CATALYTIC UP-GRADATION OF BIO-OIL BY PYROLYSIS OF BIOMASS

A Thesis submitted for partial fulfillment of the requirements
for the degree of Master of Technology in
"Chemical Engineering"

By

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CERTIFICATE

This is to certify that the thesis entitled "**Catalytic up-gradation of bio-oil by pyrolysis of bio-mass**", submitted by **Tanvidkar Priya Shreedatta (213CH1127)** in partial fulfillment of the requirements for the award of **Master of Technology** in **Chemical Engineering** during session 2014-2015 at National Institute of Technology, Rourkela. A bona-fide record of research work carried out by her under my supervision and guidance.

The candidate have fulfilled all the prescribed requirements.

The Thesis which is based on candidates' own work, have not been submitted elsewhere for a degree.

In my opinion, the thesis is of standard required for the award of a master of technology degree in Chemical Engineering.

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Priya Shreedatta Tanvidkar

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ABSTRACT

The depleting oil reserves impose a threat to ever-increasing energy requirements all over the world. This necessitates the research on alternative sources of energy. Naturally, biomass is converted to oil over a period of thousands of years. But to meet the demands, pyrolysis of biomass to produce bio-oil can be a promising method for generation of alternative energy sources. Because of high oxygen content is present in the bio-oil, it has low stability. It also has low heating value. To remove the oxygen, up-gradation of the bio-oil becomes necessary. The up-gradation of bio-oil helps in improving its chemical and physical properties and makes it resemble more to the crude oil. There are two widely known methods of bio-oil up-gradation: hydro-deoxygenation (HDO) and zeolite cracking. The hydro-deoxygenation is done by pyrolyzing biomass or bio-oil in presence of catalyst, which removes oxygen in the form of water. In this report study of Catalytic Pyrolysis on biomass viz. castor seed by using CaO, MgO, Fe_2O_3, ZnO, and TiO2 as catalyst. Different catalytic ratios such as 1:2, 1:6, 1:8, 1:10 & 1:14 have been employed at pyrolysis temperature of 550°C, with heating rate 20°C/min for approximately 60 min.

The bio-oil yield, bio-char yield, residence time for different catalysts with different ratios have been recorded. The maximum yield has obtained by using Fe_2O_3 in the ratio 1:10 with lowest char formation. Different physical & chemical tests have done for bio-oil & bio-char. According to this comparably good yield with upgraded qualities is obtained by using Fe_2O_3 as catalyst in ratio 1:10. After Fe_2O_3, it has noticed good yield is obtained from CaO, TiO_2.

1 INTRODUCTION

The energy resources can be divided into three types: fossil fuels, nuclear resources and renewable resources. Among these three, fossil fuels are vastly used in each sector of life. The demand for fossil fuels has increased rapidly due to increased industrialization and increased world population. This increased demand has put added load on the fossil fuel reserves, which are limited. It has also affected the environment adversely and increased threat to global climate change and health risks.[1]

Global warming or global climate change is a major problem of 21st century. It has various adverse effects on health and socio-economic issues, for example, increased global temperature, increase in average sea level, increased droughts and floods, and effects on the risk of calamities and malnourishment. The higher concentration of greenhouse gases such as N_2O, CH_4, CO_2, ozone, CFCs and per oxy-acetyl nitrate in the atmosphere is resulting in trapping of heat radiated from the surface of the Earth and thus increasing the Earth's surface temperature. A schematic diagram elaborating the of problem of global climate change is shown in figure1.1.[2]

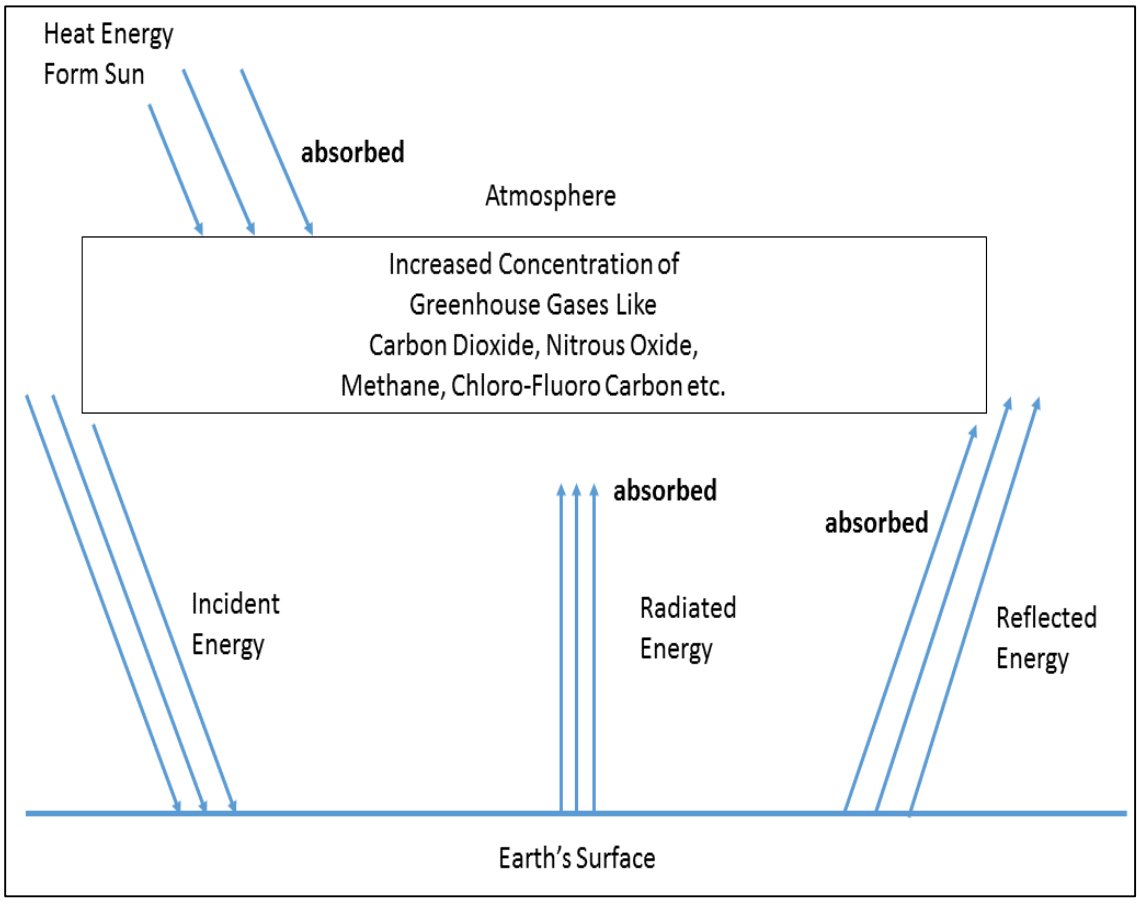

Figure 1.1 Schematic illustration of Green-House effect

Excessive consumption of fossil fuels has resulted in global warming, because burning of fossil fuels generate carbon dioxide as a byproduct. As many scientific studies divulge, in the past 200 years, global CO_2 levels have increased 31%. From 1800, deforestation added 20 Gt of carbon to the atmosphere. Also, concentration of another gas, methane, which causes ozone layer depletion has doubled since 1800[2]. The mean surface temperature has globally increased above baseline of 14^0C by 0.4–0.8^0C in the last century. This increase in global temperature caused the global sea levels to rise at an average rate of 1–2mm annually. The thickness of Arctic sea ice has reduced by 42%. Also the total ice has decreased by 10–15% since 1950[3].Thus, it is necessary to look forward to sustainable methods of producing alternative fuels. It is also imperative that these alternative fuel options contribute less to air pollution and waste. Thus this issue goes hand-in-hand with other major issues such as waste minimization, reduction of greenhouse emission, conservation of forests.

This has aroused great interest in encouraging research on alternative fuels which would be capable enough to meet world's ever increasing energy requirements. The renewables are the primary, domestic and clean or inexhaustible energy resources. These renewable technologies are also known as non-conventional or alternative energy sources. Some of the examples include solar energy, tidal energy, geothermal energy and wind energy. As opposed to non-renewable energy sources, the renewable sources are clean sources of energy and careful use of such resources reduces the hazardous impacts on the environment, produce less wastes and can be sustainable models of energy generation based on current socio-economic situations. Currently, 14% of world's total energy demand is fulfilled by renewable energy sources [4]. Conversion of various forms of biomass and bio-degradable waste can produce renewable transportation fuels. Renewable energy sources, like biogas, which are mostly used in domestic applications definitely have the ability to provide energy with almost no emissions of both air pollutants and greenhouse gases, thus truthfully it is clean source of energy. The RES energy sources and its usage is given in table 1.1[4].

Table 1.1 Main resources of renewable energy and their usage form

Sr. No.	Energy sources	Applications and Conversion
1	Solar	Solar cookers, solar home system ,solar dryers
2	Wind	Power generation, windmills, wind generators, water pumps
3	Geothermal	Power generation, urban heating, hydrothermal, hot dry rock
4	Hydropower	Generation of power
5	Direct solar	Thermal power, photovoltaic, water heaters
6	Modern biomass	Digestion, pyrolysis, heat generation, power generation, gasification
7	Tidal	Barrage, tidal stream

Generation of renewable energy will help to deal with the currently most serious tasks like reliability in improving of fuel economy and supply of energy; solving problems related to local water and energy supply; improving the living standard and employment level of the local people; guaranteeing sustainable development of the distant regions of population; employment of the responsibilities of the countries related to satisfying the agreements regarding environmental protection and international laws. Development and implementations of different projects related to renewable energy in rural areas that can create job opportunities, which in turn can minimize migration towards urban areas. Decentralization of the renewable energy can be one of the choices to meet the small-scale and rural energy needs in an affordable, environmentally sustainable and reliable way. The contribution of renewable energy sources is likely to increase considerably, about30–80% up-to 2100. The estimated scenario of consumption of renewable energy sources globally by 2040 is presented in Fig 1.2.[3]

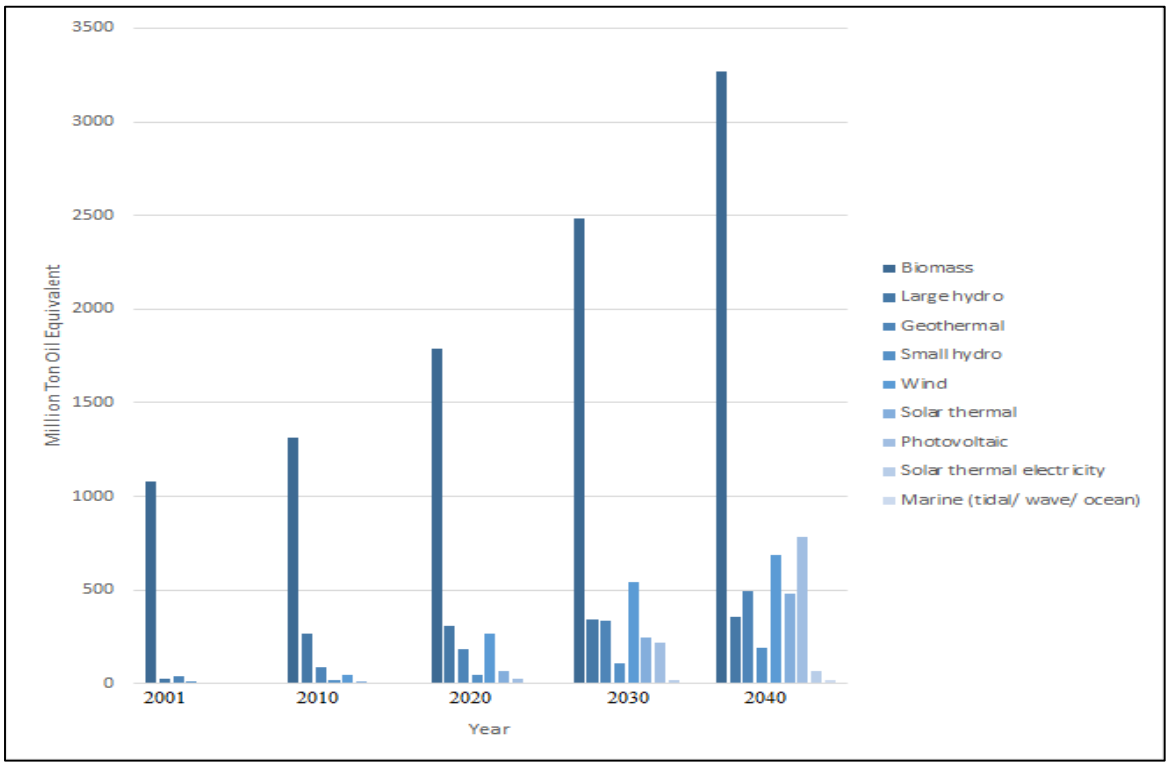

Figure 1.2 Global renewable energy scenario by 2040 (Estimated)

Renewable energy growth will help in solving the presently most critical and important tasks of enhancing energy supply dependability and economy of organic fuel; resolving problems of local water and energy supply; increasing level of employment of the local population improving the standard of living; ensuring ecological development of the isolated regions in the mountains and desert zones; employment of the responsibilities of the nations with esteem to satisfying the international assurances relating to environmental protection. Minimizing relocation towards urban areas as development and establishment of renewable energy project in countryside areas

can create job openings. Congregation of the renewable energy in distributed manner is one of the options to cope up the rural and small scale energy needs in affordable, reliable and environmentally bearable way.

1.1 BIOMASS

Biomass energy is the form of energy that is confined inside animals and plants. This can consist of organic matter of all kinds: animals, plants, or waste products from different organic sources. These natures of energy sources are recognized as bio fuels and typically include wood chips, sewage, manure, mulch, rotted trees & its components. In the process of photosynthesis, chlorophyll pigments present in leaves of plants absorbs carbon dioxide (CO_2) from the atmosphere and water from the Earth. This similar energy is then passed to animals when they consume them. When they are burned, it is considered to be as a renewable source of energy as water and carbon dioxide confined inside animals and plants are unconfined back in to the atmosphere. Also, biomass energy can be created by growing more plants and crops. Biomass is a renewable as well as CO_2 neutral resource, thus regarded as key choice to substitute fossil fuels. This fact has inspired great interest in biomass.

Biomass is organic material resulting from living, or recently living organisms. Most often it refers to plants or plant-based materials which are precisely called ligno-cellulosic biomass. The chemical composition of biomass is given ahead. Biomass is carbon based and is comprised of a mixture of organic molecules containing hydrogen, oxygen, nitrogen and also small quantities of other atoms, including heavy metals, alkaline earth and alkali metals. Chlorophylls are porphyrins and contain magnesium. The above metals are found in functional molecules like chlorophylls or porphyrins. As an energy source, biomass can either be used straight via combustion to produce heat, or indirectly by converting it to various forms of bio fuel[3].

Types of Biomass are as follows:-

1. Virgin wood: - wood processing, forestry etc.
2. Energy crops:- grass that is use specially for energy application
3. Food Waste:- by preparation, consumption and usage of food
4. Industrial waste and co-products:- industrial manufacturing waste
5. Agricultural residue:- agricultural activity's residue

Chemical constituents of Bio-mass

Ligno-cellulosic biomass contains cellulose, hemi-cellulose, and lignin, along with minor amounts of lipids (fats, waxes, and oils), proteins and minerals. Approximately two thirds of the dry mass of cellulosic materials exist in the form of hemicellulose and cellulose with lignin making up the bulk of the remaining dry mass.

1. Lignin: -

Lignin is a cross-linked racemic macromolecule. It has molecular mass in excess of 10,000 Daltons. It is aromatic and comparatively hydrophobic in nature. The degree of polymerization is

challenging to measure. Polymers get breakdown during extraction. These polymer molecule contains of various types of sub-arrangements that appear to reprise in an arbitrary manner. There are three mono-lignol monomers which are methoxylated to various degrees: sinapyl alcohol, coniferyl alcohol and p coumaryl alcohol. These lignols are integrated into lignin in the form of the phenylpropanoids guaiacyl (G), syringal (S) and p-hydroxyphenyl (H) respectively. Lignin are most difficult to pyrolysed [5][6].

2. Cellulose:-

Cellulose is a crucial organic constituent of the biomass cell wall. It is signified by generic formula $(C_6H_{10}O_5)_n$. Cellulose is a strong structure of crystal that is unaffected by hydrolysis. It has long chain of polymer with a high degree of polymerization (~10,000). Also its molecular weight is large (~500,000). Cellulose is principally made up of d-glucose, which is composed of six carbons (fig. 2.1). Cellulose is extremely insoluble. Although it is carbohydrate is not consumable by human being. It is a principal component of wood, making up about 42 to 45% by dry weight. It's amount differs from 92% (by weight) in cotton to 34% for most other plants[7]

3. Hemicellulose:-

Hemicelluloses are cell wall components. They are denoted by the generic formula $(C_5H_8O_4)_n$. It is a group of carbohydrates with a branched chain structure having lower degree of polymerization (~100–200). It constitutes nearly 24 to 36% of the dry weight basis for most wood. The structure and composition of hemicelluloses differs for different types of biomass. Most of the hemicelluloses contain some simple sugar residues like D-glucose,D-xylose (the most common), D-galactose, D-mannose, D-glucurnoic acid and D-ababinose. These normally contain 55 to 210 entities in branched structures. It is soluble in weak alkaline solutions and is easily hydrolyzed by base or dilute acid. The presence of hemicelluloses produces more gases and less tar than cellulose during decomposition[7].

