

CHARACTERIZATION OF BIO-OIL & UPGRADATION TO DIESELOIL

**A Thesis submitted for the degree of
Bachelor of Technology**

**In
Chemical Engineering**

**By
Sujit Kumar Mohanty**

Roll no. 111CH0080

**Under The Supervision of
Prof.(Dr.) R. K. Singh**



**Department of Chemical Engineering,
National Institute of Technology, Rourkela
Rourkela-769008, Odisha, India**



National Institute of Technology, Rourkela

CERTIFICATE

This is to certify that the project entitled, “**Characterization of bio-oil & Up-gradation to diesel oil**” submitted by **Sujit Kumar Mohanty** is an authentic work carried out by him under my supervision and guidance for the partial fulfillment of the requirements for the award of **Bachelor of Technology (B. Tech) Degree in Chemical Engineering** at **National Institute of Technology, Rourkela**.

Place:

Date:

Prof. R. K. Singh

Dept. Of Chemical Engineering

National Institute of Technology Rourkela-769008

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SUJIT KUMAR MOHANTY

Roll No- 111CH0080

Dept. Of Chemical Engineering

National Institute of Technology Rourkela-769008

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ABSTRACT

Because of the shortage of the conventional fuels, the price is increasing at a higher rate and a time will come when all will be deprived of these resources. Due to these fuels there is also increase in pollution; hence there is a requirement to find alternative energy sources for the automobile and industrial uses. So taking the above mentioned problem into account, the present analysis is done by taking tyre oil which was produced by the pyrolysis of the waste bicycle tyres. Thermal pyrolysis is one of the renewable advancements where waste tyre is pyrolysed into fuel oil, carbon dark, and ignitable gas under the activity of sensible mechanical conditions. This innovation sensibly and successfully arranges waste tyre without contamination, and is successful in delivering fuel that can lessen energy emergency. In a semi batch reactor thermal pyrolysis of waste tyre was carried out at a temperature range of 450°C to 800°C. The ideal pyrolytic oil of 49.6% was obtained at 600°C for tyre. Standard test techniques were used to found out the physical characteristics of the tyre oil and the chemical constituents were analyzed by using GC-MS, FTIR analyzer.

Crude bio-oil formed by quick pyrolysis comprises of a complex mixture of different oxygenated compounds which keep its utilization specifically as a fuel. The target of this examination is to enhance the bio-oil quality. Besides, the troubles and scope were briefly described along with some suggestions based on upgrading and applications of bio oil.

Keywords: conventional fuels, tyre oil, pyrolysis, GCMS, FTIR

CHAPTER 1

INTRODUCTION

1.1 CURRENT ENERGY SCENARIO

Energy is one of the significant inputs for the financial progress of any country. On account of the rising nations, the energy division expects a discriminating significance in perspective of the regularly expanding energy needs obliging immense speculations to meet them.

Energy can be arranged into a few sorts in light of the accompanying criterion:

- Primary Energy and Secondary energy
- Commercial Energy and Non-commercial energy
- Renewable Energy and Non-Renewable energy

PRIMARY AND SECONDARY ENERGY

These are the sources that are either discovered or put away in nature. Basic essential energy sources are natural gas, oil, coal and biomass. Other energy sources includes thermal, nuclear and potential energy.

COMMERCIAL ENERGY AND NON COMMERCIAL ENERGY

Commercial Energy: These are available in the market for a distinct cost. Most vital forms are coal, electricity and refined petroleum products.

Non-Commercial Energy: The energy forms which are not subjected to a commercial trade; they are hard to record for in energy offsets, despite the fact that they are in light of physical and not fiscal streams, in light of the fact that claim account generation and utilization of energy can for the most part just be measured by method for buyer reviews are called non-commercial energy. Wellsprings of non-commercial energy incorporate

fuels, for example, cattle dung firewood & horticultural wastes, which are normally assembled, & not bought at a cost utilised in particular as a part of rustic family units.

RENEWABLE AND NON-RENEWABLE ENERGY

Renewable energy is the form of energy that comes from a source which is not exhausted when used. These include solar power, tidal power, wind power, geothermal energy, etc. Non-renewable energy consists of conventional fossil fuels such as oil, coal & gas, which are expected to exhaust with time.

Today, the world runs on fossil fuels. The fundamental driver for quick advancement in 20th century is without a doubt this puzzling energy treasure, the petroleum. In the event that we look the present supply of worldwide energy from different sources, still the fossil fuel rules the supply with oil is the biggest source with around 32% offer, trailed by coal and natural gas.

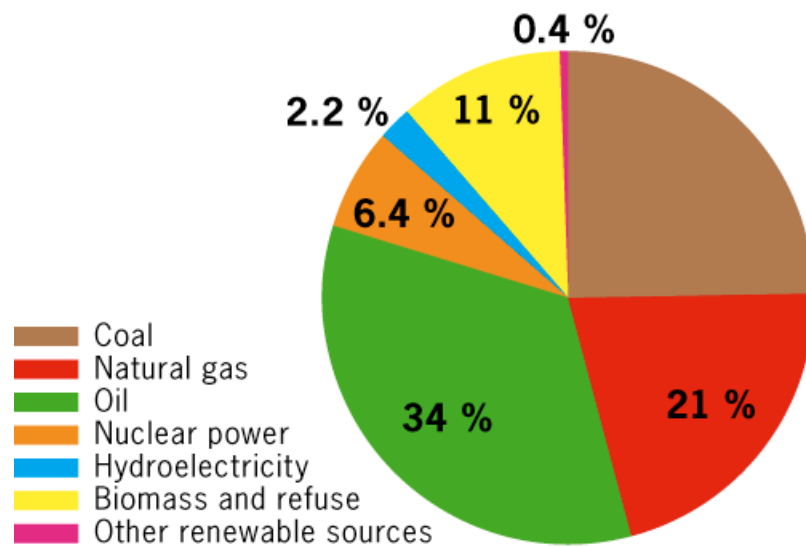


Figure 1.1: Total world energy supply by source

Source: Key world energy Statistics, IEA

1.2 PROBLEMS WITH FOSSIL FUELS

Fossil fuels as the name recommends are subordinates of animal and plant fossils that are million years of age. These are basically shaped from the remaining parts of the rotted animals and plants of the carboniferous time. The three fuel sources coal, oil/petroleum and natural gas serves to meet the energy and power requests of today's reality. The interest for energy will never be in the declining chart. Industrial revolution has demonstrated the way's despite everything it going on.

They are non-renewable wellsprings of energy as they are obtained from ancient fossils and are not accessible if once utilized. Their source is restricted and they are draining at a quicker rate. Exactly when removed it speaks to a genuine damage to the scene as they are to be reveal from underground wells.

DEMERITS OF FOSSIL FUELS

1. **Environmental Impact:** Pollution is the vital damage that is framed due to fossil fuels. Exactly as soon as blasted they give out carbon dioxide which is the primary cause for a worldwide temperature alteration.
2. **Rising Prices:** Middle-east states have enormous storage of oil and characteristic gas and several nations are relying on them for consistent supply of these energizes. This outcome in overall value changes, as indicated by the U.S. Division of Energy.
3. **Human Health Getting Affected:** Depletion of ozone layer occurs because of the arrival of nursery gasses from the fuels. Thus UV beams enter the earth's surface that has a hazardous impact on human health causing ailments like tumour.
4. **Non-Renewable:** As the fossil fuels are separated to a boundless level it is without a doubt that they will exhaust some time or another or the other. Since they are non-renewable it is likely that powers costs will confront a trek in not so distant future. It

would take a large number of years to supplant coal, and oil, and we are utilizing them rapidly.

5. Coal Mining: Coals when extracted from ranges that have immense stores is a troublesome and perilous errand as well as posture well-being danger to the lives of a few specialists who work there. The coal mining obliterates wide regions of area and results in natural unevenness.
6. Need Huge Amount of Reserves: The coal plants needs immense and standard supply of coal to deliver widespread measure of power on a steady basis. This implies they need stores of coal just about train-heaps of fuel close power stations to do the methodology of creating power. This is needed since today likewise numerous countries are subject to coal as a significant wellspring of creating energy.

