

**A REPORT ON
CO-PYROLYSIS OF LIGNOCELLULOSIC BIOMASS AND SYNTHETIC
POLYMER**

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CERTIFICATE

This is to certify that the project work entitled “**Co-pyrolysis of lingo-cellulosic biomass and synthetic polymer**” submitted by Ashish Kumar Dewangan (110CH0464) has been carried out under my supervision towards the partial fulfilment of requirement for the award of B. Tech Degree in Chemical Engineering, National Institute of Technology Rourkela. This is his original work and has not been published anywhere else for any purpose.

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CONTENTS

Chapter	Title	Page No.
	List of Tables	v
	List of Figures	vi
1.	Introduction	1 – 3
1.1	Overall Background	1
1.2	Trends in Energy Resources	1-2
1.3	Problem Statement	2
1.4	Solution Strategy	3
2.	Literature Review	4 – 12
2.1	Biomass	4 – 6
	2.1 Sources of Biomass	4
	2.1 Types of Biomass	4
	2.3 Constituents of Biomass	4 – 6
2.2	Biofuel	6
2.3	Types of Pyrolysis	6 – 7
2.4	Factors Affecting Pyrolysis Liquid Yield	7
2.5	Application of Pyrolysis Products	7 – 8
	2.5.1 Application of Pyrolysis Liquid	7
	2.5.2 Application of Pyrolysis Gas	7
	2.5.3 Application of Pyrolysis Char	8
2.6	Upgrading of Bio-Oil	8 – 9
2.7	Sugarcane Bagasse	9 – 10
2.8	Low Density Polyethylene	10 – 11
2.9	Co-pyrolysis of Biomass and Plastic	11 – 12
3	Objective of the Work	13
4	Materials and Methods	14 – 17
4.1	Materials	14
4.2	Methods	15 – 17
	4.2.1 TGA	15

	4.2.2	Proximate Analysis	15
	4.2.3	Ultimate Analysis	15
	4.2.4	Experimental Procedure	15 – 16
	4.2.5	Reactor Specification	16
	4.2.6	Sample Pyrolysis Runs	16
	4.2.7	Water Content of Liquid Product	17
	4.2.8	GC – MS	17
	4.2.9	FTIR	17
	4.2.10	Calorific Value of Bio-Oil	17
5	Results and Discussion		18 – 36
5.1	Characterization of Raw Materials		18 – 26
	5.1.1	Proximate Analysis and Ultimate Analysis of SB and LDPE	18 – 19
	5.1.2	TGA of SB and LDPE	19 – 21
	5.1.3	Effect on temperature on reaction time and yield of pyrolysis products of SB	21 – 23
	5.1.4	Effect on temperature on reaction time and yield of pyrolysis products of LDPE	23 – 24
	5.1.6	Effect of different blends of SB and LDPE on reaction time and yield of products	25
	5.1.5	Effect of temperature on product yield of different ratios of SB and LDPE	25 – 26
5.2	Characterization of Liquid Products		26 – 38
	5.2.1	Proximate Analysis of Liquid Products	
	5.2.2	Calorific Value of Liquid Products	
	5.2.3	FTIR Analysis of Liquid Products	
	5.2.4	GC – MS of Liquid Products	
6	Conclusion		39
7	Future Scope		40
	References		41 – 43

LIST OF TABLES

Table No.	Name	Page No.
Table No. 1	Major Constituents of Bagasse	10
Table No. 2	Elemental Analysis of Bagasse & LDPE	19
Table No. 3	Proximate Analysis of 1:1 & 1:3 Blend	19
Table No. 4	Yield of Pyrolysis Products with temperature for Bagasse	22
Table No. 5	Yield of Pyrolysis Products with temperature for LDPE	24
Table No. 6	Yield of Pyrolysis Products for different ratio of Bagasse and LDPE	25
Table No. 7	Yield of Pyrolysis Products with temperature for different ratio of Bagasse and LDPE	26
Table No. 8	Water Content of Liquid Products	26
Table No. 9	Calorific Value of Liquid Products	27
Table No. 10	Result of FTIR of Bagasse	28
Table No. 11	Result of FTIR of LDPE	29
Table No. 12	Result of FTIR of 1:1 Blend	30
Table No. 13	Result of FTIR of 1:3 Blend	31
Table No. 14	GC – MS Analysis of Liquid product Bagasse, LDPE & Mixtures	33 – 35
Table No. 15	Uses of some of the major chemical compounds detected in 1:1 Blend	36 – 37

LIST OF FIGURES

Figure No.	Name	Page No.
Fig 1	Molecular structure of cellulose	5
Fig 2	Molecular structure of hemicellulose	5
Fig 3	Structural units of lignin	6
Fig 4	Structure of LDPE	11
Fig 5	LDPE	11
Fig 6	Bagasse	14
Fig 7	LDPE	14
Fig 8	Experimental Set-up	16
Fig 9	TGA Characteristics of Bagasse	21
Fig 10	TGA Characteristics of LDPE	21
Fig 11	Effect of Temperature on Yield of pyrolysis products of Bagasse	22
Fig 12	Effect of Temperature on Reaction Time of Bagasse	23
Fig 13	Effect of Temperature on Yield of pyrolysis products of LDPE	24
Fig 14	Effect of Temperature on Reaction Time of LDPE	24
Fig 15	FTIR Spectrum of Bagasse	28
Fig 16	FTIR Spectrum of LDPE	29
Fig 17	FTIR Spectrum of 1:1 Blend	31
Fig 18	FTIR Spectrum of 1:3 Blend	32
Fig 19	GC – MS of Bagasse	36
Fig 20	GC – MS of LDPE	36
Fig 21	GC – MS of 1:1 Blend	36
Fig 22	GC – MS of 1:3 Blend	36

ABSTRACT

This project was carried out to determine a simple method to produce high-grade pyrolysis oil by maximizing the use of biomass wastes. In this study, the results of pyrolysis of sugarcane bagasse alone are compared with pyrolysis of sugarcane bagasse and LDPE mixtures. Pyrolysis was carried out in a semi-batch reactor with different temperature range of 350 to 550 °C, different Biomass : Plastic ratio of 9:1, 3:1, 1:1 and 1:3, with heating rate of 20°C/min. The maximum pyrolysis liquid yield of sugarcane bagasse alone was 47.15% at 500 °C. Whereas, when the co-pyrolysis of sugarcane bagasse and LDPE was done yield of liquid product increased to 52.75% with 1:1 blend. The pyrolysis temperature was 500 °C and it was selected based on results from thermo gravimetric analysis of the studied samples. Due to the synergistic effect in the pyrolysis of the biomass/polymer mixtures, higher amounts of liquid products were obtained compared to biomass alone. The physical properties of the liquid obtained were determined by using standard test methods and the chemical composition was analyzed by using FTIR, GC-MS analyzer for its suitability as an alternate fuel.

CHAPTER 1 – INTRODUCTION

Energy is important, indirectly or directly, in the whole process of growth, evolution and survival of all life forms and it plays a crucial role in the overall development of a nation. Energy is a ‘strategic commodity’ and any inconsistency in its supply threatens the functioning of the developing countries’ economy, particularly. There is a key relationship between energy consumption and economic development, one is level of economic development which relies on energy demand whereas on the other hand, economic growth which depends upon availability of cost effective and eco-friendly energy sources.

1.1 Overall Background

In India, the demand for energy continues to rise in spite of slowing global economy, due to the rapid urbanization and outgrowth of population. The available energy sources are not sufficient to overcome the continuously increasing needs. The domestic energy production will meet around 71% by 2016-17 and 69% by 2021-22 of expected energy consumption, the rest to be imported, as projected by the Planning Commission, Government of India in the 12th Five Year Plan. ^[1] World energy demand will approximately increase 56% by 2040. ^[2] The major energy demand is fulfilled from the conventional energy resources like coal, petroleum and natural gas. These sources are in the verge of getting extinct. It has been estimated that the oil sources might get depleted by 2050.

In India, energy sector has witnessed revolutionary developments and rapid growth in areas like resource exploitation and exploration, energy sector capacity additions and reforms in order to meet its needs on its course of becoming a developed country. Still, because of the multiplying population, rapid urbanization and progressing economy India is lagging behind to meet its increasing energy demands. Indian economy is tremendously affected by these energy shortages.

1.2 Trends in Energy Resources

India is the 4th largest consumer of Crude Oil and Natural Gas in the world after United States, China and Russia in 2011-12. ^[3] Petroleum demand is expected to grow rapidly in the transport sector in the future with rapid rise growth ownership of vehicle. India’s energy reserve base is

limited, hence the nation relies on imports from other countries. Primary energy consumption between 1990 and 2011 more than just doubled.

1.3 Problem Statement

For the past couple of centuries we are relying more on fossil fuels. They boosted the industrial revolution. However, our reliance on fossil fuels will cause many problems in future. The fact is that we have a very limited amount of fossil fuels left with us, it will eventually get extinct in the near future.

The increase in demand of fossil fuels is yet another problem. As densely populated countries like India and China become more developed, they would consume a huge percentage of fossil fuels. The fuel price is going higher and higher day by day, which will tend to do great damage to the economies of the countries which are dependent upon fuel imports.

The extraction of fossil fuels from the ground as well its burning as a fuel source causes real environmental damage. The threat of global warming is alarming us to find ways to reduce the emissions, it also helped us in realizing the need for alternative energy sources.

1.4 Other alternative sources of energy

Various alternate sources of energy that can supplement the present day demand for energy are wind, solar, biomass, tidal and geothermal energy. The renewable energy generation in 2012 was 89774 MW in India which includes Wind - 54.73%, Hydro - 17.15%, Biomass - 19.54%.^[1]

Among the various renewable resources biomass is paying more attention because it's the 4th largest energy source worldwide contributing more than 14% of global energy supply. In India, biomass provides 32% of total primary energy and caters to almost 70% of the country's population.^[4] Besides that bio energy has three advantages: renewable, abundant and eco-friendly nature. So biomass is a good substitute for fossil fuels.^[5]

1.4 Solution Strategy

The utilization of biomass is important because of the increasing fuel price and depletion of fossil fuels reserves of fossil fuels accompanied by the environmental concern. Biological conversion and thermochemical conversion are two main paths for conversion of biomass into energy. Pyrolysis is an efficient way for conversion of biomass into fuel. Although its stability

is low due to high percentage of water and oxygen, but there are various methods for its up-gradation.

Synthetic polymers like Polypropylene, Polyethylene, Polyethylene Terephthalate, Polystyrene, Polyvinyl Chloride, etc. contain high amount of carbon and hydrogen. Therefore, biomass/plastic co-pyrolysis reduces the percentage of oxygen and increases its calorific value.

Co-pyrolysis is a suitable process to convert synthetic polymer and lingo-cellulosic materials into valuable feed, the advantages of which include waste reduction, chemical recovery and alternate source of fuel.

CHAPTER 2 – LITERATURE REVIEW

2.1 BIOMASS

Biomass is defined as organic material which are derived from plants or animals sources. In general it is difficult to find out the actual definition. Biomass is formed by the interaction of CO₂, water and sunlight. When a living being dies, microorganisms and bacteria break down the constituents into elementary components like H₂O, CO₂, and energy. Since, plants use the same the carbon dioxide at the time of photosynthesis, the amount of CO₂ does not increase in the earth. It is thus called greenhouse gas neutral or GHG neutral.

2.1.1 SOURCES OF BIOMASS

The common biomass sources are agricultural, forest, municipal and biological. The examples of sources are discussed below.

1. **Agricultural:** grains, bagasse, straw, nutshells, corn stalks, seeds and manure from poultry and cattle.
2. **Forest:** wood, sawdust
3. **Municipal:** sewage, food waste, paper waste
4. **Biological:** biological waste, aquatic species, animal waste,

2.1.2 TYPES OF BIOMASS

The whole biomass is categorized into two different groups:

1. **Virgin biomass:** It includes plants, wood, crops, leaves and vegetables.
2. **Waste biomass:** It includes municipal waste, human waste and agricultural waste.

2.1.3 CONSTITUENTS OF BIOMASS

The major constituents of biomass are cellulose, hemicelluloses and lignin.

Cellulose

The primary organic component of cell wall is cellulose. It is represented by generic formula (C₆H₁₀O₅)_n. It is crystalline in nature, resistant to hydrolysis, a large molecular weight (~500,000) due to the presence of a long chain polymer having high degree of polymerization (~10,000). Cellulose is primarily composed of d-glucose, which is made of six carbons.