Advantages of Biomass Energy

1. No Emissions of Harmful Gases: Biomass energy, generates almost no harmful carbon dioxide emissions. Presently, many energy sources which are in use, fight to regulate carbon dioxide emissions. Due to their CO_2 emission, result is damage of the ozone layer which ultimately results in increase in the effects of greenhouse gases, tending to potentially warming our planet. As biomass is completely natural, has no such carbon dioxide side effects in its use.
2. Clean Energy: This is good for both business as well as environment. It surely releases CO_2 carbon dioxide but again captures carbon dioxide from atmosphere for its own growth. Fossil fuels release carbon dioxide but do not recapture it again thus they are harmful to the environment. It contains very low sulphur which reduces the cause of creation of acid rain.

3. Renewable and Abundant: Biomass products are renewable and abundant. Biomass come from living sources. Life is phenomenon which is cyclical, thus these biomass products potentially never run out unless there is something which living on earth.
4. Reduce Dependency on Fossil Fuels: Because of this fuel source alternative has created for fuel at domestic level. Homeowners are more independent for fuels.
5. Decrease Landfills: In addition to this, advantage of bio-energy is it takes waste which is unsafe to the environment and converts it into useful fuels. For instance, garbage landfill can be burned to produce useable biomass energy.
6. Creating Different Product: Biomass energy is also flexible. Here, diverse forms of organic matter are used to produce different bio-products. Ethanol and similar fuels are produced from corn and other crops.

1.2 PYROLYSIS

Pyrolysis is one possible path by which we can transform biomass to higher value product. Solid biomass and wastes can be easily transformed into liquid products making pyrolysis more attractive. These liquids, crude bio-oil or slurry of charcoal, have advantages in storage, transport, combustion, flexibility and retrofitting in marketing and production.

Pyrolysis is the basic thermo-chemical process for converting biomass to a more useful fuel. Biomass in the absence of oxygen, or partially combusted in limited oxygen supply, is heated, to yield bio-oil and hydrocarbon rich gas mixture. Liquid yield is high as 75% in short residence time (0.5- 2s), moderate temperature (400-6000C) with dry feedstock (<30%moisture), small particle size (<3mm) and rapid quenching at the end of process. Reactions involved in pyrolysis are shown in fig 2.2[9]

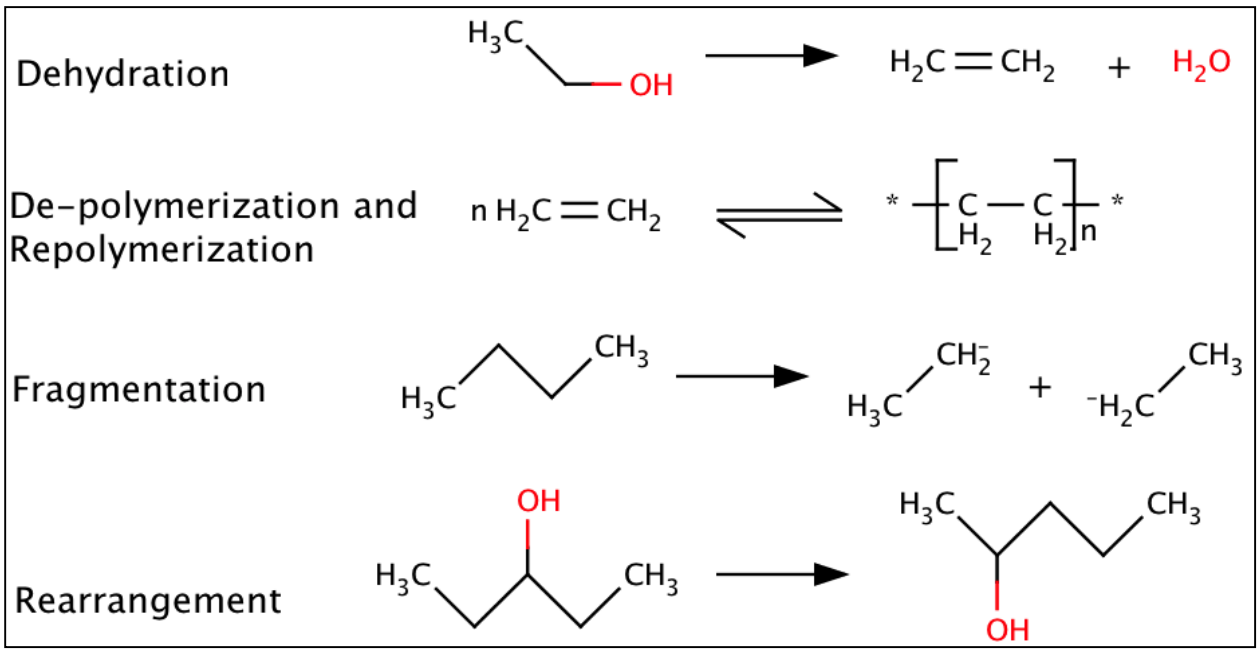

Figure 1.3 Representative pyrolysis reactions

1.3 BIO-OIL

It is viscous dark brown fluid with about 5-20% water. It is complex mixture containing oxygen, hydrogen and carbon. Bio-oil comprises of alcohols, acids, esters, aldehydes, ketones, phenols, sugars, lignin, furans, extractible terpene and derived phenols having multifunctional group. Bio-oil is not a product of thermodynamic equilibrium during pyrolysis, but is produced with short reactor times and rapid cooling or quenching from pyrolysis temperatures. This produces condensate that is also not at thermodynamic equilibrium at storage temperatures. The compound present in bio-oil are as follows.[9]

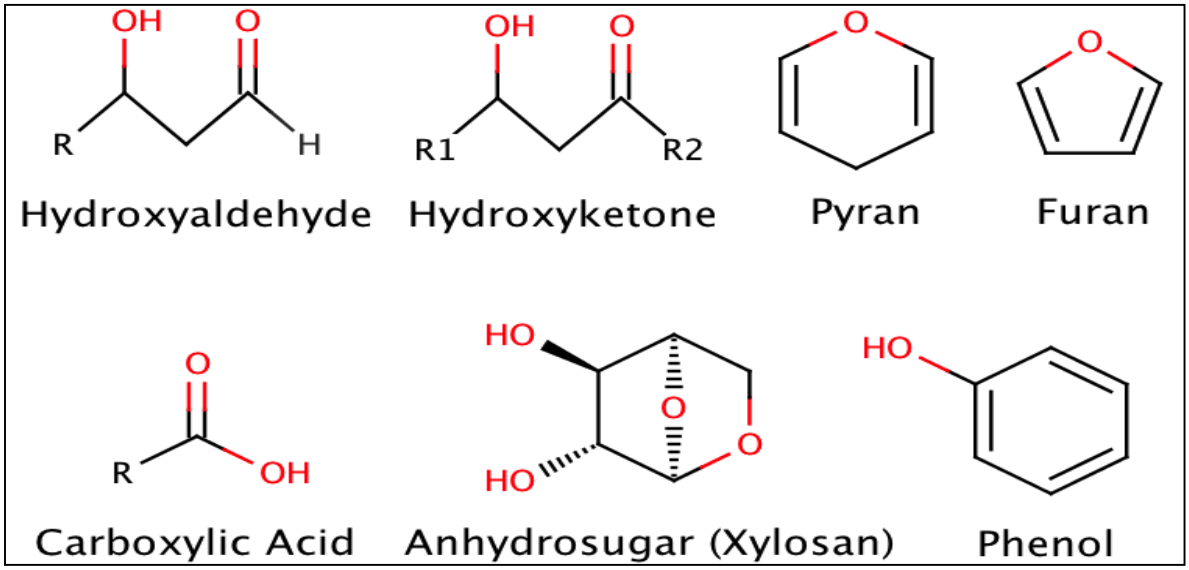

Figure 1.4 Representative compounds of bio-oil

2 LITERATURE REVIEW

2.1 CONVERSION TECHNIQUES

Key differences among generations of biofuels is in both raw material and conversion technology.

- First-generation biofuels are prepared by using conventional chemical technology in which conversion of mainly grains and oil seeds into bio-alcohols and biodiesel respectively takes place.

- Second- generation biofuels are produced from food crops (i.e. Miscanthus) and biomass residues (from crops and forests). Thus, these type of biomass provides alternative which is socially accepted. However, conversion technologies to produce Fischer-Tropsch (FT) diesel, bio-di-methyl ether (Bio-DME) and bio-hydrogen etc. are still under development.

- There is also a third-generation evolving, comprising of biofuels from algae. Also, an emerging fourth-generation which is based on the conversion of biodiesel into gasoline or on the recycling of carbon dioxide back into gasoline.

Conversion of biomass to bio-fuel are accomplished by different techniques which are broadly classified into: Thermo-chemical, Thermal, and Biochemical methods.

a) Thermal Conversion

Combustion- It is oldest method to get bio energy. Biomass combustion is a chains of chemical reactions in which carbon dioxide by oxidation of carbon and water is formed by oxidation of hydrogen. The problem with direct combustion is that huge amount of energy get wasted and cause pollution.

b) Thermo-chemical Conversion

- Gasification - It is thermal practice carried out at high temperature, to optimize the gas production, in the presence of a small quantity of oxygen. The resulting gas, known as the Syngas, is a mixture of methane, hydrogen and carbon monoxide along with nitrogen and carbon dioxide.
- Pyrolysis - It is thermo-chemical process in which thermal decomposition of biomass occurring in absence oxygen producing solid (charcoal), liquid (bio oil) and gas.

c) Bio-chemical Conversion

Adding enzymes, yeasts and bacteria to biomass causes materials to ferment which changes it into alcohol. An analogous technique is used to convert agricultural products into ethanol (grain alcohol). This ethanol is then blended with gasoline to produce an ethanol-gasoline blend. Also,

adding bacteria to break down biomass, methane is formed. Also, biomass can be taken from landfills and sewage treatment plants to yield fuel for power and heat.

The Schematic of conversion techniques is shown in fig 2.1.[8]

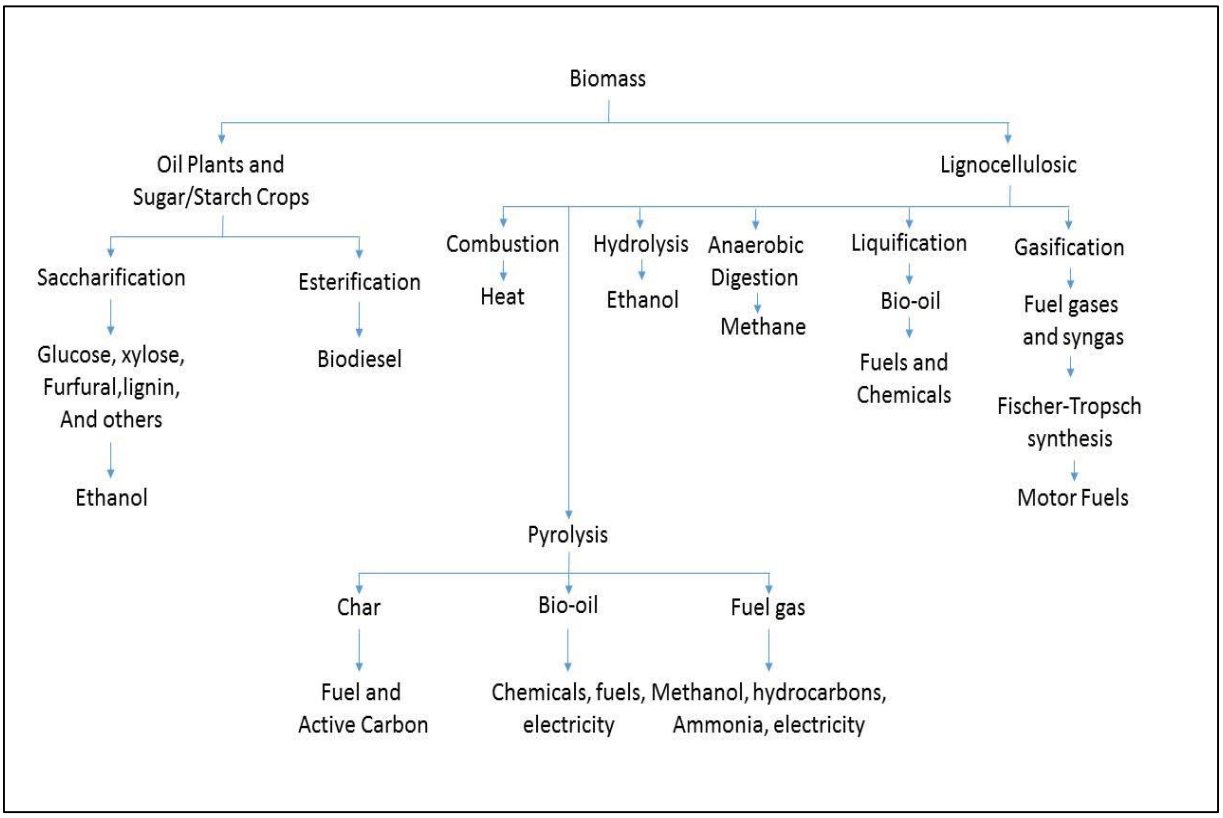

Figure 2.1 Schematic of Biomass conversion Techniques

Biochemical conversion of biomass to biofuels involves three basic steps:

a) Converting biomass to sugar or other fermentation feedstock through:
b) Fermenting these biomass-derived feed stocks using:
c) Processing the fermentation product to produce fuel-grade ethanol and other fuels, chemicals, heat, and electricity.

Advantages of Bio-oil:-

- Liquid fuel
- Decoupled conversion
- Easier to transport than biomass or syngas

2.2 UP-GRADATION OF BIO-OIL

Because of major chemical variations among petroleum and bio-oil, pyrolysis oil cannot be use straight as a transportation fuel or bio-oil cannot be "dropped-in" to existing petroleum refinery processes. Of particular note, raw bio-oil has properties of:-

(i) lower heating value
(ii) high content of oxygen
(iii) high content of solids
(iv) higher viscosity
(v) chemically instable

Thus, Bio-oil has to be upgraded. Bio-oil comprises a large number of oxygenated organic compounds with an extensive series of molecular weights, usually in lesser percentages. Because of presence of oxygenated compounds, untreated bio-oil becomes unstable in long-term storage. It is not miscible with any conventional hydrocarbon-based fuel. During storage, the chemical composition of bio-oil changes towards thermodynamic equilibrium, which causes changes in co-solubility of its many compounds, molecular weights and viscosity. Besides high viscosity problem, single phase bio-oil can separate into various thin aqueous, slurry, waxy, and sludgy phase during aging. These separation causes rapid plugging of fuel filters. The phases of bio-oil can be categorize conceptually as purification of feed, modification by chemical reaction, heteroatom removal, separation and cracking.as shown in fig 2.2. In real practice, as published in research, clean separation between the operations does not exist. However, there is a growing agreement that these components are mandatory in order to produce a finished fuel. In this, some phases can be joint in a single unit operation or scatter over multiple unit operations, The schematic of refinery integrations and bio-refinery are as in dia.2.2[9].

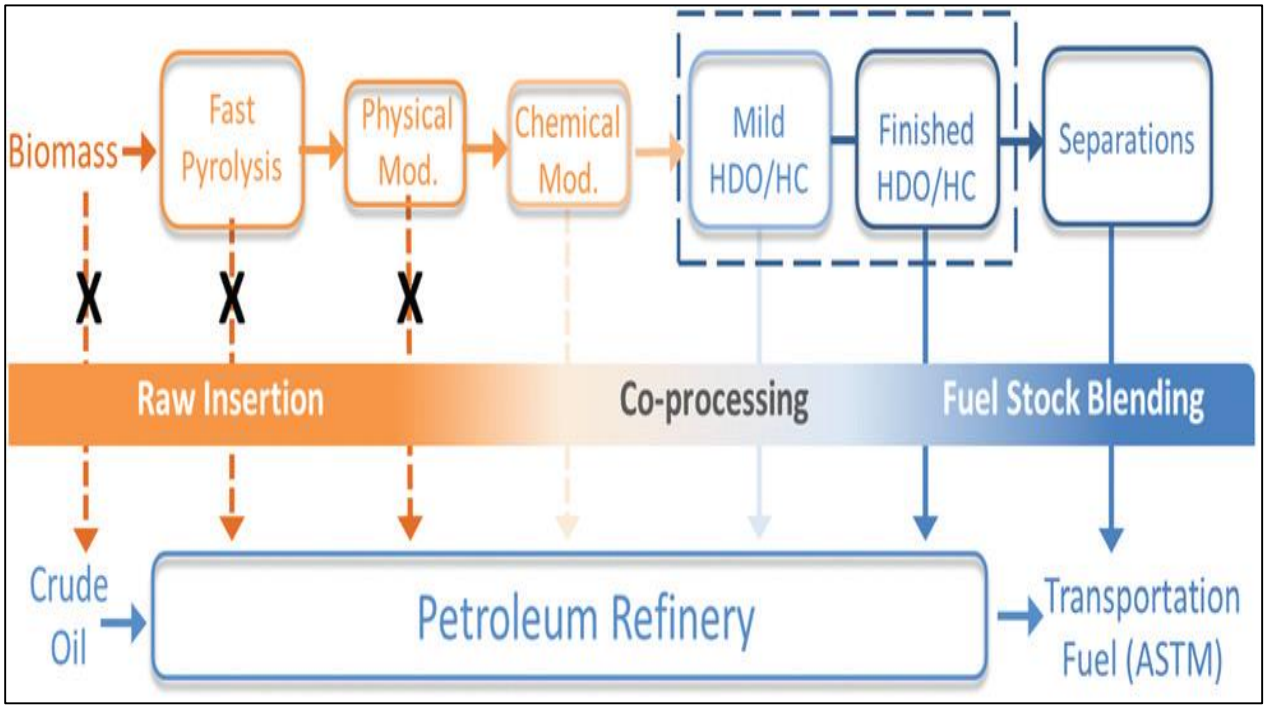

Figure 2.2 Proposed refinery integrations and biorefinery

Profitably, the deduction of chemically-bound oxygen to produce a bio-oil more similar hydrocarbon liquid

(i) Increase in heating value
(ii) Compatibility with petroleum hydrocarbons
(iii) Increase in stability
(iv) Decrease in viscosity

Particularly for the comparatively strong aryl–oxygen bonds, effective deoxygenation has proven to be exclusively challenging, (Table 2.1)[3]. Thus, deoxygenation is a critical difficulty to preventing transportation fuel manufacturing from pyrolytic oil at the industrial scale. Therefore, there is a ongoing need for new chemistries and catalytic processes.