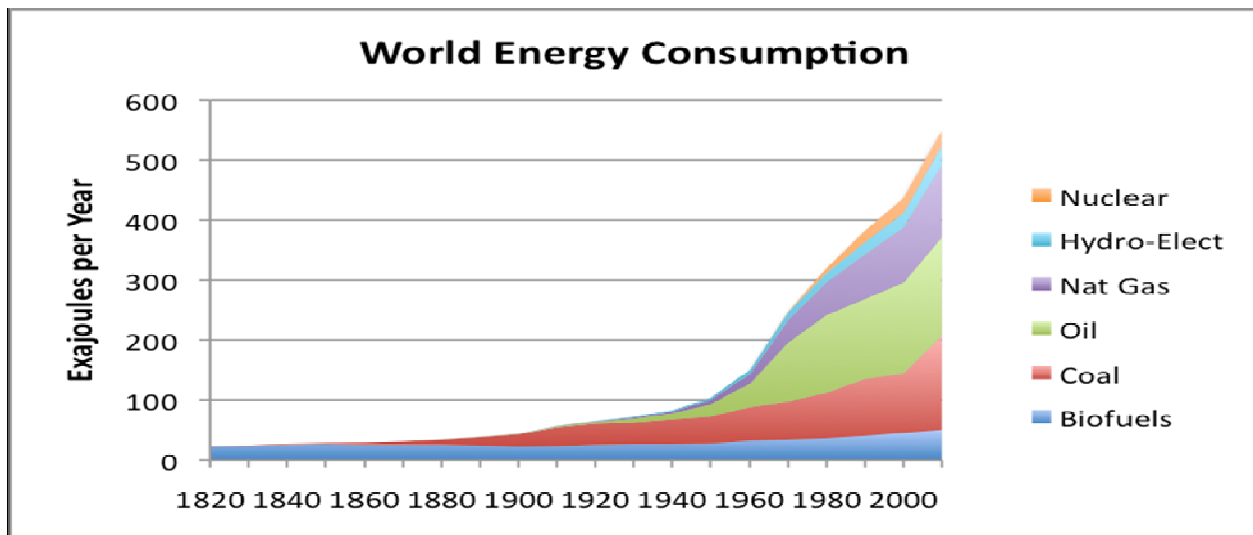


Figure 1.2 World Energy Consumption

1.3 ORIGIN OF THE STUDY

Fossil fuels are the fundamental sources of energy at present, however if their regular constraint is considered in accessibility and the way that they are not renewable, there exists a developing necessitate of growing new and renewable energy sources [1, 2]. Now a day's most nations are confronting two noteworthy issues, environmental degradation and energy crisis this is because of the developing populace, quick industrialization and dumping of various solid wastes, which are produced all the time [1]. To tackle this energy emergency and ecological debasement, researchers are putting much exertion on the possibilities of using suitable advances to recoup energy and helpful by-items from household and modern strong squanders. Consequently impressive exploration has been done to recoup energy from waste material. Such material incorporate biomass, metropolitan solid wastes, industrial wastes, farming wastes and other poor quality fuels and in addition high energy thickness materials, for example, rubber and plastics.

There is an overwhelming increment in tyre and tube wastes because of remarkable increment in number of vehicles inside India. Transforming and valorizing waste tyres has pulled in developing enthusiasm because of its expanding dumping amount and negative ecological effect. Consistently, pretty nearly 7×10^6 t of waste tyres is arranged around the world, representing 2 wt% of the aggregate waste [3]. A few components have driven thoughtfulness regarding the valorization of waste tyres: (i) the ecological harm that is brought on by uncontrolled transfer of this kind of polymer waste, alongside the non-biodegradability of tyres, (ii) the expanding interest for reusing hydrocarbons, and (iii) its high calorific worth (which could permit its utilization as fuel) [4].

The scrapping of vehicle tyre and tube speaks to a major ecological issue all through the world, particularly in developing nations. One of the basic methods for transfer is land filling, however tyres don't debase effortlessly in soil as these are cumbersome, taking up important landfill space & avoid wastes compaction [5]. Open dumping is another technique for arranging the waste tyres, but it contaminates the soil, contaminates underground water. Gives perfect rearing grounds to illness conveying mosquitoes and other vermin [6]. Further incineration is

additionally another system for arranging which includes ignition of waste tyres at profoundly controlled temperatures. Incineration of the tyre waste emanates a ton of lethal mixes, for example, Cadmium, dioxin, mercury, sulfuric acid, hydrochloric acid, nitrous oxide, fluorides and particulates that can be breathed in and amplify or stay for all time in our lung. They can bring about a show of ailments like asthma and cancer. It is realized that overwhelming metals like arsenic, lead, mercury, chromium and natural chemicals, for example, polycyclic aromatics hydrocarbons, furans and dioxins radioactive materials are not crushed by incineration [7].

One methodology which has gotten impressive late consideration is pyrolysis of the tyre which essentially includes the disintegration of the wastes at high temperatures (300-900°C) in a dormant climate to deliver gas, oil & char which has greater prospective for alternate applications. For example, derived oil may be used as fuel or may be mixed to petroleum feedstocks and it might likewise be an essential hotspot for superior chemicals [8]. Emphasis is laid on the generation of hydrocarbon fluids from tyre wastes following the manufacture of liquid product which can replace fossil fuels.

A few analysis on pyrolysis of waste tyre reasoned that the pyrolytic oil of scrap tyre contains greater convergences of polycyclic aromatic hydrocarbons, for example, toluene, benzene & xylene and so on in like manner, the oil has been indicated to contain limonene, a significant item utilized as a part of industrial applications including plan of modern diluents, saps and cements, as a dissipate specialists for pigments [9, 10].

The critical prerequisite for diesel oil is its consistency, moisture content, ignition quality, silt, and sulfur substance. Along these lines, the pyrolysis oils were obliging preparatory liquids, for example, tapping, centrifugation, desulphurization, filtration and hydro-regarding to be utilized as fuel. The treated pyrolysis oil could be utilized straightforwardly as fuel oil or mixed with diesel fuel. Thus, the atomization will be enhanced, guaranteeing a total exhaustion of the fuel. In view of its fuel properties, tyre-inferred pyrolysis oil may be considered as a profitable part for utilization with car diesel fuels.

1.4. Research Objective

In this study, bicycle tyre waste has been used as raw material for pyrolysis process. The different objectives are summarized as:

1. To obtain liquid fuel from bicycle waste by thermal pyrolysis.
2. To characterize the liquid fuel for their physical and chemical properties.
3. To characterize the diesel fuel for their physical and chemical properties.
4. To study the physical and chemical up-gradation of bio-oil.
5. To study the properties after blending of bio oil with methanol.

CHAPTER 2

LITERATURE REVIEW

2.1. BIOMASS

These are the organic materials derived from living, or as of late living life forms. As a rule it is hard to figure out the real definition. This incorporates the by-products, products, residues and wastes from horticulture, industrial, municipal wastes and forestry. Biomass likewise incorporates gases and liquids recuperated from the disintegration of non-fossilised and decomposable organic materials.

2.2 SOURCES OF BIOMASS

The Common sources of biomass are agricultural, forest, municipal & biological. Following are the examples of sources:-

- Agricultural: bagasse, food grain, corn stalks, and compost from poultry, cattle, etc.
- Forest: waste from wood, trees, sawdust, mill scrap and woody slash.
- Municipal: sewage slush, wastes from food, paper waste, etc.
- Biological: aquatic species, biological waste and animal waste.

2.3 BIO FUEL

Bio-fuels are created from living life forms or from metabolic by-items (natural or sustenance waste items). With a specific end goal to be viewed as a bio-fuel, the fuel should comprise more than eighty percent materials which are renewable. It is initially gotten from the photosynthesis handle & can hence frequently be alluded as a wellspring of solar energy. The term bio fuel incorporates solid biomass, liquid and gaseous fuels. Solid bio-fuel fuses grass cuttings, wood, sawdust, charcoal, cultivating waste, non-food energy harvests and dried fecal matter where bio diesel, bio liquor, bio-ether, pyrolytic oil are liquid bio-fuels and syngas and bio gas are gaseous bio-fuels. [11]

2.4. BIOMASS CONVERSION PROCESS

Biomass is in general converted to useful products mainly by two process:

1. Thermo-chemical process.
2. Bio-chemical processes.

2.4.1. THERMOCHEMICAL PROCESS

The thermo-chemical process include mainly process like

1. Torrefaction
2. Liquefaction
3. Combustion
4. Gasification
5. Pyrolysis

TORREFACTION

It is the moderate warming of biomass in an inactive or lessened atmosphere to a most extreme temperature of pretty nearly 300°C. It can likewise be characterized as a gathering of items coming about because of the part of the way controlled and isothermal pyrolysis of biomass happening in a temperature scope of 200–280°C.

LIQUEFACTION

It is a procedure of change of biomass into bio fuel and chemicals where transformation happens in vicinity of catalyst and solvent at 350 °C temperature and 12-20 MPa pressure. The additive

may be glycerol, phenol and water in hydrogen or nitrogen air. In order to advance organic conversion, alkali may be added to the fuel. The key thing is organic liquid with less oxygen content. The method for these blends was found to be dependent on the catalyst, however not clearly on the physical conditions used. [12]

COMBUSTION

It is an exothermic reaction joined by expansive warmth and glow, and is a marvel in which the response is suddenly proceeded by the heat produced by the response. At the point when utilizing biomass as fuel, the heat creating oxidation response, where hydrogen, carbon, oxygen, burnable nitrogen, and sulphur contained in biomass respond with oxygen or air, is known as combustion, industrially. This methodology continues by gas stage response, surface response, or both, after techniques, for example, combination, vanishing, and pyrolysis. In real combustion response, diffusion, convection, heat conduction, evaporation, mixture, radiation, and luminescence progress impressively at a high speed. Gas fuel smolders specifically in gas stage as premix ignition or diffuse burning. Heavy oil and so forth smolders in dissipation burning however decay ignition additionally continues, where breaking down the fuel bit happens by the delivered heat.

GASIFICATION

It is a process that changes over fossil fuels or organic based carbonaceous material into H_2 , CO and CO_2 . In this case the temperature is about $>700\text{ }^\circ\text{C}$, without combustion. The product formed in this case is called syngas (from synthesis gas or synthetic gas) or producer gas and is itself a fuel. On the off chance that the gasified compounds were gotten from bio mass, then the vitality got from ignition and gasification of the resultant gases is thought to be a wellspring of renewable energy. Pyrolysis is the initial step of this process, where carbonaceous particles are heated up & volatiles are released and char is produced. In the second step combustion methodology happens as the volatile items & a portion of the char responds with oxygen to

frame CO and CO₂, which gives heat to the resulting gasification responses, $C + \frac{1}{2} O_2 \rightarrow CO$. In the third step, char reacts with CO₂ & steam to produce H₂ and CO, i.e., $C + H_2O \rightarrow H_2 + CO$.