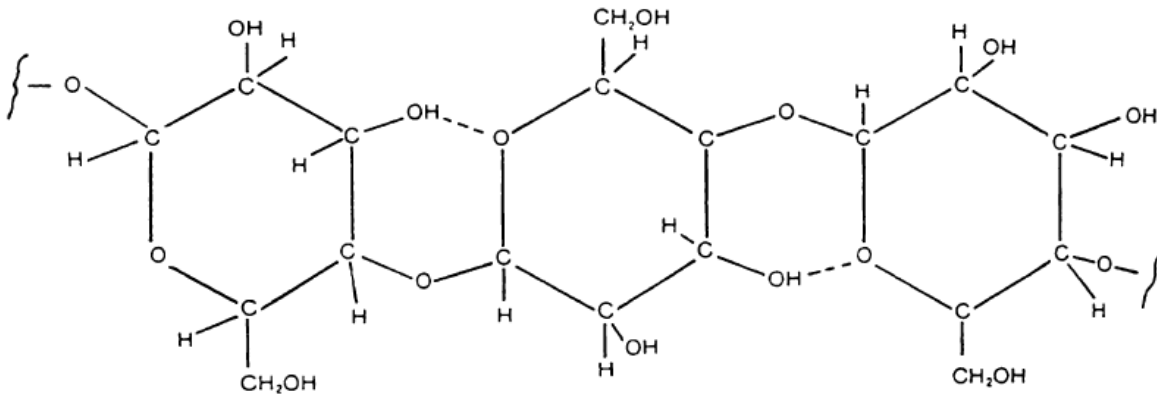


Fig 1. Molecular structure of cellulose

Hemicellulose

Hemicellulose is also one of the constituents of cell wall. It is represented by the generic formula $(C_5H_8O_4)_n$. It has a branched chain structure with groups of carbohydrates and a lower degree of polymerization (~100–200). The composition and structure of hemicelluloses varies from biomass to biomass. Most of the hemicelluloses contain D-xylose, D-galactose, D-glucose, D-glucuronic acid, D-mannose and D-arabinose. These typically contain 50 to 200 units in their branched structures. It can be hydrolysed by base or acids. The presence of hemicelluloses yields more gases than cellulose during decomposition.

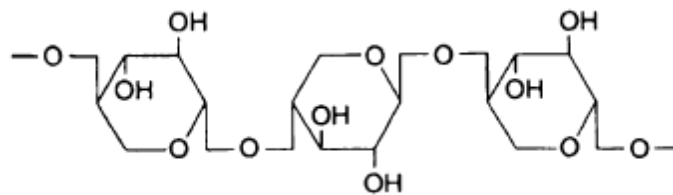


Fig 2. Molecular structure of hemicellulose

Lignin

The third important constituent of woody biomass is lignin, which is complex in nature, highly branched polymer of phenyl propane. It is a three dimensional polymer. Lignin is the binding agent for cellulose. It is highly insoluble, it does not even dissolve in sulphuric acid.

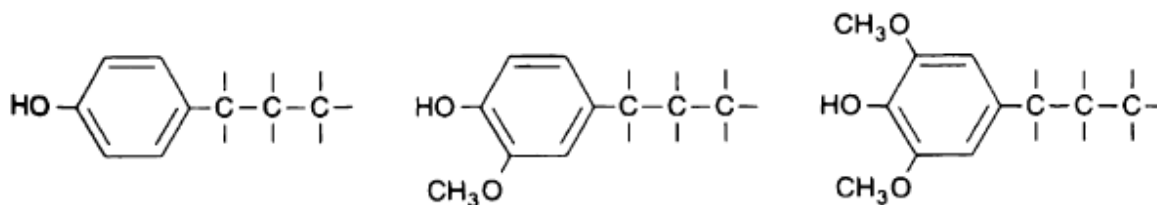


Fig 3. Structural units of lignin

2.2 BIO-FUEL

Bio-fuels are obtained from living organisms. The fuel should consist of more than 80% renewable materials to be considered as a bio-fuel. The term bio-fuel covers solid biomass, liquid fuels and gaseous fuel. Solid bio-fuel includes sawdust, wood, domestic refuse, agricultural waste, charcoal and dried manure where biodiesel, bio-alcohol, bio-ether, pyrolytic oil are liquid bio-fuel and syngas and bio gas are gaseous bio-fuel.

The yields of solid, liquid and gaseous products varies with variation in pyrolysis temperature or heating rate. Higher yields of volatiles are obtained when the sample is rapidly heated, while slow heating process yields more reactive char. When the residence time is increased secondary char is produced by the reaction of primary char and volatiles.

2.3 TYPES OF PYROLYSIS

The process pyrolysis occurs in three different ways, namely fast pyrolysis, slow pyrolysis and flash pyrolysis.

1. Fast pyrolysis

In fast pyrolysis process the feed stock is rapidly heated (high rate of heating) in absence of oxygen at high temperature. During the decomposition, vapours and char are formed. After condensation of the vapours, a dark brown liquid is obtained. Fast pyrolysis is an advanced process which can be controlled to produce higher yields of liquid products. Fast pyrolysis process produces 60-75% liquid bio-oil, 15-25% char and 10-20% non-condensable gases. The bio-oil and char can be used as source of fuel and the non-condensable gases can be recycled back in the process.

2. Slow pyrolysis

In slow pyrolysis, pyrolysis is carried out at a slow heating rate of 5-10 °C/min. In this process yield of char increases and bio-oil yield decreases.

3. Flash Pyrolysis

In flash pyrolysis the reaction time is in the range of 30 – 1500 ms. This process increases the amount of liquid product decreasing the char amount. Upon cooling, the condensable vapor is then condensed into a liquid fuel known as bio-oil. Such an operation increases the liquid yield (70 – 75%) while reducing the char production. There are four different methods of flash pyrolysis viz, flash hydro-pyrolysis, solar flash pyrolysis, vacuum flash pyrolysis and rapid thermal process.

2.4 FACTORS AFFECTING PYROLYSIS LIQUID YIELD

The yield of liquid product depends upon the following factors:

- ❖ Design of reactor
- ❖ Type of biomass
- ❖ Heating rate
- ❖ Pyrolysis temperature
- ❖ Residence time in the reactor
- ❖ Pressure
- ❖ Presence of catalysts

2.5 APPLICATION OF PYROLYSIS PRODUCTS

The application of the common products obtained from pyrolysis of biomass is given below:

2.5.1 Application of pyrolysis oil

The bio-oil obtained from pyrolysis can have the following industrial applications:

- ❖ fuel
- ❖ power generation
- ❖ extraction of chemicals and resins
- ❖ production of laevoglucose
- ❖ binding agents
- ❖ blending with diesel
- ❖ bio-oils can be used in making adhesives

2.5.2 Application of gas

Pyrolysis gas consists of carbon dioxide, methane which can be used as fuel for combustion.

2.5.3 Application of char

The char obtained has following applications:

- ❖ Solid fuel in boilers after briquetting
- ❖ Production of activated carbon.
- ❖ For gasification process to obtain hydrogen rich gas.

2.6 Upgrading of Bio-Oil

The properties of bio-oil like high viscosity, corrosiveness and thermal instability are hindrance for substitution of fossil fuels. So, the up-gradation process is required which involves reduction of oxygen content. The various upgrading techniques are:

a. Hydrodeoxygenation

The hydrodeoxygenation process is carried out in solvents which provide hydrogen. They are activated by catalysts like Ni-Mo, Co-Mo and their oxides on aluminium oxide (Al_2O_3) under pressurized condition of hydrogen or CO or both. Oxygen is removed as water and carbon dioxide hence, the calorific value of bio-oil increases.

Pindora et al ^[6, 7] hydro-treated the volatile fraction from fast pyrolysis of eucalyptus using a two stage reactor. The first stage operated without catalysts and with catalysts in the second stage. The deactivation of catalyst did not result due to carbon decomposition, instead the activated sites of zeolite catalyst was blocked by the volatile components. This hydro process produced much water bio-oil got complicated with many impurities.

Zhang et al ^[8] hydro-treated the oil phase of bio-oil catalysed by Al_2O_3 with sulphide Co-Mo-P. The oxygen content of bio-oil decreased from 41.8% to 3% besides, the bio-oil was methanol soluble while the upgraded oil was oil soluble.

Apparently complicated instruments, excess cost and superior techniques are required in the hdro-treating process and usually is stopped by reactor clogging and catalyst deactivation.

b. Catalytic Cracking of Pyrolysis Liquids

Bio-Oils containing oxygen are catalytically decomposed to hydrocarbons with the removal of oxygen as CO_2 , CO or H_2O .

Adjaye and Bakshi et al ^[9, 10] studied the catalytic performance of different catalysts for upgrading bio-oil. HZSM-5 was the most effective catalyst among the five catalysts studied, for producing organic distillate fraction, aromatic hydrocarbons, overall hydrocarbons and lest coke formation.

Although, this method is regarded as a cheaper route by conversion of oxygenated feed stocks into lighter fractions, the results are not promising due poor quality and high coking (8 – 25%) of fuels obtained.

c. Emulsification

The simplest way of using bio-oils as a transportation fuel is to directly combine it with Diesel. Although, they are immiscible in hydrocarbons but, they can be emulsified with the aid of surfactants.

Chiaramonti et al ^[11, 12] prepared emulsified bio-oils in the ratios of 25, 50 and 75 weight % and found that emulsions were more stable than the original bio-oils.

Ikura et al ^[13] separated light fractions of bio-oils by centrifugation and emulsified them in Diesel by CANMET surfactant in the ratios of 10, 20 and 30 weight %. The viscosity of 10-20 weight % emulsions were much lower than that of original bio-oil, and their corrosiveness was about half of bio-oil.

Emulsification does not demand expendable chemical transformations, but high cost and energy consumption can't be neglected.

d. Steam Reforming

Hydrogen is source of clean energy and very important gas in the chemical industry. The focus on reforming water fraction of bio-oils looks very much promising.

Czernik et al ^[14] obtained hydrogen from carbohydrate derived fraction of wood pyrolysis oil in a fluidized bed reactor with a theoretical yield of about 80%, which means approximately 6 kg of hydrogen from 100 kg of wood pyrolysis.

Takanabe et al ^[15] completely converted acetic acid by steam reforming over Pt/ZrO₂ catalysts and a hydrogen yield close to thermodynamic equilibrium was found.

e. Chemicals extracted from the Bio-Oils

Hundreds of components of bio-oil are determined and different kinds of small and valuable chemicals. There are many chemicals which can be extracted from bio-oils like phenols, volatile organic acids, additives applied in pharmaceuticals, fertilizer industry, fibre synthesizing and flavouring agents. ^[16, 17] Commercialization of these special chemicals from bio-oils requires reliable and low cost refining and separation techniques.

2.7 SUGARCANE BAGASSE

Bagasse is the fibrous residue left after extraction of juice from sugarcane. It is used in the manufacture of pulp and as boiler feed. Since it is a by-product of sugar industry, the production

depends upon the cultivation of sugarcane. Bagasse is an extremely non-homogeneous.^[18]
The composition of bagasse is shown in Table 1

Table 1. Major Constituents of Bagasse

Constituent	Mass %
Cellulose	45 – 55
Hemicellulose	20 – 25
Lignin	18 – 24
Ash	< 1

Sugarcane is the world's largest agricultural crop. There are over 1200 sugarcane factories in 80 countries located in in tropical and sub-tropical parts of the world. Crushing 1000 kg of sugarcane produces approximately 255 of moist bagasse (50 wt% moisture content). India is the second largest producer of sugarcane in the world with 342,382 TMT after Brazil. The major sugarcane producing states in India are Uttar Pradesh, Maharashtra, Orissa, Karnataka and Tamil Nadu. ^[4]

Manuel Garcia Perez et al ^[19, 20] found out that with 15% of PR mixed with bagasse maximum charcoal and minimum oil yields were obtained. The bio-oil obtained with upto 15% PR were stable emulsions and from the 30% PR an unstable emulsion was produced. However, the bio-oil obtained at 50% PR was again stable.

2.8 LOW DENSITY POLYETHYLENE

Low Density Polyethylene (LDPE) is a thermoplastic made from ethylene monomer. It was produced in 1933 by Imperial Chemical Industries as the first grade of polyethylene via free radical polymerization using a high pressure process. ^[21]

LDPE consist of the polymerized units of the monomer ethylene with repeating (C₂H₄) units. It is commonly recycled and has the number '4' as its recycling symbol. It has the chemical formula – (C₂H₄)_nH₂.

