Pyrolysis of Biomass of Different Nature in Various Reaction Environment: Fuel, Physicochemical and Qualitative Analysis of Their Products

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भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
Indian Institute of Technology Guwahati

Dedicated

To

My Parents, My Wife and My Mentor

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STATEMENT

I hereby declare that the content embodied in this thesis entitled **“Pyrolysis of Biomass of Different Nature in Various Reaction Environment: Fuel, Physicochemical and Qualitative Analysis of Their Products”** is the result of investigations and experiments carried out by me at the C1 Lab, Transit Complex, Department of Chemical Engineering, Indian Institute of Technology Guwahati, India, under the guidance of Prof. Nanda Kishore. In keeping with the general practice of reporting scientific observations, due acknowledgments have been made wherever the work described is based on the findings of other investigators.

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CERTIFICATE

It is certified that the work contained in this thesis entitled **"Pyrolysis of Biomass of Different Nature in Various Reaction Environment: Fuel, Physicochemical and Qualitative Analysis of Their Products"** done by **Mr. Harshal Dnyandeo Kawale** (Roll No. 166107114) has been carried out under my supervision and this work has not been submitted elsewhere for a degree.

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Harshal Dnyandeo Kawale

Contents

Abstract

Fossil-fuels are heading towards extinction, and their extensive use is deteriorating environmental synchronization. With this there is also an immense need for energy in the forms of heat, electricity and fuels. To overcome all these burning issues, it is time to make up a setback for clean fuels generation. In this regard, 'lignocellulosic waste biomass' is one such renewable source which can withstand the responsibility as new generation energy giant. In this dissertation, a rarely researched biomass Delonix Regia has been selected as one of the feedstock for pyrolysis at different temperatures, for catalytic pyrolysis, for hydropyrolysis and as co-feed for its co-pyrolysis along with pinewood saw dust and butyl rubber tube waste individually. This dissertation also considered another rarely researched biomass, *Oscillatoria* green algae, for its non-catalytic, catalytic and hydropyrolysis. This thesis reports that, with increase in temperature the yield of bio-oil and its calorific value has improved. The catalytic pyrolysis results in upgraded product quality of the bio-oil than non-catalytic pyrolysis bio-oil whilst catalytic hydropyrolysis delivers more phenolic product. This algal biomass is producing good quantity as well as quality bio-oil including constituent elements of popular hydrocarbons such as BTX etc. The fuel quality of two different lignocellulosic biomass materials is tested using one extensively researched biomass. The results of co-feed pyrolysis of Delonix Regia and Pinewood sawdust conveyed to go for co-feed pyrolysis rather than single feed at 1:1 ratio. Also, as the waste is increasing rapidly, there is need of waste valorization, minimization and management. Accordingly, two general solid wastes present in the vicinity of IIT Guwahati campus are chosen i.e., lignocellulosic waste (DR) and butyl rubber tube waste (TW). Both the waste materials delivered best quality bio-oil resulting average HHV of 32.61 MJ/kg. Bio-chars obtained from all the pyrolysis approaches can be activated at higher temperatures such as 600 °C to 900 °C for further utilization. In addition, advanced characterization techniques are utilized for the qualitative determination of produced bio-oil and biochar along with physico-chemical characteristics. Bio-oil was analyzed by Fourier Transform Infrared Radiation (FT-IR) Spectroscopy, Gas Chromatography and Mass Spectrometry (GC-MS), Proton Nuclear Magnetic Resonance (^{1}H-NMR). Biochar was characterized by Field Emission Scanning Electron Microscope (FESEM), and X-Ray Diffraction (XRD). Finally, the bio-oil with such enchanting calorific values also contain popular hydrocarbons such as benzene, toluene, xylene, styrene, phenols (cresol, guaiacol, catechol, Phenol, 2-methoxy etc.) in good amount. Overall, the bio-oils

are good to go for direct applications as furnace oil, heating oil, feed for boiler etc. Whereas the bio-char obtained from the aforementioned experiments possesses fuel properties, fertilizer quality and can be used in separation technology if activated. The non-condensable gases from these system has good syngas amount which can be used to make self-sustainable setup for energy utilization and production with the help of initial external heat energy. Thus, the objectives of the study are successfully completed and directed towards actual production of biofuels by utilization of waste biomass.

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Abbreviations

DR: Delonix Regia

PW: Pinewood Sawdust

TW: Butyl Rubber Tube Waste

HHV: Higher Heating Value

CV: Calorific Value

C: Carbon

H: Hydrogen

N: Nitrogen

S: Sulphur

O: Oxygen

TGA: Thermogravimetric Analysis

DTG: Differential Thermogravimetric Analysis

FT-IR: Fourier Transform Infrared Spectroscopy

GC-MS: Gas Chromatography Mass Spectroscopy

NMR: Nuclear Magnetic Resonance

XRD: X-ray Diffraction

FESEM: Field Emission Scanning Electron Microscope

BET: Brunauer – Emmett - Teller

Introduction

The significant rise in oil prices, decreasing crude-oil reserves, the increasing energy consumption with the ever increasing population and the growing concern about the environment has recently brought the need of improved utilization of renewable energy resources [1–7]. Non-renewable energy resources, like petroleum, coal, and natural gas meets about seventy-six percent of the world's main energy demand and supply, each analogous to 33, 24, and 19 %, respectively [2]. As the precursor of fossil feedstock, biomass which is rich in carbon appears to be one of the best choices for the substitution of fossil resources in many applications [4,8]. The term biomass refers to all organic material which has an origin of plants (counting algae), trees, and crops whilst they collect and store sun's energy via photosynthesis [4,9,10]. Biomass is recognized as the largest renewable energy resource and it accounts for 12 - 15 % of total world energy supply [2–4,11]. "National policy on biofuels India 2018" categorically describes biofuels as "Basic Biofuels" and "Advanced Biofuels". This policy allows use of surplus food grains for manufacture of biofuels to reduce the financial risk of framer during surplus production of the crops [12]. Producing energy from biomass has lead low emissions in form of gases like sulphur oxides (SO_x), nitrogen oxides (NO_x) which are environmentally detrimental in comparison with that of fossil fuels, on the basis of plants carbon cycle [2,9,10]. Typically, biomass contains organic matters such as lipids, proteins, sugars, starches, cellulose, hemicellulose, lignin with some inorganic matters and water [13,14]. For typical biomass, carbon and oxygen together constitute over 90 % of dry weight of the biomass [13]. The biomass-based renewable energy will anticipate in a chief role of global energy demand and supply in near future. The diminution of fossil-based fuels and at the same time burning of fossil based fuels, encounters climate change worldwide makes bio-based fuels a promising sustainable energy resource in various part of the world for the 21st century [15]. Moreover, approximately 220 billion dry tons of feedstock of biomass are available each year [16,17].

Bio-fuels from biomass can be achieved by different techniques which are divided into three groups i.e., (a) thermo-chemical conversion, (b) biochemical conversion, and (c) oil extraction [18,19]. Thermo-chemical conversion technique mainly comprises of combustion, pyrolysis and gasification, whilst in biochemical conversion, microbial and bacterial actions lead to anaerobic digestion of biomass to generate biogas and to generate alcoholic fuels, phenomenon of fermentation can be applied. In oil extraction, edible and non-edible oils can be extracted from various seeds and grains. The reaction of biomass combustion chemically converts carbon into carbon dioxide and hydrogen into the water by a series of primary and secondary reactions by directly burning biomass in combined heat and power plant [18,20]. Gasification converts the biomass in syngas by the reaction of partial oxidation whereas syngas contains hydrogen, and carbon monoxide, other gases will also be produced during this reaction such as carbon dioxide, methane and organic vapours which condenses to form tar in some amount [18,20,21]. Pyrolysis is the thermo-chemical degradation of biomass in inert media or no media. The reaction of pyrolysis eventually produces bio-oil, bio-char, and non-condensable volatile gases [18,20–23]. This thermo-chemical conversion techniques are more energy efficient compared to that of other techniques with flexibility in feed and their products [24]. Midst of all other thermo-chemical techniques, pyrolysis is considered as more effective and viable technique for conversion of biomass because of its high yielding of condensate with less smoky, clean-burning fuel quality without generating much tar and having a higher calorific value product than other techniques. In addition to the pyrolysis oil, pyrolysis process also produces char (solid product). Char can also be used as a fuel or can be upgraded to activated carbon and gaseous product which is of high calorific value may be used for power generation [8,25,26]. These products distribution, composition and yield of the pyrolytic process mainly depends on the temperature and heating rate values [8].

Further advanced research in biomass pyrolysis has the potential to solve the problem of finding an energy efficient and at the same time environment-friendly renewable and sustainable energy resource [27]. The main drawback of conventional pyrolysis product is that the bio-oil contains hundreds of oxy-functional groups [28–30]. So, to convert these oxy-functional compounds into hydrocarbon and to produce high quality bio-oil, incorporation of zeolite as a catalyst is getting attention of researchers worldwide [28,31]. In pyrolysis of biomass and upgradation of bio-oil technique, catalyst can be incorporated for an upgrading of bio-oil [32]. Very few studies focused on in-situ upgrading by biomass cracking using the catalyst to directly generate green chemicals [14]. From previously performed studies on pyrolysis, it can be emphasized that the liquid product obtained is not suitable for direct use as transportation fuel and is needed to be upgraded [33,34]. So, to obtain improved bio-oil quality catalytic biomass pyrolysis is the best thermo-chemical treatment and the bio-oil obtained doesn't require any costly pre-upgradation and thus they can be directly used for the purpose of transportation fuels or as for blending with chemicals [35,36]. Researchers adopted the catalytic hydrotreating of pyrolytic bio-oil to enhance their fuel properties. Nevertheless, these are found to be possible only under extreme temperature and pressure conditions in the presence of a suitable catalyst (usually expensive noble metal catalysts) and hydrogen gas which makes process unsuitable economically. Thus, there were approaches to combine pyrolysis and hydro-treating, which gave rise to investigations on catalytic and hydropyrolysis of biomass feedstock expecting to achieve some degree of deoxygenation during the pyrolysis process itself [37]. In catalytic pyrolysis, volatile compounds are processed in-situ where dehydration, decarboxylation, and decarbonylation reactions are expected to take the lead to reduce the oxygen content in the form of water thereby increasing contents of hydrocarbons and olefins in the bio-oil. However, by catalytic pyrolysis only 20 - 30 % of biomass carbon is found in bio-oil liquid product whereas approximately 30 % of biomass carbon leads to coke formation thereby leading to catalyst deactivation; and thus utilization of hydrogen gas can substantially lower the coke formation on the catalysts during pyrolysis [4,37]. Higher the hydrogen content of any feedstock, higher is the fuel potential of such material [38,39]. Based on this knowledge, hydro-processing technologies are believed to be the most promising routes for developing biofuels from biomass; and hydro-pyrolysis is one of such methods [37].

Another captivating yet economical and feasible pyrolysis process is co-pyrolysis of lignocellulosic biomass with different sources such as coal, plastics, and other biomasses that is studied by various researchers. Kibet et al. [40] mentioned a different study of co-pyrolysis of tobacco biomass and its components as tobacco contains lignin, tyrosine, ethyl cellulose, sodium alginate and laminarin. They have conducted co-pyrolysis of these compounds with one another and found that the reduction in harmful phenolic compounds are dependent on the mass fraction of tyrosine with lignin and ethyl cellulose and its synergistic effects. The results are useful for tobacco industry in which ethyl cellulose derivative cigarette paper can reduce the concentration of phenolic compounds after tobacco burning. Chen et al. [41] studied the co-pyrolysis of a lignocellulosic biomass of bamboo with microalgae of *Nannocholopsis* sp. in a fixed bed reactor. The bio-oil yield at the ratio of 1:1 resulted in 66.63 wt. % with the long chain fatty acids are increased in bio-oil, the oxygen containing and nitrogen containing compounds are decreased. Song et al. [42] studied co-pyrolysis of pine sawdust and lignite coal, where they found an increase in percentage of volatile matter and subsequently increase in contents of phenols and guaiacols. Similarly, Yilgin et al. [43] studied co-pyrolysis of sugar beet pulp with lignite coal and found increase in volatile matter. Sonobe et al. [44] reported more methane production in product stream by a co-pyrolysis of corncob and lignite coal.