PYROLYSIS

It is the thermal decomposition of biomass at moderate temperature in the absence of O₂. The steps in pyrolysis includes: feed-stock preparation and feed input into the reactor, carrying out the reaction by absorption of heat or other addition of agents such as air, O₂, steam, H₂, post combustion or processing of the gases produced during the reaction step, and proper guidance of the resulting liquids, ash and char. Pyrolysis item essentially comprises of gasses like CH₄, CO₂, and NH₃ and fluids like acetone, acetic acid, ethanol, bio-oils, and solid as char. The relative extent of the yield relies on the methodology and procedure condition, attributes of biomass, ideal temperature and residence time of material. In this process the biomass is heated to a temperature range with low residence time and rapidly cooled to collect the condensed liquid which is otherwise known as bio-oil. This is done to avoid the decomposition of the intermediate products during pyrolysis. At the point when cooled, most volatiles gather to form bio-oil. This methodology is an extremely prominent procedure which makes a decent amount of fluid fuel from biomass, which is fundamentally the same to business transportation energizes and can be upgraded or adjusted to supplant transportation fuel. Longer residence times and High temperature increases biomass transformation to gas, and short vapour residence times and moderate temperatures are ideal for creating liquid. The most critical highlights for pyrolysis to jump out at give fitting bio oil yield are:

1. A Temperature of around (400-500 °C) in order to produce bio oil in maximum.
2. Finely ground biomass with about less than 3mm size with high heating rates.
3. Vapor residence time of about <2 sec to lessen the unimportant reactions to occur.
4. The remaining bio-char must be removed so as to prevent the secondary cracking reactions.
5. The vapors are rapidly cooled to produce the bio oil as the intermediate product.

FAST PYROLYSIS

The products formed from this process are gases, char & bio oil. The yield of the products depend on the pressure, residence time & temperature. The parameters which are to be maintained in order to achieve maximum yield of bio oil are temperatures (450-500°C), high heating rates (i.e., >200°C/sec), at atmospheric pressure and short residence times (1-2 secs).

SLOW PYROLYSIS

Here the temperature maintained for pyrolysis reaction is 300 - 500°C and the rate of heating is slow i.e. around 20 - 30°C/sec with a vapour residence from 5 to 30 mins. The yield of solid residue and gaseous products is more in this case as compared to fast pyrolysis. The amount of liquid product obtained is up to the mark and the quality of the liquid product obtained is good.

2.4.2. BIO-CHEMICAL PROCESS

The biochemical process involves anaerobic digestion and alcoholic fermentation which are involved for biochemical conversion of the biomasses like animal manure and bio waste. Sometimes it also deals with energy crops and paper mill residues. It combines methods like pre-treatment, enzymatic action & hydrolysis.

The other types of biochemical process involve anaerobic digestion & alcoholic fermentation process. The former process involves the decomposition of the organic material in presence of microbes without supply of air/oxygen to produce the so called biogas which comprises of methane and carbon dioxide as the prime components. Biogas is generally a product from manure of cow, It is used in producing electricity since the biogas produced from the manure has a higher calorific value .On the other hand the alcoholic fermentation process involves the production of wines from the biomass like sugar crops and starch crops. It involves the action of organisms like yeast that helps in yield of high quality fuel for transportation purpose .For this process initially the compounds needed to be broken down by hydrolysis as it contains longer

chains of Polysaccharide. In the production process of ethanol, It can be distilled and can be used as fuel as petrol.

2.5 DIFFERENT TYPES OF RUBBER USED IN TYRE

Rubber is an adaptable item with different utilizations. It is developed in different nations overall and assumes a critical part in the Indian economy as well. India is one of the main makers of rubber on the planet. India is fourth biggest maker of natural rubber alongside Thailand, Indonesia and Malaysia [13].It is a known certainty that three-fourth of rubber formed is utilized as a part of the manufacturing of tyre [14].From the Fig 2.1 it has been observed that the production of tyre has been increased year wise [13]. Three major categories of rubber are used for tyre making. They are namely natural rubber, synthetic rubber and reclaimed rubber.

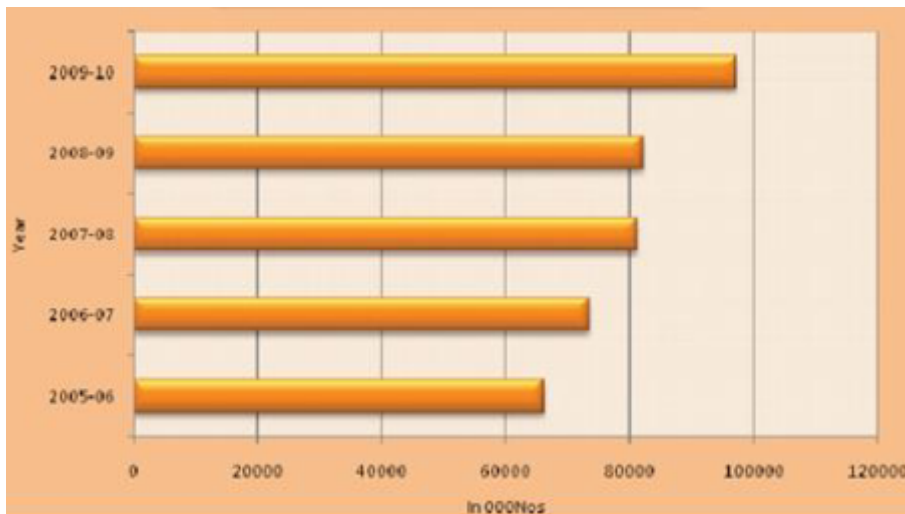


Figure 2.1Production of tyre in India

2.5.1 NATURAL RUBBER

It's a polymer of isoprene with a chemical formula (2-methyl-1, 3 butadiene).Natural rubber is produced from the sap of rubber tree (Heveabrsiliensis) which grows mainly in South East Asian nations; there are various trees from which we can get rubber as the Ficuselastica [15].It

can withstand temperature up to the range of 10-60 °C, has tensile strength 200 kg/cm² and it has high elasticity ranging from 300 to 1000 % [16, 17].

2.5.2 SYNTHETIC RUBBER

Raw materials used in the production of synthetic rubber are styrene, chloroprene, butadiene, isoprene, isobutylene, ethylene, acrylo-nitrile and propylene. More than a large portion of the world's manufactured rubber is Styrene Butadiene Rubber (SBR) produced using styrene & butadiene monomers which are copious in petroleum. Seventy five percent of all the SBR are used in the production of tyres and the rest is used for manufacturing of footwear, sponge and foamed products, waterproofed materials, and adhesives. It has greater abrasion-resistance, greater load bearing capacity and resilience. On the other hand, it gets readily oxidized, especially in presence of traces of ozone present in the atmosphere. Butyl rubber which is used in tyre inner tube, is also a synthetic rubber formed by the polymerization of isobutene with a little quantity of isoprene. It is not permeable to air and other gases, that are used in tyre inner tube and additional product which require a good obstruction in opposition to gas. These rubbers are thermally stable which makes them appropriate for use in automotive radiator hose. The ozone resistance of these makes them suitable for weather resistance and electrical insulation. Few disadvantages of these rubbers are that they tend to pick up foreign matters and impurities, they are incompatible with many natural rubber & synthetic rubber and they lose elasticity at low temperatures [15, 16, 17].

2.5.3 RECLAIMED RUBBER

Rubber recovered from vulcanized scrap rubber (as by grinding old tyres and treating with alkali, oils, and plasticizers is called reclaimed rubber. This rubber has almost the original plasticity, allowing the same to be processed and re-vulcanized. It is also used for manufacturing of new tyres. The reclaimed rubber is of less tensile strength, lower in elasticity and possesses lesser wear-resistance than natural rubber. However, it is much cheaper, uniform in composition and has better ageing properties [15, 16]. Table 2.1 shows the consumption of rubber in India

(quantity in metric tonnes). The use of natural rubber increased by 23.1%, synthetic rubber by 40.5% and reclaimed rubber by 37.1% from the year 2005 to 2010. Consumption of natural rubber is 442921 metric tonnes in the year 2005-06 which subsequently increases to 576210 metric tonnes in the year of 2009-10. In the same way production of both synthetic rubber and reclaimed rubber has increased from 141580 and 21978 metric tonnes in the year 2005-06 to 576210 and 34986 metric tonnes in 2009-10. The overall consumption of rubber in tyre sector has increased by 32.1% from the year 2005-06 to 2009-10.

Table 2.1: Rubber consumption in India sector wise (Quantity in Metric Tonnes) [1]

Year/Sector/Rubber		2005-06	2006-07	2007-08	2008-09	2009-10
Tyre sector	Natural	442921	462081	495526	508121	576210
	Synthetic	141580	1708091	190987	185094	238153
	Reclaim	21978	23714	27319	29191	34986
Grand Total		606479	656604	713904	722406	894331

2.6 WASTE GENERATION OF TYRE

Tyre and tube are the foundation of the bike and rickshaw. Bike and rickshaw keep on being the primary method of transport for the low and center wage families. This is on the grounds that the bike is both environment and individuals' cordial. India is the biggest maker of bike by just China. The fate of the bike business is splendid. Nonetheless, for survival the organizations need to effectively rebuild and modernize to accomplish worldwide aggressiveness regarding quality, expense and appropriation framework. The tyre and tube industry is a real shopper of the household elastic generation [14]. There is very good domestic as well as export demand of bicycle and rickshaw tyre and tube. On the other hand cycling is considered to be an important mode of sustainable transport because it is cheap and eco-friendly. Bicycle production was up by 3.2% in 2007 to 130 million units. India produces approximately 10% of the world annual bicycles [14, 18]. However with increased production of bicycle the production of tyre and tube

will also be increased which is proportional to the volume production of wastes. So the generation of solid wastes like tyre is increasing steadily. According to the statistical data with the exponential growth in number of automobiles, generation of waste tyre increases. In 2009, over 400 million scrap tyres were generated and over 3 billion worldwide; which is estimated to be exceeding 1 billion in scrap piles throughout India [19]. Along these lines, from the case study by (Hird et al., 2002) it was anticipated that there is a pressing need to distinguish reasonable reusing courses for waste tyres. As demonstrated in Fig 2.2 tyre reusing is anticipated to stay level in the UK until 2012 with the main development being in energy recuperation. A real use in energy recovery is as a fuel hotspot for bond ovens, where tyres create 20% more energy than coal [20]. Nearly 80% of people living in rural areas use bicycle. There is also restriction of use of car and motor bikes indifferent places particularly in educational institutes increasing the demand for the use of cycle. This will produce a lot of tyre and tube wastes. Production of these wastes can cause many environmental and hygiene problems. The mass up of this waste in the land filling sites leads to various harms such as:

- Emissions of pollutants and harmful gases.
- Breeding of insects.
- Contamination of water
- Requirement of more land filling sites.