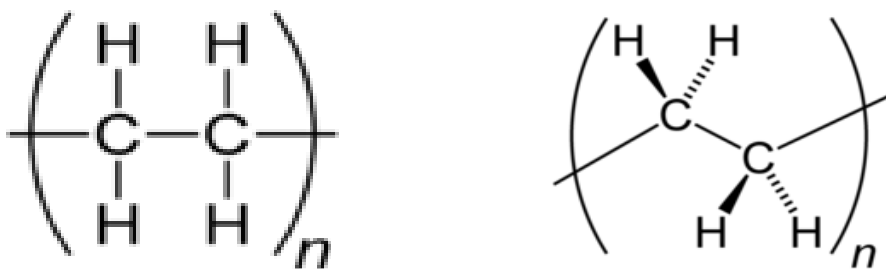


Fig 4. Structure of LDPE



Fig 5. LDPE

LDPE has more branching than HDPE, so its intermolecular forces are weaker. Also, since its molecules are less crystalline and less tightly packed because of the side branches, it has a lower density. Its density ranges from 0.910 g/cm³ to 0.940 g/cm³. It has low tensile strength and high resilience. It is non-reactive at room temperature, although strong oxidizing agents and some solvents cause swelling. It is made in opaque or translucent variations, it is quite flexible and tough but breakable. It can withstand temperature of 80 °C continuously and 95 °C for short duration.

It is widely used in the manufacturing of containers, wash bottles, dispensing bottles, plastic bags for computer components and molded laboratory equipment. It is most commonly used as plastic bags.

2.9 CO-PYROLYSIS OF BIOMASS AND PLASTIC

It has been suggested by many researchers that with co-pyrolysis of biomass with synthetic polymer the yield and quality of pyrolysis liquid increases as they act as good hydrogen source during pyrolysis which leads to the decrease in oxygen content of the product.

Mihai Brebu et al ^[22] reported that co-pyrolysis of pine cone and PP, PS and PE gave polar oxygenated compounds. The char obtained after co-pyrolysis had higher calorific value than biomass pyrolysis.

V I Sharypov et al ^[23] found out that the optimum temperature for biomass/plastic co-pyrolysis was 400 °C. for 20/80 weight ratio of biomass/aPP the yield of liquid product was about 40%.

N Marin et al ^[24] concluded that Low Beech–a-PP ratio (0.25) produced substantial amount of benzene.

Cao et al ^[25] reported that a great deal of free radical species were generated by the biomass pyrolysis and they suppress the formation of undesired matters and high molecular compounds.

Cornelissen et al ^[26, 27] investigated co-pyrolysis of PLA and biomass. The advantages of co-pyrolysis were low water content of bio-oil, high calorific value and yield of liquid products

Piotr et al ^[28] testified co-pyrolysis of cellulose/polystyrene improves the quality of the bio-oil. The bio-oil had low acid value, density and pour point. The fraction of hydrocarbons increases with the decrease in cellulose/PS ratio.

Priyanka et al ^[29] investigated PS, HDPE and PP. They were co-pyrolyzed individually with pine wood at 525 °C, 450 °C and 450 °C, respectively. The liquid product had higher carbon and hydrogen contents, calorific value and significantly lower water content, viscosity and acid values than pine bio-oil.

CHAPTER 3 – OBJECTIVE OF THE WORK

1. To investigate the decomposition behavior of sugarcane bagasse and Low Density Polyethylene (LDPE) by using thermo-gravimetric analysis.
2. To study the co-pyrolysis of sugarcane bagasse and Low Density Polyethylene (LDPE) with different ratios using various parameters.
3. To characterize the product obtained from co-pyrolysis of sugarcane bagasse and Low Density Polyethylene (LDPE) with their various chemical properties (GC-MS, FTIR, CHNS) and physical properties (Calorific Value, Water Content)

CHAPETR 4 – MATERIALS & METHODS

4.1 Materials

The raw material to be used is sugarcane bagasse which is collected from the 'Sakti Sugar Ltd., Cuttack Road, Bhubaneshwar, Orissa'. The raw material was in the form of fibres, it was dried at 40 °C for 24 hours and then crushed. The dried bagasse was then sieved. The size range of the biomass feed was 0.500 – 0.853 mm (-18 + 30 BSS Mesh Size).



Fig 6. Bagasse

Low density polyethylene was collected from 'Blowing Towers Private Ltd., Rourkela, Orissa'. The size of the LDPE grains was ≈ 2 mm.



Fig 7. LDPE

4.2 Methods

4.2.1 Thermo – Gravimetric Analysis

Thermo gravimetric analysis is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate) or as function of time (with constant temperature and/or constant mass loss). It is used to determine the characteristics of materials due to decomposition or loss of volatiles. In order to eliminate the temperature gradients within the samples small samples (10 – 20 mg) are used. The low heating rates (1-50 °C/min) are studied in normal TGA equipment and hence the conditions are similar to slow pyrolysis. Derivative Thermo-gravimetry (DTG) is also applied to TGA data, to determine the rate of weight loss as a function of temperature. The TGA and DTG data can be used to obtain kinetic parameters and devolatilization behaviour of biomass. The single component modelling for biomass is not adequate because of its complex nature.

4.2.2 Proximate Analysis

Proximate analysis is used to determine the characteristics of carbonaceous materials that is used as precursor for active carbons. Proximate analysis includes moisture content, volatile matter content, fixed carbon content and ash content. It was carried out using *ASTM D3172 - 07a* method. ^[30] The decomposition of char carbon is catalyzed by high moisture content, resulting in very low yield of the carbon. The ash content is the inorganic residue left after the burning of organic matter. The volatile matter consists of mixture of liquid and gaseous products resulting from the thermal decomposition of the sample. The fixed carbon indicates the proportion of solid carbon in final carbonization product.

4.2.3 Ultimate Analysis

Ultimate analysis is used to determine the elemental composition of the sample. The CHNSO Elemental Analyzer determines the carbon, hydrogen, nitrogen and sulphur percentage. The remaining amount is oxygen percentage.

4.2.4 Experimental Procedure

The experimental set-up consisted of a reactor furnace system in which the temperature of the furnace was maintained using a PID Controller. A condenser was attached at the outlet of the reactor, to condense the vapours coming out of it. Water was circulated as cooling liquid in the condenser using a pump. The raw was fed into the reactor which was then kept inside the

furnace for heating. The furnace was programmed to attain the temperature at which maximum yield of oil is obtained, at a specified heating rate. When the reaction starts, vapours coming out of the reactor condensed into liquid in the condenser and collected in a container however, there were some amount of non-condensable gases present which simply escaped into the surrounding. The liquid product collected was a two phase solution of heavy oil and light oil along with the water.

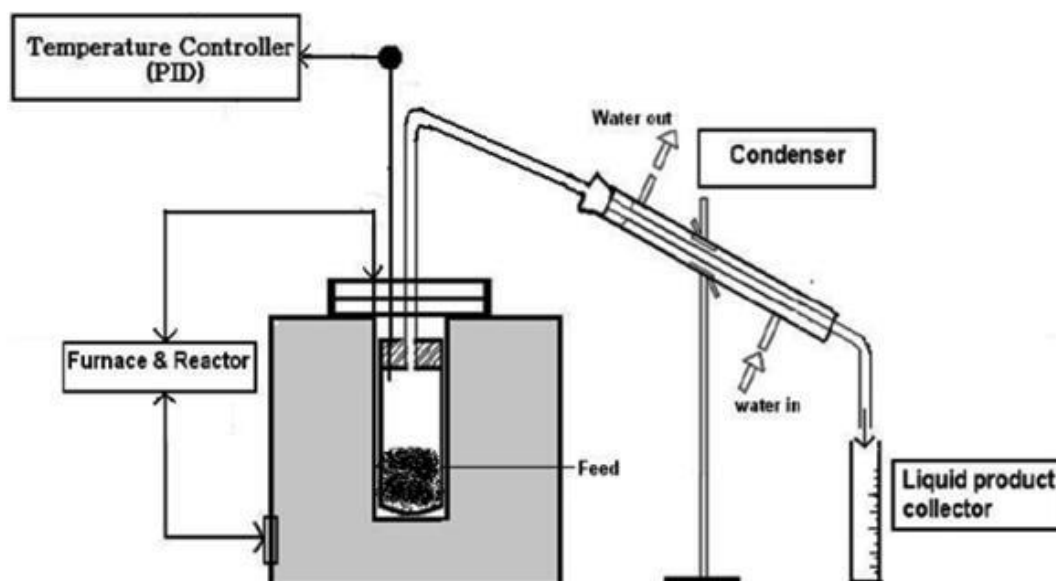


Fig 8. Experimental Set-up

4.2.5 Reactor Specification

The reactor used for pyrolysis was a semi batch reactor made up of stainless steel of length 16.5 cm, 4.7 cm internal diameter and 5 cm outer diameter an outlet tube was attached at top end and bottom end was sealed.

4.2.6 Sample Pyrolysis Runs

Once temperature range was found the pyrolysis was done using 20 gm of material at different temperatures and yield of liquid product and char were noted down. The graphs for variation of yield with various temperatures were plotted.

4.2.7 Water Content of Pyrolysis Liquids

The water of bio-oils were determined by distillation method using Dean and Stark Apparatus (IP 74/82, ASTM D95-83).^[30] After removal of water from the bio-oils they were analysed.

4.2.8 GC – MS Analysis of Pyrolysis Liquids

Gas chromatography – Mass Spectroscopy is an analytical method that combines the feature of gas – liquid chromatography and mass spectroscopy to identify different substances within a test sample.

For GC-MS the sample was first dissolved in n-Hexane in the ratio of 1:20 and a clear solution was obtained. The solution was then filtered using 2 micron membrane filter.

4.2.9 FTIR Analysis of Pyrolysis Liquids

Fourier Transform Infra-Red Analysis is done to identify the functional groups present in the sample. FTIR analysis is an analytical method based on the interactions between Infra-Red light and the sample. When molecules vibrating at their characteristics frequencies are exposed to IR radiations, the molecule absorbs IR energy only at resonance frequencies (when frequency of vibration of IR energy and molecules natural frequency match). As a result, the absorption pattern of a molecule is unique. The frequency of vibration of molecule is directly related to the structure of the molecule and nature of atoms. The absorption intensity is correlated to the concentration of molecules and to the change of dipole moment due to vibration. The symmetrical molecules which do not exhibit any change in their dipole moment due to vibration can't be identified by FTIR for e.g., O₂, N₂, H₂, Ar, He, etc.

The FTIR Spectroscopic Analysis was done using Perkin Elmer Infra-Red Spectrometer.

4.2.10 Calorific Value of Pyrolysis Liquids

The calorific value is the energy released in the form of heat when a substance undergoes complete combustion in the presence of oxygen under standard conditions releasing carbon dioxide and water. The calorific value is measured with the Bomb Calorimeter. Gross Heat Value accounts for water leaving as vapour in the exhaust and it also includes liquid water in the fuel prior to combustion. This value is important to fuels containing some amount of water prior to burning.

The calorific value of the bio-oil was determined using Parr 6100 Calorimeter.

CHAPTER 5 – RESULTS AND DISCUSSIONS

5.1 Characterization of raw materials

5.1.1 Proximate analysis and Ultimate analysis of Sugarcane bagasse and LDPE

Proximate analysis is one of the easiest ways to study the fuel characteristic of solid materials. Moisture, volatile matter and ash results are typically among the primary parameters used for assessing the quality of solid fuel material. High moisture content affects the conversion efficiency and heating value of biomass and has a potential to deteriorate its energy quality during storage as a result of decomposition. Higher value of ash content also has negative affect on the heating value. High volatile content indicates the product yield on carbonization and provides the additional information on combustion characteristic of the material. As it can be observed in Table 2, sugarcane bagasse and LDPE has very high volatile matter content of 84% and 100% respectively, therefore these materials can be used as a good source of energy. The elemental composition by ultimate analysis, in terms of carbon, hydrogen, nitrogen, oxygen and sulfur content of the selected material is essential for their pyrolysis conversion, upon which the pyrolysis product quality depends. The obtained carbon and hydrogen percentage in plastic material is more than that of the sugarcane bagasse; the oxygen percentage of biomass sample is 31.73% received as by difference, whereas the oxygen content of plastic is quite less. Calorific value of SB is less than that of coal whereas calorific value of plastic is relatively more than that of SB and coal.