Table 2.1Bond dissociation energies (BDE) for oxygenates common to bio-oil, where R= alkyl & Ar= aryl

Bond Type	BDE (Kj mol^{-1})
R-OR	339
Ar-OR	422
R-OH	385
Ar-OH	468

2.3 CATALYTIC UP-GRADATION PATHWAYS AND REACTIONS

There are two promising process proposals to catalytically upgrade pyrolysis oil to a liquid hydrocarbon transportation fuel are 1) in situ and 2) ex situ catalytic fast pyrolysis (CFP). The key difference among these methodologies is the employment of the deoxygenation catalyst in the process, either internal or external with respect to the position of pyrolysis reactor as in fig.2.3. In ex situ CFP, dried biomass is quickly heated to yield pyrolysis vapors. These pyrolysis vapors are passed through a cyclone separator to eliminate char and other solid particles, is then directed, without quenching, to a deoxygenation catalyst. After condensation these yields stabilized bio-oil. .

In situ CFP, dried biomass, in the presence of a deoxygenation catalyst, is quickly heated. Vapors gets deoxygenated after production. This results in a stabilized bio-oil when these vapors are condensed. CFP, in both cases has potential to accomplish upgrading in presence of inert carrier gas (cracking) or with a co-feed of hydrogen (hydro-deoxygenation). Organic fraction of bio-oil needs further hydro-treatment regardless of the method employed or the presence/absence of hydrogen that to in one or more stages to cope up with transportation fuel specification. The schematic of process block dia.2.5[9]

There are three general pathways to upgrade bio-oils directly to liquid transportation fuels:

(i) Hydro-deoxygenation (HDO)
(ii) zeolite cracking (ZC)
(iii)Emulsification with diesel fuel.
(iv)Steam reforming the bio-oil to produce syngas, followed by production of liquid fuels via Fischer–Tropsch or similar chemistry.

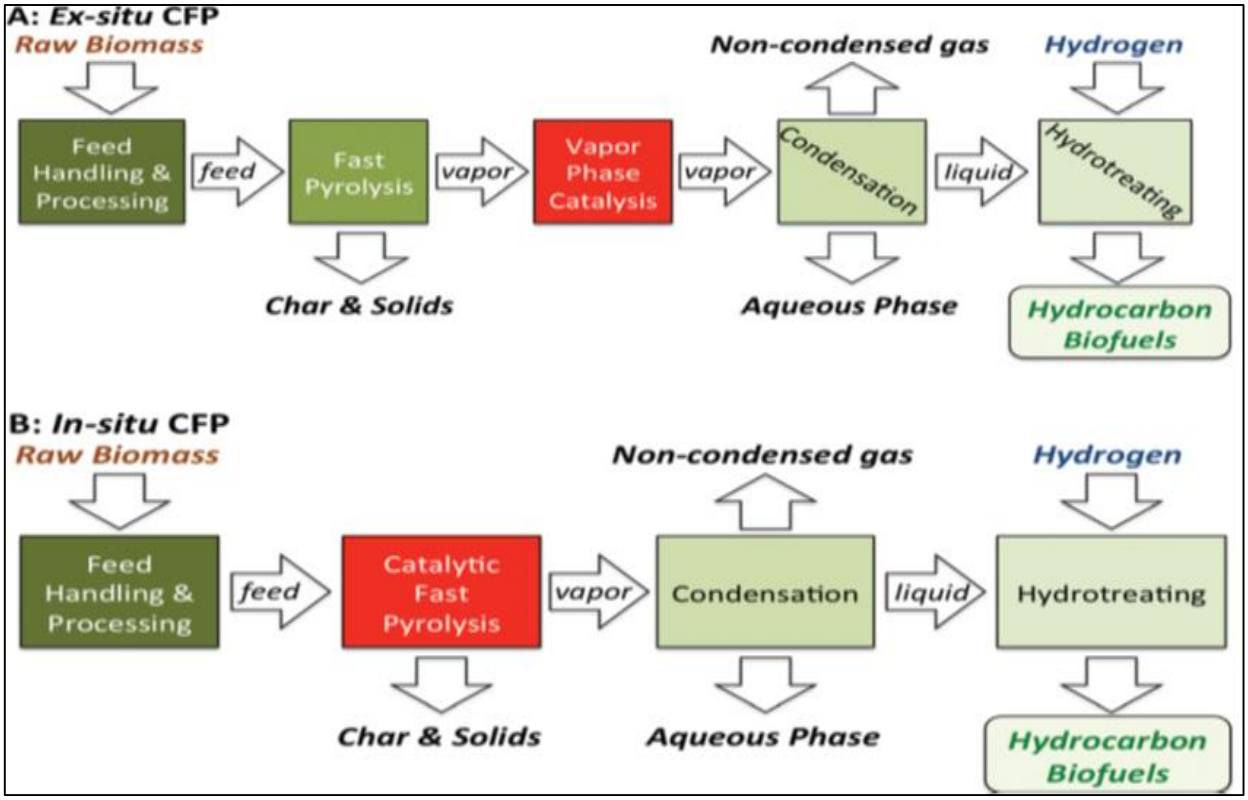

Figure 2.3 Block diagram for A) ex situ CEP process and B) in situ CEP process

ZC and HDO are catalytic upgrading methodologies, while emulsification of bio-oils into diesel fuel by using surfactants does not need a catalytic process[9]. The term "catalytic upgrading" of bio-oil complex network of many reactions, simplified by oxygen elimination products i.e. deoxygenation and hydrocarbon products. The representation of catalytic up-gradation is shown in dia.2.7[2]

DEOXYGENATION= (DCO + CRA + HCR + HYD + DDO + DAO + DMO +MT + HDO)[9]

1. DCO- De-carbonylation and Decarboxylation- eliminate oxygen as CO and CO2
2. CRA, HYD, HCR - Cracking Hydrocracking and Hydrogenation - produce alkenes, which are successively hydrogenated to alkanes, and can yield alcohols. Removal of oxygen via cracking yields CO2.
3. DDO, HDO - Direct deoxygenation (hydro-genolysis) and Hydro-deoxygenation - reactions remove oxygen as water, and preserve all carbon atoms in the original bio-oil
4. DAO, DMO – De-alkoxylation and De-alkylation - removes oxygen as an alcohol (methanol for DMO)
5. MT- Methyl transfer - another pathway to rise branching in the final mixture
6. Carbon Formation –

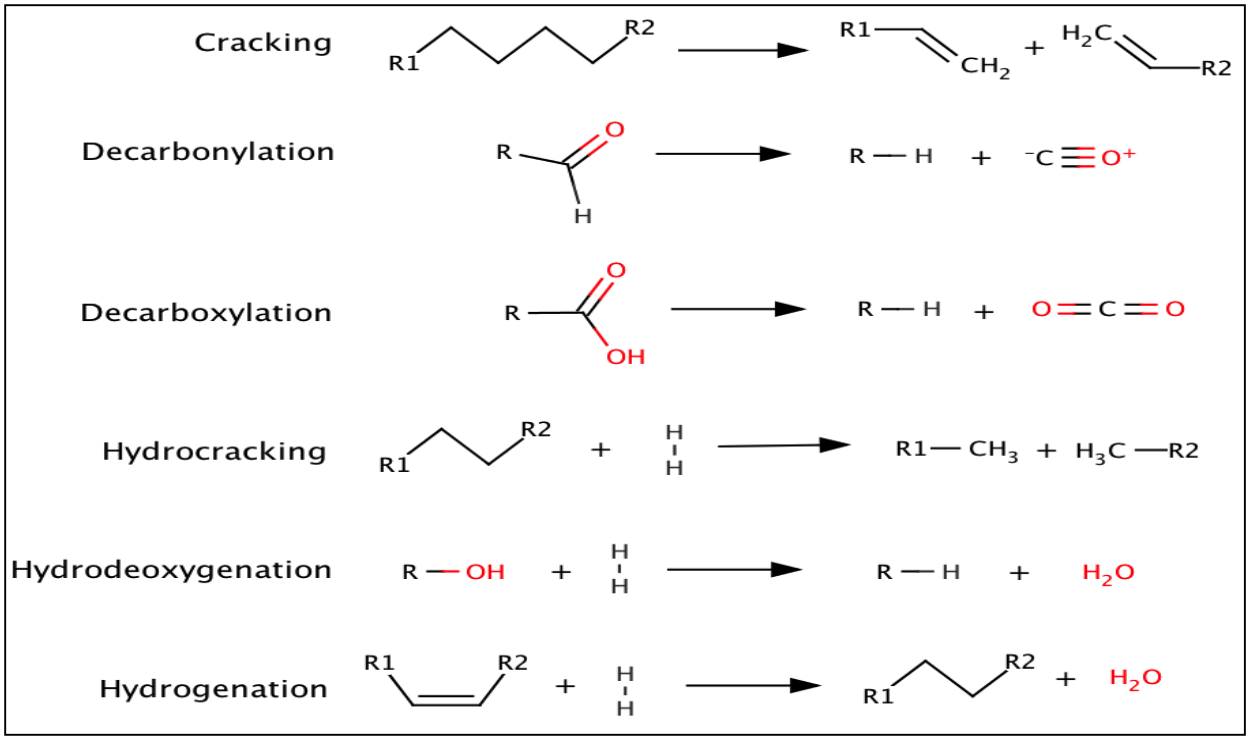

Figure 2.4 :-Representative catalytic upgrading reactions.

The refining process of lingo-cellulosic feed stocks to hydrocarbon biofuels is subdivided into two general types. First, whole biomass is decomposed and upgradeable to liquid or gaseous product which is carried out through thermochemical pathways. This produces synthesis gas (by gasification) or or by hydrolysis paths to produce sugar or bio-oils (by pyrolysis or liquefaction), monomers which are then deoxygenated to form upgradeable intermediates.[7]

Theodore Dickerson el at have discussed about developing catalyst multifunctional catalysts used in situ which are useful in both hydro-deoxygenation and zeolite cracking. Study of different catalyst in comparison is given, which includes $CoMoS_2$/Al2O3, NiMoS2/Al2O3, Pd/C, ZSM5, Al/MCM41.[8]

D. A. Ruddy et al have discussed advances in heterogeneous catalysis by structure-function relationship that defines catalyst performance (i.e. activity, selectivity, life time). Applications of transition metals sulfide catalysts for deoxygenation processes were compared with processes of noble metals, metal carbide, niride and phosphide catalysts.[9]

A. V. Bridgwater has briefly discussed conversion of biomass and up-gradation. He has briefly discussed the technologies related to use of catalysts in chemical production and use of catalytic processes in up-grading primary pyrolysis product to higher quality and higher value fuels and chemical.[10]

Dinesh Mohan et al hve reviewed the literature on woody biomass pyrolysis both fast and slow with respect to physical and chemical aspects. The effects of wood composition, structure heating rate and residence time and yield of volatiles[11]

A.V. Bridgwater, in his paper, has discussed the potential of of biomass and solid waste to convert in the usable energy. He has discussed the techniques of converting biomass to liquid or gaseous fuel. All these thermochemical processes are influenced by many factor such: catalyst, feed pretreatment, contact time, heating rate, feed material, moisture content of feed, particle size of feed, pressure, reactor geometry, temperature and residence time. [12].

J. Wildschut et al. have done experimental study on hydro-treatment of fast pyrolysis oil at 350^0 C and 200bar in a batch reactor. It has shown that, performance of Ru/C is a function of number of recycles. The oil yield (55-30%) and H/C ratio (1.24 to 1.08) has been noticed. The catalyst has shown lowest decrease in BET area and dispersion after reaction.[13]

Changjun Liu et al estimated catalytic fast pyrolysis is most efficient method for to pyrolyse lingo-cellulosic biomass which is high in oxygen content. Reactions such as de-carbonylation, de-carboxylation, de-hydrogenation and ketonization can be employed to remove oxygen and to produce hydrocarbons with desired carbon backbone. Oxygen removed in the form of CO_2 is most desirable which preserves most of hydrogen in bio-oil.[14]

Douglas C. Elliottet et al have described range of experiments done for range of catalysts and range of operating parameters like temperature, pressure and flow rate with bio-oil derived from different bio-mass. Palledium on carbon catalyst was used in bench scale, fixed bed reactor to hydrogenate bio-oil and produce partially upgraded bio-oil prepared for processing at more severe hydrocracking processes.[15]

Ofei D. Mante et al have focused on developing understanding of impact of biomass feedstock and catalytic pyrolysis on physiochemical properties of upgraded bio-oil. Different biomass feedstock like woody pine, hybrid poplar, pinyon juniper etc. have been treated with are treated with HZSM5.[16]

Richard French et al in their work evaluated a set of profitable and laboratory-synthesized catalysts for their hydrocarbon production performance via the pyrolysis/catalytic cracking means. Three types of biomass feedstocks; cellulose, wood and lignin were pyrolyzed (batch experiments) in quartz boats in physical contact with the catalyst at temperature ranging from 400°C to 600°C and catalyst-to-biomass ratios of 5– 10 by weight.The highest yield of hydrocarbons (approximately 16 wt.%, including 3.5 wt.% of toluene) was achieved using nickel, cobalt, iron, and gallium-substituted ZSM-5. De-oxygenation activity decreases as time passes because of coke deposition.[17]

Biomass of pine wood was catalytically pyrolysed in A Aho et al in fluidized bed reactor at 450^0C with different structures of acidic zeolites like beta Y, ZSM5 mordenite. It was found that

ketones and phenols were dominating compounds and smaller quantity of polymerized hydrocarbons.[18]

Paul T Williams et al have pyrolyzed rice husk in fluidized bed reactor at 400 to 600^0C with 50^0C interval wit zeolite catalyst. The pyrolysed oil were collected in series of condensers and cold trap and determined the yield as well as composition in relation to process conditions. It was observed that Polycyclic aromatic hydrocarbons (PAH) were present in low concentration and increases with increase in temperature.[19]

Qi Dang et al have employed different reaction conditions like initial hydrogen pressure (0.5 MPa- 2.0MPa), mass ratio of ethanol to bio-oil (5:1,3:1, 2:1, 1:1), reaction temperatures (260^0C, 280^0C, 300^0C) and catalysts 5%Pt/SO_4^{2-}/ZrO_2/SBA-15. The hydrogen pressure inhibit coke formation and increase mass ratio of ethanol to bio-oil (5:1, 3:1).[20]

Jelle Wildschut et al have estimated study of series of experiments using heterogeneous nobel metals as catalysts (Ru/C, Ru/TiO_2, Ru/Al_2O_3, Pt/C and Pd/C) and results were compared with typical hydro-treatment catalyst (sulfide NiMo/Al_2O_3, CoMo/Al_2O_3). The reactions were carried out at temperatures of 250^0C and 350^0C with pressure of 100 and 200bar. The Ru/C were found to be superior to classical hydro-treatment catalyst in the perspective of bio-oil yield and de-oxygenation level.[21]

Peng Lim Boey et al have discussed various issues related to CaO catalyzed transesterification. The diverse performance of CaO in neat, loaded and mixed forms, as well as support for other catalyst, CaO tolerance are suitably addressed.[22]

The experimental set up consists of Inconel tubular continuous down flow micro reactor with temperature range of 650^0C to 800^0C. The product gases essentially consist of H_2, CO, C_2H_4, C_2H_6, CH_4 and C_4^+ compounds. The process used can be employed for producing hydrocarbon and synthesis gas for applications.[23]

Kaiqi Shi et al discussed five types of catalysts such as metal oxide, molecular sieve, mineral, transitional metals. Molecular sieves such as HZSM-5, ZSM-5, MCM-41, SBA-15 and their modified forms are mostly used as catalysts. Type of catalyst produces markedly influence on bio-oil product, variety of catalyst and properties makes generalization difficult.[24]

R.H. Venderbosch et al have employed thermal treatment step/ direct hydro-processing at temperature 250^0C in the presence of H_2 and catalyst. The parallel reactions take place including re-polymerization, decarboxylation and hydro-treating.[25]

Mark Wright et al have developed techno-economical model for biomass pyrolysis and bio-oil up-gradation. It was done on the basis of 2000 MT/day up-gradation of bio-oil. The results showed that pyrolysis derived bio-oil is competitive with other alternative fuel. But technology is relatively immature resulting in higher level of uncertainty.[26]

Xuejun et al have done transesterification soybean oil using CaO. The experimental results showed that a 12:1 molar ratio of methanol to oil, addition of 8% CaO catalyst, 65^0C reaction temperature and 2.03% water content in methanol gave the best results, and the biodiesel yield exceeded 95% at 3 h. CaO maintained sustained activity even after being repeatedly used for 20 cycles and the biodiesel yield at 1.5 h was not affected much in the repeated experiments.[27]

Solid acid $40SiO_2/TiO_2$-SO_4^{2-} and solid base $30K_2CO_3/Al_2O_3$-NaOH were prepared and compared with catalytic esterification activity according to the model reaction. Upgrading bio-oil by solid acid and solid base catalysts in the accustomed experiment was investigated. The ester reaction was promoted by both solid acid and base catalysts. [28]

Suping Zhang Et al have done experiment of fast pyrolysis of saw dust with fluidized bed unit 5kg/h. The liquid product formed was separated into water phase and oil phase. The oil phase was upgraded using sulfided Co-Mo-P catalyst in autoclave. [29]

Michael Nolte et al have showed the pyrolysis oils are emulsion-like fluids, containing aqueous and phenolic phases, and can be more than 400 times more viscous than water at 25^0C. A strong dependence of viscosity upon the temperature showed that the viscosity of poplar and oak 500^0C oils increased over 220-fold between 55 and -5^0C. Generally, the oils that had higher water contents had lower viscosities.[30]

Wu jun liu have employed method of catalytic pyrolysing with zero valent metals (Al, Fe, Mg and Zn) at ambient temperature and pressure. In the upgraded bio-oil, the CvO compounds are reduced from 9.8 to 3.1 mol%, and the pH value was elevated from 3.53 to 4.85, which significantly increased the chemical stability and decreased the corrosiveness of bio-oil.[31]

The following table gives the brief idea of some of catalyst used in different papers. Some of them are transition metal catalyst, some are noble with support. The reaction conditions, reactor, ratio etc. are given in following table2.2

Table 2.2 Overall Review of Catalyst used in the Different papers.