Thus, researchers have put many efforts in developing different ways of reusing them.

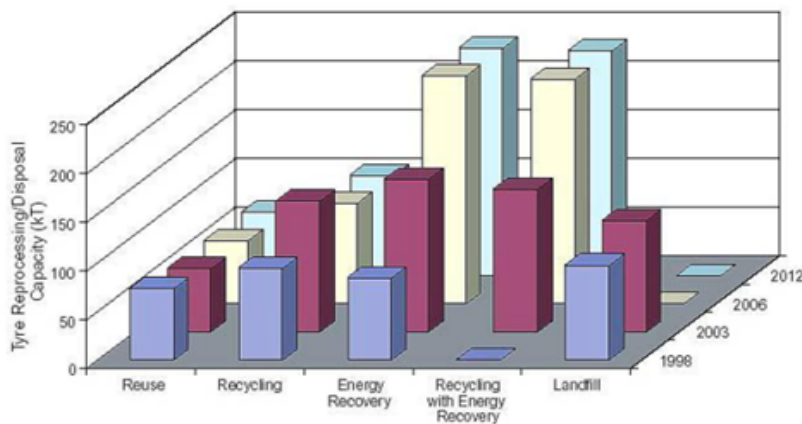


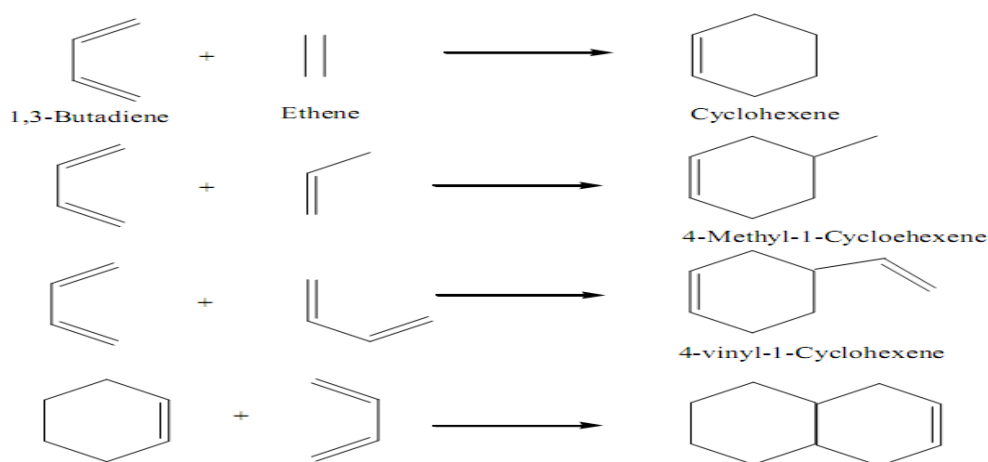
Figure 2.2 Predicted (best case) tyre reprocessing capacities by category

2.7 DIFFERENT TYPES OF RECYCLING PROCESS TO REDUCE THE TYRE WASTE

Pyrolysis, gasification and liquefaction are the thermo-chemical processes that can be used to convert waste tyre as well as other carbonaceous feed stocks such as coal, wood waste, or municipal solid waste into usable products.

2.8 REACTION MECHANISMS OCCURRED DURING PYROLYSIS OF TYRE

Pyrolysis of tyre depends on the various parameter and reactor type. Tyre is made up of different type of rubber compounds such as Butadiene Rubber (BR), Natural Rubber (NB) or Styrene Butadiene Rubber (SBR) & these rubbers basically consists of different types of polymer. During the pyrolysis of tyre different types of polymerization reactions occurs inside the reactor. Cypres and Bettens [21] suggested that the pyrolysis of tyres leads to the formation of ethene, propene and 1, 3-butadiene, which react to form cyclic olefins. The reactions are mentioned below:

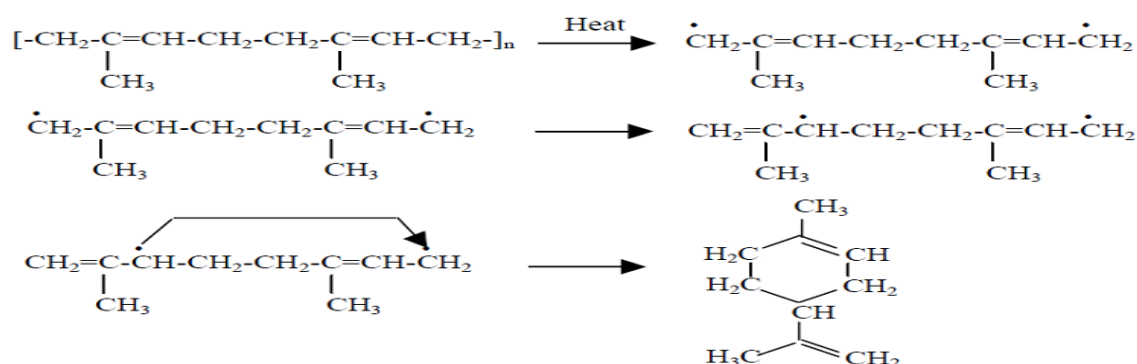


Scheme-1 Reaction mechanism during pyrolysis of tyre

Tamura et al. have additionally demonstrated that dipentene & isoprene are shaped in high focus in characteristic elastic pyrolysis & have proposed that both are created by depolymerization from the polymer radical happening by β -scission at two fold bonds. The polymer radical is obligated to shape six-membered ring, particularly under slow pyrolysis condition, so the dipentene is shaped prevalently at lesser temperature [22]. Bhowmick likewise analyzed pyrolysis of characteristic elastic utilizing TGA. They concluded that degradation initiated at a temperature $\sim 330^\circ\text{C}$ in N_2 , with a peak weight loss at $\sim 400^\circ\text{C}$. [23].

The thermal decomposition mechanism of waste tyre has been described by M Rofiquil et al and they concluded that polyisoprene has depolymerized forming dimeric species. According to the following mechanism, the dimeric species, a short-life radical, could be stabilized by pyrolytic isomerization, i.e., converting from propylene to cyclopropane [24, 25].

Scheme 2 Reaction mechanism during pyrolysis of tyre



Scheme 2 Reaction mechanism during pyrolysis of tyre

2.9 UPGRADING OF BIO OIL

The properties of high viscosity, greater oxygen content, low volatility and corrosiveness serves as a hindrance to the replacement of fossil fuels by bio-oils. In this way, bio-oils ought to be redesigned utilizing legitimate systems before they can be utilized as a part of diesel or gas motors. We can upgrade bio oil by physically, chemically and catalytically [26, 27, 28].

2.9.1 PHYSICAL UPGRADING OF BIOOIL

The most critical characteristics influencing bio oil fuel value are inconsistency with conventional fuels from the high viscosity, high O₂ content of the bio oil, high solid content, etc [26].

2.9.1.1. FILTRATION

Hot-vapour filtration can lessen the ash substance of the oil to under 0.01% & the alcohol substance to under 10 ppm. This gives a better quality item with lower char [29].

Liquid filtration to low molecule size of beneath around 5 mm is extremely troublesome because of the physic-chemical nature of the fluid & generally requires self-cleaning filters & high pressure drop [30].

2.9.1.2. SOLVENT ADDITION

Polar solvent can reduce the viscosity and homogenize bio oils. When methanol was added to bio oil, a vital impact on the oil stability was observed. Diebold & Czernik [31] concluded that the viscosity rate increased for the oil with methanol (10 wt. %) was almost 20 times lower as compared with the bio oil in which no solvent was added.

2.9.1.3. EMULSIONS

Normally pyrolysis oil is immiscible with fuel derived from hydrocarbons but we can emulsify them with the help of surfactants. CANMET [32] developed a process to form stable micro-emulsion with 5-30% of bio-oil in diesels [32]. In order to produce either a fuel for power generation or a transport fuel in engines, the University of Florence, Italy, has been working on

emulsion of 5-95% bio-oils in diesel [33, 34]. High energy requirement and the cost of surfactants serve as a major drawback for emulsification.

