited area for food production to feed a population of about 1.1 billion [8].

In such case, non – edible oil seeds and the wastes constituting cellulosic feedstock which remain out of the human food chain have become major biomass resources for production of bio-oil. Cellulosic resources are in general very widespread and plentily available. As they are not consumed by humans, their cost is relatively low. Some examples are – paper, cardboard, wood, fibrous plant material etc. Cellulosic materials are comprised of lignin, hemicelluloses, and cellulose and are thus called lignocellulosic feed stocks. These structural characteristics along

with the encapsulation by lignin make cellulosic materials more difficult to hydrolyze than starchy materials [9].

Paper and cardboard make up over 40% of the solid waste buried in North American landfills. Of that 40%, a disproportionate amount is attributable to disposable coffee cups. Unlike newspaper and cardboard boxes, disposable paper cups are not recyclable. The thin lining that makes a paper cup waterproof also keeps it from being recycled. All of those cups end up in the nation's landfills [10].

2. LITERATURE REVIEW

The conversion of biomass results in following categories of biofuels:

2.1. Solid Biofuels

These include the use of trees, crop residues, animal wastes, household or industrial residues which are used for direct combustion to provide heat. Often the solid biomass will undergo physical processing such as cutting, chipping, briquetting, etc. but retains its solid form. Also compressed peat and dry bagasse come under this category which can be burnt to get heat as a form of energy [11].

2.2. Liquid Biofuels

Liquid Biofuels are obtained from organic materials by the application of one of the various chemical and physical processes. Biofuels such as vegetable oils or ethanol are often processed from industrial or commercial residues such as bagasse or from energy crops grown specifically for this purpose. Biofuels are aimed to be used in place of petroleum derived liquid fuels. Liquid biofuels basically contains valuable and useful chemicals like ethanol, acetone, acetic acid etc., which can also be extracted from it. This liquid stream consists of bio fuels called bio-oil. The bio–oil is dull black-brown liquid and remains in liquid form at room temperature [11].

2.3. Gaseous Biofuels

Gaseous fuels such as biogas are obtained by an-aerobically (in an air free environment) digesting organic material to produce a combustible gas known as methane. Animal waste and municipal waste are two common feed-stocks for anaerobic digestion. Gaseous bio-fuels obtained from biomass decomposition contain primarily hydrogen, methane, carbon monoxide, ammonia and other gases depending upon the organic nature of biomass and the process condition [11].

2.4. Process for Biomass Conversion

- Mechanical
- Thermo – chemical
- Bio - chemical

Two methods are most promising: thermo-chemical & Bio- chemical conversions.

2.4.1. Thermo-chemical Conversion process

In thermo-chemical conversion, biomass is converted into gas & liquid intermediates that can be used for fuels and chemical synthesis. The term Biomass to Liquid (BtL) is applied to synthetic fuels produced from biomass via thermo-chemical route. The objective is to produce fuel components that are similar to those of current fossil-derived petrol (gasoline) and diesel fuels and hence can be used in existing fuel distribution systems and with standard engines. They are also known as syn-fuels [12].

The two main technologies under thermo chemical conversion are listed below

- Gasification
- Pyrolysis

The intermediate products include clean syngas ($CO+H_2$), bio-oil (pyrolysis or hydrothermal product), and gases rich in methane or hydrogen. These intermediates can further be synthesized to gasoline, diesel, alcohols, ethers, synthetic natural gas etc. and also high purity hydrogen, which can be used as fuels in electric power generation [6].

2.4.1.1. Gasification

When biomass is heated with only about one-third the oxygen needed for efficient combustion, it gasifies to a mixture of carbon monoxide and hydrogen—synthesis gas or syngas.

2.4.1.2. Fischer–Tropsch Process for Liquid Fuels

Gasification at higher temperatures of 1200^0C - 1600^0C leads to few hydrocarbons in the product gas and a higher proportion of CO & H2. If the ratio of H2 to CO (syngas or biosyngas) is 2:1then Fischer – Tropsch synthesis is an option to convert syngas into high quality synthetic biofuels which are compatible with conventional fossil fuel engines [6].

2.4.1.3. Pyrolysis

Pyrolysis is the thermal de-polymerization of biomass at modest temperatures in absence of added oxygen. The steps in pyrolysis includes: feedstock preparation and introduction into the reactor, carrying out the reaction by application of heat or other addition of reactants such as air, oxygen, steam, hydrogen, post combustion or processing of the gases produced during the reaction step, and the management of the resulting liquids, char, and ash [6].

Fast pyrolysis

The products of fast pyrolysis include gases, bio-oil, and char which depend on the process temperature, pressure, and residence time of the liberated pyrolysis vapors. The production of bio-products is maximized by fast pyrolysis, typically performed at temperatures (~450-500ºC) at atmospheric pressure, high heating rates (i.e., 500ºC/sec) and short residence times (1-2 sec) [6].

Slow Pyrolysis

Here the temperature maintained for pyrolysis reaction is 300 - 500ºC and the heating rates is slow i.e. around 20 - 30ºC/sec and the residence time allowed is more. In this case, the yield of gaseous product and solid residue is more as compared to fast pyrolysis. But the quality of liquid product is better [13].

2.4.2. Bio–Chemical Conversion Process

The bio-chemical conversion process deals with agricultural residues, energy crops and to some extent paper & pulp mill residues. It is a combination of pretreatment, enzymatic hydrolysis, and fermentation [12].

Thermal chemical conversion was believed to be the most prominent way for biomass high-efficiency conversion, converting biomass feedstock into gaseous, liquid, and solid energy products under thermal conditions. Several types of technology have been developed, including pyrolysis, gasification, combustion, etc., with controlling the process parameters. Pyrolysis is the most basic process in thermal chemical conversion of biomass, and it is also the original and accompanying reaction in gasification and combustion. The analysis of pyrolysis of biomass is helpful for the control and optimization of an efficient biomass thermal chemical conversion process [14, 15].

2.5. Paper Cups – Cellulosic Feedstock

Paper cups used as coffee cups or for cold drinks are accumulating as wastes on the earth surface at a rapid rate. Considering only America, 14.4 million disposable paper cups are used for drinking coffee each year. Placed end-to-end, these cups would wrap around Earth 55 times and weigh around 900 million pounds.

Most paper cups are designed for a single use and then disposed or recycled. A comparison between paper and plastic cups show environmental effects of both with no clear winner. One paper cup represents 4.1g equivalent petrol with a production cost 2.5 times higher than plastic cups. Paper cups are not specifically recycled. They come under regular waste and burnt or put on landfills. Recycling paper cups is difficult because of its composition as a complex of paper and paraffin. Hence they need about 150 years (same as plastics) to degrade because of their plastic foil [16].

The paper cups for hot drinks are produced from wood pulp (cellulose) and polyethylene plastic film, made out of petrol or paraffins, to improve its water resistivity and resistance to heat. They have a coating of 8-18 g/m^2 on one side. Cups for cold drinks have 6-15 g/m^2 on the top side and 8 – 18 g/m^2 on the reverse side [17].

A basic hot beverage cup is typically made of 95 % (by wt) of paper and 5 % (by wt) of polyethylene lamination. In cold drink cup, polythene used is 10% and fibre is 90%. There is a tendency of condensation on the exterior surface, so second layer of PE is given on the outside surface. The paper used is produced from valuable 'bleached kraft' fibers [17].

Mixed Paper Wastes (MPW), represents a valuable source of energy. Hence it is studied to determine the quantity of energy obtained from waste of known amount and composition. For a waste to become an energy system, the heating value of waste is one of the important characteristics that determine the energy obtainable from wastes [18].

Mixed paper wastes comprising of a mixture of Newspaper, Cardboard, Kraft, Beverage and Milk Boxes, Boxboard, Tissue, Colored Office Paper, White Office Paper, Envelopes, Treated Paper (NCR), and Glossy Paper were studied for their combined calorific value (Table 2) [18].