Based on the detailed literature studied in the pyrolysis area, the objectives of this thesis are decided based on the knowledge gaps on research of biomass/materials and their pyrolysis approach. The thesis work covered pyrolysis at variable temperature, catalytic pyrolysis, catalytic hydropyrolysis and co-feed pyrolysis. With these various pyrolysis reaction environment, the vast range of materials are successfully tested. The scarcely researched lignocellulosic biomass of Delonix Regia is extensively researched in this work along with it green algal biomass *Oscillatoria* of good product quality has also been researched. Other than this, two different lignocellulosic biomass materials viz., Delonix Regia and Pinewood saw dust are tested to reveal their synergistic effects. The Co-feed pyrolysis study of Delonix Regia with Butyl rubber tube waste material at variable ratios has also been researched. This work thus follows waste minimization and management, energy conversion from waste to biofuels and renewable energy resources approach. The results obtained from these studies are captivating and industry oriented as well as practical. For determination of functional group analysis FTIR is used, to know the presence and concentration of hydrocarbons present in bio-oil samples GCMS analysis of the samples has been conducted. To verify the concentration via proton assignments ^{1}H (proton) NMR is carried out. In this way, it is understandable that which condition is more relevant to produce precursor grade fuels or chemicals for downstream processing from the feed materials. Also, the FESEM and XRD analysis of bio-chars w.r.t. biomass defines the structural analysis of the solid materials as well as catalysts used in the study and at the same time confirms the thermal bond breaking of biomass.

CHAPTER 2

Literature Review

2.1 Biomass as a Renewable Energy Resource

Biomass is getting immense interest for generating renewable fuels as ‘biofuels’ because of their abundances and quite good energy density. The foundation behind the biomass to biofuels research forces us to study the basics of biomass and its constituents as to select the appropriate conversion technology to get most of it. The study reveals the prospective of biomass towards biofuel production. There is a deep interest in utilisation of biomass resources for the generation of energy. Which is focused on: the conversion of energy crops to produce transport fuels, the direct combustion of resource to generate heat, or the co-firing of biomass with other fossil fuels to produce power. Compared to other renewable energy supplies, biomass offers the distinct advantage of being a readily storable energy resource, with a wide geographic spread [45]. Amount of energy generated from biomass and its conversion products, represents an ever-increasing proportion of today’s energy scenario. Biomass materials can be converted into liquids, solids or gaseous fuels; through a series of conversion processes, in order to enhance its energy content. The ability to convert biomass materials through physical, chemical or biological processes, allows the transformation of carbonaceous solid materials that may be difficult to handle, bulky and of low energy concentration; into fuels with enriched physicochemical characteristics, with the added options for economic storage and transferability [46]. The energy within biomass originates from the Sun, as a result of the processes of photosynthesis. Essentially, CO_2 from the air is converted into other Carbon based molecules such as sugars. As the Sun’s energy is intercepted by the photosynthetic active elements within plants, it is ‘fixed’ through this process. These sugars or ‘Carbohydrates’ are stored within plants, or in animals when eaten; to be expelled as their wastes [47]. Biomass resources are harvested or collected as part of a constantly refilling system as renewable and sustainable development; like the crops grow, wastes continue to be generated, and residues collect. This cycle creates a closed Carbon loop, effectively making biomass materials Carbon neutral fuel sources [48]. Lignocellulosic biomass resources are typically: low-cost crops, forestry residues, arboricultural residues, wood process wastes, ‘woody’ vegetation, and the partial organic matter fraction of municipal solid wastes. Wherever these materials are available, there is potential to produce biofuels and generate energy, with minimal if any impact on food or fibre crop production. Structural information of lignocellulosic biomass represented in Figure 2.1.

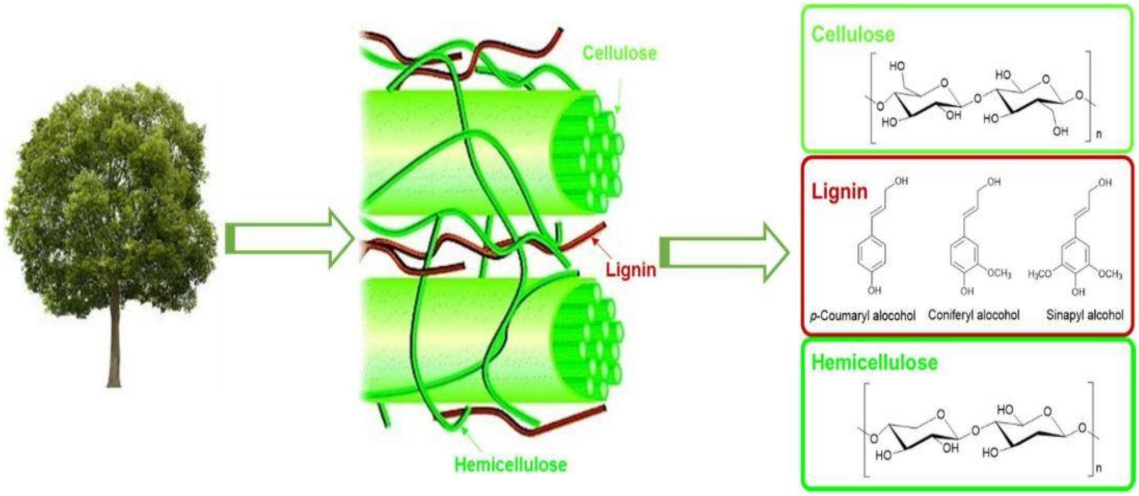

Figure 2.1. Schematic illustration of lignocellulosic biomass (adopted from Zhang et al. [49]).

Lignocellulosic biomass materials are made up of three major components: lignin, cellulose and hemicellulose [48]:

- Cellulose: Made up of linear polysaccharides in the cell walls of wood fibres. Biomass typically comprises 40 - 50 % cellulose.
- Hemicellulose**:** Surrounds the cellulose fibres and provides the linkage between cellulose and lignin within plant structure (15 - 30 %).
- Lignin: A highly complex material that is concentrated between the outer layers of plant fibres. This provides structural rigidity, holding polysaccharides fibres together (15 - 30 %).

2.2 Energy Generation from Biomass and Conversion Pathways

The processes in which biomass resources and feedstock materials are utilised for energy generation and how they are converted into alternative products, is crucial to the bioenergy sector. This section introduces the main energy pathways, and builds on the previous section by analysing how specific biomass types are best processed for optimum energy utilisation.

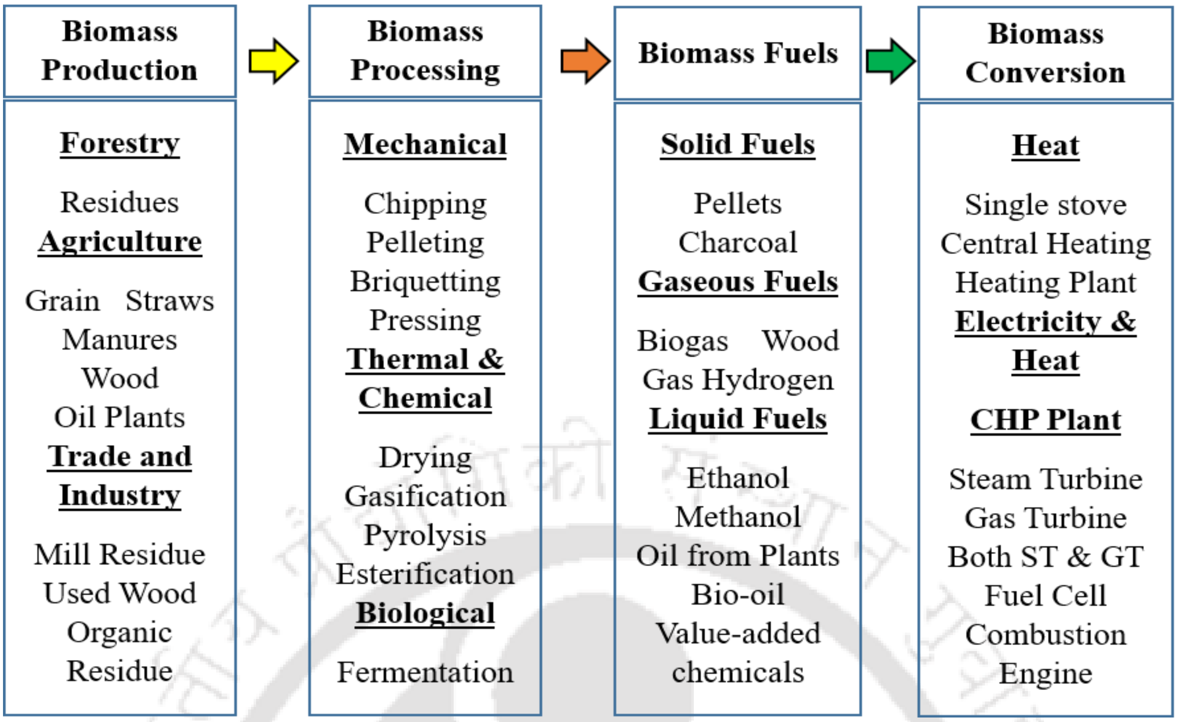

Figure 2.2. An overview of biomass production, processing and conversion to energy (adopted from Chum et a. [50]).

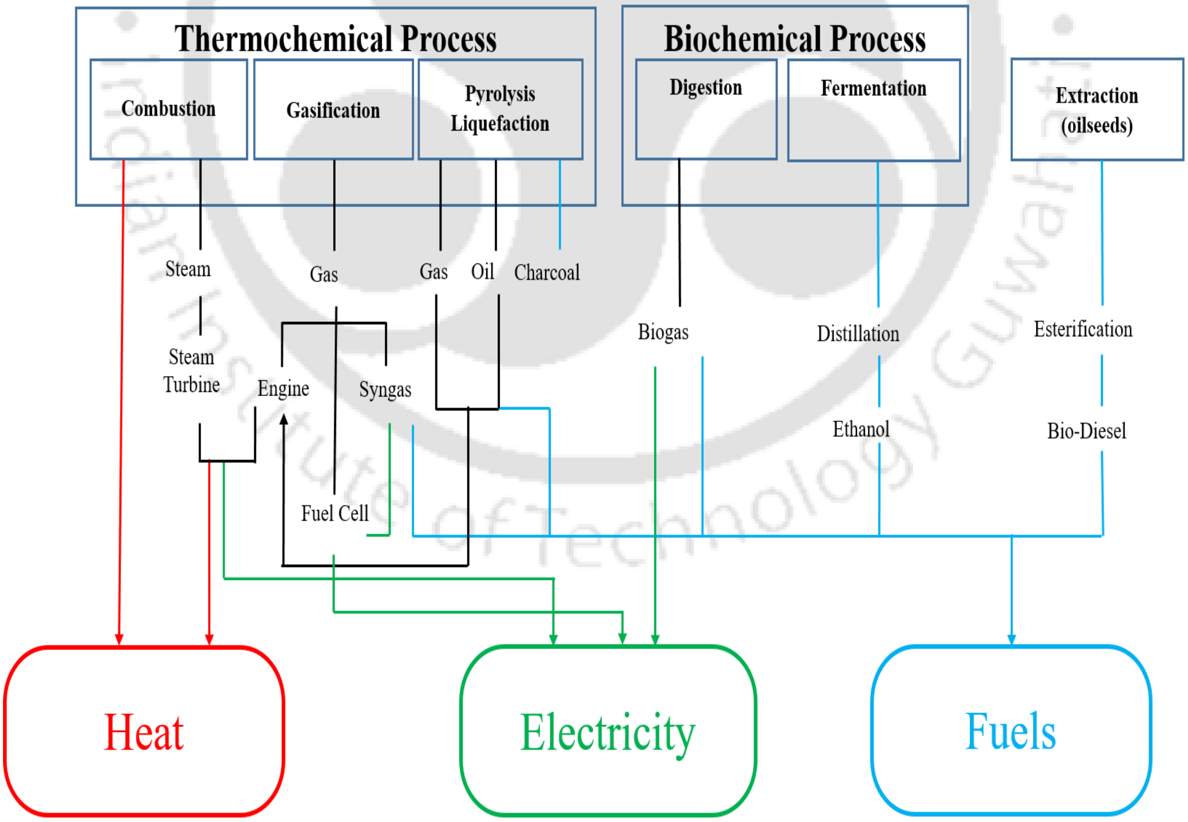

Figure 2.3. Summary of Biomass conversion pathways and end use (adopted from Faaij et al. [51]).

2.2.1 Biomass Conversion Pathways

It is the high versatility of biomass that allows so many products to be produced and derived; depending on the different conversion technologies and processes applied. Many products are flexible and can be adapted to compete with fossil fuel based products, using the existing energy and vehicle fuel infrastructures. Figure 2.2 provides an overview of the different products, and forms of energy typically generated through each conversion pathway. Biomass materials in their primary forms are not always the ideal fuels ready for utilisation. To maximise the levels of energy potentially generated, biomass material can be ‘enhanced’ using various conversion pathways. These primary conversion pathways can be separated into four basic process categories: Direct Combustion, Thermochemical, Biochemical, and Agrochemical. Figure 2.3 shows the summary of biomass conversion pathways with its end use as the resource of heat, electricity and fuel.