2.9.2. CATALYTIC UPGRADING OF BIO-OIL

2.9.2.1. HYDRODEOXYGENATION (HDO)

It is a hydrogenolysis process for removing O₂ from O₂ containing compounds. Commonly used catalysts in this case are Ni-Mo or Co-Mo. Various parameters for this process are greater pressure (up to 20 MPa) & temperature (up to 400 °C) and it also needs source for supply of hydrogen [35]. Full hydrotreating results in naphtha-like products which needs refining to get conventional transport fuels. An anticipated regular yield of naphtha proportionate from biomass is around 25% by weight or 55% in energy term barring procurement of H₂ [36]. Reaction involved in the above process is:



However various central issues emerged including that the catalyst support of commonly alumina were discovered to be unsteady in the greater H₂O content atmosphere of bio-oil & the sulfur was removed from the catalyst obliging consistent re-sulphurisation. More recently, focus is shift towards precious metal catalyst on less susceptible support. Model compounds were utilized at first to comprehend the essential procedures [37] and both entire oil and divisions have been assessed. Tests have been done on both continuous & batch stream methodologies and work to date has been in light of low-temperature (up to 380 °C) catalytic hydrogenation of bio-oil utilizing diverse metal catalyst and preparing condition to give a scope of items including petroleum refinery feedstocks. [30]

Now we need hydrogen for the hydrotreating process and we can get it by preparing an extra measure of biomass to give the H₂ to sample by gasification process. This is around 80% of that needed to create the bio-oil. The methodology is therefore less proficient than basic execution figure frequently exhibited.

Here the upgraded product should be subjected to refining to deliver marketable items and this would be required to occur in conventional refineries [30].

2.9.2.2. ZEOLITE CRACKING

Zeolite cracking gives out O_2 as CO_2 , as summarised in the overall reaction below:



The zeolite upgrading can work on the fluid or vapors inside or close coupled to the pyrolysis methodology, or they can be decoupled to upgrade either the fluids or re-vapourised fluids.

A report via hydrocarbon handling for the eventual fate of FCC and hydroprocessing in cutting edge refineries expresses that "Biomass-inferred oils are by and large best upgraded by HZSM-5 or ZSM-5, as these zeolitic catalysts advance significant returns of fluid items and propylene. Tragically, this nourishes have a tendency to coke effectively, and high TANs (Total Acid Number) & unwanted side effects, for example, water and CO_2 are extra difficulties [30].

2.9.2.3. INTEGRATED CATALYTIC PYROLYSIS

There is expanding enthusiasm for enhancing the nature of bio-oil and there have been various improvements in the most recent couple of years that incorporate or consolidate catalysis with pyrolysis.

A fractional pyrolysis process was developed by Agblevor at Virginia Polytechnic Institute & State University which is based on in-bed catalysis [38] and it has been patented [39].

A catalytic thermochemical process was claimed by Exelus which was carried at a lower temperature (200 °C) and longer residence time (20 min) to convert biomass into gasoline [40].

2.9.3. OTHER METHODS FOR CHEMICAL UPGRADING OF BIO-OIL

This section includes various methods which are not covered in hydrotreating and zeolite related processes and are described below [30].

2.9.3.1. AQUEOUS PHASE PROCESSING

Dumesic et al. proposed a method in which H₂ and alkanes are produced by aqueous phase reforming and dehydration/hydrogenation from aqueous solutions of oxygenated hydrocarbons [41-43]. The bio oil produced water soluble and mostly oxygenated hydrocarbons compounds were present in its aqueous fraction [30].

2.9.3.2. MILD CRACKING

A substitute to zeolite cracking is mild cracking over base catalyst that discourses only the cellulose and hemicellulose derived product. Here the goal is to minimise coke and gas production. Crofcheck at University of Kentucky [44] used Zinc Oxide and freshly calcined Zinc/Aluminium and Magnesium/Aluminium double layer hydroxide to upgrade synthetic bio-oils [45].

2.9.3.3. AQUEOUS PHASE REFORMING

Dumesic at the University of Wisconsin first proposed upgrading the aqueous fraction of bio-oil for H₂ and alkanes [46].

2.9.3.4. GASIFICATION FOR SYNFUELS

In this case decentralised production of bio-oil or bio-oil-char slurries is done for transportation to a process plant for gasification and synthesis of hydrocarbon transport fuel by Fischer Tropsch synthesis, or alcohol. Fast pyrolysis plants up to 100,000 tons/yr or 12 tons/hr are economically

viable. Synthetic hydrocarbons include gasoline, diesel, LPG, kerosene and methane (synthetic Natural Gas- SNG). These liquid fuels are entirely compatible with conventional fuels in all proportions, but are much cleaner [30].

Table 2.2 Comparison of characteristics of bio-oil, crude oil and catalytically upgraded bio-oil

	BIO OIL	HDO	ZEOLITE CRACKING	CRUDE OIL
Upgraded Bio Oil				
Y _{Oil} [wt %]	100	21-65	12-28	-
Y _{Gas} [wt %]		3-15	6-13	-
Y _{Waterphase} [wt %]	-	13-49	24-28	-
Y _{Carbon} [wt %]		4-26	26-39	
Oil Characteristics				
pH	2.8-3.8	5.8	-	-
Water [wt %]	15-30	1.5	-	0.1
Density[g/cm ³]	1.05-1.25	1.2	-	0.86
Viscosity _{50°C} [cP]	40-100	1-5	-	180
HHV [MJ/Kg]	16-19	42-45	21-36	44
C [wt %]	55-65	85-89	61-79	83-86
O [wt %]	28-40	<5	13-24	<1
H [wt %]	5-7	10-14	2-8	11-14
S [wt %]	<0.05	<0.005	-	<4
N [wt %]	<0.4	-	-	<1
Ash [wt %]	<0.2	-	-	0.1
O/C	0.3-0.5	<0.1	0.1-0.3	~0
H/C	0.9-1.5	1.3-2.0	0.3-1.8	1.5-2.0

Note: Adapted from Applied Catalysis A: General 407 (2011) 1– 19 [47]

Table 2.3 Carbon deposition on different catalysts after operation, given in wt% of total catalyst mass Data for zeolites in rows 1 and 2 are from Park et al. [48]. Data for HDO catalysts in rows 3 and 4 are from Gutierrez et al. [49].

Catalyst	Carbon [Wt %]
Co-MoS ₂ /Al ₂ O ₃	6.7
Rh/ZrO ₂	1.8
Meso-MFI	21.3
HZSM-5	13.6

Note: Adapted from Applied Catalysis A: General 407 (2011) 1– 19 [47]

Table 2.4 Oil composition on a water-free basis in mole% through the bio-oil upgrading process as specified by Elliott et al. [50].

	Bio-Oil	HDO Oil	Hydrocracked Oil
Alkanes	0	4.45	82.85
Ketones/Aldehydes	13.77	25.08	0
Aromatics	0	0.87	11.53
Alcohols	3.5	5.29	0
Guaiacols etc.	34.17	10.27	0
Acids/Esters	19.78	25.21	0
Furans etc.	11.68	6.84	0
Phenolics	10.27	18.55	0
Unknown	6.83	3.44	5.62

Note: Adapted from Applied Catalysis A: General 407 (2011) 1– 19 [47]

CHAPTER 3

EXPERIMENTAL WORK

3.1 MATERIALS AND METHODS

3.1.1 RAW MATERIALS

The raw material used for production of oil was tyre of bicycle collected from nearby cycle repair store. These are cut into approximate 1 cm size and remove the thread.

3.1.2 PROXIMATE AND ULTIMATE ANALYSIS OF RAW MATERIAL

ASTM D3173-75 method was used for the proximate analysis and the ultimate analysis was done by using CHNS analyzer. ASTM D5868-10a. was used for finding the calorific value of the raw material . The sample such as tyre was identified with the following characteristics using proximate and ultimate analysis. Table 3.1 gives an idea for thermal degradation of the sample showing more volatile content along with moderate fixed carbon composition. From ultimate analysis bicycle tyre shows less carbon content and more oxygen content when compared with tyre (of motor cycle). Hence the GCV of bicycle tyre was varying a small difference as compared to the motor cycle tyre but in appreciable range to recover when compared with coal [51, 52].

Table3.1 Proximate and ultimate analysis of raw material

Types of Raw material Used	Tyre	Motorcycle Tyre [51]
Proximate analysis		
Water content (wt %)	0.55	1.53
volatile matter (wt %)	62	57.50
Ash content (wt %)	18.73	20.85
Fixed carbon (By difference)	18.72	20.10
Ultimate analysis		
Carbon (C) (wt %)	57.38	75.50
Hydrogen (H) (wt %)	5.50	6.75
Nitrogen (N) (wt %)	0.67	0.81
Sulphur (S) (wt %)	3.24	1.44
Oxygen (O) (wt %)	33.21	15.50
H/C Molar ratio	0.10	N/A
C/N Molar ratio	86.26	N/A
GCV (Mj/Kg)	27.68	29.18

3.1.3 SEMI-BATCH PYROLYSIS REACTOR

The reactor was made of stainless steel (SS).

- Dimension:-

Length: 16 cm

Diameter: 5 cm (Outer)

4.8 cm (Inner)

One end was sealed & other end has two outlets. One outlet is for oil & other for nitrogen purging.

3.1.4 PYROLYSIS SETUP

The pyrolysis setup was consisting of batch reactor and furnace (which is shown in fig. 3.1). The furnace was control by PDI controller. Two 500 ml condenser in series was attached to one outlet for condense the vapours coming out of it and other outlet for nitrogen purging. At the end of condenser a flask was placed for collection of oil.