Table 2: Calorific value of paper waste [18]

Type Of Paper	Mean Gross Calorific Value (Btu/lb)
Newspaper	7540
Cardboard	6907
Kraft	6897
Beverage and Milk Boxes	6855
Boxboard	6703
Tissue	6518
Colored Office Paper	6348
White Office Paper	6234
Envelopes	6160
Treated Paper(NCR)	5983
Glossy Paper	6370
Mixed	6477

The expected calorific value of any unknown sample of mixed paper can be calculated by using the calorific values of each individual category of Mixed Waste Paper (MWP) and the weight fraction of each in a MWP sample [18].

As paper cups are LDPE coated so study of pyrolysis of LDPE could be of some help. It is a case of catalytic pyrolysis where used LDPE was pyrolyzed in a home assembled batch reactor under atmospheric pressure using a wide range of acidic and basic catalyst like silica, calcium carbide alumina, magnesium oxide and homogenous mixture of silica and alumina. CaC_2 proved advantageous on basis of reaction time while the efficiency of conversion to liquid was more for SiO_2 at optimum conditions. Hence, these two can suitably used for catalytic pyrolysis of polyethylene (Optimum weight – 1g/5g of LDPE). Oxide containing catalyst could be best suited for selective conversion into polar and aromatic compounds while CaC_2 could be adopted for selective conversion into aliphatic products [19].

The liquid product obtained from catalytic pyrolysis was characterized by physical and chemical tests. Physical test include density, specific gravity, API gravity, viscosity, aniline point, Flash point, gross calorific value etc. These were determined according to IP and ASTM standard methods for fuel values. The liquid fraction obtained is comparable with the standard

results of physical tests for gasoline, kerosene and diesel fuel oil. From chemical tests like Bromine water and $KMnO_4$ tests the presence of mixture of olefin and aromatic compounds can be obtained. Components of different hydrocarbons in the oil mixture were separated by column chromatography and fractional distillation followed by characterization with FT-IR spectroscopy [19].

3. MATERIALS AND METHODS

3.1. Raw Material

Waste paper cups have been collected from NIT campus area in Rourkela, Orissa (India). The cups were cut into small square shaped pieces (about 1 cm side).

3.2. Thermo-Gravimetric Analysis

Pyrolysis is the thermal degradation of a substance carried out in absence of air at a particular temperature. For determining the temperature range for effective pyrolysis i.e. for maximum thermal degradation, TGA of paper cup was carried out using a DTG60 instrument. TGA of the raw material sample was carried out in air medium at a heating rate of 25°C/min and 30°C/min both in air and nitrogen atmosphere. A specific amount of sample is taken and heated up to a final temperature of 700 °C for a residence time of 1 min at 700 °C. In air medium, 4.4 mg of sample is taken and for Nitrogen medium, around 5.88 mg of sample is taken. Thermo-gravimetric weight loss curve was plotted against temperature which provides the range of temperature for maximum thermal degradation of sample.

3.3. Experimental Procedure

Pyrolysis is the chemical decomposition of organic materials by heating in the absence of oxygen or any other reagents, except possibly steam. In some cases catalysts are used to enhance the efficiency. The temperature ranges from around 350°C to 700°C and the products are vapors, char and bio-oil which can further decompose into tar. Pyrolysis products basically consist of gases like CH_4, CO_2, and NH_3 and liquids like acetone, acetic acid etc. and solid char. It is a thermally initiated depolymerization process also known as "Thermolysis" which doesn't involve any oxidizing agent. Sometimes with limited supply of oxidizing agent and controlling the reaction leads to partial gasification.
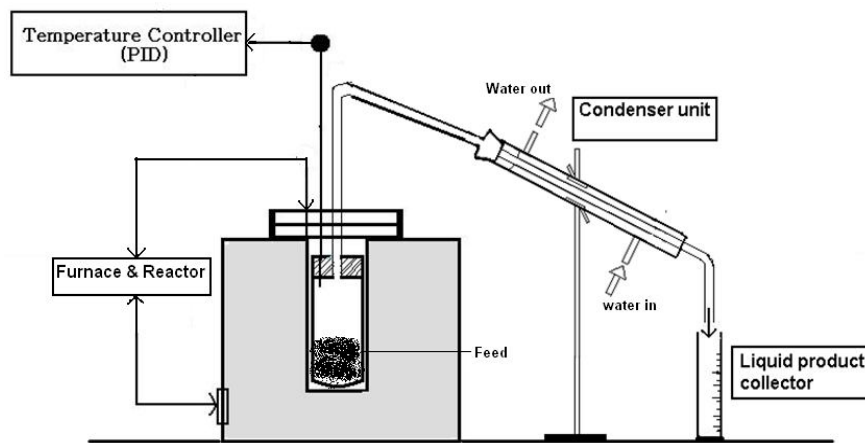
Figure 2: Experimental set-up for pyrolysis of paper cup

Paper cups pieces are taken in a reactor which is set for pyrolysis inside a furnace. The reactor-furnace system (Figure 2) is maintained at a particular temperature by using a PID controller. The outlet of the reactor is connected to a condenser. Water is circulated through the outer jacket of condenser by a pump for cooling the vapors coming out from the reactor due to pyrolysis reaction and hence condensed pyrolytic oil is collected at the other end of the condenser. Some amount of non-condensable gases also evolves which is let go into the atmosphere. The liquid product is called the bio-oil.

3.4. Sample Pyrolysis Runs

Sample pyrolysis runs aim to obtain an optimum temperature at which the liquid product attains maximum yield. The runs are taken at specific temperatures within the temperature range obtained from TGA. 15 grams of paper cup pieces are taken for pyrolysis runs at intervals of 25°C starting from 325°C to 425°C. During these runs various parameters were recorded such as reaction time, yield of liquid product, yield of char and yield of gaseous material that escape into air. The variation of these parameters was plotted against time.

3.5. Characterization of Raw Material and char

The paper cup and its char obtained after pyrolysis were analyzed through various methods in order to observe the changes in the properties of paper cup after pyrolysis.

3.5.1. Proximate Analysis

It is used to calculate moisture content, volatile matter, ash content and fixed carbon amount in the raw material and char used. ASTMD 3172-07 method [20] was used.

3.5.2. Ultimate Analysis

This analysis gives the elemental composition of the material i.e. % composition of Carbon, hydrogen, nitrogen, sulphur. % composition of oxygen is obtained by subtracting the sum of compositions of other elements from 100. The analysis was carried out by a CHNSO elemental analyzer (Variael CUBE Germany) for both paper cup and its char.

3.5.3. Calorific Value

Calorific value is defined as the amount of heat liberated by the complete combustion of a unit mass of fuel. Calorific value was determined for the paper cup using a bomb calorimeter (Model: AC-350, LECO Corporation, USA).

3.5.4. SEM Analysis

Scanning Electron Microscope (Model: JEOL-JSM-6480LV SEM) analysis of char was done in order to observe the pores on its surface at different magnification values.

3.6. Physical Characterization of Bio-Oil

This involves determination of physical properties of the pyrolytic oil by the help of standard methods for physical properties analysis which is listed in Table 3.

Table 3: Standard methods for physical property analysis [21]

Physical Property	Method
Density	ASTM D1298 – 99
Kinematic Viscosity	ASTM D445 – 11
Conradson Carbon	ASTM D189 - 06(2010)e1
Flash Point	ASTM D6450 - 05(2010)
Fire Point	ASTM D1310 - 01(2007)
Pour Point	ASTM D5853 – 09
Calorific Value	ASTM D5468 - 02(2007)
Distillation Boiling Range	ASTM D2887 – 08
Cetane Index	ASTM D4737 – 10

3.7. Chemical Characterization of Pyrolytic oil

3.7.1. FTIR

Fourier Transform Infrared Spectroscopy of the pyrolytic oil is done to determine the functional groups present in it. Functional groups like alcohols, ketones, carboxylic acids, esters, alkanes, alkenes, alkynes, amide, nitriles, nitro compounds, ethers, aromatic rings etc can be identified by FTIR using a Perkin-Elmer infrared spectrometer.