Catalyst	Reactor	Temp.	Pressure	Oil Yield	Oxygen	Paper Title
Ru/C 5 wt% Beech wood oil	Autoclave 100ml	350°C 16°/min. 4h	N_2 flush H_2 -20bar up to 200bar	55-30 wt.%	up to 85wt%	Catalyst studies on Hydro-treatement of fast pyrolysis[13]
Pd/C Popalar biomass	Fixed Bed Catalytic Reactor 0.28LHSV	300°C 8h	H_2-140bar	59 wt.%	up to 60wt%	Catalytic Hydro-processing of biomass fast pyrolysis oil to produce Hydrocarbon[15]
Pt/Al_2O_3 5 wt%	Autoclave 30 ml	350°C 4h	N_2-100bar	81%	up to 88-90wt%	Bio-oil up-gradation over platinum catalysts using in situ generated H_2[32]
Ru/TiO_3 5 wt% Beech wood oil	Autoclave 100ml	450°C 16°/min. 4h	N_2 flush H_2 -20bar up to 350bar	67 wt.%	up to 77 wt.%	Hydro-treatment of Fast pyrolysis oil using Heterogeneous Nobel metal Catalyst[21]
$CoMoS_2/Al_2O_3$	Autoclave 100ml	450°C 16°/min. 4h	200bar	26 wt.%	up to 81 wt.%	Hydro-treatment of Fast pyrolysis Oil using Heterogeneous Nobel metal Catalyst[21]

3 EXPERIMENTAL SECTION

3.1 METHOD

To study the project and fulfill its objective, experiments were carried on biomass viz. Castor seed which is oil containing seed. The sample seed i.e. Castor seed is pyrolyzed in semi batch reactor with different catalysts. Degradation temperature was found by doing TGA. Then liquid product obtained was characterized by different physical and chemical properties. Elemental composition were obtained from EDX analysis. Fourier Transform Infrared Spectroscopy (FTIR) was done to know functional groups present while Gas Chromatography Mass Spectroscopy (GCMS) for chemical analysis. The physical properties like flash point, fire point, pour point and calorific value were characterized to know its suitability as fuel. The pore structure, elemental compositions were investigated from SEM/EDX analysis.

3.2 RAW MATERIAL

Castor seeds as shown in fig. 3.1 were used as biomass and obtained from local supplier. Castor seeds obtained are sundried for 2 days, then dried in oven at temperature 105^0 C and used as feed.

Figure 3.1 Castor seeds which are used as biomass

3.3 CATALYST

The catalyst used here were CaO, MgO, Fe_2O_3, ZnO, TiO_2 obtained from Merk. The catalyst used were supplied as a fine powder.

3.4 CHARACTERIZATION OF RAW MATERIAL

Raw material was characterized by their proximate, ultimate and thermo-gravimetric properties.

3.4.1 Thermal Properties using TGA

Thermo-gravimetric analysis or thermal gravimetric analysis is a type of testing for samples which determines changes in weight to a temperature, programmed in a controlled atmosphere. Thermal gravimetric analysis is a process which involves heating a mixture to a high enough temperature so that one of the components decomposes into a gas that dissociates into the air.

The thermos-gravimetric analysis (TGA) of raw material was done using DTG 60 device. The analyzer consists of a high-precision balance with a pan of platinum loaded with the sample. Pan resides in a furnace and gets heated or cooled during the experiment. Different process using a quartz crystal microbalance is devised for measuring smaller samples on the order of a microgram versus milligram with conventional TGA. Sample was placed in a small electrically heated oven with a thermocouple for accurate measurement of the temperature. The atmosphere may be supplied with an inert gas to prevent oxidation or other undesired reactions. A computer was employed to control the instrument.

Pyrolysis involves heating of a substance in absence of air at a particular high temperature. Therefore, the temperature for effective pyrolysis of the castor seeds was determined using TGA. Around 20-30 milligrams of sample was taken and heated up to a final temperature of 700°C and a residence time of 1 minute at 700°C was allowed. TGA were performed at a heating rate of 20°C/Min. Thermo-gravimetric weight loss curve was plotted against temperature. It provides a range of temperature in which maximum thermal degradation of castor seed takes place. The TGA analysis of sample depends on the amount of cellulose, hemicellulose and lignin content of sample.

3.4.2 Proximate Analysis

Proximate analysis (defined by ASTM), is the estimation of %moisture, volatile matter, fixed carbon (by difference) and ash by prescribed methods. This is primarily carried out to establish the quality of the feed. It gives speedy and valuable information concerning commercial classification and determination of suitability for industrial use.

- **Moisture content:-**Moisture content is calculated by measuring a known quantity of air dried biomass ASTM D-871-82. Finely ground castor seed was taken on petri dish and kept at a temperature of 1030C for one an hour. Before and after heating weight of sample were measured and noted. The difference in weight divided by initial sample weight gives moisture content. Maximum the moisture content, maximum is the transportation cost and lower is the calorific value. Thus, low moisture content in biomass is preferable.
  % moisture content = (Loss in weight / weight of sample taken) *100

- **Volatile matter:-**When fuel is heated, volatile matter of a fuel are released in form of condensable and non-condensable vapor. The amount of released vapors i.e. volatile matter depends on the rate of heating and the temperature to which it is heated. The applicable ASTM standard for determination of volatile matter is ASTM D-3157-07. 1g powdered sample after removing moisture was taken in a crucible covered with lid and kept at 9500C for seven minutes. Difference of Weight of sample before and after heating divided by initial sample weight gives the %volatile matter. Volatile matter is a complex mixture of various organic and inorganic gaseous and liquid products result from thermal decomposition. Determination of % volatile matter provides us with some fuel properties related to smoke forming tendency, length of flame and ignition.
  % volatile matter = (Loss in weight due to removal of matter / weight of sample taken) * 100

- **Ash content:-**The final residue left after the complete combustion of sample is ash. It was found out by heating 1 gm of sample at 650-750^{0}C for one and half hour without lid. Ash, the inorganic solid residue left after the fuel is completely burned, has primary ingredients such as silica, aluminum, iron, and calcium and sometimes small amounts of magnesium, titanium, sodium, and potassium. Ash content is determined by ASTM test protocol D-1102.
  % ash = (Weight of ash left / weight of sample taken) * 100

- **Fixed carbon:-**Moisture, volatile matter, ash content together subtracted from 100 gives the fixed carbon content. Fixed carbon represents the solid carbon in the biomass that remains in the char in the pyrolysis process after de volatilization. It is determined as:
  % Fixed Carbon = 100- (% Moisture - % Volatile matter - % Ash content)

3.4.3 Ultimate Analysis

The ultimate analysis i.e. elemental analysis was done in CHNSO Elemental analyzer (Vario El Cube Germany) to know elemental compositions.

3.5 EXPERIMENTAL SET-UP

The schematic diagram of the pyrolysis of biomass experimental set up is given in fig. 3.2 and experimental setup is given in fig. 3.3. The pyrolysis unit comprises of PID controller, an electrically heated furnace, pyrolysis semi batch reactor, glass condenser and measuring cylinder. Highly sensitive PID controller maintains the temperature of furnace. The reactor is cylindrical shaped vessel made up of stainless steel. The vapors coming out of rector were allowed to flow through glass condenser. Water is circulated as cooling medium in the condenser via a pump.

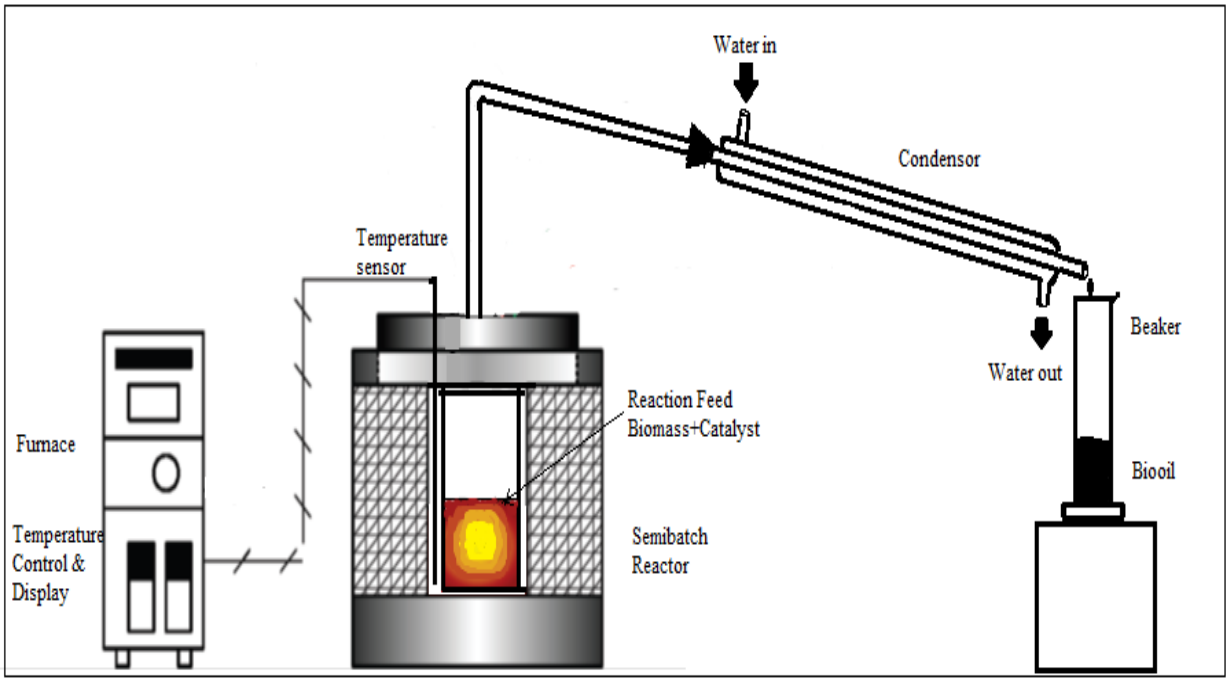

Figure 3.2 Schematic diagram of experimental setup for pyrolysis of biomass

Figure 3.3 Experimental setup for Pyrolysis

3.6 EXPERIMENTAL PROCEDURE

The seed, raw materials were purchased from market and used, after drying first in sunrays for 2 days and then in oven at 105^0C, as feed to the reactor. Biomass was pyrolyzed at different temperatures 500^0C, 550^0C and 600^0C at the heating rate of 20^0C/min. Biomass viz. castor seeds of 15gm were fed to the semi batch reactor and reactor is then placed vertically in electrically heated furnace. The temperature of furnace was controlled by PID controller. The vapors generated in reactor were condensed by water cooled condenser and condensed liquid i.e. bio-oil was collected in measuring cylinder. As liquid contained two fractions namely; aqueous phase and oil phase, were separated by gravity separator. The residue i.e. bio-char was collected from the reactor after cooling. Also series of experiments were conducted to determine the influence of different catalyst to biomass ratios between 1:14, 1:10, 1:8, 1:6 and 1:2 at 550^oC at heating rate of 20^0C/min. These series of experiments were conducted with previously mentioned catalyst. For this series of experiments, pyrolysis of biomass viz. castor seed, 15gm for each run along with different catalyst with different ratios were done. The liquid i.e. bio-oil was then collected, weighted and stored in air tight bottles. The sample of residue i.e. bio-char or pyrolytic char collected after cooling of reactor were collected, weighted and stored in air tight bags. During sample runs various data like yield of char, reaction time, yield and volume of liquid product were noted down. Variation in liquid product, yield of char, and gas (volatiles) with respect to temperature were plotted. Variation in reaction time with respect to temperature was also plotted. The bio-oil collected is shown in fig.3.4

Figure 3.4 Bio-oil collected in measuring cylinder

3.7 CHARACTERIZATION OF BIO-OIL

3.7.1 Characterization of Physical Properties

The pyrolytic oils obtained were characterized for their physical and chemical properties. The physical properties such as color density, viscosity, pH, flash point, fire point, pour point, calorific value of all pyrolytic oil were determined and stated in the result and discussion part. The viscosity of bio-oil is measured by using Redwood viscometer while flash point and fire point using flash point apparatus.

3.7.2 Characterization of Chemical Properties

3.7.2.1 Functional group analysis by FTIR

Fourier Transform Infrared spectroscopy (FTIR) is an essential analysis technique for identification of various characteristic functional groups present in fuel oil. As interaction of an infrared light takes place with chemical bond present in oil stretches, contracts, and absorbs infrared radiation in a specific wave length range in the presence of molecules. The functional groups existing in the bio/pyrolytic oil were recognized by using this principle. The FTIR spectra were generally composed in the range of 400-4000 cm-1 region, 8cm-1 resolution. The rotational and vibrational status of the molecules changes by absorption in infrared region. The absorption frequency is governed greatly on the vibrational frequency of the molecules. The absorption intensity depends on the infrared photon energy that can be transferred to the molecule which ultimately depends on the change in the dipole moment that occurs as a result of molecular vibration. A molecule will not absorb infrared light unless the absorption causes a change in the dipole moment. All compounds except for elemental diatomic gases such as N_2, H_2 and O_2 have infrared spectra. Thus most components present in a flue gas were also analyzed by their characteristic infrared absorption.

To determine the functional groups present in the pyrolytic oil, Fourier Transform Infrared spectroscopy of the oil is being analyzed in a Perkin-Elmer infrared spectrometer.

3.7.2.2 Chemical compounds by GC-MS

Gas Chromatography – Mass Spectrometry for the pyrolytic or bio-oil was accomplished using a GC-MS OP 2010 analyzer [SHIMADZU] to investigate the chemical compounds existing in the bio-oil i.e. product. Chromatography is specifically designed for components identification by separating mixtures of chemicals into individual components. After isolation, evaluation of components is done individually. In nearly all chromatography, after introduction or injection of sample mixture in mobile phase, separation occurs. In liquid (LC) chromatography, the mobile phase is solvent whereas in the gas (GC) chromatography, an inert gas behaves as mobile phase e.g. helium. Mobile phase is the one who carries the sample mixture across stationary phase. The stationary phase is actually a chemical that can attracts components present in mixture of a sample. The column tube made up of glass or stainless steel with various dimensions. The mobile phase comprises mixture of compounds which interacts with the stationary phase. The rate of interaction for is different for individual compound in a mixture. The compounds with fastest interaction rate will elute from column first & those with slowest interaction rate will elute from the column last. With examination of the changing characteristics

for the mobile phase as well as the stationary phase, the different mixtures of chemicals are able to get separated. Additional enhancements to this separation process are also made by altering the temperature and pressure for the stationary phase and the mobile phase respectively.

GC is equipped with a thin, long column having a thin interior stationary phase solid coating (5% phenyl-, 95% dimethyl siloxane polymer). The capillary column has 0.25 mm diameter. This particular column is used for non-polar, semi volatile organic compounds. The capillary column will be held in an oven which is provided with the system of increasing the temperature steadily (or in GC terms, ramped). With gradual increase in the temperature, the compounds with lesser boiling points exit from column faster than those having greater boiling points. After separation, compounds exit from column and move in a detector. Detector generates an electronic signal in the presence of a compound. Higher the concentration of compound in present sample the greater is the signal. Then, the computer processes this signal. The Retention time (RT) is a time when the sample is injected i.e. time zero to when exit of sample takes place. Meanwhile the instrument goes on running, the computer produces a graph by making use of these signals. These peaks of chromatogram are representative of signal developed at point when compound exits from column of GC into detector. The Retention Time (RT) is represented by x-axis, and intensity (abundance) of the signal is represented by y-axis.