2.2.2 Thermochemical Conversion Processes

The core Thermochemical conversion processes applied to biomass materials, are combustion, pyrolysis and gasification. These processes convert biomass into biofuels and directly into energy.

A. Combustion

A.1 Direct Combustion Processes

Despite the growth in prominence of a series of conversion processes, the direct combustion of biomass still accounts for ~97 % of global bio-energy generation [51]. The direct combustion conversion pathway is the complete combustion of biomass material, to convert biomass energy to heat and/or electricity. Heat generation through direct combustion, is the most common use of biomass material; ranging from small scale domestic bioenergy systems up, to large scale 100MW plants. This biomass conversion pathway also includes the combustion of biomass materials within existing and new generation coal fired power plants [51]. The electrical efficiencies of biomass combustion power plants range from 20 - 40 %, with the typical trend of efficiency increasing with plant size. At the other end of the scale, smaller systems are typically inefficient in comparison, with heat transfer losses up to 30 - 90 % [10]. Before biomass materials are combusted, it is typical for pre-treatment processes to take place to ready the material as particularly related to the removal of water. Due to the high water content typically associated with virgin biomass materials; without pre-treatment, the calculated heat content of the material would have to be corrected, to correspond with the extent of water content. Research demonstrating that high water content within biomass material, can reduce the net heat generated by as much as 20 % [10].

A.2 Co-firing Biomass Resources with Coal

Co-firing simply refers to the combustion of biomass material alongside coal for the generation of power. As biomass material is classified as being carbon neutral; the dual combustion of biomass with coal brings down the total carbon emissions per unit of energy produced, compared to the scenario where coal is combusted on its own. Coal and biomass materials are quite different in composition, and as a result, the content of the emissions produced during co-firing are different to the conventional combustion of either fuel. Research has shown that the co-firing of biomass material with coal is capable of reducing both NO_x and SO_x emissions from those of conventional coal plants. Co-firing may also result in reduced fuel costs, reductions in wastes, and also lower soil and water pollution; dependent on the properties of the biomass material utilised. Co-firing can therefore have a positive effect on both the environment and the economics of power generation [51]. Also, it enhances the properties of fuel.

B. Gasification

Biomass gasification is a form of extreme pyrolysis conversion that is carried out at high temperatures, in order to maximise the production of gases. These expelled gases are known as ‘synthesis gases’ and are composed of: Carbon Monoxide, Hydrogen, Methane, Carbon Dioxide, and Nitrogen. The biogas produced has high versatility compared to the original solid biomass, and can be combusted to produce heat and/or steam for electricity generation, or used in further bio-refining processes. Biomass gasification systems are part of the latest generation of biomass energy conversion processes that are being applied to enhance the efficiency, and reduce the investment costs of bio-electricity generation. Gasification plants are produced in a range of sizes and types that can operate on a variety of fuels, ranging from woods and charcoal to coconut shell and even rice husks. Efficiencies up to 50 % have been found to be achievable, using combined-cycle gas turbine systems where waste gases are recovered to operate steam turbines; demonstrating that such biomass plants can be as economical as conventional coal-fired plants. The power output being determined by the economic and ready supply of the biomass fuels [17].

C. Pyrolysis

Pyrolysis is the thermal decomposition of biomass in the absence of Oxygen. It is the first step in the combustion and gasification of biomass materials, although in these processes the pyrolysis stage is followed by the total or partial oxidation of the primary products. In pyrolysis, the biomass material decomposes to generate: aerosols, vapours, and some charcoal – each having value in energy terms. In summary, pyrolysis is the thermal degradation of biomass material into more useful fuels. The pyrolysis of biomass material is an attractive conversion option as it enables solid biomass and waste materials, to be readily converted into liquid products. Liquid fuels having advantages in terms of transportation, storage, combustion, retrofitting, and flexibility in production and marketing [52].

C.1 Conversion Modes

Depending on the conversion reaction conditions and the specification of the biomass material reacted, pyrolysis conversion will produce a wide range of products with differing attributes; the predominant products being: bio-oil/crude (liquid), charcoal, and non-condensable gases. Conventional slow pyrolysis of biomass materials has been undertaken for 1000's of years in the production of charcoal. In this mode of pyrolysis, the feedstock is held at constant temperature or slowly heated. This process enables vapours to be continually removed – the resulting products having high charcoal content. Alternatively, during flash pyrolysis, small dried biomass particles are thermo-chemically converted into a range of products that are up to 75 % liquid fuels, with smaller quantities of charcoal and non-condensable gases [52]. Therefore, depending on the types of end products desired, the parameters of the pyrolysis process can be tailored. The pyrolysis process can be varied greatly in order to generate different end products, with a typical fuel-to-feed efficiency of 95.5 %. This high 'fuel to feed' ratio makes pyrolysis the most efficient process for biomass conversion, and also a process with great potential of competing with non-renewable fossil fuels. At present, the preferred pyrolysis methodology is fast or flash pyrolysis; at high temperatures with very short residence times, resulting in proportionately high liquid fuel end products [52].

C.2 Production of Bio-Oil

Extractives from biomass materials following pyrolysis include oils and other valuable chemicals, which can be converted into biodiesel through a trans-esterification process with methanol. These bio-oils are highly valuable conversion products, as they have high energy densities compared to those of most other biomass materials, and are readily available [25]. Bio-oils are an important source of fuel for remote areas, where it is economical to convert biomass into bio-oil. Further refinement of bio-oils can then result in a long list of potential products, most noticeably those used as transport fuels, either as a blend, or through sole combustion. Bio-oil can be upgraded to the value added products and thus being a precursor for production of bio-based petrochemicals.

C.3 Production of Bio-Char

The slow heating of wood in air tight conditions is known as carbonisation, and results in the production of char or charcoal end products. Char is an extremely important principal fuel for many households, both across the developed and developing world [52]. Wood carbonisation typically occurs at ~400^{0}C, and produces char with approximate content of: 80 % Carbon, 1 - 3 % ash, and 12 - 15 % volatile compounds. Although the typical end products and compositions are highly dependent on the feedstock input and the conversion parameters applied [52].

2.3 Various Modes of Pyrolysis

The research on non-catalytic and catalytic pyrolysis and co-feed pyrolysis is voluminous, but on hydropyrolysis the same is limited. However, a precise course of their review presented below, though several review articles suggested the scope of research work done in this particular area of pyrolysis.

2.3.A Pyrolysis

Pyrolysis of lignocellulosic biomass depends on biomass type, pretreatment, reaction atmosphere, temperature, heating rate, and vapour residence time. Pyrolysis of biomass follows three-step mechanism listing that dehydration or moisture removal, primary reactions, and secondary reactions followed by depolymerization, dehydrogenation, and fragmentation [53].

Primary pyrolysis reactions occurs between 200 - 400 °C, while secondary reactions occurs at the higher temperatures [54]. Lee et al. [55] studied slow pyrolysis of pinewood biomass in the temperature range of 300 - 720 °C with a heating rate of 10 °C/min. The time of reaction is 2 hours, and the reaction was carried out in a static bed batch reactor. The effect of temperature was researched and found that as the temperature and heating rate increases the yield of the product also increases. Li et al. [56] used legume straw and apricot stone biomass for pyrolysis in a free-fall reactor at a temperature range of 500 - 800 °C with a heating rate of 10 - 40 °C/min. They reported that the yield and composition of hydrogen-rich gas as a product from fast pyrolysis depends on the structure of biomass and said that cellulose and hemicellulose produce more hydrogen-rich gas than lignin. Sun et al. [57] used two kinds of biomass samples - rice husk and sawdust (from Chinese walnut) for pyrolysis at a temperature range of 700 - 1000 °C and heating rate of 10^4 °C/s in an entrained flow reactor and reported that optimal temperature for LHV varies with the type of biomass. Alvarez et al. [58] used rice husk of a specific brand as feedstock in a conical spouted bed reactor at 400 - 600 °C. They observed that the yield of bio-oil was high with continuous removal of char. Mullen et al. [59] reported pyrolysis of corn cobs and corn stover biomass at an operating of temperature 500 °C in a bubbling fluidized bed reactor. They found 60 % of the bio-oil yield from corn crop residue with an HHV of 20 MJ/kg.

A conical spouted bed reactor was used by Amutio et al. [60] for flash pyrolysis of pinewood (Pinus insignis) biomass at an operating temperature 800 °C and heating rate 15 °C/min. Choi et al. [61] used sawdust of bald cypress biomass at an operating temperature of 480 °C in a bubbling fluidized bed reactor. Authors studied the effect of biomass feeding rate and temperature of condensation on the yield of bio-oil. Demirbas [62] used seven types of biomass namely hybrid poplar-aspen bark, eastern red maple wood, wheat straw, corn stover, bagasse, commercial cellulose, and peat moss for their pyrolysis at a temperature range 400 - 700 °C and residence time of 0.44 s. They reported that the moisture in bio-oil significantly influences the thermal degradation of the biomass during pyrolysis. Flash hydropyrolysis of pine wood at a temperature range of 600 - 1000 °C and heating rate of 10^4 - 10^6 °C/s studied by Steinberg et al. [37]. Lappas et al. [27] studied the flash pyrolysis of biomass in a circulating fluid bed reactor at the temperature range of 400 - 600 °C with a heating rate of 2000 °C/s and feed rate of 2 - 30 g/min. The residence time is 0.3 - 1 second, and the pressure is between 1.6 to 3.3 atm. The system thus resulted in a very high liquid yield of approximately 70 wt. %

relative to that of biomass weight. Demirbas [63] studied conventional pyrolysis and fast pyrolysis of ground beech wood in variable heating rate conditions in a fluidized bed reactor. The temperature range for both the pyrolysis reaction is 675 - 975 °C with a heating rate of 6 K/s. The residence time for fast pyrolysis is 0.5 to 5 seconds, while the residence time for conventional pyrolysis is 5 to 30 minutes. The increase in liquid yield is shown from 90 to 170 second, and thus the pyrolysis process, and blending of pyrolytic products are controllable by the irregular heating rate. Therefore, from the above literature survey, it is clear that the performance of the pyrolysis of given lignocellulosic biomass can be affected by temperature, heating rate, residence time, an atmosphere of the reaction and type of the reactor. The major reactions involved in the pyrolysis mechanism are reversible and presented here [64].

$$CO_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2\,(g)} + H_{2\,(g)} \qquad (1), \text{ Water - gas shift reaction}$$

$$2\,CO_{(g)} \leftrightarrow C_{(s)} + CO_{2\,(g)} \qquad (2), \text{ Boudouard reaction}$$

$$CH_4 + CO_2 \leftrightarrow 2\,H_2 + 2\,CO \qquad (3)$$

$$CH_4 + H_2O \leftrightarrow 3\,H_2 + CO \qquad (4)$$

$$C + H_2O \leftrightarrow CO + H_2 \qquad (5)$$

$$C + 2\,H_2O \leftrightarrow 2\,H_2 + CO_2 \qquad (6)$$

$$CO_2 + C \leftrightarrow 2\,CO \qquad (7)$$

$$CH_4 \leftrightarrow C + 2\,H_2 \qquad (8)$$

2.3.B Catalytic Pyrolysis

However, bio-oil obtained from the pyrolysis of biomass possesses many undesirable components such as high content of volatile acids, water, and other oxygenated compounds in large fractions which in turn lowers the heating value [65]. To use bio-oil in fuel applications, upgrading of bio-oil is necessary. Nevertheless, catalytic pyrolysis is a promising way to improve bio-oil quality by substantially removing oxygenated compounds during pyrolysis of biomass, thereby increasing calorific value, lowering viscosity, and increasing stability [66]. From the various catalysts studies of catalytic pyrolysis of biomass, zeolites have shown to be effective for reducing oxygenated compounds of pyrolysis oil and converting the bio-oil in aromatic compounds and olefins [67].

Zheng et al. [65] reported an overview on fast catalytic pyrolysis of lignocellulosic biomass focussing mainly on reaction chemistry, reactor type and operating condition, catalyst type and new processes for solving technical barriers in the field. They summarized that the reaction chemistry provides the rational design of reactor and preparation of highly effective catalyst as the acid sites of zeolites display multifunctioning roles besides catalysing the reaction. Agblevor et al. [66] worked on fractional catalytic pyrolysis of hybrid poplar wood, and HZSM-5 zeolite used as a catalyst for the study. The temperature of the reaction is in between 450 to 500 °C, and the reaction carried in a fluidized bed system. The liquid yield decreased than that of conventional pyrolysis, whereas the gas yield increased. In another experimental study, conducted by Yildiz et al. [68] on fast catalytic pyrolysis of biomass; The feed used for their research is pinewood, and the temperature is 500 °C. The oxygenate functional compounds which were present in the bio-oil were then excluded in the form of water, carbon monoxide, and carbon dioxide by use of catalyst and the overall acidity of bio-oil decreased. Aho et al. [69] experimented woody biomass in a fluidized bed with the influence of zeolite structure. The biomass used for the study is pine wood, the temperature set at 450 °C, and the zeolites used were H-Beta, H-Y, HZSM-5, and Mordenite. They have reported the results as the chemical composition of the bio-oil was dependent on the structure of acidic zeolite catalysts. Ketones and phenols are the leading products in the bio-oil obtained from catalytic pyrolysis of biomass.