Table 2. Proximate Analysis and Ultimate Analysis of Bagasse & LDPE

Characteristics	Bagasse	LDPE
Moisture Content	4.5	0
Volatile Matter	84	100
Fixed Carbon	6	0
Ash	5.5	0
C	56.16	84.627
H	3.512	14.407
N	6.213	0.044
S	2.380	0
O	31.73	0.234
Calorific Value (cal/g)	4400.54	11035.72

Table 3. Proximate Analysis of 1:1 & 1:3 Blend

Characteristics	1:1	1:3
Moisture Content	2	1
Volatile Matter	91	95
Fixed Carbon	5	2
Ash	2	1

5.1.2 Thermo-gravimetric analysis of sugarcane bagasse and plastic (LDPE)

Thermo-gravimetric analysis (TGA) is one of the most common techniques used to investigate the thermal decomposition characteristic of solid raw materials such as coal, biomass and plastic. It provides a measurement of weight loss of the sample as a function of time and temperature. The decomposition characteristic of SB and LDPE samples are given in the Fig 9. From the TGA curves it can be seen that weight loss increased with the increase in pyrolysis temperature for both the samples. By comparing TGA curves, it can be obviously observed that bagasse and LDPE samples have different thermal behaviour trends due to their structural difference.

It is generally accepted that the decomposition of biomass involves three main stages such as drying of moisture, degradation of unstable polymers and continuous slight devolatilisation. [31, 32] .

It can be seen that the bagasse sample started decomposing at a much lower temperature than LDPE. The TGA curve of bagasse shows that there are three stages of decomposition which happens due to various composition of biomass which consists of moisture, cellulose, hemicellulose and lignin. In the first stage the decomposition of bagasse started at room temperature up to 142°C with 5.5% weight loss which indicated that release of inherent water and hydrolysis of some extractives. In the intermediate stage, cellulose and hemicellulose which are the main constituent of biomass decomposes within the temperature range 200°C to 380°C and 61.13% weight loss was obtained. The final stage is the most complicated as lignin the most complex structural fraction of the biomass began to decompose. This stage is most vital for the pyrolysis mechanism as it leads to charcoal formation. In the temperature range of 380°C to 430°C weight loss of 21.9% was observed. After that a constant weight loss of biomass occurred up to 500°C because of some extractive and non-combustible material present in biomass material. From the previous study it was proved that in the temperature range of 280°C to 500°C, depolymerisation reaction occurs which is predominated by the integration of bonds causing the formation of liquid products containing a wide variety of organic compounds. [32, 33] .

Similarly, from the TGA curve of LDPE in Fig 10 it can be noticed that the decomposition of LDPE occurred in a single stage with higher temperatures as compared to bagasse and also the plastic decomposition is completed in short interval of temperature. However the maximum decomposition of LDPE occurred in the temperature range of 300°C to 450°C and no further decomposition was observed after this temperature.

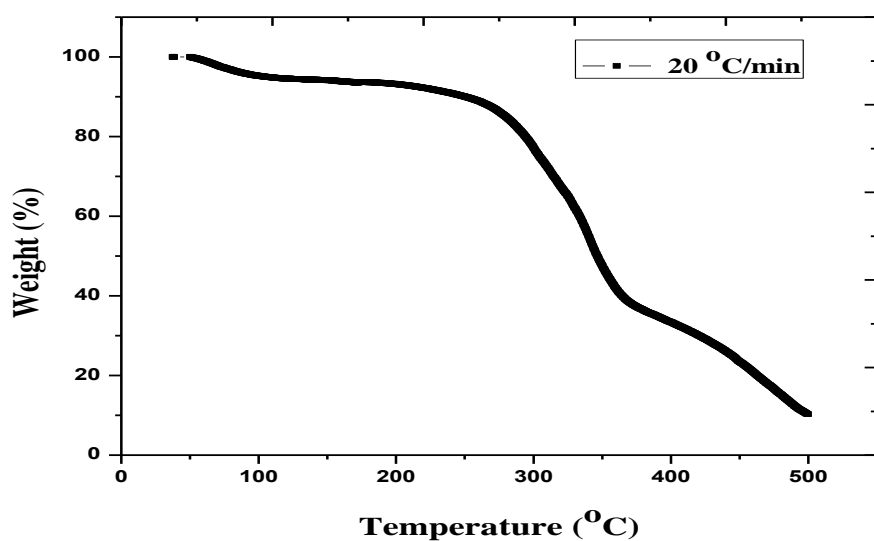


Fig 9. TGA Characteristics of Bagasse

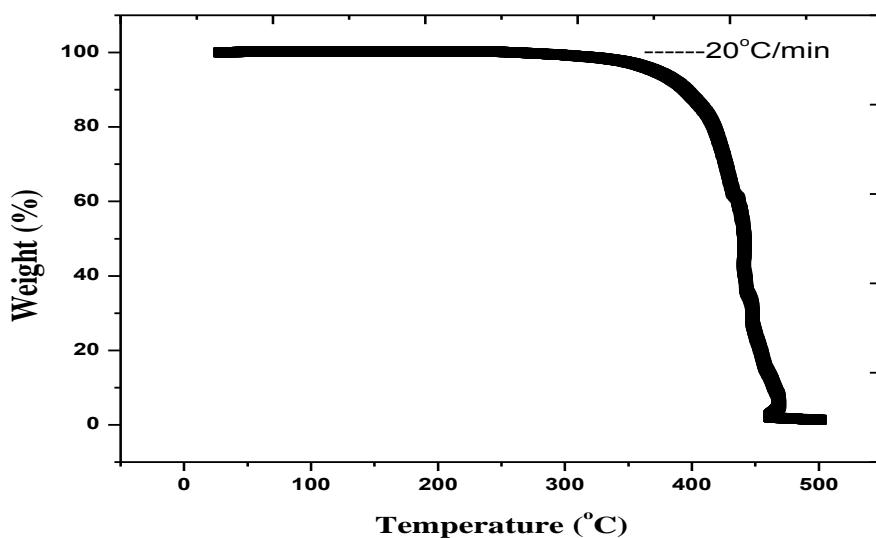


Fig 10. TGA Characteristics of LDPE

5.1.3. Effect of temperature on reaction time and yield of pyrolysis products of sugarcane bagasse

The various product yields obtained from the pyrolysis of sugarcane bagasse at different temperatures with average heating rate of 20°C/min using semi-batch reactor are given in Fig 11. Pyrolysis temperatures were selected according to the results of TG analysis. From the figure it is clearly evident that when the temperature increases from 350°C to 500°C the yield of liquid product increased to a maximum value of 47.15% at 500°C. At this temperature strong cracking takes place inside the reactor and complete decomposition occurs since it is

maximizing the liquid yield. The gas yield increased over the whole temperature range which is probably due to the decomposition of some liquid vapours into non-condensable gases. The decrease in char yield at higher temperature is consistent with the increase in the volatile matter. However secondary tar destruction at the higher temperature causes the decrease in liquid yield while the gas and total conversion increases. It can be easily recognized that 500°C is the convenient pyrolysis temperature. With increase in temperature reaction time is decreases.

Table 4. Yield of Pyrolysis Products with temperature for Bagasse

Temperature (°C)	% Liquid	% Char	% Vapour	Reaction Time (min)
350	37.65	46.75	15.60	76
375	39.65	42.95	17.40	72
400	44.15	37.50	18.35	69
425	45.15	32.35	22.50	65
450	45.85	30.90	23.25	61
475	46.40	29.95	23.5	58
500	47.15	28.30	24.55	55
550	43.55	26.30	30.05	48

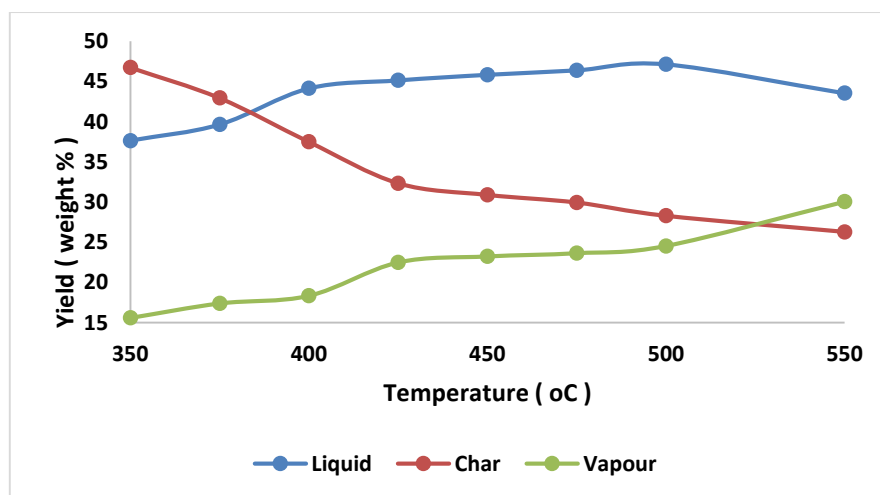


Fig 11. Effect of Temperature on Yield of pyrolysis products of Bagasse

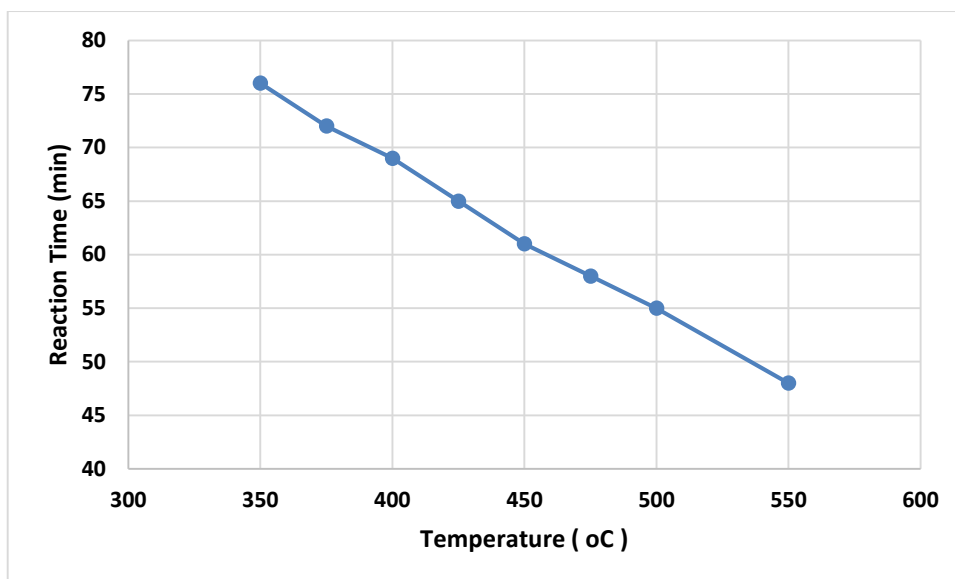


Fig 12. Effect of Temperature on Reaction Time of Bagasse

5.1.4 Effect of temperature on reaction time and yield of pyrolysis products of LDPE

The effect of pyrolysis parameters such as temperature and reaction time on the product yield of pyrolysis was investigated. The yields of each fraction obtained in the pyrolysis process are shown in Table 5. It was found that the yield of liquid product gradually increases with the increase in temperature and it increased to 74.40% at 500°C. The growing yield of volatile components (gases and liquids) could be caused by the differences in the thermal stability of polymer chains. Both the linear and branched hydrocarbons have decreasing thermal stability with increasing temperature.

Therefore at 500°C the C=C bonds cracked more likely than at lower temperature and this resulted in higher yields of volatile products. With increase in temperature char yield decreased. Subsequently, yield of gaseous products with increasing pyrolysis temperature is irregular. The reaction time decreased with increasing temperature.