GC-MS is used for both the qualitative and the quantitative identification and measurement of semi volatile, volatile organic compounds in complex mixtures. The pyrolytic oil obtained was characterized by using GC/MS- QP 2010 SHIMADZU. It was also armed with the flame ionization and the mass spectrometry (GC-FID-MS) detection. A capillary used here was coated with DB-5 film 0.25 μm thick and has diameter 0.25 mm with length of 30 m. The GS was provided with split injector at 200ºC and with 1:10 as split ratio. The carrier gas used was helium gas with flow rate 1.51 ml/min and having 99.995% purity. The initial temperature in oven was set at 70 ºC for 2 min and increased up to 300 ºC with rate of 100 ºC/min and maintained for time of 7 min. The NIST library facilitate the acknowledgement of all compounds. Mass spectrometer was generally operated for interface temperature about 240ºC & ion source temperature of 200 ºC for range of 40-1000 *m/z.*

3.8 BIO-CHAR CHARACTERIZATION

3.8.1 Proximate Analysis

Proximate analysis for bio-char was done according to ASTM D3173-75. In this analysis, %moisture, volatile matter, ash, fixed carbon was determined.

3.8.2 Ultimate Analysis

Ultimate analysis for bio-char was carried out with the aid of elemental analysis or CHNSO analyzer. In this analysis elemental percentage was determined.

3.8.3 SEM Analysis

Scanning Electron Microscope (SEM) is instrument use to define morphology of material under view. Energy-dispersive X-ray spectroscopy (EDS or EDX) is the diagnostic technique which is used for chemical characterization or elemental analysis or of a sample. EDX bank on the examination of X-ray excitation and interaction of some source with sample. Each component has a distinctive atomic structure. The representative capabilities are because of this fundamental principle. This permits distinctive set of peaks for X-ray spectrum which arouses the emission of typical or characteristic X-rays of specimen. Charged particles such as protons or electrons a beam of X-rays, with high energy was concentrated into the sample to be examined. An atom belonging to the sample comprises ground state electrons which were bound to the nucleus in discrete energy levels. The incident beam excited an electron in from an inner shell which ejected from shell by generating an electron hole at its site. Then, that hole is filled by an electron from a higher-energy shell. Difference between the energy of the shell at higher-energy and that of shell at lower energy was unconfined in X-ray form. The energy and number of the X-rays discharged from a specimen was measured by using an energy-dispersive spectrometer. The X-rays energy are representative of the difference in energy among the two shells. The elemental configuration of the specimen was measured, by atomic structure for elements through they were allowed. Scanning electron microscopy images were captured by using JEOL microscope (JSM-6480 LV) and acceleration voltage of 15 kV at altered magnification values to get the perfect view of pore density and diameter.

4 RESULT & DISCUSSION

4.1 RAW MATERIAL CHARACTERIZATION

4.1.1 Proximate and Ultimate Analysis

Proximate and ultimate analysis were done to characterize the raw materials. The moisture, ash, volatile matter, fixed carbon content in the fuel was determined by proximate analysis. The fuel's quality and type can be determined quickly and easily by this analysis. Conversion efficiency and heating value drastically depend upon the moisture content of biomass. Biomass, during storage, decomposes more rapidly if the moisture content is higher. After combustion, volatile matter converts in the form of light hydrocarbon, gas and tars. Biomass contains around 75% of volatile matter, which is higher than the coal. Due to higher content of volatile matter, biomass devolatilizes readily than solid fuel. Also, biomass liberates less fixed carbon, which is for pyrolysis and gasification. Along with moisture content, ash content also affects the heating value. As the plant structure includes of a wide variety of mineral matter namely salt of potassium, calcium, magnesium, silica and ash content are vital part of biomass. Ash content varies with plant and soil condition, weather conditions. The proximate as well as ultimate analysis results of all raw materials are given in table 5.1 and table 5.2 respectively. From proximate analysis, it was noted that raw material i.e. castor seed contains higher percentage of volatile matter and less amount of ash content and moisture. From ultimately analysis, it was noted that, higher is the oxygen content which is trailed by carbon C and hydrogen H with a less amount of sulphur.

Table 4.1 Proximate Analysis results of Castor seed

Sr. No.	Content	Weight percentage
1	Moisture	26.86
2	Volatile matter	15.74
3	Ash	8.32
4	Fixed carbon	2.8

Table 4.2 Ultimate analysis of Castor seed

Sr. No.	Element	Weight percentage
1	Carbon	58.762
2	Hydrogen	6.438
3	Nitrogen	2.416
4	Oxygen	30.394
5	Sulphur	0.04
6	C/N	24.322
7	C/H	9.127

4.1.2 Thermo-gravimetric Analysis using TGA

In fig 4.1, TGA thermograph of bio-mass i.e. castor seed with the heating rate of 20^0C/min under atmospheric air condition is displayed. The representative parameters of de-volatization are described here. In this case, three step weight loss was noticed with the primary decomposition or 1st. decomposition occurred between 35^0C to 200^0C castor seed. This region signifies 6.71% weight loss at the heating rate of 20^0C/ min for castor seed. The 2nd and the rapid decomposition of the sample occurred between 200^0C to 500^0C signifying 79.24% for castor seed and rest 15.77% of residue for castor seeds respectively. The 1st. step decomposition characterizes the evaporation of water i.e. moisture content in biomass, 2nd. Decomposition characterizes principally the development of volatiles and during the 3rd step, the pyrolysis residue i.e. bio-char gradually decomposed, with the weight-loss rate getting reduced also residue ratio remains constant during end the decomposition. As the decomposition rate is high for the rapid decomposition region or 2nd step, it is called as active pyrolytic zone. In the course of this active pyrolytic zone, the weaker chemical bonds and intermolecular links were destroyed. Some small gaseous molecules were produced because of the lower temperature and the side aliphatic chains might had broken. In the 3rd step, chemical bonds had broken because of high temperature along with damage of skeletons of the parent molecules. Thus, lesser molecules in the form of gas phase formed from larger molecules with the formation of coke.

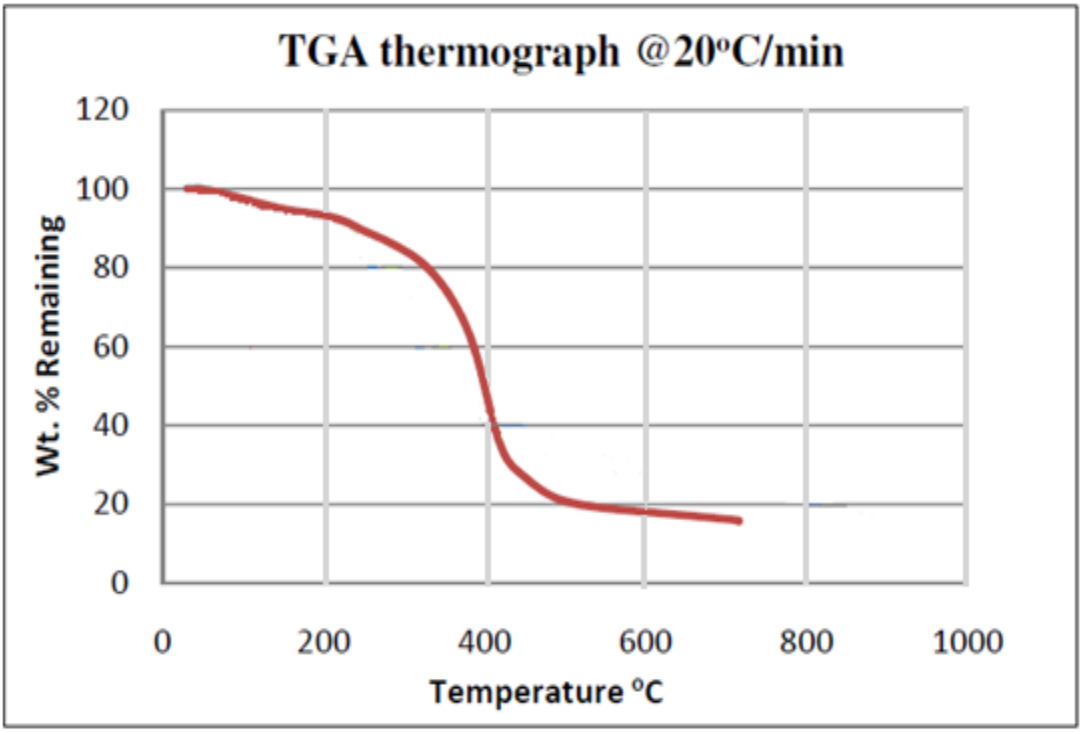

Figure 4.1 TGA graph for Castor seed

4.2 EFFECT OF TEMPERATURE ON YIELD PRODUCT / BIO-OIL

Fig. 4.2 shows the product i.e. bio-oil yield of slow pyrolysis for castor seed at a heating rate with 20^0C/ min. It was noticed that, with increment in temperature, yield of liquid product increases. It was observed that, up to certain temperature here 550^0C, the liquid i.e. bio-oil yield increased gradually and after then started decreasing with increment in temperature beyond 550^0C. This might had happen because of increased quantities of non-condensable gases and volatiles. The yield of char decreased as temperature increased. This occurs due to secondary reaction taking place in pyrolysis, representing that char materials decomposes as temperature gets higher. From the fig 4.2, it was noticed that, the liquid yield i.e. bio-oil increases from 49.16% to 60.12% by volume and 47.35% to 61.32% by weight with increase in final temperature from 475- 550^0C along with the decrease in char yield from 26.54 to 20.25%. For pyrolysis after temperature 550^0C, increase in the density of oil had noted with increase in temperature i.e. for same volume oil was weighting more. This might had happened due to development of denser liquid product at high temperatures as the residence time is lesser compared to lower temperatures. Fig.4.2 shows the effect of temperature on completion time i.e. Residence time. With increase in temperature, the decrease in Residence time or completion time was observed. This might be due to the emerging of more quantities of volatiles in a short time period. It was observed that, both yield of liquid and completion time i.e. Residence time of pyrolysis are functions of temperature. The optimum temperature for production of pyrolytic oil can be obtained by comparing the volumetric yield of pyrolytic oil, completion time or residence

time of pyrolysis with pyrolysis temperature. Thus, to obtain maximum yield of bio-oil with low density in optimum completion time, 550^0C found appropriate temperature for pyrolysis of castor seed.