Carlson et al. [34] communicated the green gasoline by fast catalytic pyrolysis of solid biomass-derived compounds where they indicated that the selective production of aromatics could obtain from solid biomass by selecting proper catalyst, using high heating rates and using a high catalyst to feed ratios. The obtained biofuel has an octane number of 111, and thus, used as an alternative fuel. French and Czernik [70] researched cellulose, lignin, and wood at the temperature range of 400 to 600 °C and the catalyst to biomass ratio were five and ten by weight. The study stated that the catalytic cracking of biomass leads to multiple reactions such as deoxygenation, dehydration, decarboxylation, decarbonylation in the presence of zeolite catalyst. They found 16.5 wt. % of hydrocarbons as the highest yield in which toluene was present in 3.5 wt. %. Another study on catalytic pyrolysis of white oak wood in bubbling fluidized bed by Mullen et al. [71] where they used Y zeolite and β zeolite as catalysts. The authors presented basic chemistry behind the catalytic conversion of primary pyrolysis vapours into value-added chemicals. With the help of bubbling fluidized bed, it is easy to regenerate zeolite and allows to add the same zeolite in reactant stream for its reuse. This system replicates the fluid catalytic cracker unit (FCC) of the petroleum industry. Zang et al. [72] compared non-catalytic and catalytic fast pyrolysis of corncob in a fluidized bed reactor. The optimal condition for the catalytic reaction is 550 °C temperature, the gas flow rate of 3.4 lpm bed height of 10 cm and particle size of 1 to 2 mm which resulted in a liquid yield of 56.8 % and HZSM-5 zeolite used as a catalyst for the study.

2.3.C Hydropyrolysis

Higher the hydrogen content of any fuel more is the fuel quality. Based on this knowledge, hydroprocessing technologies are believed to be the most promising routes to develop biofuels from biomass; and hydropyrolysis is one of such methods.

Sharypov et al. [38] studied direct hydropyrolysis of biomass and plastic waste to generate distillable liquids as hydrocarbons in a batch type stirred autoclave reactor with haematite and pyrrhotite ore materials as a catalyst. The process conditions were similar to that of the co-pyrolysis experiment, but the hydrogen pressure was 3 MPa. Hydrogen atmosphere slightly reduced the olefin content, but with the help of a catalyst, the reduction degree was large and thus, it converts olefins into hydrocarbons. This co-hydropyrolysis process is a fascinating technology to generate environment-friendly distillate hydrocarbon fraction, which can be used as a raw material to produce valuable chemicals. Chen [39] reviewed on green oil production by hydroprocessing and spreads the light on the co-processing of bio-oil with petroleum oil in already available hydroprocessing units at petroleum industries. Presently, in a refinery, mild conditions of hydroprocessing can be considerable with a specific type of catalyst to make an economic scheme. Noble metal catalyst on alumina support is a well-proven catalyst for hydro-decarbonylation while the base catalyst is best suitable for hydrodeoxygenation. Co-processing of bio-oil with petroleum crude/oil can produce enhanced cetane no. diesel distillate. Liu et al. [36] reviewed the hydropyrolysis of biomass, which stated that hydropyrolysis suppressed the char formation and at high pressures, it increased the liquid yield. When Mo-sulfide catalyst incorporated into the system, then the catalytic hydropyrolysis yields more liquid with reduced oxygen and more straightforward composition. Thus to overcome the bio-oil complexity, it is recommended to opt for catalytic hydropyrolysis. Furthermore, from hydroprocessing, we can generate valuable biofuels in the form of lower hydrocarbon molecules which are best suitable for use as a transportation fuel, and they can also serve the purpose of production of bio-based petrochemicals. With respect to these pyrolysis types, few literature studies are presented in Table 2.1.

Based on the literature studies followed, the novel biomass of algal material can be tested other than lignocellulosic biomass and its literature study is presented as Table 2.2.

Table 2.1. Conscript of different biomass feedstock materials and their Pyrolysis, Catalytic Pyrolysis, and Hydropyrolysis behaviour.

A. Pyrolysis

Biomass feedstock	Temperature	Pressure (bar)	Atmosphere	Reactor	Remarks	Reference
Bamboo	300 °C - 700 °C	-	Nitrogen	Fixed Bed	As temperature increases the CV decreases and water content increases for bio-oil but biochar CV increases with increase in temperature. Highest calorific value for bio-oil and biochar is 13.95 MJ/kg at 400 °C, and that of biochar is 29.56 MJ/kg at 700 °C. The highest yield is 36.57 % at 500 °C.	Chen et al. [73]
Walnut shell	600 °C	-	Nitrogen and Carbon dioxide	Fixed Bed	In a nitrogen atmosphere, the yield of tar is 60.3 wt. % which contains 20.9 wt. % oxygenated aliphatic with 74.9 wt. % benzenes and phenols. In the carbon dioxide atmosphere, the yield is 62.7 wt. % with 24.3 wt. % oxygenated aliphatic and 66.6 wt. % benzenes and phenols.	Senneca et al. [74]
Hazelnut shell	500 K - 1200 K	-	Inert	Tubular	The highest liquid yield of 37.2 % is obtained at 650 to 800 K, and at 900 K it decreases to 19.2 wt. %.	Demirbas [75]
Beechwood					The highest liquid yield of 38.6 % is obtained at 650 to 800 K, and at 900 K it decreases to 12.8 wt. %.	
Spruce wood					The highest liquid yield of 37.5 % is obtained at 650 to 800 K, and at 900 K it decreases to 19.6 wt. %.	

Municipal solid waste					The highest liquid yield of 35.2 % is obtained at 650 to 800 K, and at 900 K it decreases to 16.1 wt. %.	
Geodae-Uksae 1 (Giant Miscanthus)	300 °C - 700 °C	-	Nitrogen	Batch	The highest bio-oil yield obtained is 50.57 wt. % at 550 °C and HHV of bio-oil is 18.72 MJ/kg at 600 °C.	Lee et al. [76]
Rice husk (Brillante)	400 °C - 600 °C	-	Nitrogen	Conical spouted bed	High bio-oil yield at 450 °C.	Li et al. [56]
Corn Cobs	500 °C	-	Inert	Bubbling fluidized bed	40.9 % bio-oil yield with a calorific value of 19.5 MJ/kg.	Mullen et al. [59]
Corn Stover					58.2 % bio-oil yield with a calorific value of 22.1 MJ/kg.	

B. Catalytic Pyrolysis

Biomass feedstock	Temperature	Catalyst	Atmosphere	Reactor	Remarks	Reference
Hybrid Poplar wood	500 °C	HZSM-5	Nitrogen	Fluidized Bed	In Catalytic pyrolysis, the HHV of bio-oil is 30.5 MJ/kg while for non-catalytic pyrolysis it is 24.48 MJ/kg on moisture free basis. The yield of bio-oil obtained is 33 wt. %.	Agblevor et al. [66]
Pinewood	450 °C	H-Beta-25, H-Y-12, H-ZSM-5-23, H-MOR-20	Nitrogen	Fluidized Bed	Oil yield is influenced by a different catalyst, whereas maximum yield is obtained by H-ZSM-5-23 catalyst.	Aho et al. [32]
Lignocellulosic biomass	600 °C	ZSM-5	Helium	Pyroprobe	These conditions give high aromatic selectivity compared to other conditions.	Carlson et al. [34]
Aspen wood		ZSM-5				

Cellulose Lignin	400 °C - 600 °C		Helium, Argon	Tubular quartz reactor	The maximum amount of yield of hydrocarbons with 16 wt. % is obtained with a composition of 3.5 wt. % toluene in the presence of Ni, Co, Fe, Ga - substituted ZSM-5.	French and Czernik [70]
White oak wood	500 °C	CaY-zeolite, Beta-zeolite	Nitrogen	Bubbling Fluidized bed	CaY-zeolite reduces oxygenates in product bio-oil and the dehydration with dehydrogenation are the main mechanisms performed by Beta-zeolite.	Mullen et al. [71]
Corncob	400 °C - 700 °C	HZSM-5	Nitrogen	Fluidized bed	Optimum conditions for bio-oil with 56.8 wt. % yield and HHV of 34.6 MJ/kg are 550 °C with N_2 flow rate of 3.4 LPM.	Zhang et al. [72]

C. Hydropyrolysis

Biomass feedstock	Temperature	Pressure/ Catalyst	Atmosphere	Reactor	Remarks	Reference
Canadian White Pine	500 °C	Na_2CO_3/Al_2O_3 and Pt/Al_2O_3	Hydrogen, n-Butane	Quartz tube reactor	Na_2CO_3/Al_2O_3 catalyst reduced oxygen but produced harmful carbonyls. Pt/Al_2O_3 catalyst resulted in bio-oil of 19 MJ/kg HHV which is same as non-catalytic case. However, dual catalyst bed resulted in 43 MJ/kg bio-oil.	Nguyen et al. [77]
Cellulose Sugarcane bagasse Eucalyptus wood	520 °C	10 MPa/ FeS catalyst	Hydrogen	Fixed Bed	High pressure reduced the oxygen content of bio-oil up-to 20 wt. % and iron sulfide are responsible for nearly 100 % conversion of all three biomass materials.	Yaman [78]

Table 2.2. Literature details of pyrolysis on algal biomass.

Biomass	Reaction Conditions	Result	Reference
Blue-green algae blooms (BGAB)	Temperature: 300 - 700^{0}C Reactor: fixed bed reactor	Maximum oil yield of 54.97 wt. % at a temperature of 500^{0}C.	Hu et al. [79]
Green algae	Catalyst: HZSM-5 Reactor: fixed bed reactor	Bio-oil yield of 52.7 wt. %, HHV of 18.6 MJ/Kg.	Suchithra et al. [80]
Algal and lignocellulosic	Reactor: fixed bed reactor	Bio-oil yield of 32.69 wt. % at a temperature of 500^{0}C	Yuan et al. [81]
Algal biomass	Reactor: batch reactor	At 450^{0}C produced bio-oil 24 – 45 wt. %.	Vardon et al. [82]
Algal biomass	Reactor: fixed bed reactor	Yield 11 -17 wt. % seaweed species.	Yanik et al. [83]
Micro-algae	Catalyst: cobalt–molybdenum Reactor: fixed bed reactor	Bio oil yield 36 wt. %.	Tran et al. [84]
Microalgae Dunaliella tertiolecta	Reactor: stainless autoclave with 100 ml capacity and a magnetic stirrer	Maximum bio-oil yield of 36.9 wt. % at temperature of 360^{0}C and a holding time of 30 min, heating value of 26.62 MJ/kg.	Zou et al. [85]
Algal and lignocellulosic	Reactor: fixed bed reactor	HHV- 15.3 MJ/Kg.	Maddi et al. [86]
Microalgae	Reactor: fluid bed reactor	Yields of 18 and 24 wt. %, HHV 29 MJ/kg	Miao et al. [87]
Spirulina	Reactor: fixed bed reactor	HHV 21.68 MJ/kg, water content 32.42 wt. %	Chaiwong et al. [88]
Green algae	Reactor: fixed bed reactor	Maximum yield of bio-oil and bio-char was found to be 24.10 and 44.01 wt. % respectively at a temperature of 500 °C, HHV 19.91 MJ/kg.	Aboulkas [89]
Heterotrophic *Chlorella protothecoides*	Reactor: fluid bed reactor	57.9 wt. % yield of bio-oil.	Miao et al. [90]

2.3.D Co-feed pyrolysis

Co-pyrolysis is a process in which two or more materials are used as feedstock. Many studies have shown that co-pyrolysis of biomass has improved the characteristics of bio-oil such as increase in oil yield, lowering of oxygen content, increase in higher heating value (HHV), etc. Co-pyrolysis is found to produce high grade bio-oil and also contributed to solve some problems of solid and hazardous waste management [91]. Thus, the study of co-pyrolysis is more effective in terms of lucrative technology for biofuels production. The detailed literature study of co-feed pyrolysis on lignocellulosic biomass with algal biomass, coal, synthetic polymers, rubber waste (tyre waste) is discussed and presented as Table 2.3.