Table 5. Yield of Pyrolysis Products with temperature for LDPE

Temperature (°C)	% Liquid	% Gas	% Char	Reaction time (min)
450	68.75	20.5	10.75	120
500	74.40	20.7	4.9	90
550	65.25	31	3.75	75
600	60.60	36.9	2.5	55

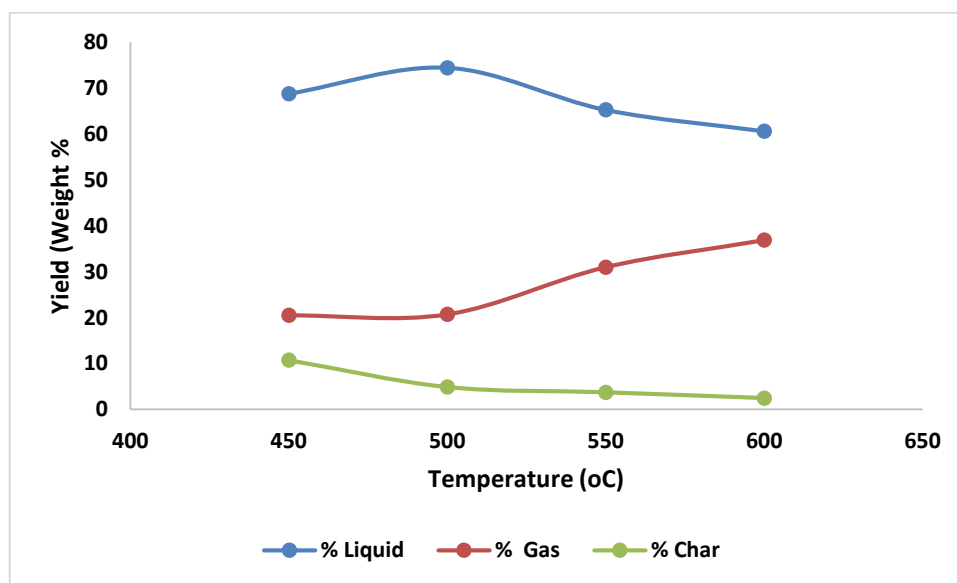


Fig 13. Effect of Temperature on Yield of pyrolysis products of LDPE

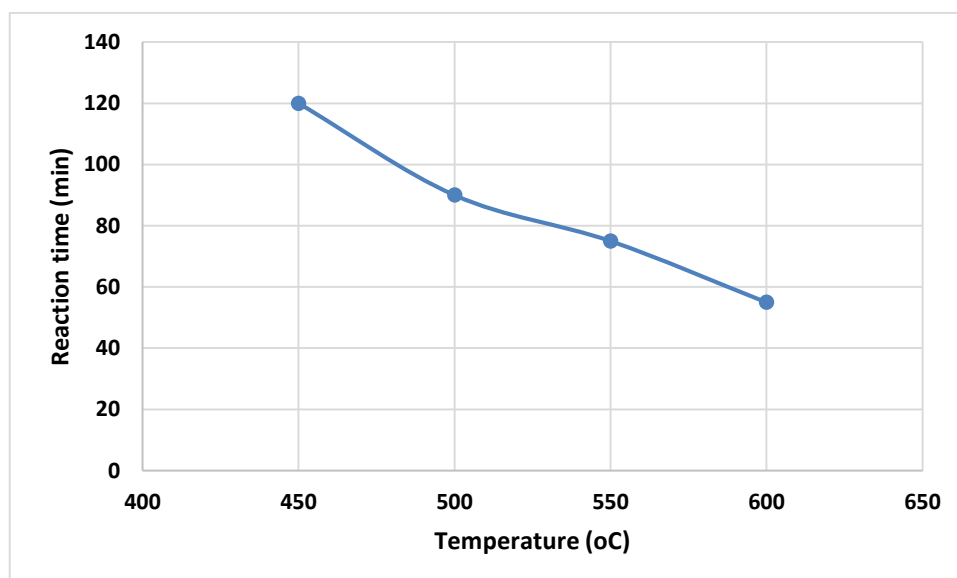


Fig 14. Effect of Temperature on Reaction Time of LDPE

5.1.5 Effect of different blends of sugarcane bagasse and LDPE on reaction time and yield of pyrolysis products

Figure 2 shows the product yield of sugarcane bagasse and LDPE thermal co-pyrolysis with different feed ratios of 9:1, 3:1, 1:1 and 1:3 at 500°C temperature. The 1:1 blend produced around 52.75% of liquid yield which may be because the addition of LDPE is playing an important role in the rise of liquid production. It is clear from Table 6 that an increase in plastic ratio leads to a decrease in the residual char yield. It means that the conversion degree of the biomass and plastic mixtures is increased. The gas yield also increased with the addition of LDPE because of the secondary decomposition reaction of the liquid fraction into non-condensable gases and the stabilization of radicals by hydrogen released from the LDPE. Also, it has been suggested by previous literature that synthetic polymer is an excellent hydrogen source hence it could provide hydrogen during thermal co-processing with biomass which can lead to an increase in the liquid yield. ^[34] Reaction time increases with increase in the ratio of the plastic.

Table 6. Yield of Pyrolysis Products for different ratio of Bagasse and LDPE

Ratio	Temperature (°C)	% Liquid	% Char	% Gas	Reaction time (min)
9:1	500	37.25	32.40	30.35	69
3:1	500	37.25	26.95	35.80	73
1:1	500	52.75	10.1	37.15	78
1:3	500	46.85	12.95	40.20	85

5.1.6 Effect of temperature on product yield of co-pyrolysis of sugarcane bagasse and LDPE

From figure it can be observed that 500°C is the suitable pyrolysis temperature. The maximum liquid yield of 52.75% and 46.85% were obtained with 1:1 and 1:3 blend, respectively. So, the liquid obtained by co-pyrolysis of 1:1 blend has been used for further characterization.

Table 7. Yield of Pyrolysis Products with temperature for different ratio of Bagasse and LDPE

Ratio	Temperature (°C)	% Liquid Product	% Char	% Vapour	Residence Time (min)
1:1	475	39.90	14.65	45.45	83
1:1	500	52.75	10.1	37.15	78
1:1	525	44.00	14.10	41.90	70
1:3	450	39.80	7.55	52.65	92
1:3	500	46.85	12.95	40.20	85
1:3	550	34.80	5.95	59.25	80

5.2 Characterization of liquid product

5.2.1 Water content of pyrolysis liquid product

Due to the relatively high percentages of water in the liquid product, the water content of the sugarcane bagasse pyrolysis liquid and co-pyrolysis liquid of 1:1 and 1:3 blends of sugarcane bagasse and plastic is measured using the Dean-Stark method. Around 5–10 ml sample is introduced into a 250 ml flask together with approximately 60 ml toluene. Water is separated from the sample under azeotropic conditions into a calibrated reservoir, indicating the amount of water present in the sample. Table 8 indicated that the water percentage of pyrolysis liquid obtained from sugarcane bagasse is higher than that obtained from co-pyrolysis.

The water content of bio-oils are shown in table 7

Table 8. Water Content of Liquid Products

Material	% Water Content
Bagasse	33.33
1:1 (Bagasse : LDPE)	18.18
1:3 (Bagasse : LDPE)	7.14

5.2.2 Calorific Value of pyrolysis liquid of sugarcane bagasse and 1:1 blend

From Table 8, it can be summarized that the addition of plastic clearly showed an additional increase in the calorific value of pyrolysis liquid produced from sugarcane bagasse/LDPE (1:1) blends compared to the pyrolysis liquid of sugarcane bagasse .

Table 9. Calorific Value of Liquid Products

Sample	Gross Calorific Value
Bagasse	8491 cal/g
1:1 (Bagasse : LDPE)	9420 cal/g

5.2.3 FTIR analysis of pyrolysis liquid

FTIR spectroscopy provides information about the functional groups present in a molecule such as COR, COOR, CN, NO₂, etc. This method of spectroscopy does not provide information regarding the location or connectivity of these functional groups. It also helps to determine the structural and compositional changes in the pyrolysis liquid. The formation of new type of compounds can also be detected from FTIR spectrum. The functional groups which were detected in FTIR for different pyrolysis liquid are shown in Table 10, 11, 12 & 13. From co-pyrolysis liquid it was identified that acyl halides and esters were formed which were not present in liquid product of individual pyrolysis of bagasse and LDPE. The alkynes which were present in pyrolysis liquid of bagasse and LDPE was not identified in the co-pyrolysis liquid of both blends indicating that it gets converted into more saturated hydrocarbons. Most of aliphatic compounds were present in pyrolysis liquid of LDPE as compared to sugarcane bagasse pyrolysis liquid. The amines (C-N) were also not present in the blend. So it can be concluded that it gets transformed to different type of compounds during co-pyrolysis. The liquid product obtained from blends consisted mainly of organic aromatic hydrocarbons like alcohols, phenols and carboxylic acid derivatives.

Table 10. Result of FTIR of Bagasse

Wavelength	Wavelength Range	Functional Group	Class of Compounds
3437.91	3400 - 3500	N-H (primary amines)	Amines
2924.24	2850 – 3000	CH ₃ , CH ₂ & CH	Alkanes
2093.57	2000 - 2250	C≡C	Alkynes
1711.91	1710 – 1720	C=O	Saturated Ketone
1513.77	1500 – 1560	N-H (secondary amines)	Amines
1379.80	1330 – 1430	O-H bending (in-plane)	Alcohols & Phenols
1270.38	1210 – 1320	O-C (acids)	Carboxylic Acids & Derivatives
1052.34	1000 – 1250	C-N	Amines
720.04	720 – 725	CH ₂	Alkanes

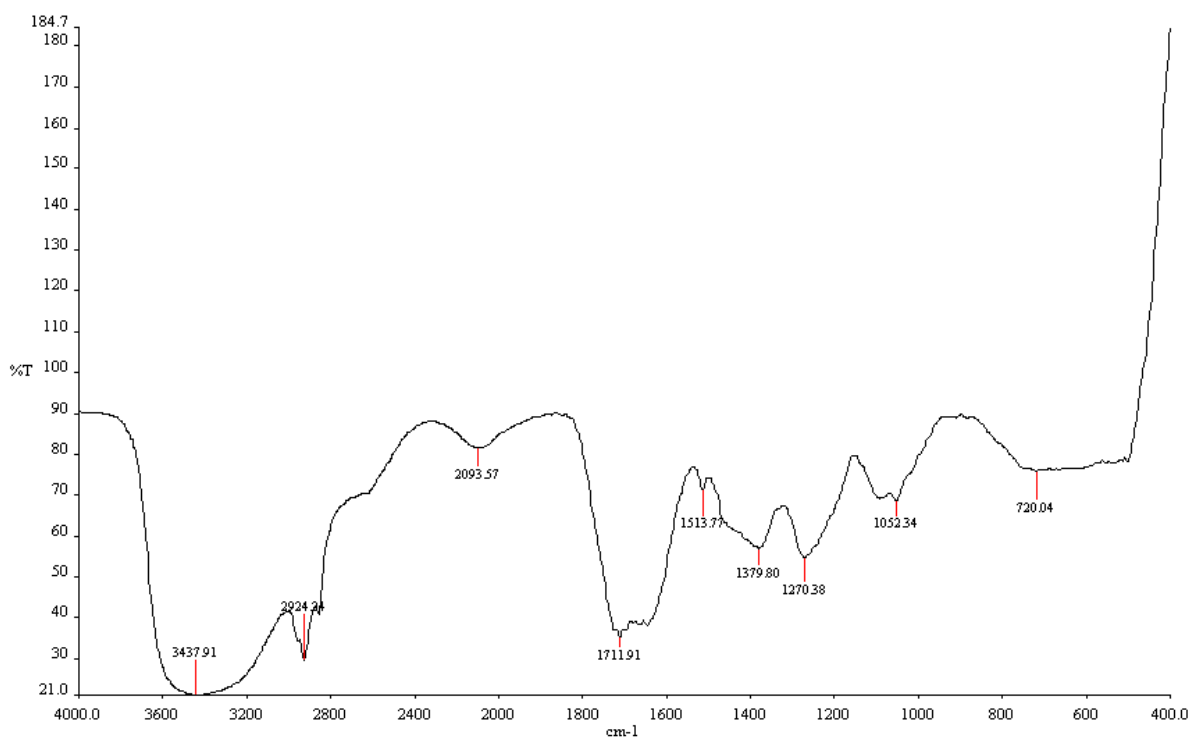


Fig 15. FTIR Spectrum of Bagasse

Table 11. Result of FTIR of LDPE

Wavelength	Wavelength Range	Functional Group	Class of Compounds
3074.88	3020 – 3100	=C-H & =CH ₂	Alkenes
2921.37	2850 – 3000	CH ₃ , CH ₂ & CH	Alkanes
2853.01	2850 – 3000	CH ₃ , CH ₂ & CH	Alkanes
1702.90	1705 – 1720	C=O (H Bonded)	Carboxylic Acids & Derivatives
1640.42	1550 – 1650	NH ₂ (primary amines)	Amines
1460.36	1350 – 1470	CH ₂ & CH ₃	Alkanes
1376.67	1330 – 1430	O-H bending (in-plane)	Alcohols & Phenols
991.44	970 – 1250	C-O	Alcohols & Phenols
964.00	880 – 925	=C-H & =CH ₂	Alkenes
908.56	880 – 925	=C-H & =CH ₂	Alkenes
721.20	720 – 725	CH ₂	Alkanes
698.15	600 – 700	C-H	Alkynes