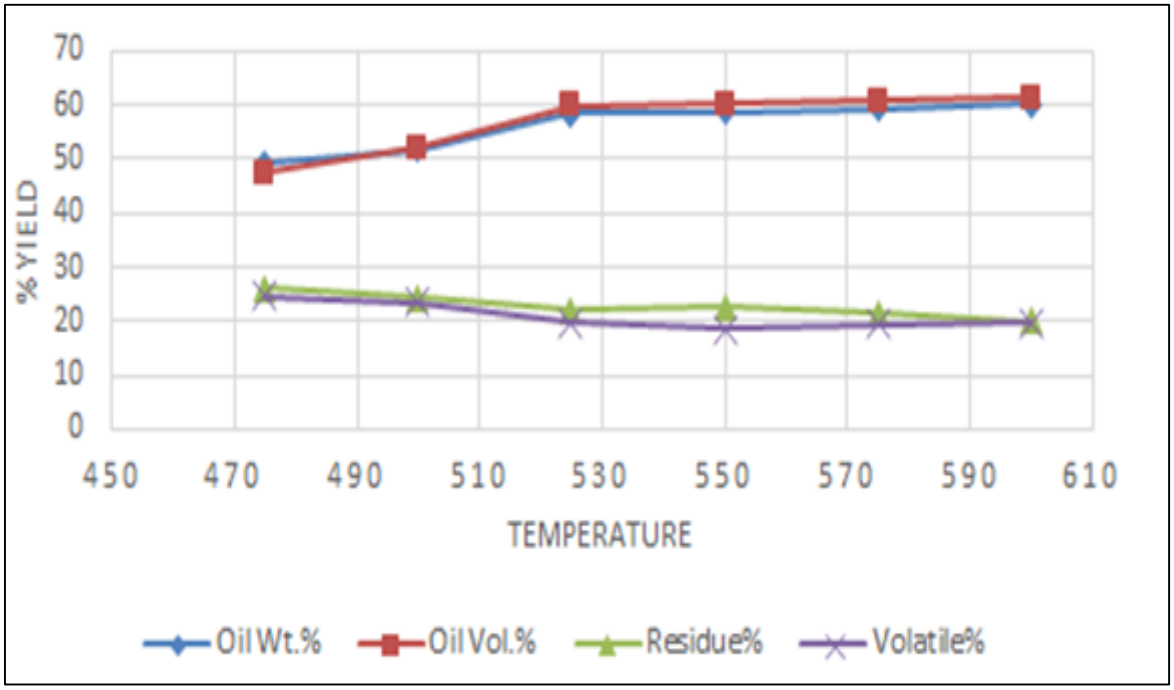

Figure 4.2 Effect of Temperature on yield of Product /Bio-oil

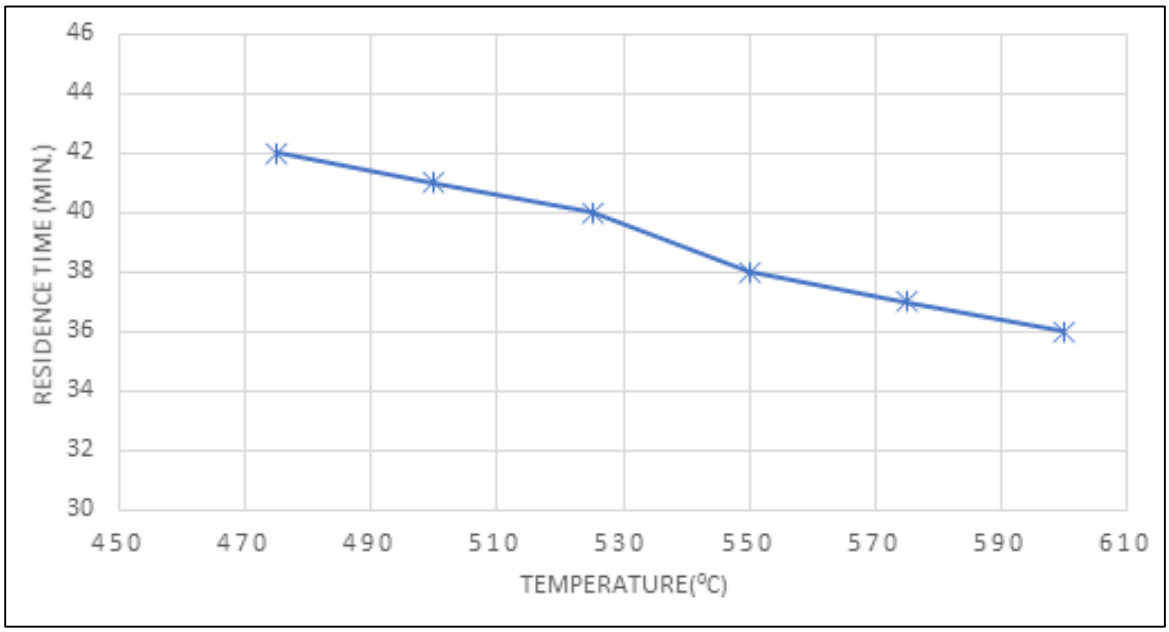

Figure 4.3 Effect of Temperature on Residence/ Completion Time

4.3 INFLUENCE OF CATALYST ON YIELD OF PRODUCT / BIO-OIL

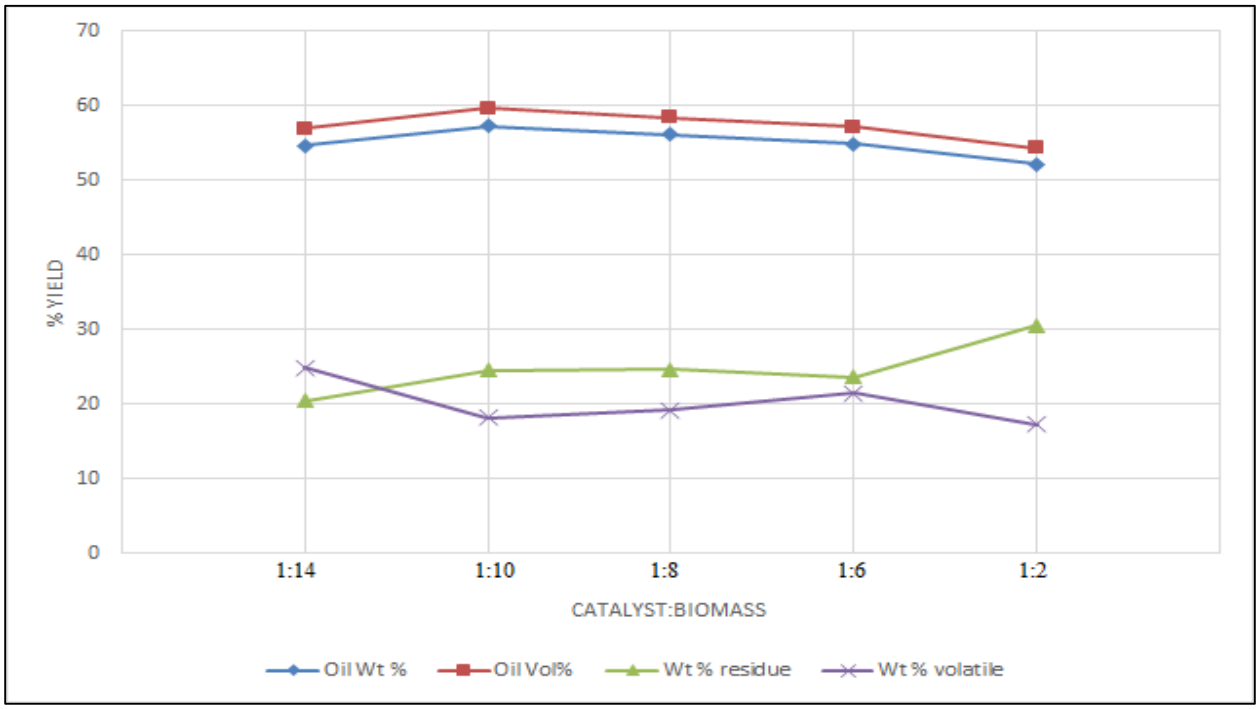

Figure 4.4 Influence of CaO on Bio-oil yield

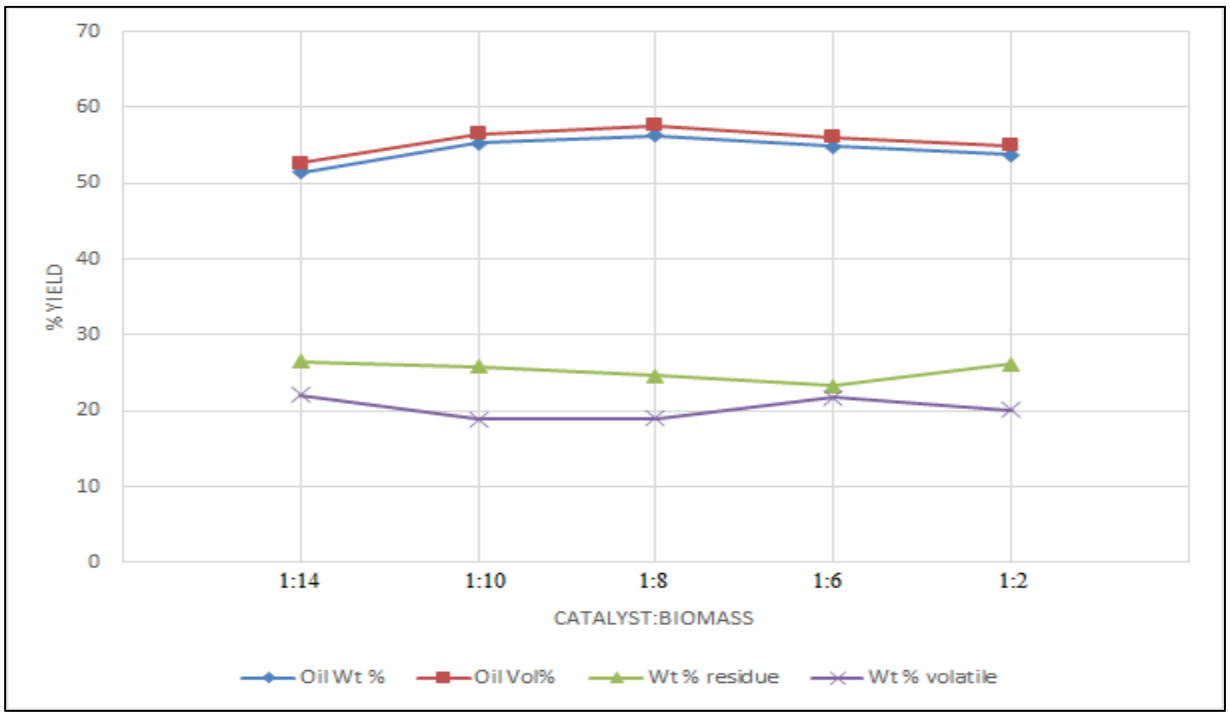

Figure 4.5 Influence of MgO on Bio-oil yield

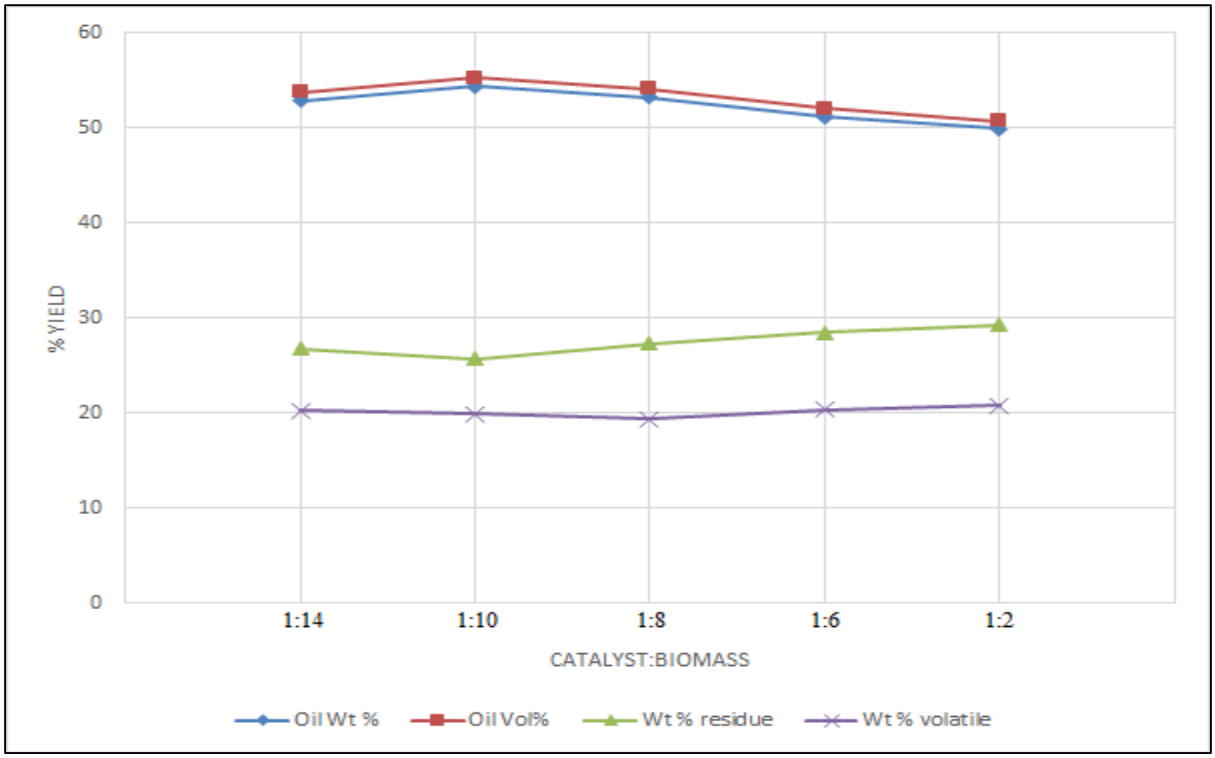

Figure 4.6 Influence of ZnO on Bio-oil yield

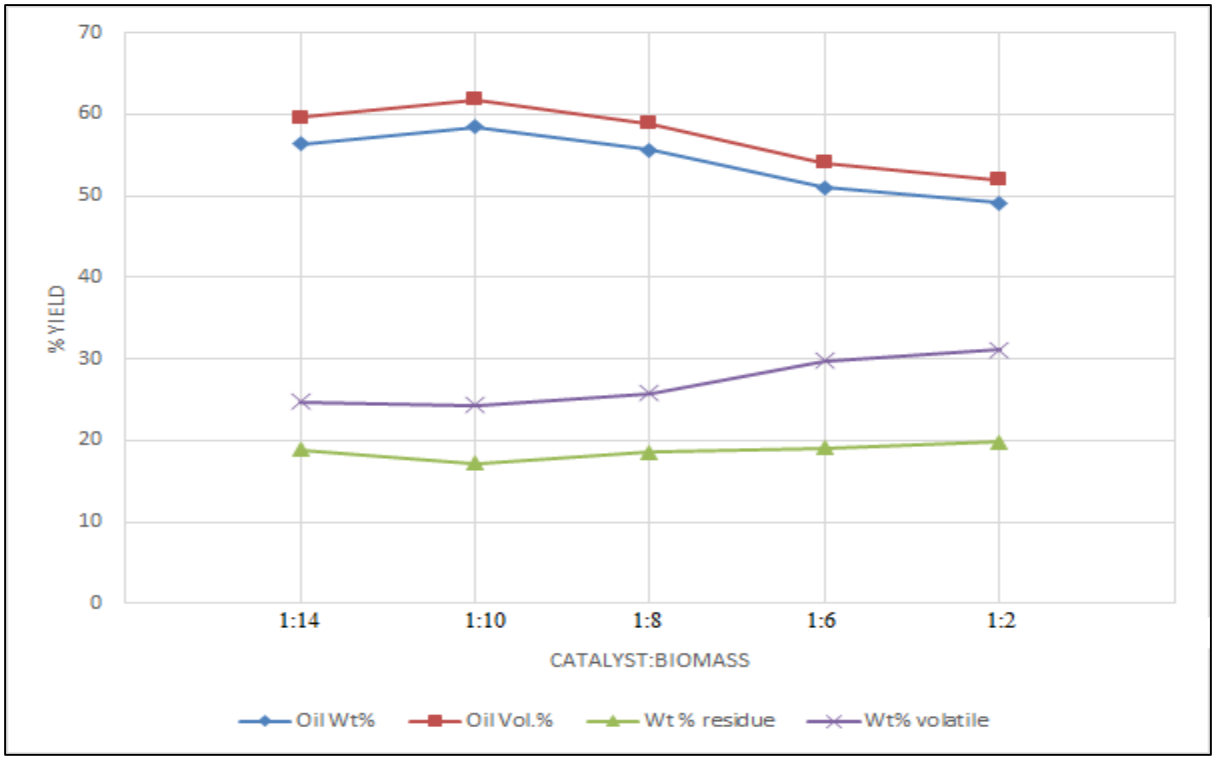

Figure 4.7 Influence of Fe_2O_3 on Bio-oil yield

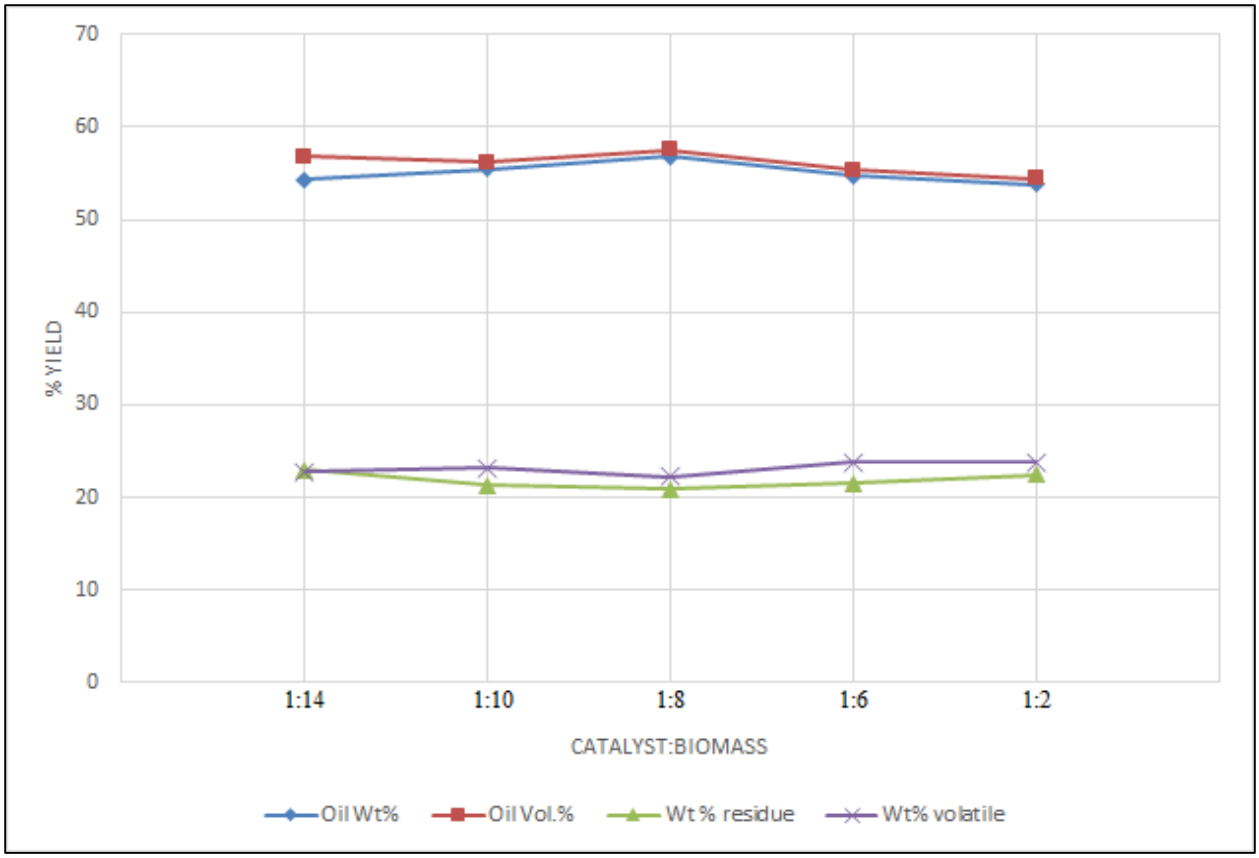

Figure 4.8 Influence of TiO_2 on Bio-oil yield

4.4 BIO-OIL CHARACTERIZATION

4.4.1 Physical and Chemical properties of Bio-oil

Characterization of bio-oil was done, according to Physical/fuel properties, for bio-oil by slow pyrolysis of castor seed, as defined in the experimental division. The physical/fuel properties of fuel layer, given in table 4.3 shows the optimum temperature of pyrolysis to get maximum volumetric yield and the comparison between castor bio-oil and diesel with castor up-graded bio-oil. The color of bio-oil was dark reddish brown having distinguishing smoky smell. The pyrolytic oil or bio-oil was separated into two layers viz. fuel layer and aqueous layer. All physical properties like density, viscosity, calorific value, fire point and flash point are found to be comparable with diesel. The pyrolytic oils are soluble in petroleum products like diesel, petrol, methanol and toluene along with its calorific values identical to diesel. So the pyrolytic or bio-oil is analogous with diesel and can be used by adding to diesel in transportation purpose. The CHNSO analysis of the pyrolytic or bio-oil represents that the pyrolytic oil contains maximum amount of C, H and O. Higher the C/H ratio, better the calorific value of oil.

Table 4.3 Physical properties of Bio-oil

Sr. No.	Properties	Castor up-graded bio-oil	Castor bio-oil	Diesel
1	Max. volumetric yield	63.89%	65.16%	-
2	Optimum temperature for max. yield	550^0C	550^0C	-
3	Appearance	Free flowing dark brown liquid	Free flowing dark brown liquid	yellowish
4	Odor	A distinctly smoky smell	A distinctly smoky smell	Aromatic
5	Calorific value	7678Kcal/Kg	6519Kcal/Kg	10700Kcal/Kg
6	Flash point	31^0C	33^0C	76^0C
7	Fire point	37^0C	35^0C	-
8	Pour point	$<5^0$C	$<5^0$C	-16^0C
9	Density	0.921gm/cc @^{0}C	0.968gm/cc @ 30^0C	0.85gm/cc
10	Viscosity	11.28CST @ 40^0C	18.79CST @ 40^0C	2.5CST
11	pH	8.4	3.9	-
12	Conradson carbon residue	1.502%	2.632%	-
13	Miscibility	Methanol, Toluene, Ethanol, Diesel and petrol	Methanol, Toluene, Ethanol, Diesel and petrol	

Table 4.4 Chemical properties of bio-oil

Elements	Castor up-graded bio-oil	Castor bio-oil	Diesel
C	69.86%	60.09%	85.72
H	5.17%	9.87%	13.2
N	7.35%	6.59%	0.18
O	17.62%	23.45%	0.3
C/H	13.51%	6.12	6.49

4.4.2 FTIR Analysis of Bio-oil

The FTIR analysis for castor pyrolytic or bio-oil states that the bio-oil is having similar functional group as most of the fuel. The functional groups, existing in pyrolytic oil, detected in the FTIR analysis are specified in Table 4.4. It was observed from the analysis that, presence of broad –OH stretching vibrations in the range of 3600- 3000 cm^{-1} represents the presence of Alcoholic and Phenolic group in the pyrolytic oil. The peaks in the range of 2930-2850 cm^{-1} are representative of the C-H stretching i.e. presence of alkane. Along with this, C-H bending vibration i.e. presence of CH2, CH3 groups with peaks in the range of 1460-1380 cm^{-1} were observed. The peaks in the range of 1760-1680 cm^{-1} gives confirmation of the presence of C=O (Carbonyl) Aldehyde, Ester and Ketone. The peaks between the range of 1675-1575cm^{-1} represents C=C stretching vibration i.e. presence of alkene group. Those several peaks were observed in the range of about 910-605cm^{-1} indicating the existence of some substituted groups in the Phenolic and Aromatic form.