Uzoejinwa et al. [92] reviewed co-pyrolysis of biomass and waste plastics and there study is mainly focused on the operating conditions like mixing ratio and temperature. The study states that the co-pyrolysis technique is economical and more result oriented than that of single feed pyrolysis. Yuan et al. [93] studied the synergistic effect of cellulose and HDPE at various mass ratios of 3:1, 1:1, 1:3 on weight %. They stated that the cellulose degrades between 260 °C - 410 °C and HDPE degrades in the range of 410 °C - 527 °C. This study reveals that the ratio of less than 1:1 for cellulose to HDPE results the production of more alkane and alkene by minimizing production of furans, aldehyde, and carbohydrate which are main products of cellulose degradation. Chang et al. [94] studied the co-pyrolysis synergy of *Nannochloropsis* sp. and palm kernel shell to produce various hydrocarbons. When both the biomass materials are studied separately they resulted in the 11.79 area % and 2.96 area % for *Nannochloropsis* sp. and palm kernel shell respectively but when these two materials are mixed the ratio of 1:1, at 600 °C they resulted in 30.39 wt. % aromatic hydrocarbons. They also explained that the reason behind the synergistic effect of the biomass materials resulting in more aromatic bio-oil is that the substitution reaction of the free radicals playing with primary vapours of bio-oil consisting mainly phenols and it is applicable to most of the co-feed studies. Yuan et al. [95] experimented the rapid co-pyrolysis of rice straw and bituminous coal individually and in the ratio of 1:4 and 4:1 respectively in a high-frequency furnace. They found the synergy between rice straw and bituminous coal at ratio of 1:4 where volatiles yield increases and char yield decreases which suggests that the low biomass to coal ratio is recommended for production of efficient products. Johansson et al. [96] co-pyrolysed woody biomass with plastic waste and reported that the pyrolysis of woody biomass and plastic waste affects product composition and property.

The reactive oxygenate compounds get suppressed to increase the production of alcohols and esters. Kibet et al. [40] mentioned a different study of co-pyrolysis of tobacco biomass and its components as tobacco contains lignin, tyrosine, ethyl cellulose, sodium alginate and laminarin. They have conducted co-pyrolysis of these compounds with one another and found that the reduction in harmful phenolic compounds are dependent on the mass fraction of tyrosine with lignin and ethyl cellulose and its synergistic effects. The results are useful for tobacco industry in which ethyl cellulose derivative cigarette paper can reduce the concentration of phenolic compounds after tobacco burning. Chen et al. [41] studied the co-pyrolysis of a lignocellulosic biomass of bamboo with microalgae of *Nannocholopsis* sp. in a fixed bed reactor. The bio-oil yield at the ratio of 1:1 resulted in 66.63 wt. % with the long chain fatty acids are increased in bio-oil and the oxygen containing and nitrogen containing compounds are decreased. Several studies reported co-pyrolysis of plastic waste with biomass to produce high-quality bio-oil with increased percentage of yield. Above studies of the co-pyrolysis study reveals that this technology has a major breakthrough to put on as a benchmark technology for the production of valuable hydrocarbons and alternative fuel for engines. The technology can be implemented in the existing systems of boilers, coal thermal power plants for production of more efficient products with the upper hand of economic benefit.

The production of biofuels from biomass alone cannot replace the need for tremendous energy, because of their low calorific value and more oxygen content; thus, it requires an alternative hydrogen and carbon source to improve its quality and durability [92]. Butyl rubber is used in various applications like vehicles' inner tubes, rubber stoppers, automobile parts [97] and the huge amount of waste generated by them is treated by various ways which are environmentally hostile like incineration and direct combustion. Thus, the proper mechanism for the utilization of waste is required that can be environment benign and co-feed pyrolysis is the prosperous technology in that manner [98,99]. The co-pyrolysis of biomass with other carbon-containing wastes, like rubber tubes and plastics, plays a vital role in obtaining a stable oil by synergistic effects due to radical interactions occurring during the process [100]. Co-pyrolysis is a simple and effective waste management strategy for valorization of the plastics, waste tyres and tubes [22,101]. It is a technique for the conversion of biomass and other waste materials to produce condensable and non-condensable products along with solid carbon-rich bio-char as residue, whereas it generates a clean-burning fuel having a higher calorific value and less oxygen content [92,100,102]. Also, it utilizes same amount of energy and operating conditions as that of single feed pyrolysis but results in much more upgraded (or deoxygenated) products [46,100].

Martinez et al. [103] studied co-pyrolysis of forestry wastes and waste tyres in fixed bed reactor and continuous auger reactor. The co-pyrolyzed bio-oil showed evidence of upgrading by portraying an increase in calorific value and pH while a decrease in oxygen content and density. This is because of the interaction of radicals during the reaction of vapors generated from biomass and tyres. The decreased phenolic compounds and aldehydes showed stable bio-oils. The authors also found that the auger reactor was seen to result in synergistic effects between biomass and tyres, which produces bio-oil with improved properties. Duan et al. [104] pretreated lignin and soapstock that is co-pyrolyzed under microwave irradiation to upgrade the pyrolysis vapors and obtained an effective biomass conversion. The optimum quality of bio-oil was reported at 150 °C for 60 min duration of microwave heating in the presence of 0.5M hydrochloric acid. The gasoline fraction in the oil ranged from 57.38 to 71.98% under various conditions of pretreatment, while diesel fraction varied from 13.16 to 22.62%. A brief review of the literature pertaining to co-feed pyrolysis of biomass and plastic/tube wastes, etc. is presented in Table 2.3.

Table 2.3. A transitory observation of Co-feed Pyrolysis of different materials.

Feed	Experimental Conditions	Type of Reactor	Findings	Author
Lignite and sugar beet pulp	Temp.: 600 °C Feed ratio: 50/50	-	Bio-char contains significant amt. of volatiles and can be further treated.	Yilgin et al. [43]
Algal biomass seaweed with lignocellulosic biomass sugarcane	Temp.: 550 °C Feed ratio: 50/50	Cylindrical quartz fixed bed reactor	(a) Acidity and density decreased, (b) CV increased, (c) At the ratio of 50:50, the highest bio-oil yield obtained.	Hua and Li [105]
Biomass and crude glycerol	Temp.: 600 °C Feed ratio: 20, and 40 wt. % of glycerol	Batch reactor	The optimum percentage of glycerol is less than 20 wt. % to get more liquid yield.	Bartocci et al. [106]
Nannochloropsis sp. and palm kernel shell	Temp.: 600 °C Feed ratio: 9:1, 7:3, 1:1, 2:3, 3:7, 1:9	Batch reactor	1:1 ratio resulted in 30.39 wt. % of aromatic hydrocarbons.	Chang et al. [94]
Enteromorpha clathrata with rice husk	Temp.: 550 °C Feed ratio: 1:1, 1:2, 1:3, 2:1, 3:1	Fixed bed reactor	The synergistic effect of both the material at 1:1 results in 30 % gas, 42 % char, and 28 % bio-oil.	Wang et al. [107]
Sewage sludge with lignocellulosic biomass	Temp.: 500 °C Feed ratio: 50/50	Conical spouted bed reactor	With high bio-oil yield, the bio-oil is ready to use as a fuel and chemical precursor.	Alvarez et al. [108]
LDPE with the biomass residue	Temp.: 600 °C	-	It gave maximum bio-oil yield with a significant amount of phenols and alcohols.	Yang et al. [109]
Biomass with coal	Temp.: 400 °C Feed ratio: 0 – 100 %	Freefall reactor	Water present in biomass reacts with CO from coal and increase the H_2 amount in gas.	Quan et al. [110]
Cellulose and HDPE	Feed ratio: 1:0, 3:1, 1:1, 1:3, 0:1	TG/MS	Cellulose degrades between 260-410 °C, and in ratio 1:1 results more alkane and alkene.	Yuan et al. [93]

Pine, plastics and tyre wastes	Temperature: 350-450°C Reaction time: 5-30 min	Stainless Hastelloy C276 Autoclave reactor	Liquid yield increased from 33% to 92% with increase in the plastics content of feedstock. There was decrease in CO_2 in the gas with increase of hydrocarbons content.	Paradela et al. [111]
Rice straw, pine wood, waste rubber tyres	Temperature: 500°C Reaction time: 20s (Flash)	-	H/C_{eff} ratio of products varied for the two feedstock though the product distribution was similar. High value of this ratio increased the percentage of hydrocarbons. Optimal biomass and waste tyre blending ratio was 6/4 (mass/mass).	Wang et al. [112]
Microalgae Chlorella, waste tyre	-	Microwave assisted pyrolysis set up	50 mass % of tyre was suitable for better quality and quantity of liquid and solid products from co-pyrolysis.	Fang et al. [113]
Grape seeds, waste tyres	Temperature: 550°C Reaction time: 30 min. with calcined calcite (CaO) catalyst	Stainless steel fixed bed reactor	Around 40 mass % of waste tyres increased organic phase yield upto 73 mass % with reduction in oxygen content upto 4.2 mass %. HHV increased from 15.3 to 27.3 MJ/kg. CaO catalyst promoted dehydration reaction of acids and phenols to produce hydrocarbons. CO_2 capture effect is also made possible with CaO producing less polluting gases to be released to the environment.	Veses et al. [114]
Pine nut shell and scrap tyre	Temperature: 500°C	Fixed bed reactor	Bio-oil yield is increased with increasing blending ratio as well as the quality of bio-oil is improved by adding scrap tyre to pine nut shell.	Uçar, S. and Karagöz [115]

Based on above detailed literature on non-catalytic pyrolysis, catalytic pyrolysis, hydropyrolysis, and co-feed pyrolysis firstly the novel biomass is chosen. The selected biomasses are scarcely researched such as Delonix Regia and *Oscillatoria* whereas Pinewood sawdust and Tube waste are taken just for comparative study with lignocellulosic biomass of Delonix Regia. Pyrolysis of Delonix Regia is carried out at various temperatures to determine the temperature effect on bio-oil production and properties. The study of non-catalytic, catalytic and hydropyrolysis is conducted on Delonix Regia and *Oscillatoria*. Whilst the co-feed study is conducted on Delonix Regia biomass with Pinewood and Tube waste. For the catalytic pyrolysis study of Delonix Regia biomass 10 wt. % Sodium Y, Zeolite is taken and for algal biomass of *Oscillatoria*, 10 wt. % of TiO_2: ZnO (1:1) is taken as to get lighter hydrocarbons.

Motivation and Objectives

3.1 Motivation for the Research

It will be a radical step to achieve biofuels from biomass with the quality of fossil based fuels. On the background of the research, it is the well-known fact that the fossil-fuels are generated from biomass itself underneath the earth's surface. The biomass was previously buried and naturally processed under the earth's surface over a long period of time to form non-renewable but essential energy resources which are now on the verge of extinction due to high consumption rate increasing day by day. So, on the basis of this background the focus is on creating such conditions that, fuel grade renewable energy resources in laboratory scale, pilot scale as well as on industrial scale can be produced to meet every day's energy need. Recently, Indian state Karnataka is gained attention by acquiring first position in producing renewable energy in world, by leaving behind previous giants of the field, Denmark and Netherland [116]. But from the prospective of environmentalists and local farmers it is not the one methodology which will change the way of production of sustainable energy. Because, India is an agrarian country so, to engage a fertile piece of land for renewable energy production leads to another crisis. On the other hand, the burning of agricultural residues in most of the parts of India are causing air pollution where they can be utilized for farmer's profitability other way around. Thus, the most suitable practice for getting lucrative biofuels on large scale are the thermochemical routes, accordingly one such renowned thermochemical conversion method which is pyrolysis, to generate bio-oil is opted out in this thesis work. Lot of work have already been done in this regard, as studying pyrolysis reaction within a specific temperature range, increasing pressure, different catalyst and heating rates. But, the study didn't set any long-lasting application oriented scenario. Apart from this, the biofuels obtained from pyrolysis technology are best alternative for furnace oil or heating oil and it can be possibly utilized for boilers. Therefore, this research study is focusing on the novel biomass which are narrowly researched within a most economic framework. The main focus is on solid waste biomass, forest residue, arboricultural residue, agricultural residue and some hazardous waste materials that are present around the vicinity in large scale.

3.2 Objectives of the Research Study

Based on the above discussion, the strategy of work is to experimenting with variable parameters such as temperature, pressure, reaction atmosphere, heating rate and catalyst medium. Overall objectives of this research study are stated below:

Various Pyrolysis approach to get biofuels and valuable hydrocarbons from scarcely researched novel lignocellulosic and algal biomass. Comparative study of novel lignocellulosic biomass by the co-feed using other lignocellulosic biomass and tube waste material.