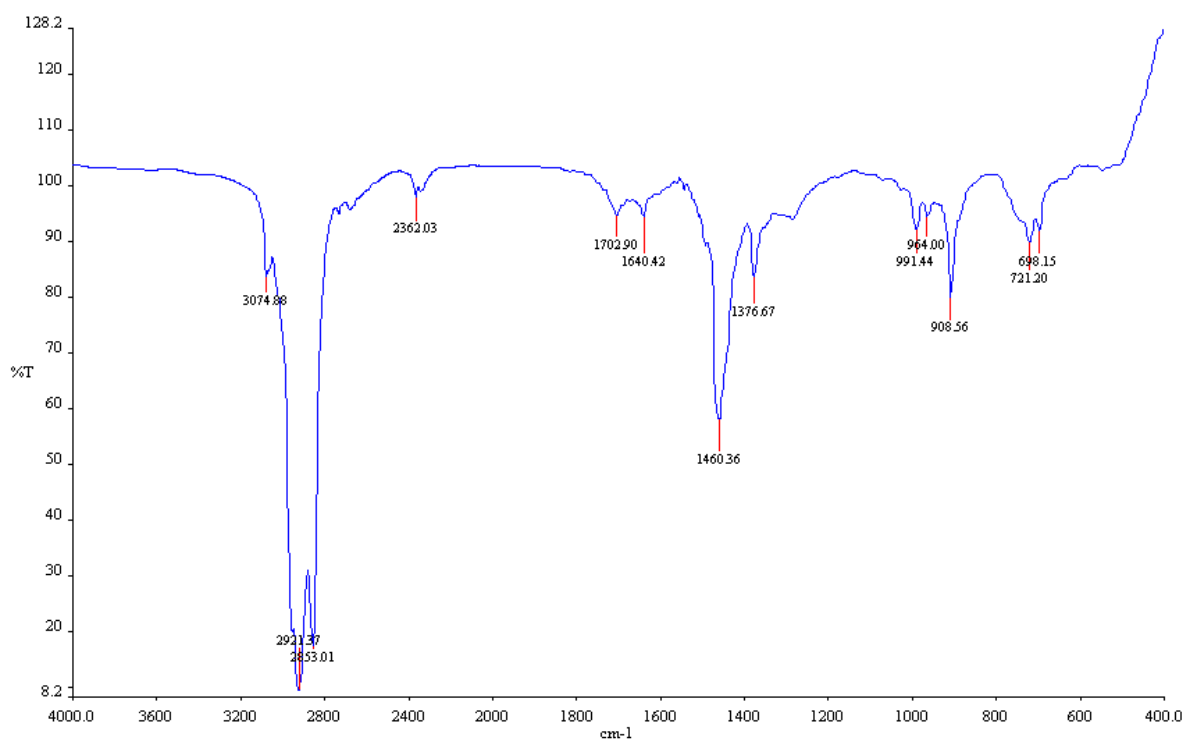


Fig 16. FTIR Spectrum of LDPE

Table 12. Result of FTIR of 1:1 Blend

Wavelength	Wavelength Range	Functional Group	Class of Compounds
3075.21	3020 – 3100	=C-H & =CH ₂	Alkenes
2954.56	2850 – 3000	CH ₃ , CH ₂ & CH	Alkanes
2922.94	2850 – 3000	CH ₃ , CH ₂ & CH	Alkanes
2852.39	2850 – 3000	CH ₃ , CH ₂ & CH	Alkanes
1771.58	1750 – 1820	C=O (acyl halides)	Carboxylic Acids & Derivatives
1740.62	1735 – 1750	C=O (esters)	Carboxylic Acids & Derivatives
1710.66	1710 – 1720	C=O (saturated ketone)	Aldehydes & Ketones
1640.45	1630 – 1695	C=O (amides)	Carboxylic Acids & Derivatives
1609.58	1550 – 1650	NH ₂ (primary amines)	Amines
1513.45	1500 – 1560	N-H (secondary amines)	Amines
1462.51	1350 – 1470	CH ₂ & CH ₃	Alkanes
1375.93	1330 – 1430	O-H bending (in-plane)	Alcohols & Phenols
1214.42	1330 – 1430	O-H bending (in-plane)	Alcohols & Phenols
1111.76	970 – 1250	C-O	Alcohols & Phenols
991.62	970 – 1250	C-O	Alcohols & Phenols
964.71	970 – 1250	C-O	Alcohols & Phenols

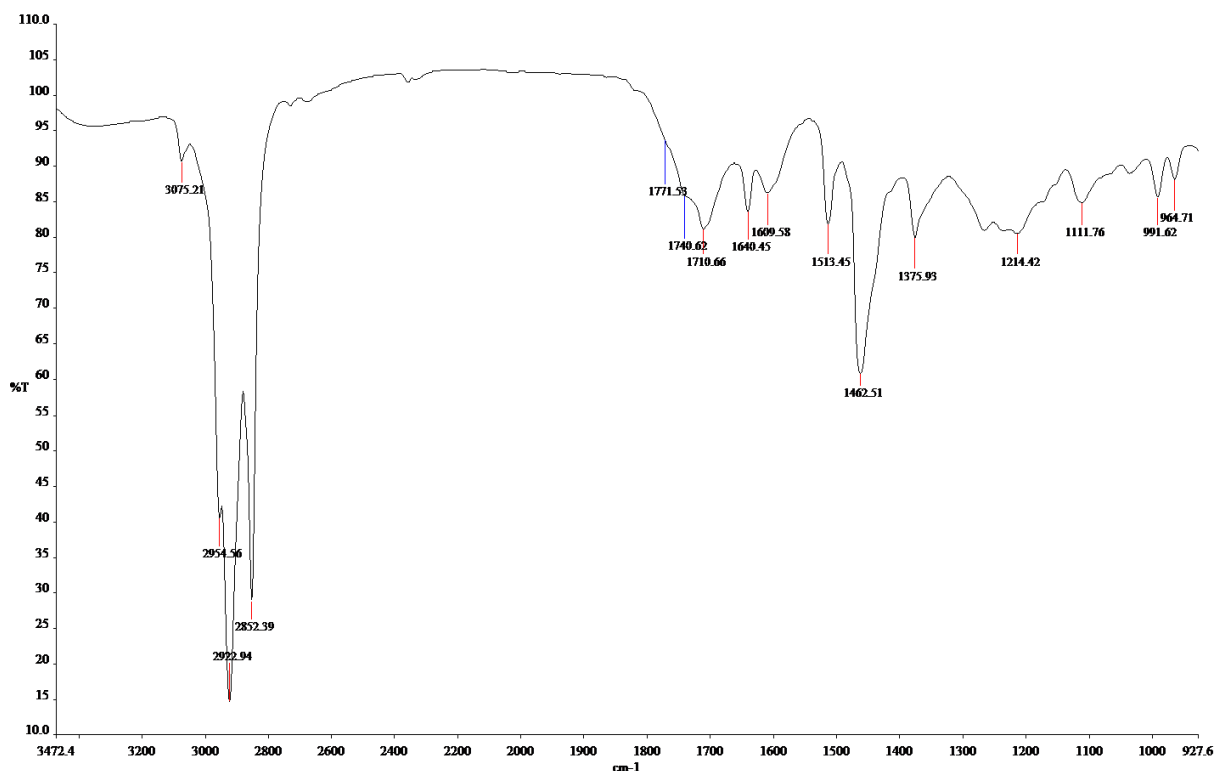


Fig 17. FTIR Spectrum of 1:1 Blend

Table 13. Result of FTIR of 1:3 Blend

Wavelength	Wavelength Range	Functional Group	Class of Compounds
3413.54	3400 - 3500	N-H (primary amines)	Amines
2922.60	2850 – 3000	CH ₃ , CH ₂ & CH	Alkanes
2852.91	2850 – 3000	CH ₃ , CH ₂ & CH	Alkanes
2083.70	2000 - 2250	C≡C	Alkynes
1641.52	1550 – 1650	NH ₂ (primary amines)	Amines
1460.51	1350 – 1470	CH ₂ & CH ₃	Alkanes
1376.89	1330 – 1430	O-H bending (in-plane)	Alcohols & Phenols
1275.22	1210 – 1320	O-C (acids)	Carboxylic Acids & Derivatives
1083.97	970 – 1250	C-O	Alcohols & Phenols
991.70	970 – 1250	C-O	Alcohols & Phenols
908.18	880 – 925	=C-H & =CH ₂	Alkenes
720.14	720 – 725	CH ₂	Alkanes

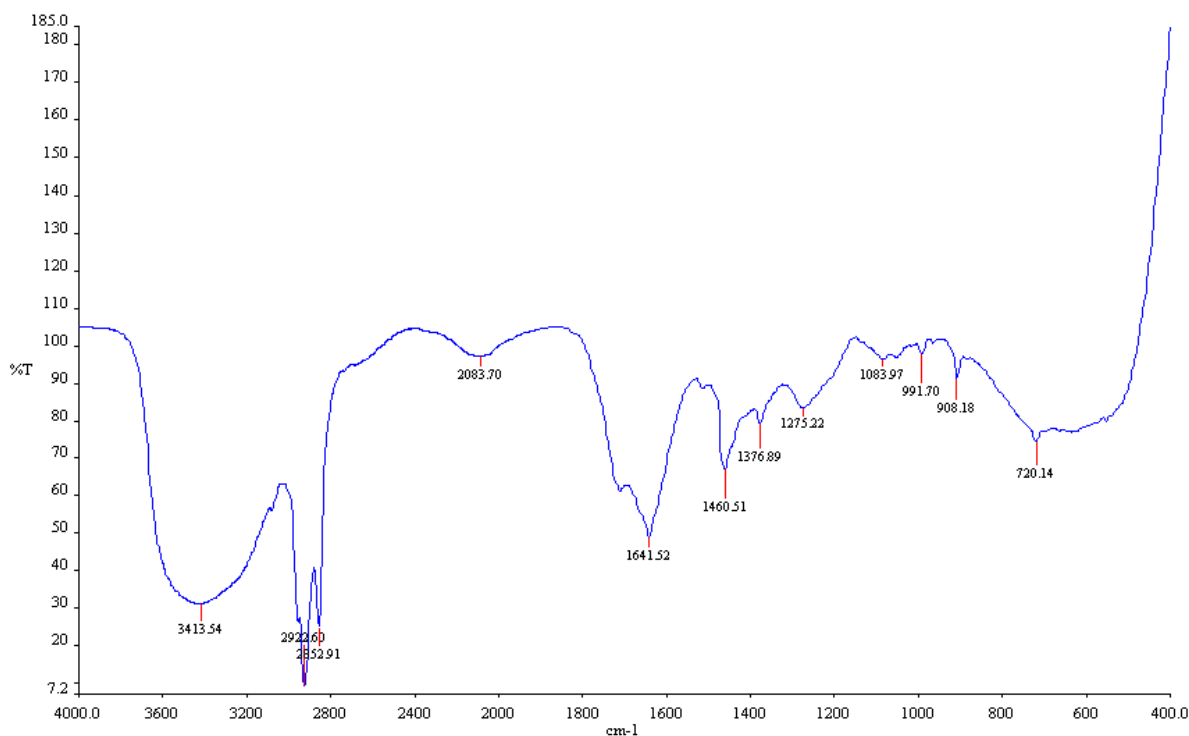


Fig 18. FTIR Spectrum of 1:3 Blend

5.2.4 GC – MS analysis of pyrolysis liquid

GC-MS is one of the modern analytical techniques to identify the possible compound present in the pyrolysis liquids derived from pyrolysis. GC-MS analyses were carried out with the pyrolysis liquid obtained at 500°C temperature for bagasse, LDPE and their blends of 1:1 and 1:3. From the Table 14 it can be analyzed that almost 32, 26, 61, and 55, compounds were present in pyrolysis liquid of SB, LDPE, 1:1 and 1:3 blends, respectively. The area percentage also gives a rough estimation about the amount of compound present in the pyrolysis liquids. It can be observed that pyrolysis liquid of sugarcane bagasse contains many aliphatic and aromatic compounds such as C₉-C₂₀ alkanes of (16.78%), 2, 6-Dimethoxy-phenol (8.91%), 2,6-Dimethoxy-4-(2-propenyl)-phenol (8.18%), 2-Methoxy-benzeneethanol (6.71%), 2-Methoxy-phenol (6.28%) and others aromatic compounds. The composition of pyrolysis oil from LDPE was C₉-C₂₀ alkenes (45.72%), C₉-C₂₀ alkanes (21.15%), 1,3-Diphenylpropane (10.62%), Behenic alcohol (5.3%) and other aromatic hydrocarbons. The major compounds present in co-pyrolysis of 1:1 blend of bagasse and LDPE are C₉-C₂₀ alkanes (47.18%), Dibenzyl disulphide (5.45%), 2-Methoxy-phenol (4.22%), 1,2-Benzenediol (4.03%), 2,6-Dimethoxy-phenol (3.51%), Kaempferol (3.4%). Similarly from 1:3 blend of bagasse and LDPE the major compound were obtained as C₉-C₂₀ alkenes (49.13%) and C₉-C₂₀ alkanes (14.92%). According to the GC – MS Analysis it is very clear that co-pyrolysis blends of bagasse and LDPE leads