3.7.2. GC-MS

Gas Chromatography – Mass Spectrometry is done to determine the chemical compounds present in the oil. For this analysis some amount of sample of the oil is sent to Sargam Laboratory, Chennai and the analysis is done using a GC-MS-OP 2010[SHIMADZU] analyzer. The results of GC-MS give a confirmation to the results obtained in FTIR. The GC-MS conditions are as follows:-

GC Conditions:

Column Oven Temperature: 70˚C

Injector Temperature   :   240˚C

Injection Mode   :   Split

Split Ratio   :   10

Flow Control Mode   :   Linear Velocity

Column Flow   :   1.51 ml/min

Carrier Gas   :   Helium   99.9995% purity

Injection volume   :   1 micro liter

Column Oven Temperature Program:

Rate	Temperature (˚C)	Hold Time (min)
-	70.0	3.0
10	300	9 [35.0 mts total]

Column: VF-5ms

Length: 30.0m

Diameter: 0.25mm

Film Thickness: 0.25um

MS condition:

Ion source temp: 200 °C

Interface temp: 240°C

Scan range: 40 – 1000 m/z

Solvent cut time: 5mins

MS start time: 5(min)

MS end time: 35 (min)

Ionization: EI (-70ev)

Scan speed: 2000

4. RESULTS AND DISCUSSION

4.1. Thermo-Gravimetric Analysis

From the TGA curve (Figure 3), the maximum thermal degradation of the paper cups was observed to be in the temperature range of 300–400°Catboth the heating rates and also in both the mediums (air and nitrogen). In this active pyrolytic zone, 68% weight loss was observed. Another range of thermal degradation was also observed from 400 – 520°C. But this range is not of interest because at such high temperatures, the vapors formed are generally higher hydrocarbons and non- condensable gases as a result, the liquid yield is minimized. Thus, the temperature range of 300 – 400°C was chosen for further experimentation.
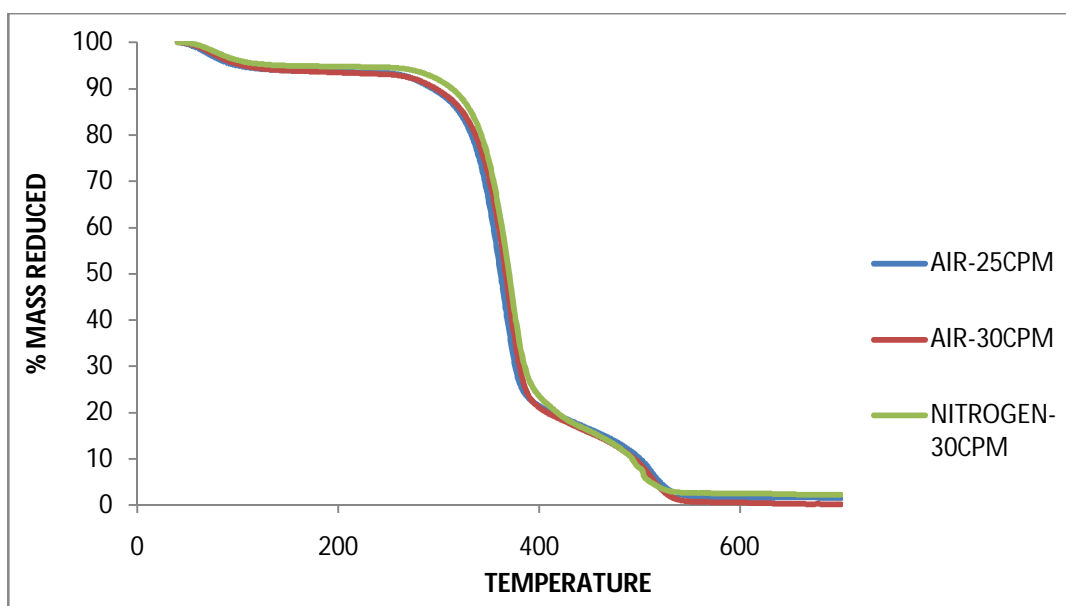
Figure 3: TGA curve for Paper cup

4.2. Sample Pyrolysis Runs

Table 4 gives the distribution of different fractions of paper cup pyrolysis products at different temperatures. Maximum yield of the bio-oil is 52 wt% at the temperature 400 ℃. Thus, the optimum temperature was fixed to be 400°C as our interest is to maximize the yield of liquid product. From the graph of liquid yield vs. temperature (Figure 4), the yield increases with increase in temperature up to 400°C and then decreases. Also the curves for gas yield and char were plotted with respect to temperature (Figure 4) and as observed the gaseous yield decreased up to 400°C and increased suddenly after 400°C where as solid yield decreased with increase in

pyrolysis temperature. This proves that after 400°C the vapors formed are mostly non–condensable which result in decrease of liquid yield. The reaction time vs. temperature curve (Figure 4) shows a decreasing trend with increase in temperature.

Table 4: Distribution of different fractions at different temperatures in thermal pyrolysis of paper cup

Temperature (^{0}C)	Oil(wt.%)	Gas/volatile (wt.%)	Residue (wt.%)	Reaction time (min.)
325	30.33	26.67	43	24
350	39.23	21.27	39.5	20
375	47.13	16.87	36	18
400	52.53	13.87	33.6	15
425	42.33	26.87	30.8	8

Figure 4: Variation of Yields vs. Temperature and Reaction Time vs. temperature
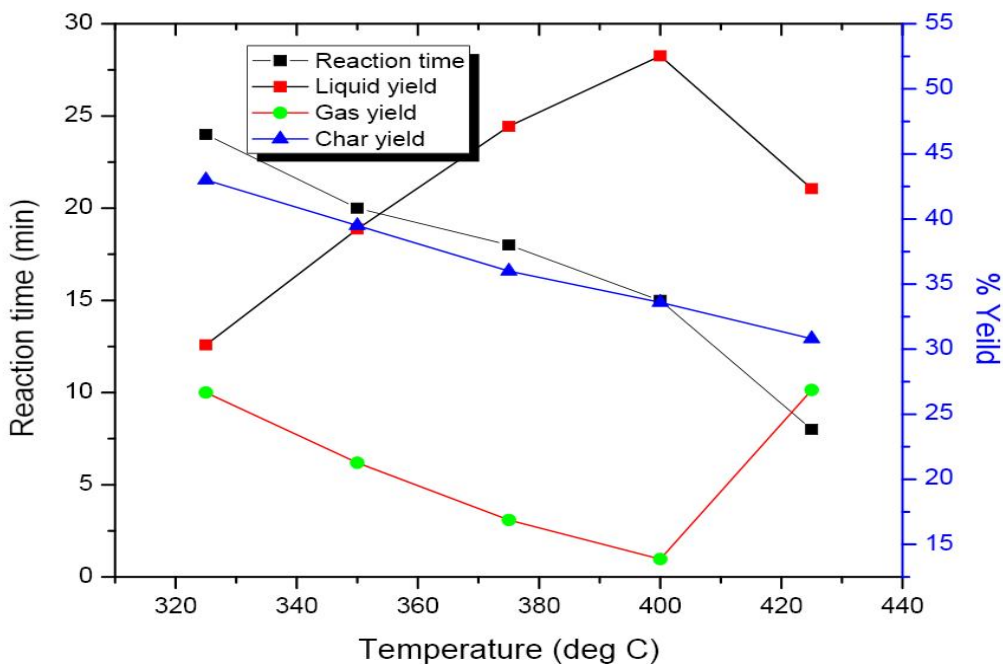
17

4.3. Characterization of Paper cup and its char

The proximate analysis is a quick and easy way of estimating fuel quality. Negligible moisture content of paper cup indicates negligible effect on the conversion efficiency and the heating value of the cellulosic biomass; low ash content also indicates less impact on the heating value of paper cup; volatile matter is not very high whereas the high percentage of fixed carbon owes to its cellulosic nature. These properties make paper cup an efficient raw material for good quality fuel. The proximate analysis of paper cup and the obtained char (Table 5) shows a decrease of volatile matter from 52% to 12% and in turn results in increase of ash content and fixed carbon content.