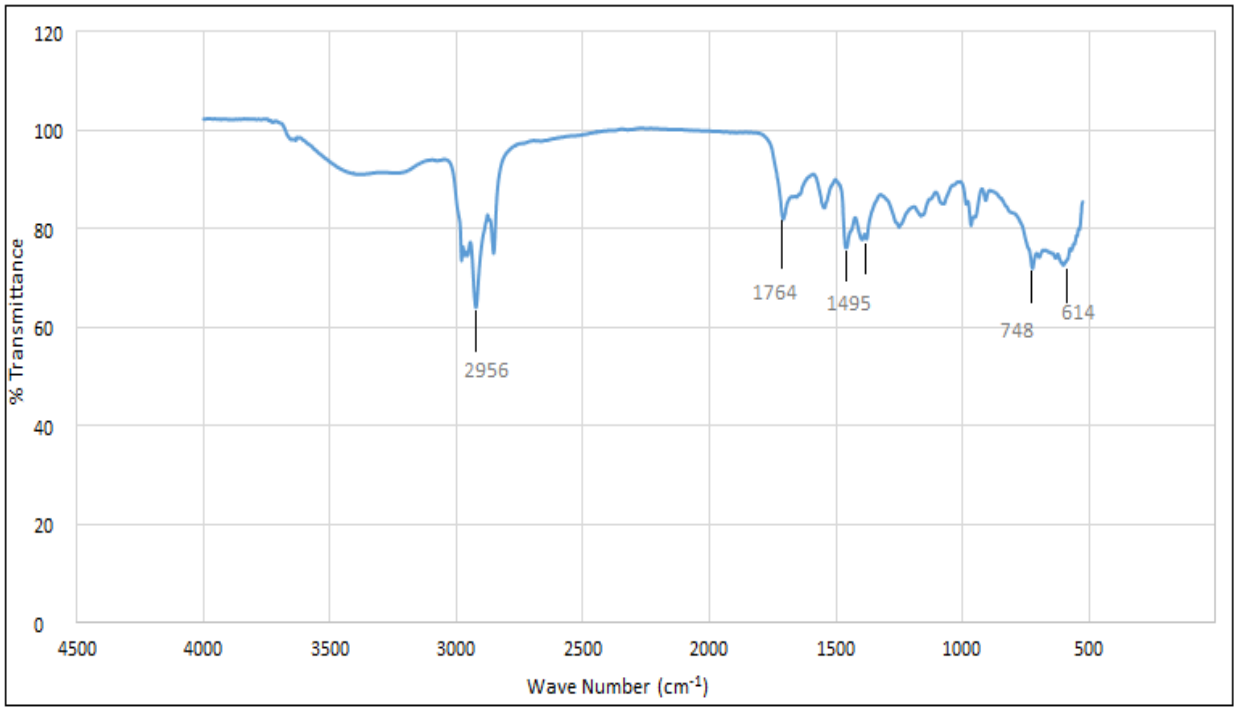

Figure 4.9 FTIR Analysis of castor bio-oil

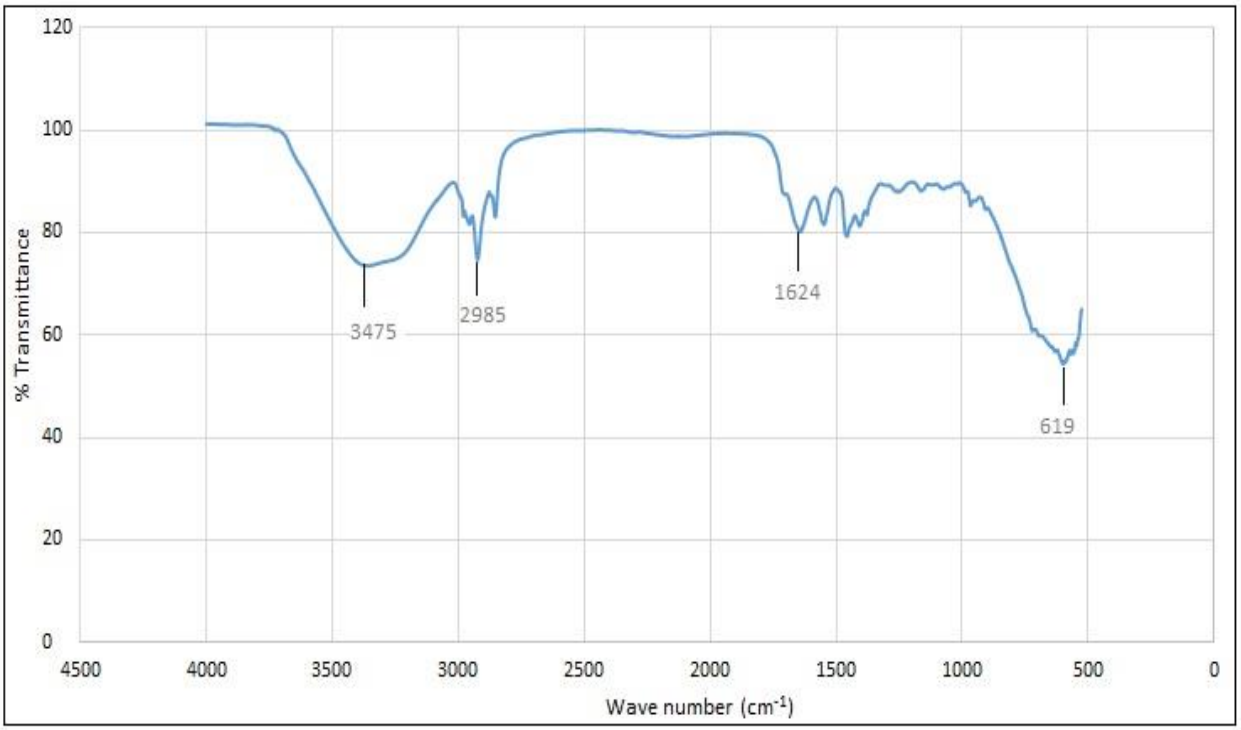

Figure 4.10 FTIR analysis for bio-oil with catalyst ratio 1:10 & CaO as catalyst

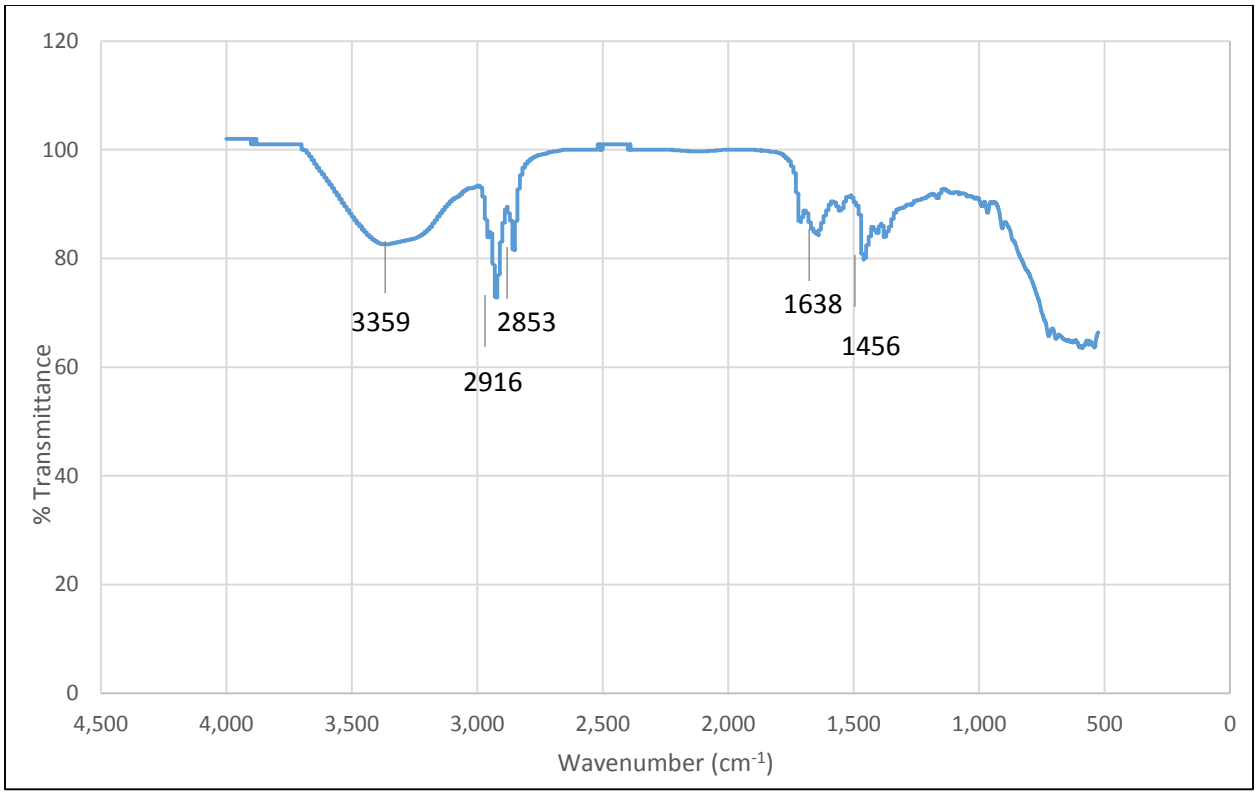

Figure 4.11 FTIR analysis for bio-oil with catalyst ratio 1:8 & MgO as catalyst

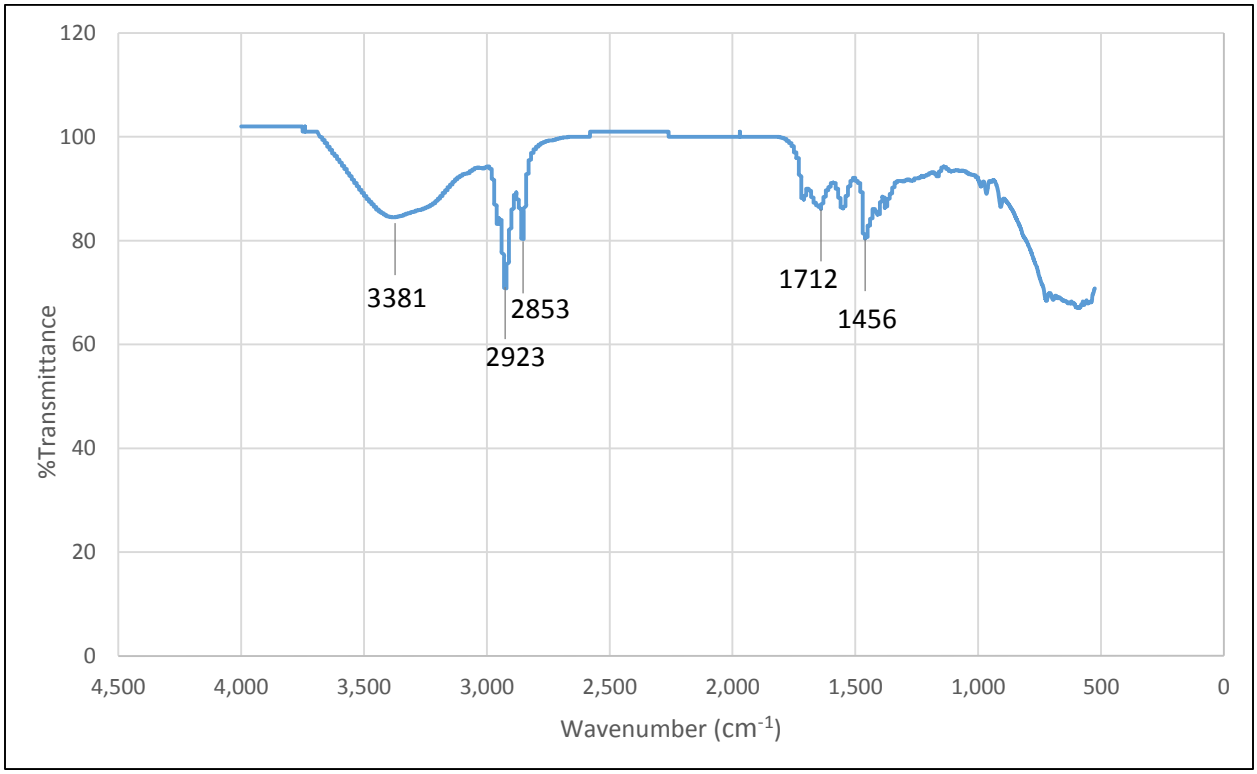

Figure 4.12 FTIR analysis for bio-oil with catalyst ratio 1:10 & ZnO as catalyst

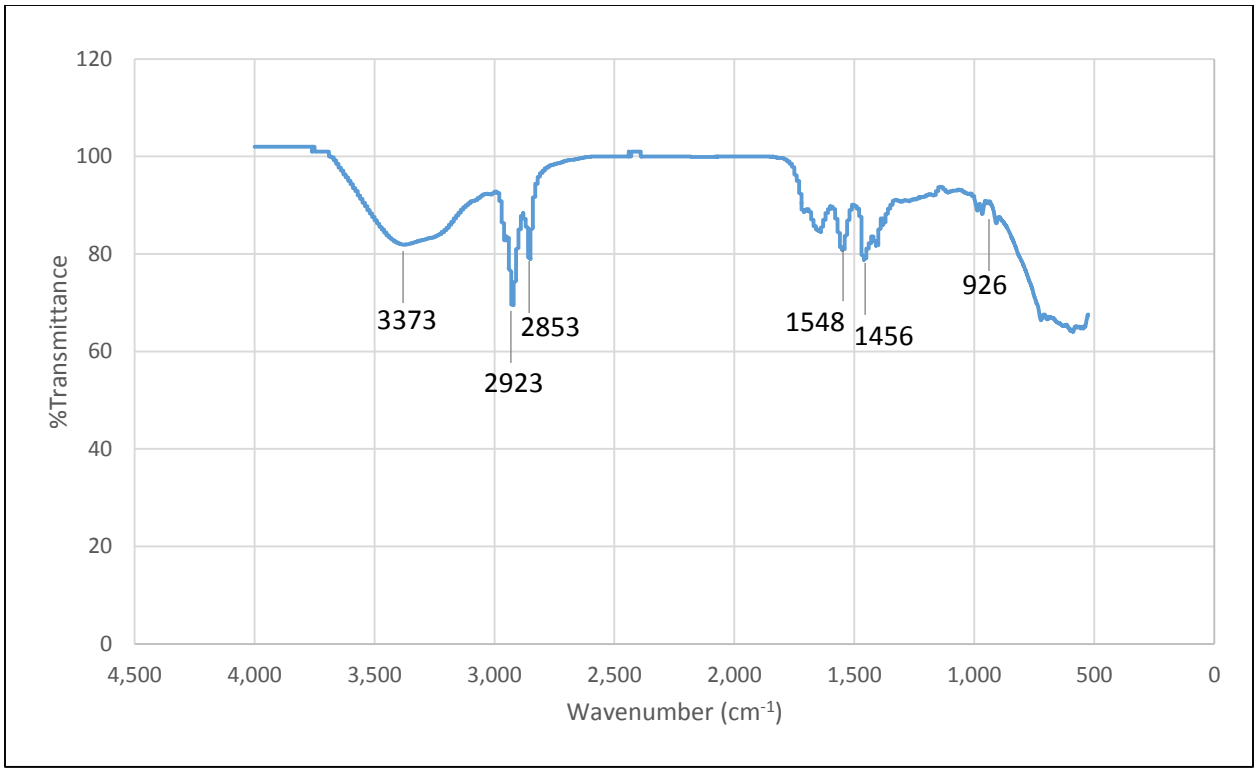

Figure 4.13 FTIR analysis for bio-oil with catalyst ratio 1:10 & Fe_2O_3 as catalyst

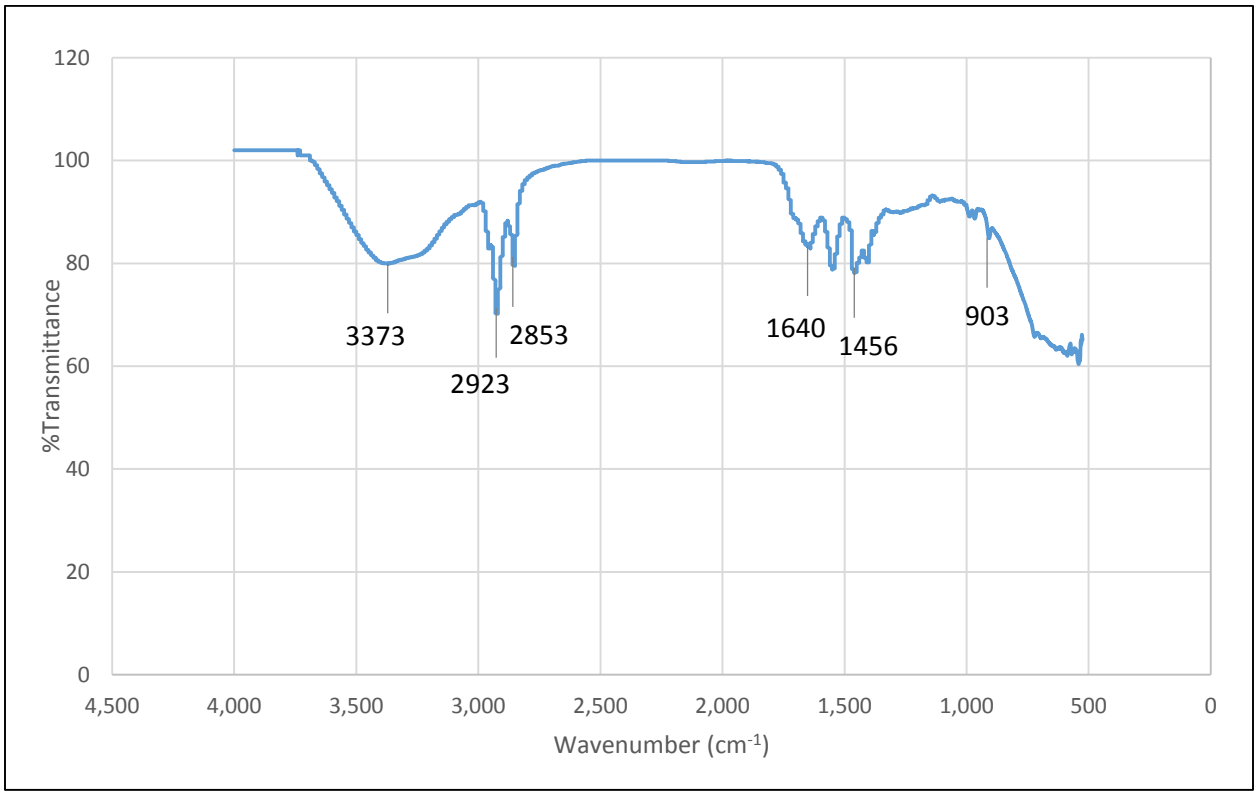

Figure 4.14 FTIR analysis for bio-oil with catalyst ratio 1:8 & TiO_2 as catalyst

Functional groups existing in both upgraded bio-oil and bio-oil are given in table 4.5.