to an increase in both alkane and alkene fractions comparing the results obtained from individual bagasse pyrolysis liquid. C₉-C₂₀ alkanes are very desirable component of fuel as they form the major part of aviation fuel and diesel also, they are the most important component of fuel oil and lubricating oil and act as anti-corrosive agents in lubricating oil. It can be inferred that free radicals produced from pyrolysis of LDPE is stabilized by the hydrogen from bagasse and hence, the amount of alkanes increased considerably in 1:1 blend. As, in 1:3 blend the amount of bagasse was less so less amount of alkanes were formed.

Table 14 GC – MS Analysis of Liquid product Bagasse, LDPE & Mixtures

Compound	Formula	M (amu)	RT (min)	Area % Blend			
				Bagasse	LDPE	Blend 1:1	Blend 1:3
Heptadecane	C ₁₇ H ₃₆	240.282	15.1	-	-	5.9	-
Dibenzyl disulfide	C ₁₄ H ₁₄ S ₂	246.054	18.9	-	-	5.45	-
Hexadecene	C ₁₆ H ₃₂	224.25	13.9	-	10.38	4.89	8.14
Tetradecane	C ₁₄ H ₃₀	198.235	11.4	-	-	4.28	-
Octadecane	C ₁₈ H ₃₈	254.297	16.1	-	7.01	4.24	-
2-Methoxy-phenol	C ₇ H ₈ O	124.052	6.8	6.28	-	4.22	-
1,2-Benzenediol	C ₆ H ₆ O ₂	110.037	8.5	5	-	4.03	-
Pentadecane	C ₁₅ H ₃₂	212.25	12.7	-	-	3.61	-
Eicosane or Icosane	C ₂₀ H ₄₂	282.329	18.2	4.07	0.37	3.61	4.58
2,6-Dimethoxy-phenol	C ₈ H ₁₀ O ₃	154.063	10.8	8.91	-	3.51	0.95
Kaempferol	C ₁₅ H ₁₀ O ₆	168.042	12.1	-	-	3.4	-
4-Ethyl-phenol	C ₈ H ₁₀ O	122.073	8.0	4.76	-	3.37	1.11
Nonadecane	C ₁₉ H ₄₀	268.313	17.2	1.7	7.3	3.29	4.76
1,2,5-Trimethoxy-3-methyl-benzene	C ₁₀ H ₁₄ O ₃	182.094	13.1	-	-	3.14	-
2-Methoxy-benzeneethanol	C ₉ H ₁₂ O ₂	152.084	9.8	6.71	-	2.89	-
Docosane	C ₂₂ H ₄₆	310.36	20.0	1.59	3.29	2.87	2.7
Dibenzyl trisulfide	C ₁₄ H ₁₄ S ₃	278.026	21.3	-	-	2.78	0.64
Tetracosane	C ₂₄ H ₅₀	338.391	21.7	0.52	1.56	2.44	1.33
Benzenemethanol	C ₇ H ₈ O	108.058	6.5	-	-	2.15	-
2,6-Dimethoxy-4-(2-propenyl)-phenol	C ₁₁ H ₁₄ O ₃	194.094	14.6	3.68	-	1.7	-
3-Methoxy-1,2-benzenediol	C ₇ H ₈ O ₃	140.047	9.5	-	-	1.69	-
Pentacosane	C ₂₅ H ₅₂	352.407	22.5	-	1.27	1.49	0.84
2,4-Dimethyl-phenol	C ₈ H ₁₀ O	122.073	7.7	-	-	1.34	-
2-Hydroxy-3-methyl-2-cyclopenten-1-one	C ₆ H ₈ O ₂	112.052	5.7	1.67	-	1.3	-
Benzenemethanethiol	C ₇ H ₈ S	124.035	10.6	-	-	1.28	-
Tridecane	C ₁₃ H ₂₈	184.219	10.1	-	-	1.14	-
2-Methyl-phenol	C ₇ H ₈ O	108.058	6.1	-	-	1.09	-
Triacotane	C ₃₀ H ₆₂	422.485	26.0	-	-	1.06	-

2-Ethyl-5-methyl-phenol	C ₉ H ₁₂ O	136.089	9.0	-	-	0.98	-
4-Ethenyl-2-methoxy-phenol	C ₉ H ₁₀ O ₂	150.068	10.3	-	-	0.97	-
Hexadecanoic acid or Palmitic acid	C ₁₆ H ₃₂ O ₂	256.24	17.8	2.19	0.84	0.87	-
3-Ethyl-2-hydroxy-2-cyclopenten-1-one	C ₇ H ₁₀ O ₂	126.068	7.3	1.82	-	0.75	-
2,3-Dihydro-benzofuran	C ₈ H ₈ O	120.058	8.8	-	-	0.66	-
Cyclopentadecane	C ₁₅ H ₃₀	210.235	15.7	-	-	0.55	-
Heptadecenal	C ₁₇ H ₃₂ O	252.245	17.4	-	-	0.49	-
2-Methyl-1-penten-1-one	C ₆ H ₁₀ O	98.073	6.0	-	-	0.41	-
5-Octadecene	C ₁₈ H ₃₆	252.282	16.3	-	-	0.41	0.64
Allyl Cyclohexyl carbonate	C ₁₀ H ₁₆ O ₃	184.11	19.7	-	-	0.39	-
α-Selinene	C ₁₅ H ₂₄	204.188	16.8	-	-	0.3	-
Docos-1-ene	C ₂₂ H ₄₄	308.344	20.2	-	-	0.25	-
2-(1,3-Benzodioxol-5-ylmethyl)-isoindole-1,3-dione	C ₁₆ H ₁₁ NO ₄	281.069	25.6	-	-	0.19	-
Pentacosene	C ₂₅ H ₅₀	350.391	22.6	-	-	0.13	-
2-p-Nitrophenyl-oxadiazol-1,3,4-one-5	C ₈ H ₅ N ₃ O ₄	207.028	24.9	-	-	0.09	-
2-Methoxy-2-heptene	C ₈ H ₁₆ O	128.12	7.4	-	-	0.07	-
9-Methylbicyclo[3.3.1]nonane	C ₁₀ H ₁₈	138.141	5.6	-	-	-	0.79
1-Butyl-cyclohexene	C ₁₀ H ₁₈	138.141	6.3	-	-	-	0.84
3-Methyl-cyclooctene	C ₉ H ₁₆	124.125	6.7	-	-	-	1.25
Undec-1-ene	C ₁₁ H ₂₂	154.172	6.8	4.26	-	-	5.51
Trifluoro-acetic acid	C ₂ HF ₃ O ₂	268.165	7.6	-	-	-	0.52
(1-Methyl-1-propenyl)-benzene	C ₁₀ H ₁₂	132.094	7.8	-	-	-	0.59
Benzoic Acid	C ₇ H ₆ O ₂	122.037	8.0	-	1.13	-	-
Dodec-1-ene	C ₁₂ H ₂₄	168.188	8.5	5.3	-	-	3.99
Dodecane	C ₁₂ H ₂₆	170.203	8.6	-	-	-	2.29
Dodecene	C ₁₂ H ₂₄	168.188	8.8	-	-	-	0.5
4-Vinylphenol	C ₈ H ₈ O	120.058	8.9	4.37	-	-	-
2-Cyclopenten-1-one	C ₅ H ₆ O	166.136	9.0	-	-	-	0.13
Hexyl-cyclohexane	C ₁₂ H ₂₄	168.188	9.2	-	-	-	0.69
4-Heptafluorobutyryloxyhexadecane	C ₂₀ H ₃₃ F ₇ O ₂	438.237	9.2	-	1.31	-	-
1-Hexyl-cyclohexene	C ₁₂ H ₂₂	166.172	9.5	-	-	-	1.26
Tridec-1-ene	C ₁₃ H ₂₆	182.203	10.0	-	6.46	-	6.86
1-Pentadecyne	C ₁₅ H ₂₈	208.219	10.3	-	-	-	0.61
6-Tetradecyne	C ₁₄ H ₂₆	194.203	10.4	-	-	-	0.23
5-Cyclohexyl-1-pentene	C ₁₁ H ₂₀	152.157	10.6	-	-	-	0.43
4-Ethyl-1,3-benzenediol	C ₈ H ₁₀ O ₂	138.068	11.3	3.42	-	-	-
Tetradec-1-ene	C ₁₄ H ₂₈	196.219	11.4	-	10.07	-	8.06
Cyclotetradecane	C ₁₄ H ₂₈	196.219	11.8	-	-	-	0.46
3-Methyl-4-oxo-pentanoic acid	C ₆ H ₁₀ O ₃	130.063	11.9	1.18	-	-	-
Hexylcyclohexane	C ₁₂ H ₂₄	168.188	12.1	-	0.88	-	-
2,4-Dimethoxy-3-methylphenol	C ₉ H ₁₂ O ₃	168.079	12.1	-	-	-	1.93
2,6-Di-methoxy-4-methyl-phenol	C ₉ H ₁₂ O ₃	168.079	12.2	3.96	-	-	-
Pentadec-1-ene	C ₁₅ H ₃₀	210.235	12.7	-	8.62	-	8.93
1-(4-Hydroxy-3-methoxyphenyl)-ethanone	C ₉ H ₁₀ O ₃	166.063	12.7	2.9	-	-	-
1,1'-(1,2-Ethanediyl)bis-benzene or Dibenzyl	C ₁₄ H ₁₄	182.11	13.1	-	1.42	-	-