Ultimate analysis gives the elemental composition of the raw material and its char. It shows a noticeable variation in carbon and oxygen percentage where as hydrogen content remained constant for paper cup and its char and sulphur content was not present in both paper cup and char.

Table 5: Paper cup and Paper cup char characterization

	Paper cup	Paper cup char
Moisture content	0	0
Volatile Matter	52	12
Ash content	2	8
Fixed carbon	46	80
C	46.7	77.7
H	6.7	6.7
N	2.12	0
S	0	0
O	44.4	15.6
C/H Molar Ratio	0.57	0.97
C/O Molar Ratio	1.4	6.64
Empirical Formula	$C_{1.4}H_{2.41}N_{0.05}O$	$C_{6.67}H_{6.91}O$
Gross Calorific Value(MJ/Kg)	20.102	25.4

4.3.1. SEM analysis

The SEM analysis of the char shows following images of the char surface obtained from scanning electron microscope at magnification values of 200 (Figure 5) and 1000 (Figure 6). It is observed that the paper cup char has no well-defined pores.
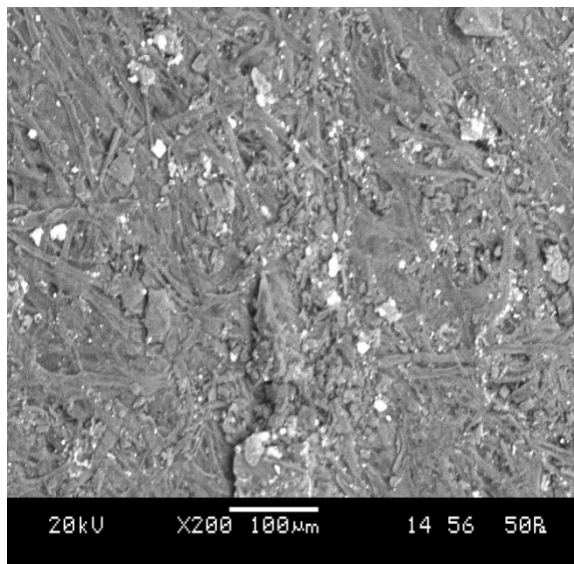
Figure 5: SEM image of paper cup char at 200x magnification
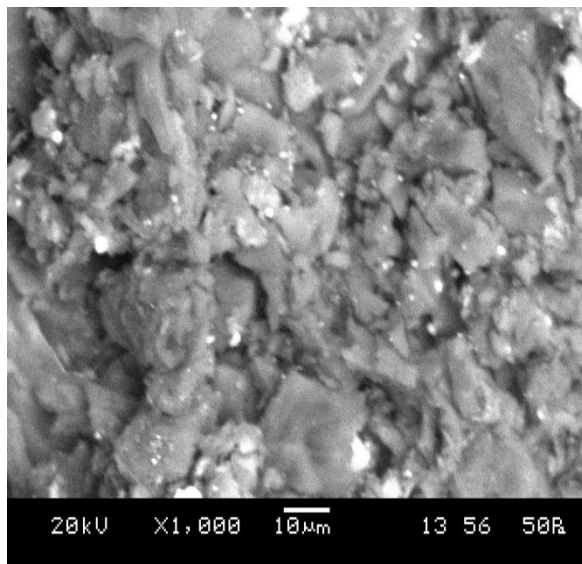
Figure 6: SEM image of paper cup char at 1000x magnification

4.4. Physical Properties of Bio-fuel

Physical properties such as density, specific gravity, kinematic viscosity, carbon residue, sulphur content, flash point, fire point, pour point, cloud point, gross calorific value, distillation boiling range and cetane index of bio-oil which helps in assessing and determining feasibility of bio-oil as commercial liquid fuels is shown in Table6.

Table6: Physical Properties of Bio-Oil

Product Properties	Paper cup Pyrolytic Oil
Density @ 15°C in gm/cc	1.0136
Specific gravity @ 15°C/15°C	1.0145
Kinematic viscosity @ 40°C in cst	0.80
Pour point	Below Minus 12°C
Cloud point	Minus 4°C
Sulphur Content	Nil
Conradson Carbon Residue	0.76%

Distillation:

Initial Boiling Point	40
Final Boiling Point	360

From comparison of physical properties of other pyrolytic oils and diesel and gasoline (table 7) it can be seen that paper cup pyrolytic oil has higher density than transportation fuels like gasoline and diesel along with a lower viscosity. Density and viscosity of bio-oil can be modified by blending it with different transportation fuels and also by using various upgrading techniques. The distillation range showed that the bio-oil starts boiling at 40°C and the distillation stops at around 360°C. It means the bio-oil contains substantial amount of volatiles as it initial boiling point is below 100°C. As it can be observed from Table 7, the properties of bio-oil were in similar range to that of other pyrolytic oils. From the comparison of carbon range it can be concluded oil obtained in this work lie between light and heavy petroleum products in this respect.

Table7: Comparison of Fuel Properties

Properties	Specific Gravity	Kinematic Viscosity	Pour Point	IBP (°C)	FBP (°C)	Chemical Formula
Fuels	15°C/15°C	@40°C (cst)	(°C)			
Paper cup Pyrolytic Oil	1.0145	0.80	< -12°C	40	360	C_6-C_{20}
Gasoline[22]	0.72-0.78	-	-40	27	225	C_4-C_{12}
Diesel[23]	0.82-0.85	2-5.5	-40 to -1	172	350	C_8-C_{25}
Bio-Diesel[23]	0.88	4-6	-3 to 19	315	350	C_{12}-C_{22}
Heavy Fuel Oil[24]	0.94-0.98	>200	-	-	-	-
Wood Pyrolytic Oil[25]	1.3	13	-12			C_5-C_8

4.5. Chemical composition of Bio-oil

4.5.1   FTIR analysis

FTIR analysis (Figure 7) gives a brief account of the functional groups present (Table 8) in the bio-oil.
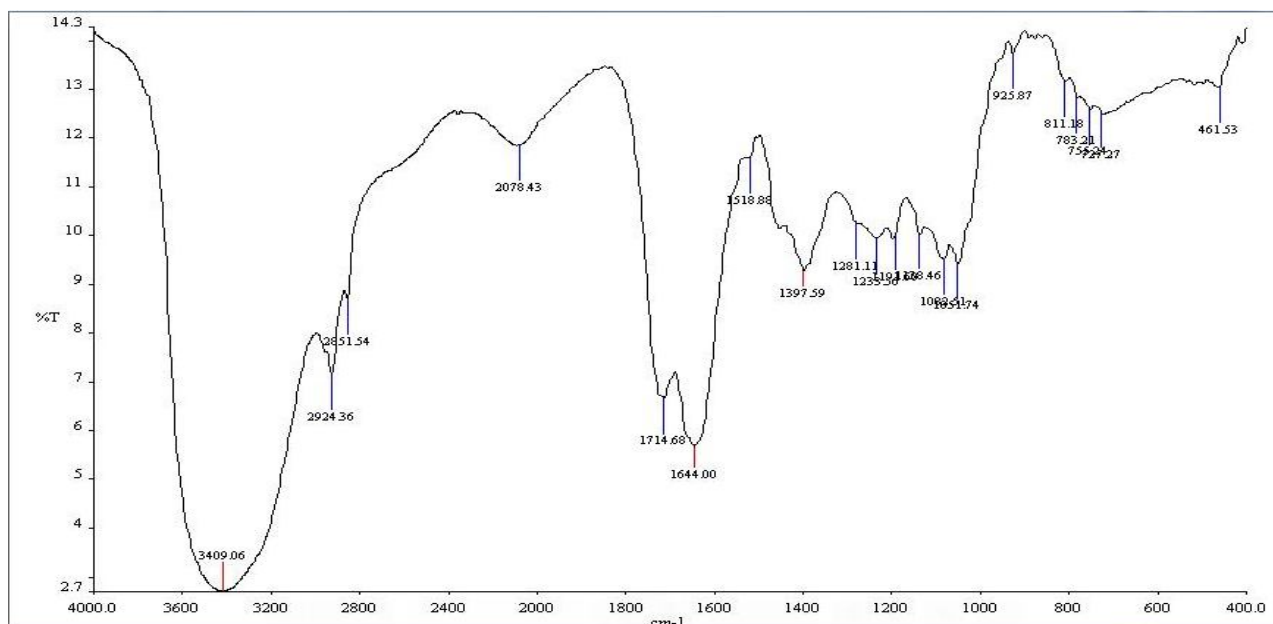
Figure 7: FTIR graph of paper cup pyrolytic oil