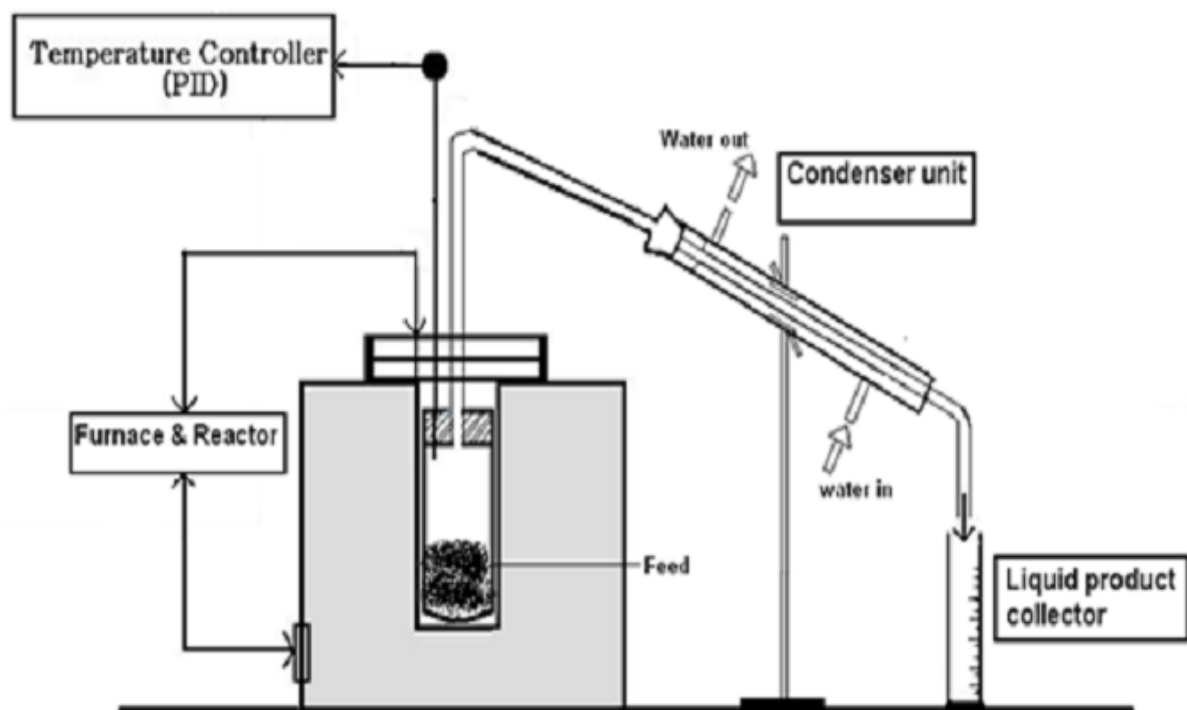


Fig 3.1 Schematic diagram for thermal pyrolysis setup

3.1.5 EXPERIMENTAL PROCEDURE

For each run 30 grams of sample was taken in batch reactor. Then it was placed in the furnace. At a rate of 20 °C/ min at various temperature (350 °C to 800 °C) pyrolysis was carried out. The

condensable liquids were collected in the flask. The non-condensable vapours were vented to the open atmosphere. The non-condensable vapours weight was calculated by mass balance.

3.2 CHARACTERIZATION OF PYROLYTIC OIL

3.2.1 CHEMICAL CHARACTERISTICS OF TYRE OIL

3.2.1.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Using FTIR method the oil was analysed. Within the range of 400-4000 cm^{-1} region with 8 cm^{-1} resolution, the FTIR spectra was collected. The FTIR imaging was carried out using Perkin Elmer RX.

3.2.1.2 GC-MS ANALYSIS

Chemical arrangement of bio-oil was tried by GC-MS (Auto System XL GC/Turbo Mass MS, PerkinElmer) with a fourfold indicator and a DB1MS narrow section (30 mm \times 0.25 mm inward width \times 0.25 μm thickness). Helium (UHP) was utilized as the bearer gas with a steady stream of 1.2mL/min. The starting temperature of oven temperature system was situated at 40°C and proceeded for 4 min, ascending by 5°C/min to 250°C, which proceeded for 10 min. The injector temperature was 250°C. The volume of infused example (10% of bio-oil in chloroform) was 1 μL . Electron ionization (EI) was utilized as a part of the MS and standard mass spectra with 70 eV ionization energy were recorded with a checked reach from 0 to 1200 amu. The computer coordinating of mass spectra was performed utilizing the NIST98 and WILEY7.0 library and the maintenance times of known species infused in the chromatographic segment were utilized for characterisation of the peaks.

3.2.1.3 CH-NS ANALYSIS

Carbon, Hydrogen, Nitrogen, Sulphur substance of bio oil was determined. In the burning procedure (heater at ca. 1000 °C), carbon is changed over to CO₂; hydrogen to H₂O; nitrogen to nitrogen gas/ oxides of nitrogen and sulphur to SO₂. On the off chance that different components, for example, chlorine are available, they will likewise be changed over to ignition items, for example, hydrogen chloride. A mixture of sponges are utilized to uproot these extra burning items and additionally a percentage of the chief components, sulphur for instance, if no determination of these extra components is needed.

The ignition items are cleared out of the burning chamber by inactive transporter gas, for example, helium and disregarded warmed (around 600 °C) high virtue copper. This copper can be arranged at the base of the ignition chamber or in a different heater. The capacity of this copper is to evacuate any oxygen not expended in the beginning burning and to change over any oxides of nitrogen to N₂ gas. The gasses are then gone through the spongy traps to leave just CO₂, H₂O, SO₂ and N₂.

Identification of the gasses can be done in a mixture of ways including (i) a GC partition took after by measurement utilizing warm conductivity discovery (ii) an incomplete division by GC ('frontal chromatography') trailed by warm conductivity location (CHN however not S) (iii) a progression of discrete infra-red and warm conductivity cells for recognition of individual mixes. Evaluation of the components obliges alignment for every component by utilizing high immaculateness 'small scale scientific standard' mixes, for example, acetanilide and benzoic corrosive.

3.2.2 PHYSICAL CHARACTERISTICS OF TYRE OIL

Physical properties for example specific gravity, density, flash point, pour point, fire point, sulphur content, Kinematic viscosity, cloud point, and distillation boiling range of the tyre oil was determined using the following standard methods, which is shown in the Table 3.2.

Table-3.2 Methods for Physical Property Analysis

Sl. No.	Physical properties	Methods
1.	Kinematic viscosity	I.S:1448 P:25
2.	Specific gravity	I.S:1448 P:16
3.	Fire point	I.S:1448 P:20
4.	Flash point	I.S:1448 P:20
5.	Cloud point	IS:1448 P:10
6.	Pour point	IS:1448 P:10
7.	Distillation boiling range	IS:1448 P:18
8.	Sulphur content	IS:1448 P:33

3.3 BLENDING PROPERTIES

Blending of tyre oil with methanol was carried out in different concentration(5 wt. %, 10 wt. %, wt. %, 15 wt. %) and different properties are measure and the graph was plotted between concentration of methanol and tyre oil vs the properties(like viscosity).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 THERMAL PYROLYSIS RESULT

The product distribution obtained from tyre for temperature range of 350°C to 800°C at every 50°C increase in temperature for an average feed size as 1cm has been shown in Table 4.1. The weight fractions of oil, reaction temperature, volatile and char along with reaction time were plotted together in the Fig 4.1. It was apparent that at lower temperatures the tyre was partially pyrolysed to give less oil and volatiles with maximum retention of material in solid form as char. With increase in temperature, more gaseous streams were observed at 500°C to 550°C along with moderately high oil products, which increases up to 600°C and that explains the effect of temperature on product yield. It was also proved that oil yield increases from 24.64% to 49.6 % by weight at 450°C to 600°C, there after no significant change occurs. It can be postulated that the optimum yield of oil was obtained at 600°C temperature, due to the strong cracking of tyre rubber and the secondary cracking which takes place inside the reactor, and that was followed by formation of more gases, with a significant decrease in residue from 68.5 % to 41.65% by weight for temperature increase from 450°C to 700°C. With increase in reaction time, results that incomplete depolymerisation of the sample that leads to production of more char and less amount of oil at lower temperature. The decrease in reaction time contributes to secondary reaction of the product with higher temperature, which leads to more oil and less char. There is no noticeable process for gas loss with reaction time.

Table 4.1 Product distribution of tyre pyrolysis

Temperature(°C)	Oil (wt%)	Char (wt%)	Volatile matter(wt%)	Reaction time(Sec)
450	21.6	71.3	7.1	60
500	38.7	48.8	12.5	54
550	42.3	46.6	11.1	42
600	45.8	42.3	11.9	41
650	48.3	42.8	8.9	37
700	47.9	41.6	10.5	34

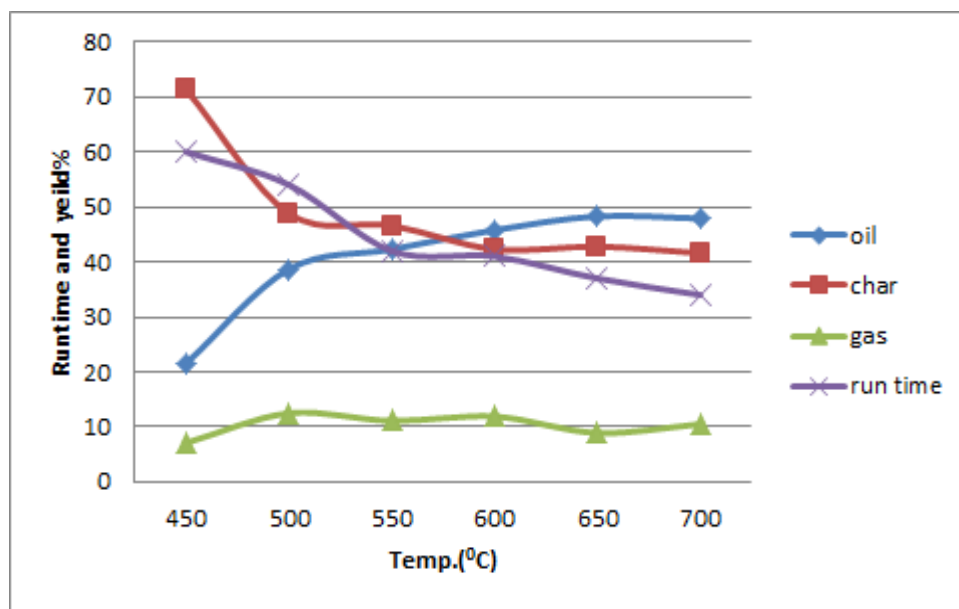


Figure 4.1 Effect of temperature on product yield and reaction time of tyre pyrolysis