Table 4.5 FTIR Analysis of bio-oil

Sr. No.	Functional groups present	Wave number (cm^{-1})
1	Broad -OH stretching vibrations, presence of alcohol group	3600-3300
2	Sp_3 –CH stretching vibration, presence of alkane group	3000-2850
3	C=O (carbonyl) Aldehydes, Esters and Ketones	1760-1680
4	C=C stretching vibration, presence of alkene group	1675-1575
5	C=C stretching, Aromatic ring	1490-1510
6	CH_2, CH_3 bending vibrations, C-H bending vibration,	1460-1380
7	Aromatic and Phenolic	910-605

4.4.3 GC-MS Analysis of Bio-oil

The bio-oil was chemically characterized by using GC–Mass Spectrometry carried at 550^0C i.e. pyrolysis temperatures. Table 4.6 gives categorization of compounds present with their retention time.

The table 4.6 indicates the compounds present in highest concentration in pyrolytic oil of castor seed. The compounds are Oleic acid, 10 undecenoic acid, Oleanitrile, Octadecanonic acid, N-hexadecanoic acid,3-phenyl-5-(pyridin-4-ylmethylidene)-2-thioxoimidazolidin-4one, Octadec-9-enoic acid. Various animal and vegetable sources contains monounsaturated omega-9 fatty acid i.e. oleic acid ($C_{18}H_{34}O_2$). The Stearic acid is saturated form of this acid. Lorenzo's oil can be made by using these steric acid. 10-undecenoic acid, ($CH_2CH\ (CH_2)_8COOH$) used in the manufacture of pharmaceuticals, perfumery and cosmetics. The cosmetics includes antidandruff shampoos, musk in perfumes, aromas and antimicrobial powders. Octadecanoic acid i.e. stearic acid which is saturated fatty acid contains 18-carbon chain which is waxy solid and its chemical formula is $C_{17}H_{35}CO_2H$.

Table 4.6 GCMS analysis of castor pyrolytic oil

Name of compound	Area%
Oleic acid	20.84
2 octanone	3.56
oleanitrile	3.06
10-undecenoic acid	25.35
Octadec-9-enoic acid	6.28
3 phenyl-5-2thioxoimidazolidin-4-one	4.96
1-dodecanesulfonyl	2.09
Methyl undec-10-enoate	1.85
N-hexadecanoic acid	6.29
1-dodecanesulfonyl	1.08
13-hexyl-oxa-cyclotridec-10-en-2-one	3.65
Undecanonic acid	1.28
Methy; 12-hydroxy-9-octadecenenoate	2.68
5-octadeceyne	1.76
Hexadecene	4.13
9-octadecenamide, (z)-	3.64
2-amino-6-n-hepthyl-4-hydroxypteridine	7.46

The table 4.7 shows the compounds present in highest concentration in catalytic pyrolysis oil of castor seed. Considering total area percentage, Total Ion Chromatogram (TIC) of compounds with the highest peak areas were $C_{18}H_{33}N$ Oleanitrile, 1Hepadecene 8 ene, Pentadecenenitrile $C_{16}H_{27}NO_2S$, Pentadecene $C_{15}H_{30,}$ 1-H indole C_8H_7N, 1Tetradecene. 1-H indole is main constituent of Natural jasmine oil. Thus also used in the manufacturing of artificial jasmine oil.

Table 4.7 GCMS analysis of catalytic pyrolysis oil of castor oil

Name of compound	Area%
Phenol,2-Methoxy	3.061
Cyclododecane	2.21
1H-indole	4.67
1 Tetradecene	6.12
Pentadecane	8.75
1 Heptadecene 8- ene	12.75
1 Heptadecene	2.32
Pentadecanenitrile	13.32
Methyl ester	2.68
N Hexadecanoic acid	5.28
Bicycloheptane	4.49
Oleanitrile	18.85
1 Heptadecanitrile	4.12
Toluene	8.37
1 Hexadecnamine	2.95

4.5 CHARACTERIZATION OF BIO-CHAR

Bio-char was characterized according to calorific value and SEM analysis.

4.5.1 Calorific Value

The calorific value for different bio-char were obtained from slow pyrolysis of the raw material. The bio-char obtained from castor seed with calorific value about 5732.48 Kcal/kg. Thus these chars can be fuel option.

4.5.2 SEM Analysis of Bio-char

The SEM graphs of the bio-char at different magnification are given in fig 4.15-4.17. A significant property of pyrolytic or bio-char is that, it has morphological similarity with natural carbon. It can be easily noted that, bio-char showed the porous structure in SEM analysis. Thus, this bio-char can be employed as an adsorbent or activated carbon.

Pyrolysis temperature, catalysts used affected the shape as well as size of particle. Increase in size of pores along with decrease in thickness of cell wall and void proportion increment has noted. The fast volatile are released during pyrolysis which causes significant internal overpressure and the conjoining a more open structure. Therefore, from SEM photograph, it was noted that porosity increased with pyrolysis temperature.

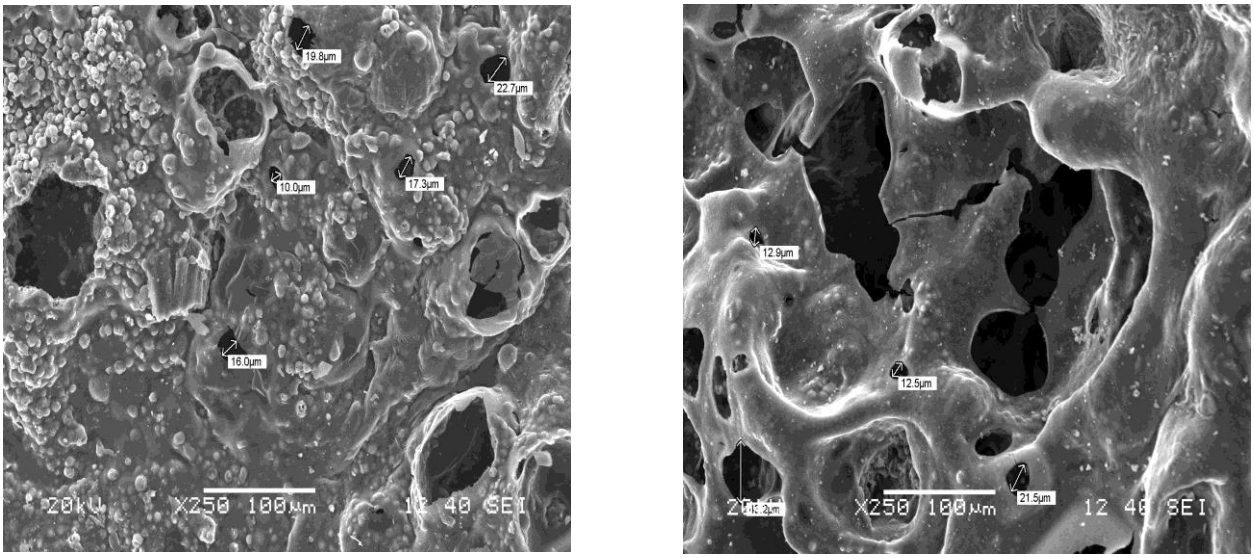

Figure 4.15 (a) SEM analysis of castor seed bio-char (b) SEM analysis for up-graded castor seed bio-char with CaO as catalyst

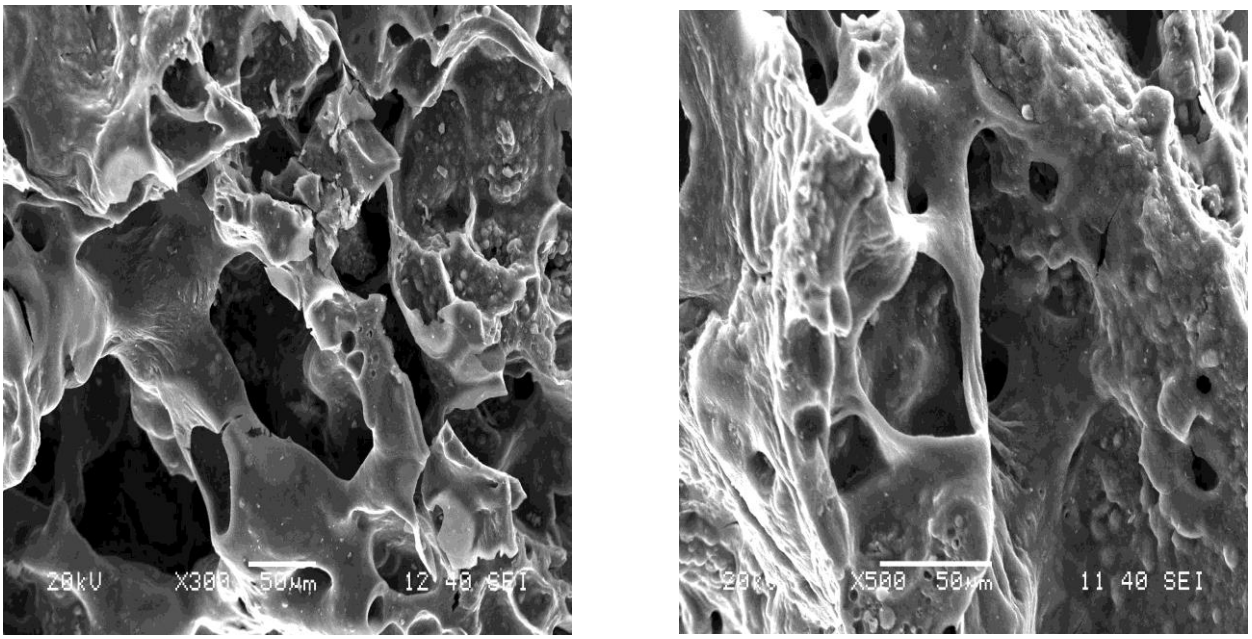

Figure 4.16 (a) SEM analysis for up-graded castor seed bio-char with MgO (b) ZnO as catalyst

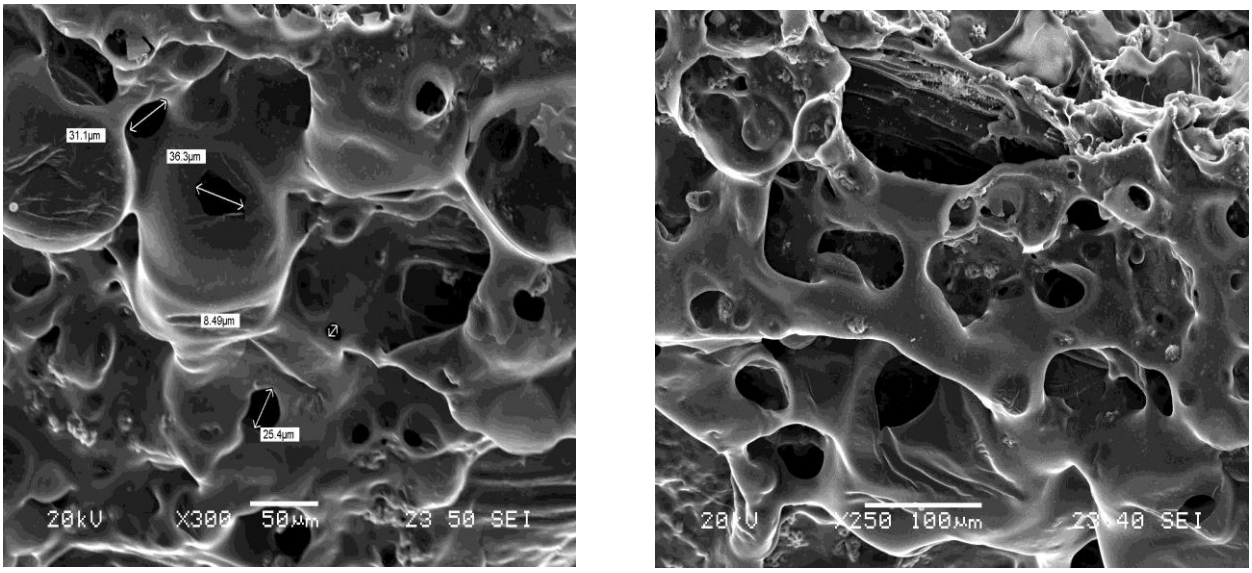

Figure 4.17(a) SEM analysis for up-graded castor seed bio-char with Fe_2O_3O (b) TiO_2 as catalyst

5 CONCLUSION

The characterization raw material i.e. castor seeds was carried. TGA showed degradation of raw material around 350-550^{0}C accordingly pyrolysis temperature range was decided.

The slow thermal pyrolysis of castor seed was done in semi-batch reactor for temperatures 475^{0}C to 600^{0}C provided heating rate 20^{0}C/min. The reactor is made up of stainless steel. On volume basis, the maximum yield of 65.16% was obtained for castor seed at 550^{0}C temperature with less completion time. The solid residue i.e. bio-char quantity decreased continuously. The non-condensable part decreased first with increase in temperature then after 550^{0}C it remained constant.

Catalytic pyrolysis of castor seeds were carried out at temperature of 550^{0}C with the heating at the rate of 20^{0}C/min, in a semi batch reactor to produce up-graded bio-oil using calcium oxide (CaO), zinc oxide (ZnO), magnesium oxide (MgO), ferrous oxide (Fe_2O_3) and titanium oxide (TiO_2) as catalyst. The catalyst to biomass ratio varies in the range of 1:14 to 1:2. The maximum bio-oil yield was obtained at with Fe_2O_3 as catalyst for the catalyst to biomass ratio 1:10. The maximum yield of bio-oil obtained was 58.46% with minimum bio-char produced i.e. 17.25% and less volatiles released i.e. 22.32%.

Physical and chemical characterization of liquid product i.e. bio-oil was done for both castor seed bio-oil and up-graded castor seed bio-oil. The difference in viscosity, pH, calorific value and carbon residue was noted. The viscosity of up-graded bio-oil was found less than bio-oil. This might had happened because of the de-oxygenation of compound due to catalyst. The increase in pH value of up-graded oil has been noticed from 3.9 to 9.16, which shows acidic nature of oil was eliminated due to use of catalysts. The calorific value of up-graded bio-oil increased from 6519Kcal/kg to7678 Kcal/kg. The carbon residue of bio-oil was found to be 1.0502% which is low, indicating that after ignition it leaves very minute residue.

The notable compounds present in pyrolytic oil of castor seed were Oleic acid, 10 undecenoic acid, Oleanitrile ,Octadecanonic acid, N-hexa-de-canoic acid, Octadec-9-enoic acid, 3-phenyl-5-(pyridin-4-ylmethylidene)-2-thioxoimidazolidin-4-one. It was detected that the bio-oil comprises compounds with carbon chain length in the series of C_4-C_{24} which is similar to most of fuels used.

The major compound present in catalytic bio-oil were Oleanitrile, 1Hepadecene 8 ene, Pentadecenenitrile, Pentadecene, 1Tetradecene, 1-H indole, Bicyclopentane. It was noted that catalytic pyrolysis oil does not contain Oleic acid, 10 undecenoic acid, octadecenoic acid.The results obtained from FTIR were found to be in consistent with GCMS results. The functional groups in both up-graded bio-oil and bio-oil were found analogous to most other bio-oil specified in literature.

Also, calorific value of bio-char was noted sufficiently high, thus can be use as solid fuel. SEM graphs, from the analysis, showed the presence of pores in solid residue i.e. bio-char, which indicates its use as adsorbent.

6 FUTURE WORK

1. Ex situ up-gradation of biomass- by upgrading bio-oil. By doing both ex situ and in situ up-gradation, finding the maximum conversion of bio-oil along with its up-graded properties.
2. For different biomass- optimizing catalyst ratio, pyrolysis temperature with in situ and ex situ conditions
3. Checking up-graded bio-oil usability in engine.
4. Detailed study of reactions occurring in up-gradation.

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