Table 8: FTIR compound and Frequency table

Frequency	Compound Type
3409.06	O-H stretch hydrogen bonded alcohol
2924.36 – 2851.54	C-H stretch alkanes
1714.68	C=O stretch Aldehydes, Ketones, Carboxylic acids, Esters
1644.0	C=C stretch alkenes
1518.88	NO_2 asymmetrical stretch nitro compounds
1281.11	C-N stretch amines
1233.56 – 1051.74	C-O stretch Alcohols, Ethers, Carboxylic acids, Esters
925.87	C-H bend alkenes
811.18 – 727.27	C-H bend Phenyl Ring Substitution Bands

4.5.2. Gas Chromatography – Mass Spectrometry

GC-MS gives the chemical composition of the paper cup pyrolytic oil. The compounds present in the oil are obtained in a chromatogram which is then compared with a standard chromatogram data available.

Table 9: Chemical composition of Bio-oil

| Compound	Area%	Formula
1-Acetoxy-2-Propionoxyethane	3.62	$C_7H_{12}O_4$
2-Furancarboxaldehyde, 5-methyl-	10.36	$C_6H_6O_2$
Phenol	2.34	C_6H_5OH
1,2-Cyclopentanedione, 3-methyl-	5.06	$C_6H_8O_2$
2,3-Dihydro-5-Hydroxy-6-Methyl-4H-Pyran-4-One	3.27	$C_6H_8O_3$
Oxetane, 2-Propyl	2.85	$C_6H_{12}O$
Maltol	5.82	$C_6H_6O_3$
2,3-Dihydro-3,5-Dihydroxy-6-Methyl-4H-Pyran-4-One	1.17	$C_6H_8O_4$
1,4:3,6-Dianhydro-.alpha.-d-glucopyranose	12.26	$C_6H_8O_4$
2-Furancarboaldehyde, 5-(hydroxymethyl)-	18.20	$C_6H_6O_3$
Tetradecane	0.72	$C_{14}H_{30}$
Pentadecane	1.51	$C_{15}H_{32}$
3-Heptadecene, (Z)-	1.55	$C_{17}H_{34}$
Eicosane	0.5431	$C_{20}H_{42}$
Hexadecanenitrile	3.08	$C_{16}HN$
Hexadecanoic Acid	6.59	$C_{16}H_{32}O_2$
Oleanitrile	7.86	$C_{18}H_{33}N$
Octadecanoic acid	1.84	$C_{18}H_{36}O_2$

From the table 9, it is observed that the oil is mainly composed of 18.2% 2-Furancarboaldehyde, 5-(hydroxymethyl)-; 12.26% 1,4:3,6-Dianhydro-.alpha.-d-glucopyranose; 10.36% 2-Furancarboxaldehyde, 5-methyl-; 7.86% Oleanitrile; 6.59% Hexadecanoic Acid; 5.82% Maltol; 5.06% 1,2-Cyclopentanedione, 3-methyl-; accounting for around 66% of the area of total ion chromatogram. It can be observed that the bio-oil contains 18 compounds in the range of $C_6 – C_{20}$ which is present in most of the fuels.

5. KINETIC STUDY OF PYROLYTIC REACTION

Kinetic analysis of a reaction process gives information on the effect of various process parameters on the feedstock conversion. As the raw material pyrolyzed here is paper cups which belongs to cellulosic feedstock, so pyrolysis of paper cup can be modeled like a cellulose pyrolysis. The pyrolysis cracking of cellulosic material can be modeled as 1st order reaction.

$$A \text{ (solids)} \rightarrow B \text{ (solids)} + C \text{ (volatiles)} \tag{1}$$
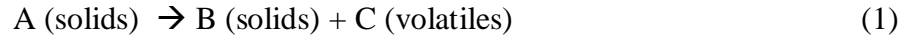
For 1st order reaction, the rate equation is given by

$$\frac{dx}{dt} = k(1 - x) \tag{2}$$

Where,

$$k = ko * e^{\frac{-E}{RT}} \tag{3}$$

$$x = \frac{Wi - W}{Wi - Wf} \tag{4}$$

Hence,

$$\frac{dx}{dt} = ko * e^{\frac{-E}{RT}} * (1 - x) \tag{5}$$

Now considering heating rate β,

$$\frac{dx}{dt} = \frac{ko}{\beta} * e^{\frac{-E}{RT}} * (1 - x) \tag{6}$$

Now taking into account the effect of variation of temperature on conversion (x), the following equation represents the pyrolysis reaction:

$$\ln\left(-\ln(1 - x)\right) = \ln\left(\frac{KoRT^2}{\beta E}\right) - \left(\frac{E}{RT}\right) \tag{7}$$

Activation energy (E) is determined from the slope of the straight line plot of ln(-(ln(1-x)) vs. 1/T (Figure 8) using the TGA data.
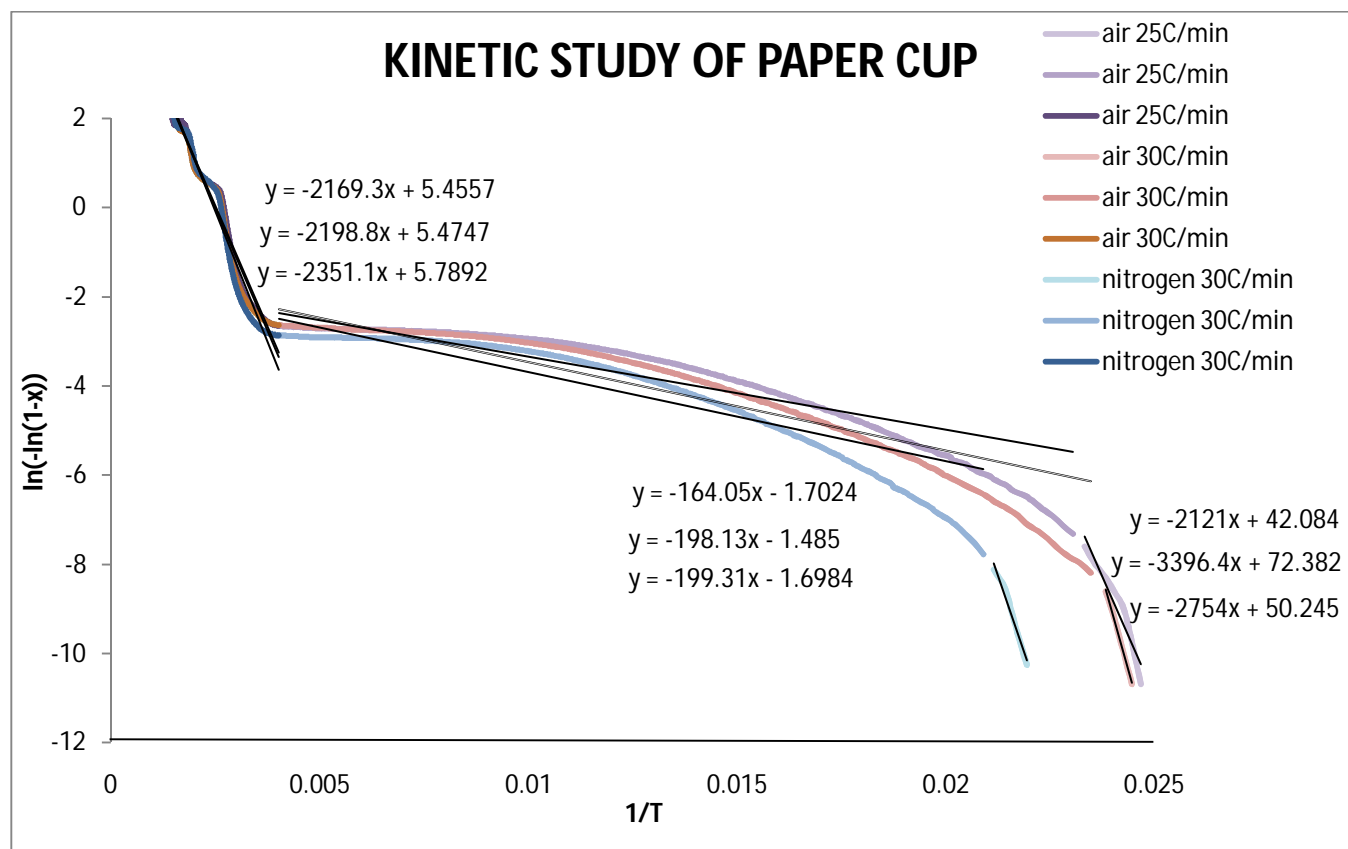
Figure 8: Kinetic analysis plot for determination of Activation Energy