A) Pyrolysis of novel lignocellulosic biomass at variable temperature.
B) Pyrolysis, catalytic pyrolysis and hydropyrolysis of lignocellulosic biomass.
C) Pyrolysis, catalytic pyrolysis and hydropyrolysis of algal biomass.
D) Co-feed pyrolysis of lignocellulosic biomass with different lignocellulosic biomass.
E) Co-feed pyrolysis of lignocellulosic biomass with tube waste material.

Materials and Methods

4.A Pyrolysis of Delonix Regia at Variable Temperatures

4.A.1 Biomass and its Characterization

The lignocellulosic biomass feedstock selected in this study is a solid waste biomass of *Delonix Regia* (DR) tree shown in Figure 4.1, as it is a fast-growing tree and abundantly available in the neighborhood of the IIT Guwahati campus that is contributing to around 100 kg of solid waste every-day. The waste biomass is collected as the arboriculture residue as it is planted for the decorative purpose of the surrounding atmosphere. The growth irrigation of this particular tree depends on the atmospheric humidity and stored moisture in the soil. The dry bark and trunk of DR are pulverized, ground and sieved to 200 - 400-micron size and then oven-dried for 2 hours at 100 °C to remove free moisture from the feedstock.

Figure 4.1. Delonix Regia tree and the crushed biomass obtained from the tree.

The moisture content, volatile matter content and ash content of DR were obtained as per ASTM standards, viz. ASTM E871, ASTM E872 and ASTM D1102 respectively; and finally, the fixed carbon content was obtained by the difference. The ultimate elemental analysis of DR was obtained by CHNS (Euro EA3000, Euro Vector, Italy) analyser. The HHV of DR was obtained by the Dulong formula as, HHV = $\{0.336 \times C + 1.418 \times H - 0.145 \times O\}$ by Buckley and Domalski [117] using elemental composition of C, H and O based on ultimate analysis. In order to select the range of pyrolysis temperature, the thermogravimetric analysis

(TGA) of DR was performed by using TGA-Model No.: TG209 F1 Libra (make: M/s. Netzsch, Germany). For this purpose, the initial and final temperatures were set at 30 °C and 750 °C respectively at a heating rate of 20 °C/min while using nitrogen carrier gas at a flow rate of 40 ml/min. The differential thermogravimetric analysis (DTG) of DR was carried out by the same equipment under the same conditions used for TGA. The X-ray diffraction (XRD) analysis of biomass feedstock was conducted by XRD-Model No.: D8 Advance (make: Bruker, Netherlands). For the XRD purpose, Cu-K-α radiation was used and the incident angle varied from 10 to 60°.

4.A.2 Experimental Procedure

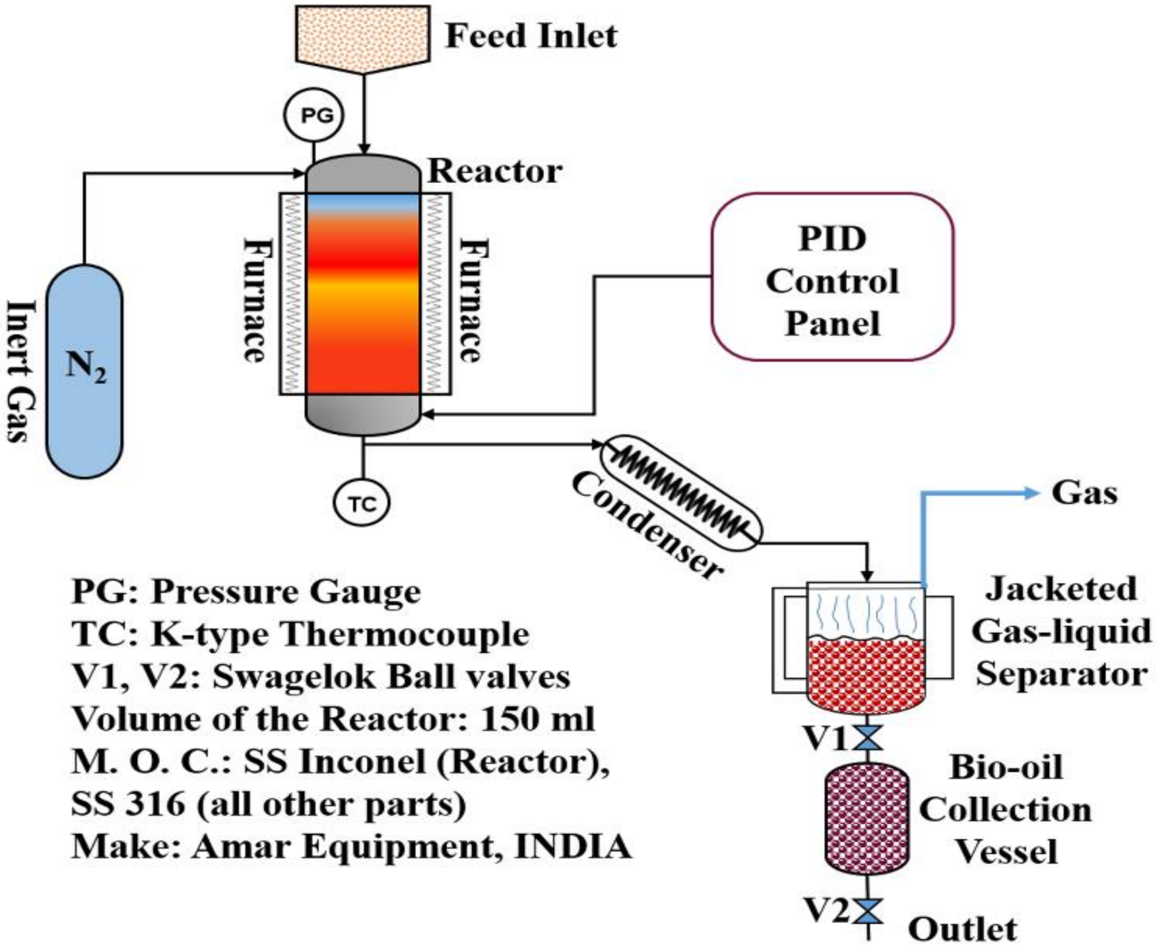

Figure 4.2. Schematic of pyrolysis setup used for DR pyrolysis at variable temperatures.

The pyrolysis of DR conducted in a tubular batch reactor (made by SS Inconel material) system of capacity 150 ml (Make: Amar Equipment, India). The reactor tube having dimensions as 38 mm OD × 25 mm ID × 300 mm L with L/D ratio of 12. This system consists of a single zone heating furnace of ATS (Make: USA) that is having a maximum heating rate of 20 °C/min, and hence this is a slow pyrolysis study. The setup also equipped with condenser, gas-liquid separator and bio-oil collection vessel as shown in Figure 4.2. The gas-liquid separator is made up of SS 316 material which separates the condensable liquid and non-condensable gases on the basis of gravity. The nitrogen gas is used as an inert gas and a mass flow controller (Brooks MFC) is provided to maintain 0.3 ml/min. constant flow of nitrogen gas throughout the pyrolysis reaction of DR. The control panel of the system monitors the temperature and pressure inside the reactor by using a k-type thermocouple for temperature and WIKA transducer for pressure, respectively. The system is also equipped with a backpressure regulator at the outlet gas stream to maintain the pressure inside the reactor system and taking gas sample out of the system as per the requirements.

Depending on particle size of the biomass, the sample was fed inside the reactor where the pre-processed biomass feedstock (DR) weighed 37 g processed for the experiment, after that the reactor is properly closed so that to have a leak-proof system. The temperature is set to a fixed temperature (500 °C, 600 °C and 700 °C for each case) and a maximum heating rate (20 °C/min) is set. The flow rate of nitrogen gas is fixed to 0.3 ml/min. Upon reaching the system temperature to pyrolysis temperature (500 °C, 600 °C and 700 °C for each case), it is maintained for 2 hours inside the heated reaction zone. The reaction time of 2 hours is best suitable time for all the reactions based on biomass conversion as tested by various trial runs of different reaction time. In addition, the system is open to atmosphere so that to maintain one atmospheric pressure inside the reaction zone. The vapours from the reaction condensed continuously by condenser for which ice-cooled water circulated by a pump. These condensed vapours separated from non-condensing gases in a gas-liquid separator, and the condensed liquid, which is bio-oil, is continuously collected in a liquid collection vessel provided in the setup, whereas the non-condensing gases are collected in a tedlar bag periodically. By the end of 2 hours reaction time, the furnace is switched off and the setup allowed cooling down to ambient temperature. Upon cooling the reactor setup, the same opened to collect solid product present inside the reactor that is bio-char. This bio-char is also analysed by XRD by the same method as the biomass feedstock was analysed. For each pyrolysis temperature, the experiments conducted three times to avoid experimental errors. The yield of bio-oil and bio-char calculated on a weight basis relative to the weight of biomass feed; and the yield of non-condensing gases is obtained by the difference.

4.A.3 Characterization of Bio-oil and Bio-char

Prior to characterization, bio-oil samples filtered by using Whatman's qualitative filter papers so that to remove if any unwanted solids present in the samples; however, no solids found on the filter paper after filtration. In order to obtain HHV of bio-oil samples by using Dulong formula [117], elemental analysis of these samples are carried out by CHNS analyser (make: Euro EA3000 Elemental, Italy) facility available at Guwahati Biotech Park (India). The acidity (pH) of the bio-oils estimated by Eutech Benchtop pH meter (make: pH 700 Thermo Fischer Scientific, India). The moisture content of bio-oils is estimated by Karl-Fischer titration (KFT) by Karl Fischer Titrator facility (model: 878 KF, make: M/s. Metrohm, Switzerland) using pyridine free KFT solution and dry methanol as a dry solvent. The density of bio-oils estimated by using a 10ml pycnometer at room temperature. Interfacial rheometer (Anton Parr, Austria) is used for obtaining the viscosity of the bio-oil samples.

The Fourier Transformation Infra-Red (FTIR) spectroscopy of bio-oils obtained by FTIR facility (model: IRAffiinity-1, make: M/s. Shimadzu, Japan). For this purpose, attenuated total reflectance (ATR) method used, which utilizes a diamond crystal as a sampler. The model analysis set at % transmittance, number of scans was 30; resolution was 4 cm^{-1} and wavenumber at 400 - 4000 cm^{-1}. Further, Gas Chromatography-Mass Spectrometry (GCMS-Model No.: 450-GC, 240-MS; Make: M/s Varian, Netherland) of bio-oil samples carried out so that to determine plausible chemical compounds present in the samples. The column used for the study is strongly polar capillary column 'VF - 5ms' having dimensions of 30 m length × 0.25 mm ID × 0.25 μm film. The initial temperature of the oven is set at 80 ºC with 2 minutes of hold. Then the ramp is set to a heating rate of 8 ºC/min to reach a temperature of 140 ºC and then above 140 ºC; the ramp is set to 4 ºC/min until it reaches 210 ºC. The bio-oil sample of two microliters injected through the liner in a capillary column by keeping the split mode of 20:1. The nature of MS is based on ions trap technology having the external source for the ionisation. The total acquisition time of the method is 29 minutes. In this system, high purity inert gas helium passed as a carrier gas at a flow rate of 1 ml/min. maintaining four bar pressure in the carrier gas line. Based on the mass of the element, it finally gives the probable compound, and the software used for the GCMS analysis is Varian WS. Finally, the bio-oil samples analysed to study the confirmation of structural configuration of its molecules and the interaction of different compounds using proton (^{1}H) nuclear magnetic resonance (NMR-Model No.: ASCEND 600, 600 MHz Nuclear Magnetic Resonance Spectrometer, Make: Bruker, Netherlands). The bio-oil samples were prepared in $CDCl_3$ solvent at a ratio of 1:3 respectively and analysed using 16 numbers of scans.

4.B Non-catalytic, Catalytic, and Hydropyrolysis of Delonix Regia

4.B.1 Biomass

The Lignocellulosic biomass feedstock used in the study is a solid waste biomass of Delonix Regia (DR) trunks. As Delonix Regia is an arboricultural residue and present in IIT Guwahati campus in abundance representing a solid-waste biomass and contributing to the waste of energy. It is thus collected to determine its fuel potential. The collected biomass is sun-dried, crushed, and ground to 250 to 500-micron mesh size and taken for the determination of proximate and ultimate analysis to explore its energy density. The calorific value (CV) of DR biomass is estimated by fully automated Toshniwal Bomb Calorimeter (IS 1350-1, India) by combusting 1 g biomass sample under pressurized conditions. Proximate Analysis of this biomass is carried out on muffle furnace (Make: VB Ceramics, Chennai, India) according to ASTM standards. Moisture content is calculated by introducing 1 g of biomass sample in oven for 12 hours at 110 ºC ASTM E871- 82. The volatile matter content is obtained by heating 1 g of biomass at 900 ºC for 7 - 8 minutes as ASTM E872-82. Where, ash content is obtained according to ASTM D1102 by keeping sample at 800 ºC for 4 hours in the muffle furnace. Finally, the fixed carbon content is calculated as a difference 100 - (Moisture + Volatile matter + Ash content). The ultimate analysis is experimented by using CHNS Elemental Analyser (EuroEA3000, Euro Vector, Italy) at Guwahati Biotech Park, India. Thus, the biomass is tested for its physicochemical properties.