4.2 CHARACTERIZATION OF PYROLYTIC OIL

4.2.1 PHYSICAL PROPERTIES

After thermal pyrolysis the oil obtained is dark brown in colour with strong acidic smell resembling petroleum fractions. The oils were characterized and compared with the properties of diesel fuel and it is summarized in Table 4.2

Table 4.2 Physical properties of tyre pyrolytic oil and Diesel

Properties	Tyre oil	Diesel
Density(kg/m ³)	916.4	832.4
Kinematic viscosity	4.2	2.47

Flash point(⁰ C)	47	49
Fire point(⁰ C)	59	57
Pour point(⁰ C)	17	-15
Cloud point(⁰ C)	22	-11
Colour	Dark brown	Light yellow

4.2.2 CHEMICAL PROPERTIES OF THE PYROLYTIC OIL

4.2.2.1 CHNS ANALYSIS OF TYRE PYROLYTIC OIL

Elemental composition of both tyre oil and diesel oil are shown in table 4.3.

Table 4.3:-CH-NS Analysis result

Element	Tyre oil	Diesel
C	56.216	85.92
H	6.725	13.1
N	0.651	0.20
S	3.010	0.28
O	33.398	0.5

4.2.2.2 FT-IR ANALYSIS OF TYRE OIL

It is a method which is utilized to get an infrared range of emission, absorption, photoconductivity or Raman scattering of a strong solid, liquid or gas. A FTIR spectrometer at the same time gathers high spectral resolution information over a wide spectral extent.

Fourier Transform Infrared (FT-IR) Spectroscopy is one of the vital systems which construct its usefulness with respect to the rule that all atoms ingest infrared light. Just the monoatomic (He, Ne, Ar, and so forth) and homopolar diatomic (H₂, N₂, O₂, and so on) particles don't ingest infrared light. On cooperation of an infrared light with oil, synthetic bond will extend, contract, and retain infrared radiation in a particular wave length go notwithstanding structure of whatever is left of the atoms. In light of this standard useful gathering present in the pyrolytic oils were recognized. The FT-IR range for tyre oils is indicated in Fig 4.2 outcomes from the transmittance ranges are displayed in Table 4.4. The information demonstrates that the present oils contain fundamentally aliphatic and fragrant mixes.

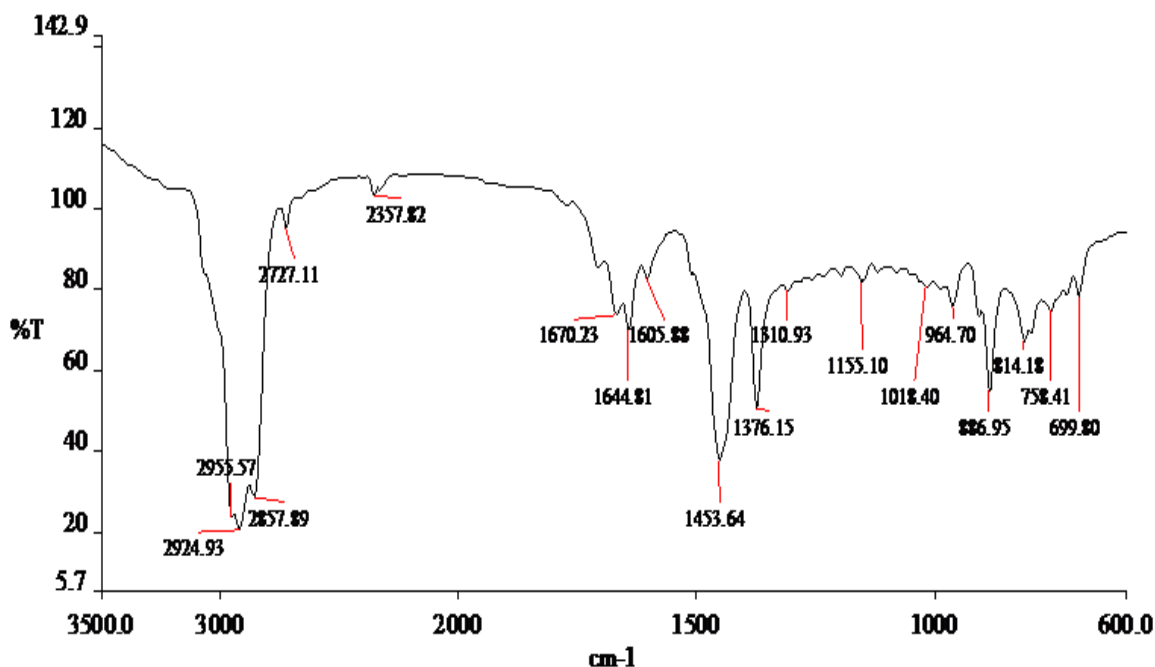


Fig4.2 FT-IR spectra of tyre pyrolytic oil

Table 4.4 : FT-IR functional groups of tyre pyrolytic oil

Wavelength Range (Cm ⁻¹)	Functional group	Class of compounds
2955.67	C-H stretching	Alkene
2727.11	C-H stretching	Aldehyde
1670.23	C=O stretching	Aldehyde or ketones
1644.81	C=C stretching	Alkene+ N-H Bend
1605.88	C-C stretching	Aromatic compound
1453.64	C-H bending	Alkene
1376.15	C-H bending	Alkene
1310.93	C-N stretching	Amines
964.70	C-H bending	Alkene
886.95	C-H bending	Alkene
814.18	C-H bending	Alkene+ Phenyl ring substitution

4.2.2.3 GC-MS ANALYSIS OF TYRE PYROLYTIC OIL

Gas chromatography–mass spectrometry (GC-MS) is an analytical method which combine the features of gas-chromatography and mass spectrometry to detect various substances within a test sample. Analysis using GCMS confirmed the composition of each fraction. GC-MS analyses were carried out for the pyrolytic tyre oil which was obtained at a temperature of 600°C. The peaks provided by the chromatogram were analysed by the NIST software. It can be observed that the tyre pyrolytic oil is a very complicated mixture of aromatic and aliphatic compounds such as 1,3-dimethyl cyclohexene, Methyl ethyl cyclopentene, Ethylbenzene, O-Dimethyl benzene, 1-Methyl-2-butylacetylene, Dimethylbenzene, Cyclohexene, Benzene, 2-Methyl-1-phenyl-1-butene, etc. And it was observed that total sixty-eight compounds were obtained in the pyrolytic oil. The maximum percentage of Cyclohexene, 1-methyl-4-(1-methylethenyl) was present as compared to other compounds. The tyre pyrolytic oil produced in a fixed-bed reactor

at 500°C claimed by Rodriguez et al. consisted of 1.7 wt % sulfur-containing compound, 4.3 wt % nitrogen-containing compound, 31.7 wt % aliphatic compounds and 62.3 wt % aromatic compounds. According to M. Rofiquel et al. pyrolytic oils are a complex mixture of aromatic and aliphatic compounds with their total concentration of 49.50% and 16.60% respectively. From the results we can conclude that the pyrolytic oil contains a high proportion of aromatic compounds.

Table 4.5 Result of GCMS analysis

Sl.no.	Area	Run time	Name
1	0.57	6.038	1,3-dimethyl cyclohexene
2	0.84	6.476	Methyl ethyl cyclopentene
3	1.68	7.263	Ethylbenzene
4	2.08	7.553	O-Dimethylbenzene
5	1.01	7.991	1-Methyl-2-butylacetylene
6	1.30	8.303	Dimethylbenzene
7	0.67	8.653	1,5-dimethyl-2-aminomethylpyrrole
8	0.79	8.905	3,5-octadiene-2-one
9	1.66	9.440	1,3,5-Trimethylbenzene
10	0.49	9.834	1-methyl-4-(1-methylethyl)-Cyclohexene
11	1.26	10.168	1,5,5-trimethyl-3-methylene cyclohexene
12	3.92	10.799	1-Methyl-3-ethylbenzene
13	1.46	11.082	1,3-Cyclopentadiene
14	2.02	11.498	2,6-Dimethyl-2,4,6-octatriene
15	2.11	11.839	1,2,3-Trimethylbenzene
16	1.97	12.196	2,3,6-Trimethyl-1,5-heptadiene
17	9.47	13.199	Cyclohexene, 1-methyl-4-(1-methylethenyl)
18	1.93	13.830	Benzene, 1-methyl-3-propyl
19	2.93	14.662	Benzene, 1-methyl-4-(1-methylethyl)
20	0.77	15.375	(4-Methylphenyl) methanol