Table 10: Activation Energy for Pyrolysis of Paper Cup

Sample	Activation Energy (KJ/Mol)		
	1st Phase	2nd Phase	3rd Phase
N2 30degree/min	22.896756	1.65706334	19.5470454
Air 30degree/min	28.2376696	1.64725282	18.2808232
Air 25degree/min	17.633994	1.3639117	18.0355602

Pyrolysis kinetic analysis is valuable for the in-depth exploration of process mechanisms. On the basis of thermo gravimetric analysis of different kinds of biomass feedstock, thermal kinetics analysis was performed to analyze the pyrolysis behavior of biomass. With the apparent kinetic parameters derived, a kinetic model was proposed for the main reaction section of biomass pyrolysis process.

From literature, Cellulosic biomass materials quickly decomposed in a very limited temperature range of 590–670 K, with larger decomposition rate. Woody materials are the most difficult for pyrolysis, with the longest duration [26].

From kinetic analysis of the pyrolysis process, kinetic parameters can be obtained for a large variety of biomass feedstock, which can provide valuable fundamental data for the development of efficient biomass thermal chemical conversion technology. Activation energy of some cellulosic feedstock is given in table 11 [26].

Table 11: Activation energy for various biomass feedstocks [26]

Biomass Feedstock	Activation Energy E (KJ/mol)
Corn Stalk	66.518
Wheat straw	70.516
Cotton stalk	71.055
Tree skin	77.316
Wood chip	85.393
Peanut shell	84.47
Seed shell	91.462
Cotton	200.9
Filter paper	227.296

Comparing the activation energy for pyrolysis of paper cup (Table 10) with other pyrolytic oils, the value is relatively very small. Hence paper cup can be used as a blend in the pyrolysis of feedstock having higher activation energy in order to reduce the overall activation energy.

6. INDUSTRIAL SCALE-UP AND ECONOMIC ASSESSMENT

6.1. Aim

Design an industrial unit of capacity 12 tons/day for producing bio-oil by thermal pyrolysis of paper cups.

6.2. Raw Material

Plastic coated paper cups

6.3. Products

Table 12: Pyrolysis products and its uses

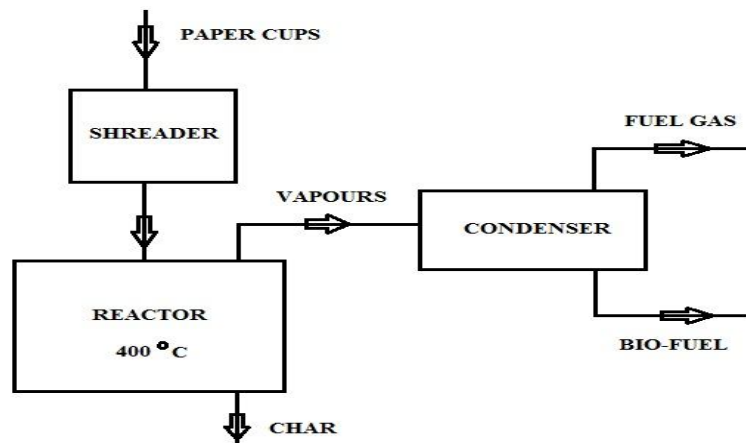| Product	Use
Paper cup Pyrolytic Oil	Used as Bio-fuel.
Fuel Gas	Non-condensable vapors having high calorific value.
Char	Source of activated carbon. Also used as solid fuel.

6.4. Process

Figure 9: Process flow diagram of Pyrolysis unit

6.5. Material Balance

1 kg paper cups produce ➡ 0.34 Kg Char

➡ 0.13 Kg Non-Condensable Vapors (Fuel Gas)

➡ 0.53 Kg Bio-Fuel

Let us design the unit to process 12 tons of paper cups in a single run.

12 tons of paper cups produce ➡ 4080 Kg Char

➡ 1560 Kg Fuel Gas

➡ 6360 Kg Bio-Fuel

6.6. Energy Balance

6.6.1. Energy Balance for Reactor

Due to the complex nature of pyrolysis processes of biomass involving lots of simultaneous reactions, it is very difficult to keep an account of all processes while doing energy balance. Thus, for the sake of convenience, we measured the overall energy required for the pyrolysis of different amount of paper cups by connecting an energy meter across the furnace. A linear relationship was found out from the plot of Mass vs. Energy consumed.

Table 13: Energy-Mass Analysis

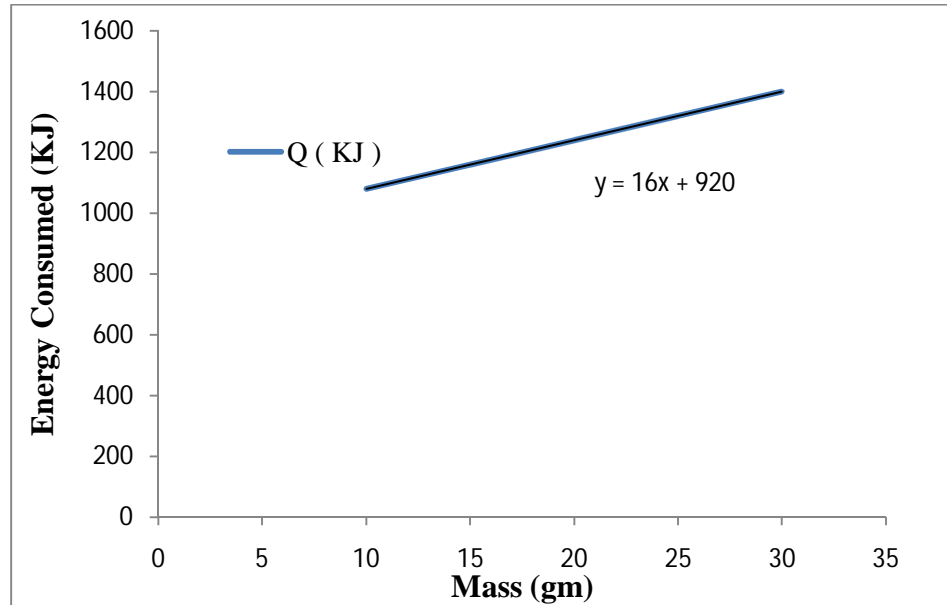| Mass (gm)	Q (KJ)
10	1080
15	1160
20	1240
25	1320
30	1400

Figure 10: Mass-Energy consumption

Now using the linear relation, a rough estimation of energy required for pyrolysis of 12tons of paper cup was found out to be 1,92,920MJ. This energy is the amount of overall energy consumed by the process, i.e. energy to raise temperature of paper cup from 35°C to 400°C along with energy consumed for pyrolysis reaction, whereas in industry the case will be different. Although the process is a semi-batch process but the furnace won't be allowed to cool down to room temperature after every run as it will cost a lot of energy loss. So, energy consumed is expected to be less than 1, 92, 920MJ. Since it is a rough estimation, so calculation are done with 1,92,920 MJ only.