4.B.2 Catalyst

Zeolite – Y, sodium commercially synthesized by Alfa Aesar is utilized as a catalyst in this study that has Si/Al ratio of 5.1:1. This zeolite is used on a large scale in petroleum refinery as a cracking catalyst. It converts crude petroleum fractions into more valuable gasoline, diesel and other valuable products.

4.B.3 Pyrolysis Procedure

The pyrolysis experiments of DR biomass are carried out using Tubular reactor (Make: Amar Equipment Ltd., Mumbai, India) consisting of ATS single zone heating furnace (USA). The reactor is equipped with a control panel, which controls the temperature and pressure of the system while the reactor setup has the system where mass flow controller (MFC) controls gas flow rate of 0.3 lpm in the present study, this particular objective is tasted for the performance of inert gas flow rate and its effect on the reaction mechanism. The system has an extended structure consisting of condenser, gas-liquid separator, and bio-oil collection vessel. The schematic of the pyrolysis reactor system is shown in Figure 4.3. In this work, three different cases of pyrolysis are studied which are viz. non-catalytic conventional pyrolysis, catalytic pyrolysis using zeolite and catalytic hydropyrolysis using hydrogen as a reacting medium and carrier gas with zeolite catalyst as explained below.

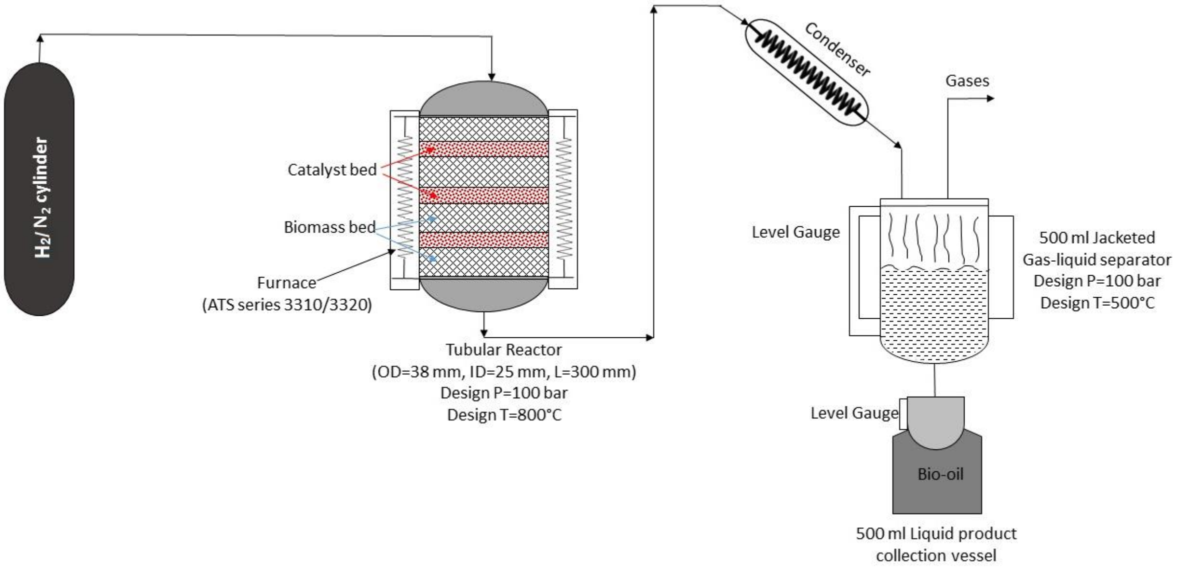

Figure 4.3. Schematic of a tubular reactor system used for the pyrolysis, catalytic pyrolysis and catalytic hydropyrolysis of *Delonix Regia* biomass.

The sun-dried solid waste DR biomass with 40 g weight is fed into a tubular reactor of capacity 150 ml as a batch feed. Then the temperature is set at 600 °C, and the pressure inside the system is maintained at 1 bar by a continuous flow of nitrogen gas adjusting 0.3 lpm. The temperature inside the reactor is maintained constant at 600 °C for 2 hours in stable condition. After 2 hours, the pyrolysis is stopped, and the liquid product is collected in bio-oil collection vessel then sent for further analysis. In second case, the dried biomass along with 10 wt. % zeolite Y sodium catalyst is fed into the tubular reactor and carried out catalytic pyrolysis in a similar manner as in the case of non-catalytic pyrolysis. The 10 wt. % is an optimized feed to catalyst ratio for performed cases w.r.t. the conversion. The product from the outlet is collected in the collection vessel, then taken for analysis to find out its fuel characteristics and other details. In third case, the reaction atmosphere is of hydrogen whereas it acts as carrier medium with 0.3 lpm flow rate and 10 wt. % zeolite, Y sodium is used as a catalyst in this experiment. Other parameters are maintained same as in the above two cases.

4.B.4 Analytical Techniques for Characterization of Products

The collected pyrolytic bio-oil after each run is characterized for pH analysis on Eutech Instruments (pH-700, India) benchtop pH meter whereas its CV is calculated using Toshniwal Bomb Calorimeter (IS 1350-1). Determination of functional groups present in bio-oil is obtained by Fourier Transform Infra-Red spectroscopy (FT-IR Model No.: IRAffinity-1; Make: M/s Shimadzu, Japan) which uses Attenuated Total Reflectance (ATR) method with 30 scans 4 cm^{-1} resolution and 4000 - 400 cm^{-1} wavelength in % transmittance measurement mode. The bio-oil sample is placed on the diamond crystal of ATR assembly and when it is attacked by IR beam, the absorbed energy of sample is converted into attenuated energy form and then gives back to IR beam that passed to the detector to generate IR spectrum. The FT-IR spectrum of the bio-oil by each case is tested in the same atmosphere to determine the variation in the functional groups present in the bio-oil of each particular case compared to other cases. For compound specification and molecular mass distribution of bio-oil, Gas Chromatography-Mass Spectrometer (GCMS-Model No.: 450-GC, 240-MS; Make: M/s Varian, Netherland) having the column specifications of VF-5ms with dimensions of 30 m x 0.25 mm x 0.25 µm at maximum operating temperature of 300 ºC is utilized. Helium gas is passed as a carrier gas in the system, the initial temperature of oven is set at 80 ºC with 2 minutes of hold up and ramp is set to 8 ºC/min to reach 140 ºC and lastly above 140 ºC ramp is set to 4 ºC/min to reach 210 ºC; which runs in total acquisition time of 29 minutes. GC-MS is a reliable tool to know the compounds present at the molecular level in a given sample. GC separates the bio-oil mixture, and MS detects the ionized molecule. Hence, to confirm the presence of functional groups shown in FTIR, GC-MS is the best suitable method of analysis. Bio-oil is then analysed using proton (^1H) Nuclear Magnetic Resonance (NMR-Model No.: ASCEND 600, 600 MHz Nuclear Magnetic Resonance Spectrometer, make: Bruker, Netherlands), using Chloroform-D as solvent. This analysis gives the corresponding structure of identified molecules and represents hydrogen assignment in that structure. X-ray diffraction (XRD) analysis of raw biomass is done using XRD (XRD-Model No.: D8 Advance; Make: Bruker, Netherlands) which uses Copper – K – α radiation, the incident angle of the radiation is studied between 10 to 60 degrees.

4.C Non-catalytic, Catalytic, and Hydropyrolysis of *Oscillatoria*

4.C.1 Biomass

The algal biomass is collected from the river bed of green algae in the Brahmaputra River. It is also available in a gigantic amount in nearby ponds and lakes of Guwahati city. The algal biomass collected for the experiment belongs to *Cyanobacteria*, of genus *Oscillatoria*. It is motile and moves by the means of microfibrils. *Oscillatoria* has a long un-branching filamentous structure that reproduces by binary fission. These cyanobacteria can conduct photosynthesis just like the other in its phylum but it can also conduct anoxygenic photosynthesis. Algal Biomass *Oscillatoria* is taken as waste from waterbody then dried and ground to the least possible particle size. Figure 4.4 is showing the photographs of (a) freshly collected algal biomass sample from the pond, (b) dried and ground algal biomass and (c) microscopic view of the algal biomass. From taxonomy using the microscopic view of collected algal biomass, it has been clear that the biomass has a filamentous structure which corresponds to the group of *Cyanobacteria* and genus of *Oscillatoria*. After confirming the structural analogy of collected algal biomass, it is then physically characterized to determine its quality before processing it for bio-fuels production.

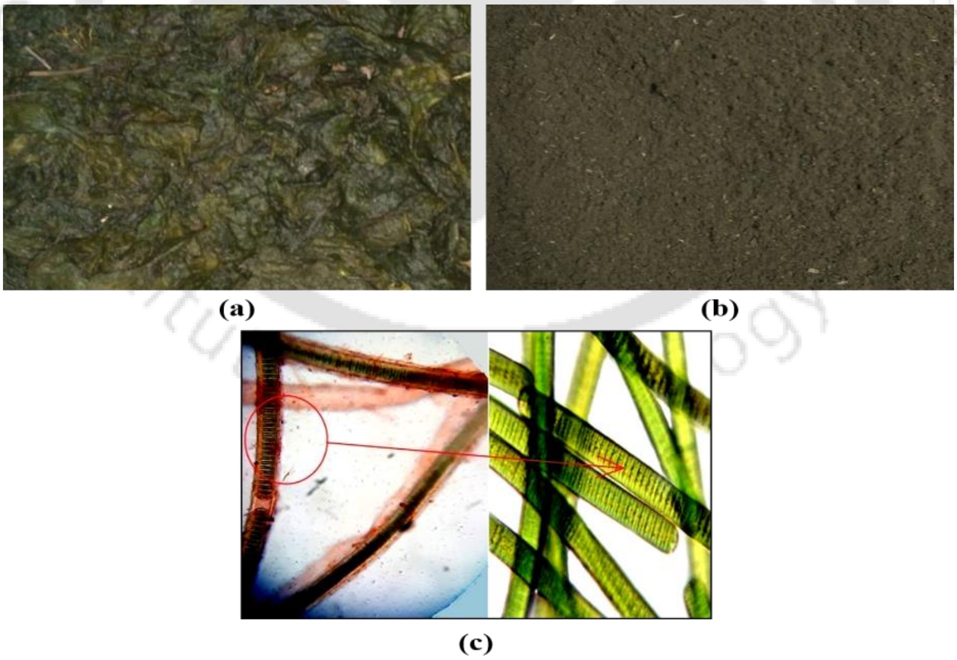

Figure 4.4: (a) Photograph of wet algal biomass, (b) photograph of grinded and dried algal biomass, (c) microscopic view of *Oscillatoria*.

4.C.2 Catalyst study

TiO_2 + ZnO are used as a catalyst for the product study from the algal biomass. The metal oxides that are another cost effective alternative were used as the experiments performed with the zeolites resulted in more coke formation for this case study. They are commercially purchased from Sisco Research Laboratories, India. The purpose of using these two catalysts together is that the petroleum industries wastewater treatment plant uses them as a photo-catalyst for degradation of heavy concentrated wastewater to extract lower molecular weight hydrocarbons. Whilst to examine the product behavior and to improve the product quality of bio-oil from algal biomass the TiO2: ZnO is used as 10 wt. % to that of biomass on 1:1 basis.

4.C.3 Pyrolysis Experiments

The pyrolysis of algal biomass *Oscillatoria* is conducted in three different atmospheres viz., (i) in inert medium using nitrogen gas, (ii) in catalytic medium using nitrogen gas with TiO_2 + ZnO on 1:1 basis as a catalyst, (iii) in hydro-catalytic medium using hydrogen gas with same 1:1 ratio of TiO_2 + ZnO as a catalyst. Non-catalytic pyrolysis of Oscillatoria is compared with the catalytic pyrolysis and then catalytic hydropyrolysis. The reaction atmospheres are similar as that of previous study of Delonix Regia biomass but the operating conditions are changed. All experiments are conducted on a fixed bed batch type reactor having an ATS furnace of a single heating zone. The feed holding capacity of the reactor for green algae of particle size 75 to 250 micron is 80 grams. The maximum attainable heating rate of the furnace is 20 °C/minute. All experiments are carried out at 1 bar pressure and 550 °C temperature, pressure is monitored using WIKA transmitter and K-type thermocouple is used for temperature determination inside the reactor. The reaction residence time is for 2 hours and for primary vapors condensation the ice-cooled water line is functioned for condenser. Non-condensable gases are separated by means of gas-liquid separator whereas bio-oil collected in bio-oil collection vessel and the bio-char is obtained after removing the batch.