1-Cyclohexylnonene	C ₁₅ H ₂₈	208.219	13.3	-	-	-	1.05
Hexadecane	C ₁₆ H ₃₄	226.266	13.9	7.93	-	-	
1,3-Diphenylpropane	C ₁₅ H ₁₆	196.125	14.7	-	10.62	-	0.73
Heptadecene	C ₁₇ H ₃₄	238.266	15.0	-	-	-	7.04
2,4-Diphenyl-1-butene	C ₁₆ H ₁₆	208.125	15.4	-	3.61	-	0.72
Octylcyclohexane	C ₁₄ H ₂₈	196.219	15.8	-	-	-	0.64
3,5-Dimethoxy-4-hydroxyphenylacetic acid	C ₁₀ H ₁₂ O ₅	212.068	16.0	3.9	-	-	-
1-Octadecene	C ₁₈ H ₃₆	252.282	16.1	-	-	-	5.81
1-Chloro-hexadecane	C ₁₆ H ₃₃ Cl	260.227	17.4	-	-	-	0.49
2-Propenyl-cyclohexane	C ₉ H ₁₆	124.125	17.9	-	-	-	0.54
1-Docosanol or Behenic alcohol	C ₂₂ H ₄₆ O	326.355	18.1	-	5.3	-	-
Heneicosane	C ₂₁ H ₄₄	296.344	19.1	-	4.34	-	4.16
1-(Cyclohexylmethyl)-2-methyl-cyclohexane	C ₁₄ H ₂₆	194.203	19.4	-	-	-	0.24
Octadec-9-enoic acid	C ₁₈ H ₃₄ O ₂	282.256	19.5	1.69	-	-	-
Oxalic acid or Cyclohexylmethyl tridecyl ester	C ₂₂ H ₄₀ O ₄	368.293	20.3	-	-	-	0.15
Tricosane	C ₂₃ H ₄₈	324.376	20.8	0.71	-	-	-
Nonadec-1-ene	C ₁₉ H ₃₈	266.297	21.0	-	-	-	0.12
4-Hydroxy-3-methoxyphenylethyl alcohol	C ₉ H ₁₂ O ₃	168.079	21.3	0.74	-	-	-
Trimethoprim	C ₁₄ H ₁₈ N ₄ O ₃	290.138	22.6	1.71	-	-	-
Hexacosane	C ₂₆ H ₅₄	366.423	23.2	-	1.19	-	0.67
4,4'-Methylenebis[2,6-dimethoxyphenol]	C ₁₇ H ₂₀ O ₆	320.126	24.3	0.77	-	-	-
Nonacosane	C ₂₉ H ₆₀	408.47	25.4	-	0.26	-	-
1,3,5-Triphenylbenzene	C ₂₄ H ₁₈	306.141	25.8	-	0.65	-	-
5'-Phenyl-1,1':3',1''-terphenyl	C ₂₄ H ₁₈	306.141	25.8	-	-	-	0.59

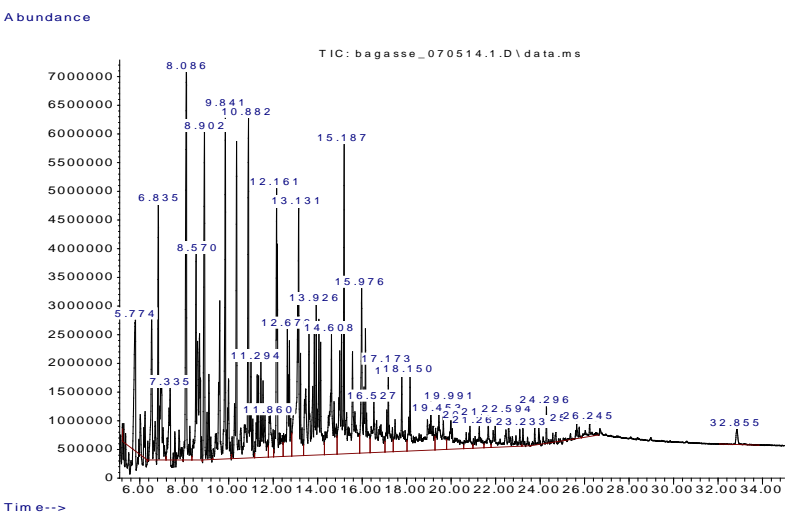


Fig 19. GC – MS of Bagasse

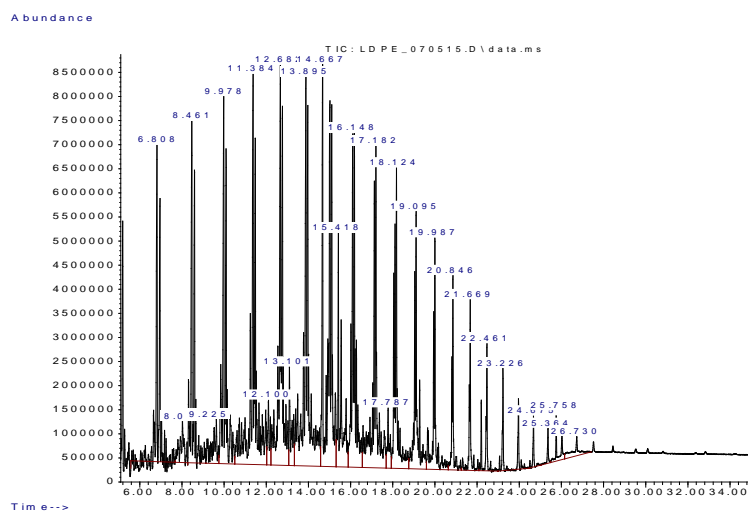


Fig 20. GC – MS of LDPE

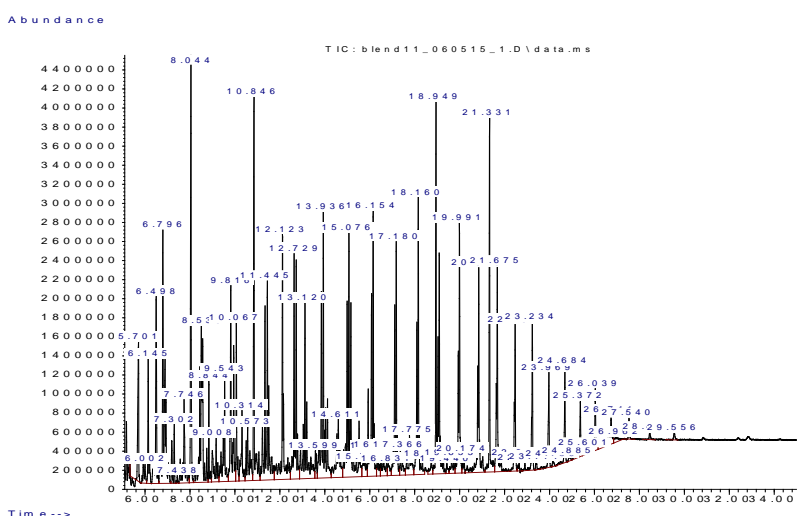


Fig 21. GC – MS of 1:1 Blend

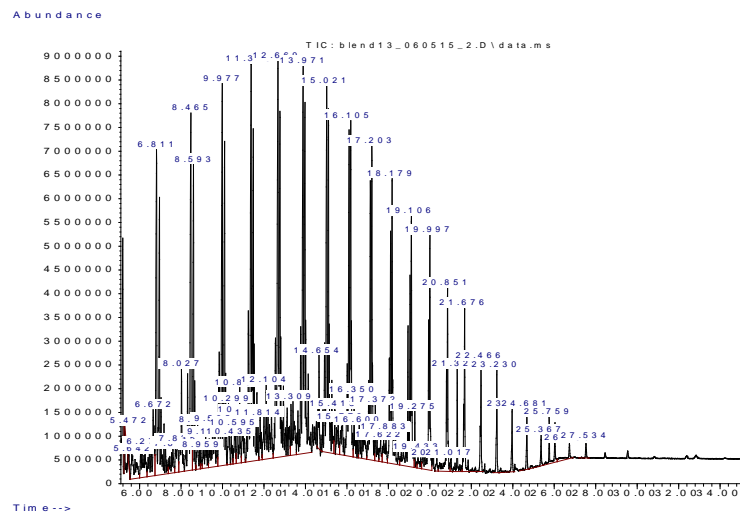
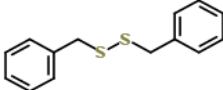
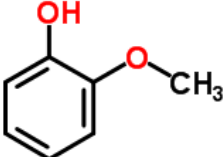
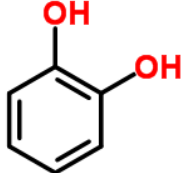
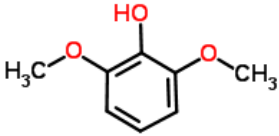
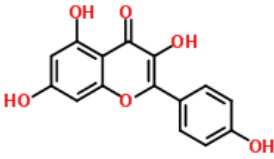
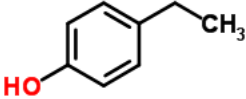
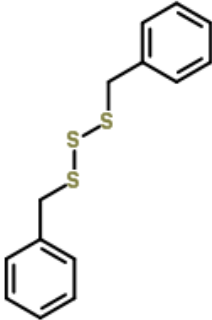
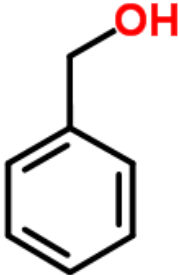


Fig 22. GC – MS of 1:3 Blend

Table 15. Uses of some of the major chemical compounds detected in 1:1 Blend

Compound	Structure	Uses
Tetradecane, Pentadecane Hexadecane	Straight Chain	Major part of diesel and aviation fuel, high viscosity less suitable for use in gasoline
Heptadecane, Octadecane, Icosane, Nonadecane, Docosane, Tetracosane	Straight Chain	Most important components of fuel oil and lubricating oil, act as anti-corrosive agents in lubricating oil due to their hydrophobic nature

Benzyl disulfide		Manufacturing of corrosion inhibitors, fragrance compounds, high-pressure lubricant additives
Guaiacol		<p>Its derivatives are used medicinally as an expectorant, antiseptic, and local anaesthetic.</p> <p>It also can be used as an indicator in chemical reactions that produce oxygen.</p>
Catechol		Production of pesticides, precursor to fine chemicals such as perfumes and pharmaceuticals, black-and-white photographic developer
Syringol		In preparation of food by smoking, it is the main chemical responsible for the smoky aroma, can serve as a substitute feedstock for phenol formaldehyde resin, a commonly used, water resistant adhesive for plywood
Kaempferol		Anti-inflammation, Anti-bacterial, Restrain cough Antioxidant, Anti-spasmodic or Spasmolytic, Anti-ulcer Choleric, Diuretic, Relieve coughing

4-Ethyl-phenol		<p>Pure 4-ethylphenol is the starting material for the production of 4-vinylphenol and of various anti-oxidants which are used in rubber and polymers.</p> <p>It is an intermediate for pharmaceuticals and dyes.</p>
Dibenzyl trisulfide		<p>Molecules with Potential for Cancer Therapy in the Developing World</p>
Benzyl alcohol		<p>It is used as a dielectric solvent for the di-electrophoretic reconfiguration of nanowires.</p> <p>It is used as a general solvent for inks, paints, lacquers, and epoxy resin coatings.</p> <p>It is also a precursor to a variety of esters, used in the soap, perfume, and flavour industries. It is also used as a photographic developer.</p>

CHAPTER 6 – CONCLUSION

The study has shown that pyrolysis of sugarcane bagasse mixed with LDPE has the potential to be a suitable method for producing high grade pyrolysis oil which obtained a high yield of 52.75% with 1:1 ratio, at an optimum temperature of 500°C. The temperature has a major effect on the production of pyrolysis yield. With increase in pyrolysis temperature of sugarcane bagasse, the liquid yield was increased up to 500°C, after that it was not in appreciable range, the gas yield increases above 500°C but, the char yield decreases. Co-pyrolysis of biomass and LDPE at 500°C resulted in an enhanced liquid yield with a lower water content and a higher calorific value. The synergistic effects are observed to increase along with the addition of LDPE. The alkane and alkene contents of the liquid obtained by LDPE pyrolysis are the highest compared to the liquid obtained by individual bagasse pyrolysis and also by Bagasse: LDPE pyrolysis blends of 1:1 and 1:3. It can be concluded that co-pyrolysis liquid yield of bagasse with LDPE blends comprises of more alkane and alkene species than that of liquid obtained by the pyrolysis of bagasse alone. The maximum co-pyrolysis liquid yield of 52.75% was obtained at 500°C with 1:1 blend. Hydrogen released from LDPE leads to this increment, stabilizing the free radicals generated under the co-pyrolysis conditions. Thus, it can be concluded that LDPE acts as a hydrogen donor media in view of liquid formation during the co-pyrolysis process. From the FTIR analysis the obtained liquid yield of blends consists mainly of the aliphatic compound and less aromatic compound as compared to the individual bagasse. According to the GC – MS analysis it is very clear that co-pyrolysis blends of bagasse and LDPE leads to an increase in both alkane and alkene fractions comparing the results obtained from individual bagasse pyrolysis liquid. Therefore, this method can be considered a simple, cheap, and effective procedure to obtain high-grade pyrolysis oil.

CHAPTER – 7 FUTURE SCOPE

- ✓ Modification of pyrolysis experimental setup
- ✓ Characterization of products such as liquid, solid and gas obtained after co-pyrolysis of biomass and plastic as per their various physical and chemical properties.
- ✓ Comparative study of sugarcane bagasse pyrolysis liquid and the liquid product obtained by co-pyrolysis of sugarcane bagasse and LDPE plastic.
- ✓ To study the improvement of quality and quantity of liquid product by catalytic co-pyrolysis process.

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