6.6.2. Energy balance for Condenser

As the operating temperature of the reactor and furnace system is 400°C so we assume temperature of the vapors coming out of the reactor to be around 350°C.

Now,

(Vapors from Reactor) = (Fuel Gas) + (Bio-Oil)   (8)

So, input for condenser = 7920 Kg of vapors which comprises of 1560 Kg of Non-condensable (Fuel Gas) and 6360 kg of condensable liquid Bio-oil. Here also a very rough estimation has to be done in order to determine energy recovered while condensing. Here, the process is condensation of mixture of hydrocarbon vapors. In order to evaluate the energy

28

recovered during condensation and design the condenser mole fraction of each component of hydrocarbon vapor mixture is required with their specific heat capacity, thermal conductivity, viscosity, heat of vaporization, etc. which are not available. So, in this estimation, the hydrocarbon vapor mixture is considered as a single component hydrocarbon vapor with specific heat of vapor as 0.5 KJ/Kg K since it varies in the range of 0.5-3 KJ/Kg K for hydrocarbon vapors at constant pressure.

From literature it has been found that Specific Heat of LDPE pyrolysis oil = 2 KJ/Kg K.

Now, distillation range for bio-oil is,

Table 14: Distillation range for Bio-Oil

Initial Boiling point	40°C
Final Boiling Point	360°C

Now,

(Total Energy Recovered)= (Energy by Fuel Gas)+(Energy by Bio-oil)   (9)

Energy by fuel gas = 1560*0.5*(350-40) = 2,41,800 KJ = 241.8 MJ

Energy by bio-fuel = 6360*0.5*(400-360) + 6360*2*(360-40)

        = 41,97,600 KJ = 4197.6 MJ

Total Energy Recovered = (241.8+4197.6) = 4439.4 MJ

Amount of cooling water @30°C required = 4439400/(4.186*40) = 26513 Kg = 27 tons

6.7. Equipment Size

6.7.1. Reactor

Cylindrical shape reactor made of carbon steel operating at 14.7 psi.

The reactor is assumed to work in a similar way to coke ovens used for coking of coal with a capacity of 12 tons processed at single run with a residence time of 20 hours.

Total Energy required for one run = 1,92,920MJ = 182.85 M Btu

Time between two consecutive runs for discharging and loading = 1 hour

Total time for one run = 21 hours

Total no of runs per year = (365*24)/21 = 417 runs

Energy required per hour, Q = (182.85)/20 = 9.14 M Btu/hr

6.7.2. Condenser

1-4 Shell and tube exchanger with 21.25 inch shell inner diameter with a baffle spacing of 5 inch and 158 no of 16 inch long 13 BWG tubes with an outer diameter of 1 inch and a square pitch of 1.25 inch. Combined dirt factor of 0.003 should be provided.

Flow rate of vapors = (7920 Kg)/21 = 377.14 Kg/hr

Flow rate of cooling water = 27000/21 = 1285.71 Kg/hr

Inlet temperature of vapors = 350°C

Outlet temperature of vapors = 40°C

Inlet temperature of cooling water = 30°C

Outlet temperature of cooling water = 70°C

LMTD = 81.03°C   R = 310/40 = 7.75   S = 40/(350-30) = 0.125 F_T = 0.85

Δt = 0.85*81.03 = 68.87°C

Shell Side (Cooling water):

Flow area = (21.25*0.25*5)/(144*1.25) = 0.1475 ft^2 = 137.03 cm^2 = 0.014 m^2

Mass Velocity =(1285.71)/(0.014) =91,836 Kg/hrm^2 = 25.51 Kg/m^{2}s

Equivalent diameter = 0.99/12 = 0.0825 ft = 0.025 m

Viscosity of water = 0.547*10^{-3} N s/m^2

Thermal conductivity of water = 0.6 W/m K

Reynolds number = (0.025*25.51)/(0.547*10^{-3}) = 1165.9

$j_H = 17$

$h_o = 17*(0.6/0.025)*((4186*0.547*10^{-3})/0.6)^{(1/3)} = 637.58$ W/m^2 K

Tube Side (Hot fluid):

Flow area = $(158*0.515)/(144*4) = 0.141$ ft^2 = 0.0131 m^2

Mass velocity = $377.14/(0.0131) = 28789.31$ Kg/hrm^2 = 8 Kg/m^2 s

Viscosity of hydrocarbon vapor @240°C = $1.9*10^{-5}$ Kg/m s

Thermal conductivity of hydrocarbon vapor = 0.1385 W/m K

Reynolds number = $(0.021*8)/(1.9*10^{-5}) = 8842.10$

L/D = $16/0.0675 = 237$

$j_H = 34$

$h_i = 34*(0.1385/0.021)*((500*1.9*10^{-5})/(0.1385))^{(1/3)} = 91.79$ W/m^2 K

$h_{io} = 91.79*0.81 = 74.35$ W/m^2 K

Clean overall coefficient, $U_C = (74.35*637.58)/(74.35+637.58) = 66.58$ W/m^2 K

Overall design coefficient:

Total Surface Area = $158*16*0.2618 = 662$ ft^2 = 61.5 m^2

$U_D = (4439.4*10^6)/((21*3600)*(61.5*68.87)) = 13.86$ W/m^2 K

Dirt Factor = $(U_C - U_D)/(U_C*U_D) = (66.58 - 13.86)/(66.58*13.86) = 0.057$ m^{2}K/W

6.7.3. Shredder

Total raw material to be shredded per year = $417*12 = 5004$ tons

Required shredder capacity = $5004/(365*24) = 0.571$ tons/hr.

A shredder of capacity 1 ton/hr is used and operated at 0.571 tons/hr.

6.8. Cost Analysis

Cost analysis provides a rough estimate of the total investment required to setup a plant of particular capacity, operating cost of the plant and production cost of the product. Cost analysis data will enable us to determine whether setting up such a plant is economically feasible and beneficial to society or not.

Total investment consists of two parts:

• Fixed Capital: - Total cost of plant ready for start-up.

• Working Capital: - Additional investment needed, over and above the fixed capital, to start the plant and operate it to the point when income is earned.

6.8.1. Factorial Method to Determine Total Investment:

$$C_f = f_l * C_e \qquad\qquad (10)$$

Where,

C_f = Fixed Capital Cost

f_l = Lang Factor depending on type of process

C_e = Total delivered cost of all major equipment.

Basic Procedure:

• Prepare material & energy balance, preliminary flow sheets, size major equipment and select material of construction.

• Estimate purchase cost of major equipment using literatures.

• Calculate Fixed Capital using Table 10.

• Working Capital = 10-20% of Fixed Capital.

• Total Investment = Fixed Capital + Working Capital.