21	1.35	15.628	Benzene, (1,1-dimethylpropyl)
22	0.59	16.200	Pyridine, 3-ethoxy- (CAS)
23	0.74	16.490	5-Methylindan
24	2.27	16.839	1-Methyl-2-propenyl)-benzene
25	1.92	17.990	2-Methyl-1-phenyl-1-butene
26	1.19	18.317	4,7-Dimethylindan
27	0.54	18.674	Cyclohexane,1-methyl-2,4-bis(1-methylethenyl)
28	1.12	19.053	3-Thiophen-2-yl-acrylonitrile
29	3.61	20.078	4,7-Dimethyl-2H-isoindole
30	1.82	20.687	Naphthalene, 1-ethyl-1,2,3,4-tetrahydro131
31	2.09	21.073	2-methylbenzothiazol
32	2.39	21.980	1,1,6-Trimethylindane
33	2.32	22.448	Benzene, 4-(2-butenyl)-1,2-dimethyl-
34	0.80	22.990	2-Chloro-4-fluoro-5-methylaniline
35	2.89	23.265	Indene, 1,2,3-trimethyl
36	0.94	23.733	4-methyl-5-isopropyliden-8-oxo-nona-1,3-diene
37	2.04	24.045	2,6-Dimethyl-naphthalene
38	3.59	24.528	2,7-Dimethylnaphthalene
39	2.51	25.077	2-Chloro-3-fluorobenzoic acid
40	4.36	25.575	Spiro[4.5]dec-7-ene,1,8-dimethyl-4-(1-methylethenyl)-, [1S-(1.alpha.,4.beta.,5.
41	2.74	26.585	2,7-Naphthalenediol, decahydro- (CAS) 121.094
42	1.44	27.254	2,3,6-Trimethylnaphthalene
43	0.80	27.655	Naphthalene, 2,3,5-trimethyl
44	0.79	27.997	4,6,8-Trimethylazulene
45	1.95	28.814	n-tri-decanene
46	0.88	29.334	2-(4-Methylphenyl)pyridine
47	0.71	29.973	3-Hydroxy-2-pyridin-3-yl-propenal
48	0.45	30.589	Naphthalene, 1,6-dimethyl-4-(1-methylethyl)
49	0.87	31.057	n -heptadecane

50	1.17	31.481	Azulene, 7-ethyl-1,4-dimethyl-
51	0.47	32.030	4,4'-Dimethyldiphenylmethane
52	0.56	32.417	Methyl-2-isopropenyl-5-anisole
53	0.32	32.907	9,13-bis(Demethyl)retinal
54	0.25	33.204	n-Pentadecane
55	0.90	33.761	1-(9H-Fluoren-4-yl)-1,2-ethanediol
56	0.76	34.155	2-Methoxyphenazine
57	0.48	34.616	1,2-epoxy-carota-1,4-dienaldehyde
58	0.48	34.987	7-Ethyl-1,2,3,4-tetrahydroacridine
59	0.69	35.359	Tetradecyl cyanide
60	0.86	35.678	Bicyclo[3.1.0] 2-hexene, 4,4,6,6-tetramethyl
61	0.52	37.899	1,7-Dimethylphenanthrene
62	1.39	39.273	Heptadecyl cyanide
63	0.64	40.165	4,6-Dichloro-7-hydroxybenzo-2,1,3-thiadiazone
64	0.28	41.197	3,4,5,6-Tetramethylphenanthrene
65	0.38	42.542	1-[3,3-Dimethyl-2-(3-methyl-buta-1,3-dienyl)-cyclopentyl]-2-hydroxy-ethanone
67	0.26	43.069	(4-(.alpha.-naphthyl)bicyclo(2.2.2)oct-1-yl)methanol
68	0.25	43.441	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl

4.3 BLENDING PROPERTIES

Table 4.6- Blending of tyre oil with methanol and their viscosity

Ratio(wt. % methanol)	Time taken(sec)	Viscosity(mm ² /sec)
1:19 (5)	198	3.94
2:18(10)	180	3.58
3:17(15)	156	3.1
100:0(100)	36	0.7164

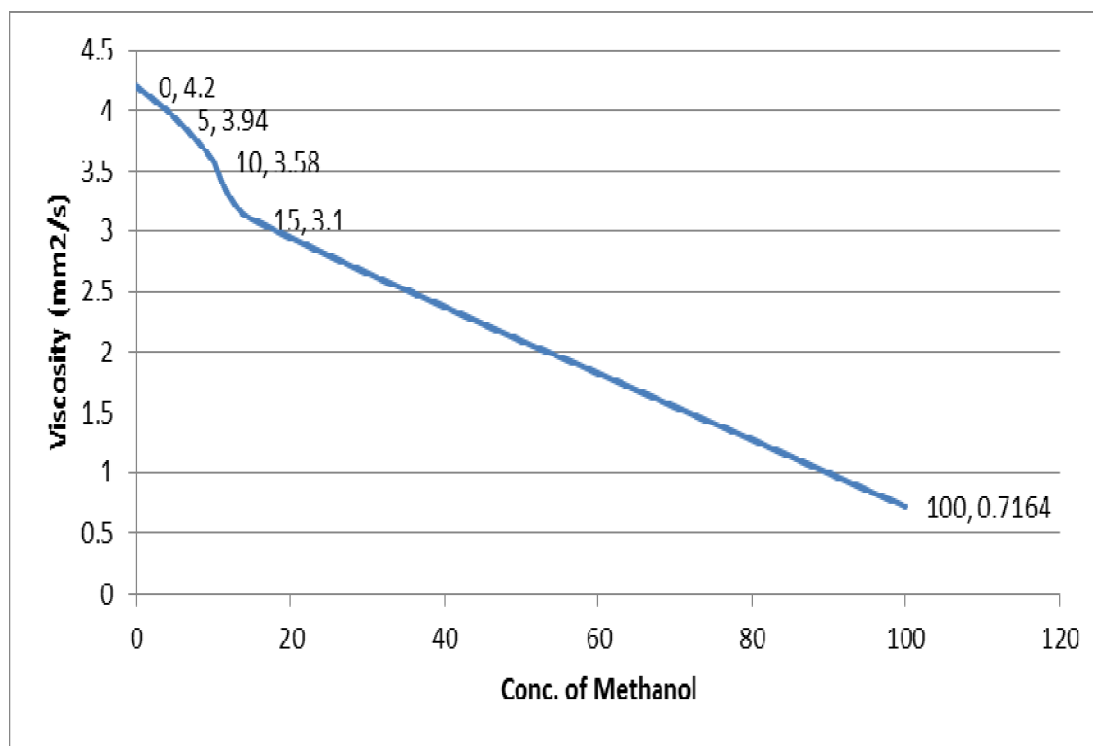


Figure 4.3Plot between concentration of methanol and Tyre Oil vs Viscosity

CHAPTER 5

CONCLUSION AND FUTURE WORK

5.1. CONCLUSION

The bio-oil formed from fast pyrolysis is transportable and storable, and in addition has the capacity to supply various profitable chemicals. Some basic and essential requirements need to be followed if you wish to have better yields of improved quality bio oil from pyrolysis.

The capability of bio-oil is progressively being perceived, with a fast development in examination into enhancing the properties of bio-oil especially for devoted applications and for bio fuel generation. Irrefutably the most captivating and potentially critical examination is on complex & more sophisticated catalytic system & these will oblige bigger scale advancement to demonstrate practicality & reasonability. Bio refineries offers extensive extension for improvement of pyrolysis based processes & products, and these will require advancement of component processes so as to advance a coordinated system. They will fundamentally incorporate procurement of power & heat for at least energy self-sufficiency.

In this project, the value added products from waste tyre pyrolysis was explored. The thermal pyrolysis has been carried out in a semi-batch reactor under distinctive temperature ranges from 450°C - 700°C.

Following conclusions were observed during the experiment:

- The greatest yield of oil acquired was 49.6% at an ideal temperature of 600°C for tyre.
- It was likewise watched that with increment in temperature both oil and gas yield was increased. This is because of the strong cracking of tyre rubber and the secondary cracking that happened inside the reactor. This demonstrates the impact of temperature on production yield.
- From GC-MS and FTIR analysis of bio oil, it was concluded that the chemical composition and the functional groups present in the pyrolytic oil was that of aromatic & aliphatic compounds. From GC-MS analysis, we can conclude that the tyre pyrolysis contains around 68 chemical compounds of varying carbon chain length.

- It was seen that viscosity of bio oil decreases with addition of polar solvents such as methanol.
- Bio oil can be upgraded both physically and chemically.
- Catalysts used in the catalytic upgrading of bio oil are zeolites, Cobalt molybdenum or nickel molybdenum, etc.
- Upgraded bio oil can be used as a fuel oil.

5.2. FUTURE WORK

Few recommendations along with some problems regarding fast pyrolysis and bio oil upgrading are mentioned below:

- Since bio oils are complex mixtures, biomass fast pyrolysis ought to compare with the qualities of the biomass feed-stocks, products utilities, suitable reactors & methodologies for the products applications.
- We need to focus more on the upgrading of bio-oils with a few adjustments to gear setup before applying them in creating energy or heat.
- Finding feasible sources of hydrogen for hdrodeoxygenation process.
- It is important to imagine adding a few solvents to diminish polymerization by esterification, acetalization and phenol/formaldehyde responses, to decrease olefin polymerization responses and emulsifiers to avert phase partition issues.

- Biomass can be a economically suitable renewable asset for productive energy utilities if utilized as a part of an incorporated methodology that additionally creates other attractive co-products to keep up practical advancements.
- New formulations regarding catalyst development need to be investigated.
- During the upgrading of bio-oil utilizing different catalysts, the system on catalyst deactivation expected to be further clarified, and the catalysts with high durability, strong renewable capacity and high productivity need to be created.
- For emulsification, we need to look for more economical and plentiful surfactants as substitutes for the high- valued surfactants.
- To advance the industrialization of upgrading of bio- oil, more focus ought to be paid to grow more experimental facilities with larger scale and larger efficiency.

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