Sl. No.	Item	Process Type		
		Fluids	Fluids-Solids	Solids
1	Major Equipment Purchase Cost (PCE)	1	1	1
f1	Equipment Erection	0.4	0.45	0.5
f2	Piping	0.7	0.45	0.2
f3	Instrumentation	0.2	0.15	0.1
f4	Electrical	0.1	0.1	0.1
f5	Buildings, Process	0.15	0.1	0.05
f6	Utilities	0.5	0.45	0.25
f7	Storage	0.15	0.2	0.25
f8	Site Development	0.05	0.05	0.05
f9	Ancillary Buildings	0.15	0.2	0.3
	Total Physical Plant Cost(PPC) = PCE*	3.4	3.15	2.8
	Total Physical Plant Cost (PPC)	1	1	1
f10	Design & Engineering	0.3	0.25	0.2
f11	Contractor's Fee	0.05	0.05	0.05
f12	Contingency	0.1	0.1	0.1
	Fixed Capital = PPC*	1.45	1.4	1.35

6.8.1.1. Major Equipment Costs

Reactor

Cost of cylindrical reactor made of carbon steel operating at 14.7 psi with an energy intake capacity (15 m^3) of 1.592MBtu/hr = \$44,312 (2004 basis, PCI = 444).

Cost of reactor @2012 (PCI = 665) = (665/444)*44312 = \$66,368

Condenser

A 1-4 fixed head shell and tube heat exchanger made of stainless steel with heating surface area of 61.5 m^2 and operating at pressure range of 10 psi is required.

Cost of exchanger @2004 = \$52,000;

Cost of exchanger @2012 = $77,882

Storage Tanks

Cost of Storage Tank of capacity 50 m^3 for storing bio-fuel (floating roof) @2004 = $37,404

Cost of Storage Tank @2012 = $56,022

Shredder

Cost of shredder of capacity 1tons/hr @2004 = $38,148;

Cost of shredder @2012 = $57,137

Thus major equipment purchase cost = reactor + condenser + shredder + storage tank

$$= \$2,38,420 = Rs\ 1,19,21,000$$

6.8.1.2. Total Investment

Major Equipment Purchase Cost (PCE) = Rs 1,19,21,000

Total Physical Plant Cost (PPC) = 1.95*PCE= Rs 2,32,45,950

Fixed Cost = 1.35*PPC = Rs 3,13,82,032

Working Capital = 0.10*Fixed Cost = Rs 31,38,203

Total Investment = Fixed Capital + Working Capital = Rs 3,45,20,235

6.8.2. Operating Cost

It is the cost of producing the product and is needed to judge viability of project and to choose between alternate processes.

$$\text{Annual Production Cost} = A + B + C \text{ (From Table 16)} \tag{11}$$

$$\text{Production Cost (per Kg)} = \frac{Annual\ Production\ Cost}{Annual\ Production\ Rate} \tag{12}$$

Sl. No.	Item	Typical Values
	Variable Costs	
1	Raw Materials	From Material Balance
2	Miscellaneous Materials	10% of item (5)
3	Utilities	From Flow Sheet
4	Shipping & Packaging	Usually Negligible
	Sub Total A =	1+2+3+4
	Fixed Costs	
5	Maintenance	5-10% of Fixed Capital
6	Operating Labors	From Manning Estimates
7	Laboratory Costs	20 – 23% of item (6)
8	Supervision	20% of item (6)
9	Plant Overheads	50% of item (6)
10	Capital Charges	10% of Fixed Capital
11	Insurance	1% of Fixed Capital
12	Local Taxes	2% of Fixed capital
13	Royalties	1% of Fixed Capital
	Sub Total B =	5+6+7+8+9+10+11+13
	Direct Production Costs =	A+B
14	Sales Expense	
15	General Overheads	
16	R&D	C= 20-30% of Direct Production Cost

Raw Materials

Cost of Raw Materials = 5*12000*417

$$= Rs\ 2,50,20,000$$

Miscellaneous Materials

Cost of Miscellaneous Materials = 0.10*0.05*3,13,82,032 = Rs 1,56,910

Utilities

Chilled Water @30°C = ((417*27*1)/100)*(665/444) = $168 = Rs 8,431

Electricity = {1.5*{(417*1,92,920) − (417*4,439.4)}}/100

$$= \$1178942 = \text{Rs } 5,89,47,120$$

Cost of Utilities = Rs 5,89,55,551

Maintenance

Cost of Maintenance = 0.05*3,13,82,032 = Rs 15,69,101

Operating Labors

Cost of Operating Labor = 20*3*500*365 = Rs 1,09,50,000

Laboratory Costs

Laboratory Costs = 0.2*1,09,50,000 = Rs 21,90,000

Supervision

Supervision Cost = 0.2*1,09,50,000= Rs 21,90,000

Plant Overheads

Plant Overheads = 0.5*1,09,50,000 = Rs 54,75,000

Capital Charges

Capital Charges = 0.1*3,13,82,032 = Rs 31,38,203

Insurance

Insurance = 0.01*3,13,82,032 = Rs 3,13,820

Local Taxes

Local Taxes = 0.02*3,13,82,032= Rs6,27,640

Royalties

Royalties = 0.01*3,13,82,032= Rs 3,13,820

Direct Production Costs = Variable Costs + Fixed Costs

$$= Rs\ 8,41,24,030 + Rs\ 2,67,67,584 = Rs\ 11,08,91,614$$

Sales Expense + General Overheads + R & D = 0.2*11,08,91,614= Rs 2,21,78,323

Annual Production Cost = 11,08,91,614+ 2,21,78,323 = Rs 13,30,69,937

Income from sales of Bio-Fuel = 417*6360*60 = Rs 15,91,27,200

Income from sales of Fuel Gas = 417*1560*4.4767*1.32 = Rs 38,44,081

Income from sales of Charcoal = 417*4080*3*1.623 = Rs 82,83,921

Total Income from Sales = Rs 17,12,55,202

Net Profit = Rs 3,81,85,265

7. CONCLUSION

1. Paper cups constitute a major portion of non-decomposable wastes which is still growing high in numbers. Hence is abundantly available and can be used for bio-oil production.

2. The optimum temperature for pyrolysis of paper cups is obtained at 400°C and the yield of liquid product is maximum with a recovery of 52.53 (wt%).

3. The pyrolytic oil yield is observed to be better when the amount of paper cup taken in the reactor is less (almost half) with respect to the volume of the reactor. It is because, all the pieces of paper cup are completely pyrolyzed and don't stick to each other.

4. The pyrolytic oil contains around 18 chemical compounds of varying carbon chain length of $C_6 - C_{20}$, the major compounds being 2-Furancarboaldehyde, 5-(hydroxymethyl)-; 1,4:3,6-Dianhydro-.alpha.-d-glucopyranose; Oleanitrile; Hexadecanoic Acid; Maltol; 1,2-Cyclopentanedione,3-methyl-; 2-Furancarboxaldehyde,5-methyl- and contains functional groups such as Aldehydes, Ketones, Carboxylic acids, Esters, nitro compounds, amines, alcohols, ethers, alkanes, alkenes, and Phenyl Ring Substitution Bands.

5. Char obtained after pyrolysis of paper cup can be used as solid fuel due to its good calorific value.

6. Activation energy of the pyrolysis reaction of paper cups is found to be less. Hence it can be blended with other biomass feedstock of higher activation energy so that the pyrolysis reaction can be made easier.

7. Industrial scale-up and economic assessment was performed for the pyrolysis of paper cups by considering all required assumptions. The result showed a profit of 3.8 crores INR annually for the production capacity of 12 tons/day.

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Paper Published:

1. Bijayani Biswal, Sachin Kumar, R. K. Singh, "Production of hydrocarbons liquid by thermal pyrolysis of waste paper cups" communicated to <u>Chemical Engineering Communication</u>, Taylor and Francis series.

2. Bijayani Biswal, Sachin Kumar, R. K. Singh, "Thermogravimetric analysis of waste paper cups" communicated to <u>International Journal of Environmental Science and Development</u>.