4.D Co-feed pyrolysis of Delonix Regia (DR) with Pinewood Sawdust (PW)

4.D.1 Biomass Materials

The lignocellulosic biomass taken for the pyrolysis study to produce biofuels is Delonix Regia which is hardly researched and available in enormous percentage as a solid waste in IIT Guwahati campus. Other biomass is Pinewood sawdust which is collected from local sawmill nearby the campus area, and extensively researched for biofuels production. Both the biomass materials are sun dried, grinded and sieved to the 250 to 400-micron mesh size. The reason for choosing this biomass is that the Delonix Regia trunks are lying on the ground, below the tree, every day in the campus and contributes to the solid waste which results in the waste of energy. No such research is done on this energetic lignocellulosic biomass to convert its energy in usable manner. Thus, to convert this waste into wealth it is decided to take an action on the biomass as to degrade it thermally to get the biofuels. For the reference study, another locally available waste biomass i.e., Pinewood sawdust is taken, which is the waste generated by sawmills when pinewood is being transformed into wooden frames and already researched by many researchers for biofuels production. Hence, to study the comparative behaviour of both biomass materials for biofuels production, pyrolysis experiments are conducted separately on each biomass and then by co-feed of both the biomass at different ratios by weight.

4.D.2 Experimental Comprehension

Single feed pyrolysis and co-feed pyrolysis are conducted in a 150 ml volume tubular reactor system (Make: Amar Equipment, India) consisting of single zone heating furnace (Make: ATS, USA) and mounted with condenser, gas-liquid separator and bio-oil collection vessel. (a) Single Feed Pyrolysis: A controlled amount of nitrogen is passed through the MFC to maintain the pressure of 1 bar inside of the reactor system. Inside the reactor, 40-gram feed of single biomass is taken and the temperature is set at 625 °C. Total reaction time of the process is of two hours and the system is open to atmosphere system. The experiments are carried out thrice to check the repeatability. (b) Co-feed Pyrolysis: In co-feed pyrolysis, Pinewood sawdust and Delonix Regia biomass (PW: DR) are taken at ratios 25PW:75DR, 50PW:50DR, and 75PW:25DR that contribute the total feed of 40-grams. The pressure inside of the reactor is at 1 bar, temperature is set at 625 °C and the reaction time is 2 hours.

4.E Co-feed pyrolysis of Delonix Regia (DR) with Tube Waste (TW)

4.E.1 Feed Materials

The primary co-feed material taken in this study is lignocellulosic biomass *Delonix Regia* (DR), which is a fast-growing, widely available evergreen tree exhibiting deciduous characteristics in large areas with variable climatic conditions. The DR biomass is collected as solid waste from the roadside of the IIT Guwahati campus area, Assam, India, then processed to cut in a wood-cutter, dried, ground by the grinder and screened to 250-micron particle size. Whereas, the variable ratio of co-feed exhibiting the variable amount of Tube waste (TW) and it is collected from the backyards of local puncture repairing shops as the place has become dump-yard. The tube waste is washed with water, sundried and then cut into pieces of about 2mm × 1mm size. Cellulose, hemicellulose and lignin are building blocks of lignocellulosic biomass DR, whereas butyl rubber has a combination of 98 % isobutylene and 2 % isoprene as a building material of bicycle tubes and popularly known as isobutylene-isoprene rubber (IIR).

4.E.2 Co-feed Pyrolysis Experimental Insights

The co-feed pyrolysis of DR with TW is carried out in tubular reactor made up of SS 316 material having 4.2 cm ID and 4.8 cm OD (Make: Lelesil, Mumbai, India) which is surrounded by single zone heating furnace having a length of 40 cm (Make: Lelesil, Mumbai, India). This reactor setup is scale-up of the previous reactor and used to understand the effect of increased feed holding capacity. Nitrogen gas is used as a carrier gas for the experiment with a constant flowrate to maintain the atmospheric pressure of 1 bar inside of the reactor. The temperature for the study of co-feed pyrolysis at variable ratios of DR with TW is kept constant for all the cases at 600 ºC. For monitoring pressure and temperature, the reactor is equipped with pressure gauge and K-type thermocouple, respectively. The heating rate of the furnace is around 12 ºC/minute. The overall feed holding capacity of the reactor according to the particle size of co-feed is 300 grams. Schematic representation of the experimental setup with reactor dimensions is shown as Figure 4.5. The variable ratios of the co-feed are tested by keeping lignocellulosic biomass of DR as base material and varying the ratio of TW material. The co-feed ratios tested are 95DR:5TW, 85DR:15TW, 75DR:25TW, 65DR:35TW and 50DR:50TW. As the temperature reaches the set-point, the counting of the residence time of the reaction starts, which is of 2 hours. This experimental procedure is optimized by repeating several experiments, which resulted in ± 5 mass % of the variation in yield. Thus, the optimized method of co-feed pyrolysis experiment is taken and all the experiments are carried out accordingly to report a generalized pilot-scale co-pyrolysis process. The series of chemical reactions take place as primary and secondary reactions inside of the reactor and generates highly actuated pyrolytic vapours. These vapours pass through the condenser in which ice-cooled water is pumped continuously, thus to cool down the pyrolytic vapours. The cooled vapours are then pass through the gas-liquid separator in which condensed liquid and non-condensable vapours are separated by means of gravity. The non-condensable vapours are driven out of the system and collected in tedlar bags. Whereas the condensed liquid is flowing down to the liquid collection vessel and collected as bio-oil, which then taken for further characteristic analysis. After the completion of the reaction, as the reactor cools down to the room atmosphere, it is dismantled through the system and the bio-char which remained inside of the reactor is collected. The bio-char is further tested for its fuel property evaluation and to study its structural characteristics along with absorption behaviour.

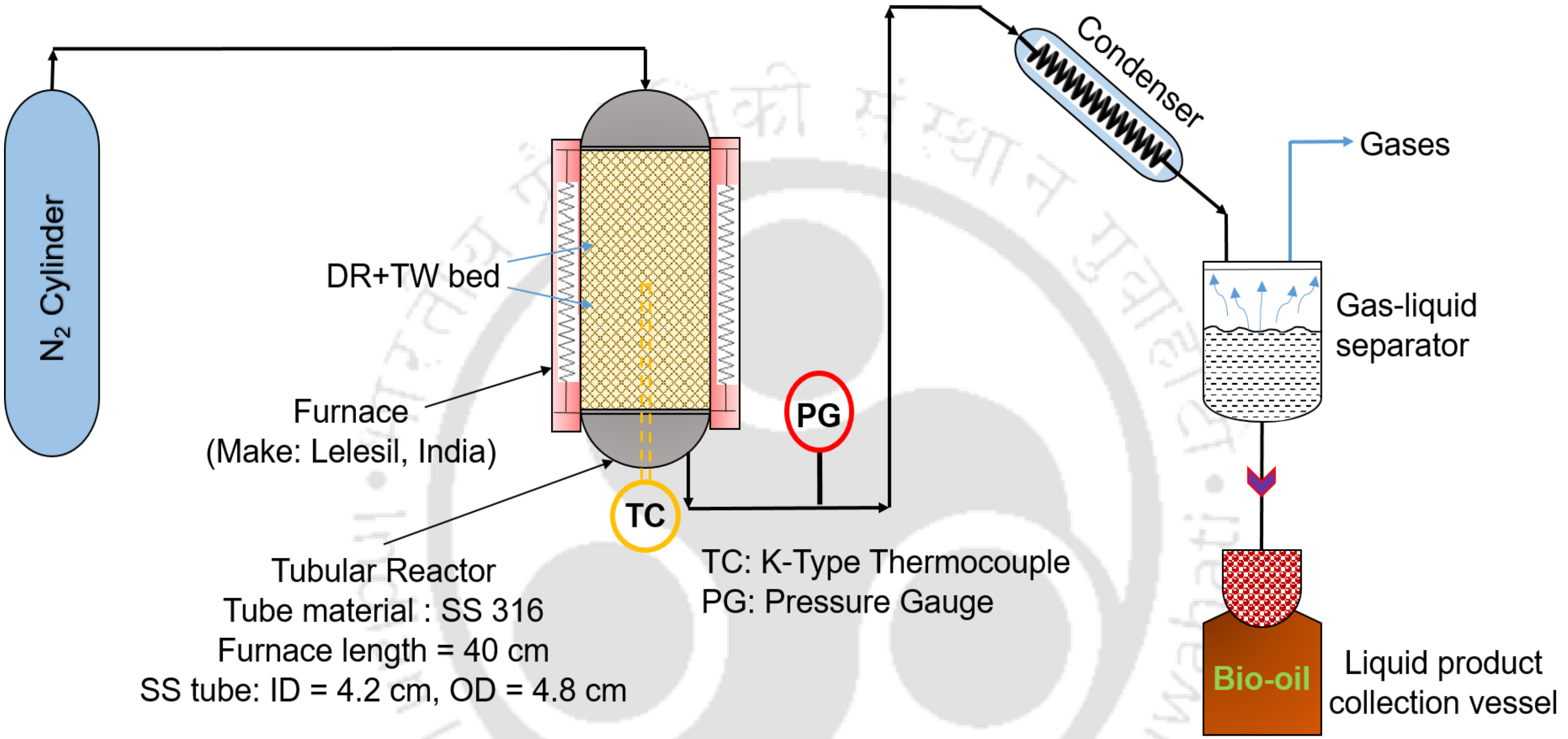

Figure 4.5. Schematic representation of pyrolysis setup for co-feed study at various ratios of Delonix Regia with Tube waste.

4.E.3 Feed and Products Characterization

DR biomass and TW are characterized by various characterization techniques to know their properties before testing their fuel prospective together at multiple ratios. The Proximate analysis of the biomass and TW is determined by ASTM standards [118]. Moisture content is obtained using ASTM E1756-08, where DR and TW are kept at 105 °C in hot air oven (Make: Remi, Mumbai, India) for 12 hours. Volatile matter content of DR and TW is obtained using ASTM E872-82 by keeping them in a muffle furnace (Make: VB Ceramics, Chennai, India) for 8 minutes at 910 °C. Further, the ash content of both the co-feed materials is obtained according to the ASTM E1755-01 where both the materials are kept at 600 °C for 4 hours in above-mentioned muffle furnace. Calorific value (CV) here referred as higher heating value (HHV) is calculated using oxygen bomb calorimeter (Make: Toshniwal, Delhi, India). 1 g of solid feed sample is taken in crucible and burnt in oxygen pressurized autoclave at 30 bar. Both the materials are then subjected to determine the mass percentage of carbon, hydrogen, nitrogen and sulphur on CHN elemental analyzer (Make: Euro Vector, Model: EuroEA3000, Italy). Thermal degradation behaviour of DR and TW along with the possible thermal decomposition temperature range and maximum thermal degradation temperature is studied on thermogravimetric analyzer (Make: Netzsch, Model: TG 209 F1 Libra, Germany) as thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG). The heating rate of the TGA and DTG study is kept at 15 ºC/minute in presence of nitrogen as carrier gas starting from temperature 30 ºC to end at 800 ºC, specifying wide thermal range. The cooling water is also continuously circulated in the system to maintain the microbalance of the closed TGA instrument. Further, the biomass and tube waste are characterized on powder x-ray diffractometer (Make: Rigaku, Model: Micromax-007HF, Japan) using Copper-K-α radiation to generate x-ray of wavelength 1.54 Å. The range of 2θ value studied is 10° to 80° for better understanding of the basic crystal structure of both the materials. For understanding the difference in surface morphology of both the materials, DR and TW are studied under field emission scanning electron microscope (Make: Zeiss, Model: Sigma 300, Germany) using internal lens at magnification of 5 - KX zoom.

The products obtained from co-feed pyrolysis of DR and TW at various ratios are basically solid char, liquid fuel and gaseous stream. This study focuses on liquid fuel and solid char characterizations to determine the overall energy potential of both the materials at the tested co-feed ratios.

All the obtained bio-oils are filtered with qualitative filter paper and then 10 mass % dichloromethane is added to the filtered bio-oils for separation of organic-phase and aqueous phase. After separation, the product yield of both the phases is recorded whereas organic phase bio-oil is taken for further characterizations. Bio-oil is firstly tested for its physico-chemical properties in which it is tested by pycnometer (Make: Borosil, India) of 10 ml volume to determine the density of the liquid. The viscosity is determined by Ostwald's viscometer (Make: Borosil, India) having around 10 ml liquid holding capacity. The bio-oil is then analyzed for its acidic nature determination by pH evaluation using benchtop pH meter (Make: Eutech, Model: pH 700, India). The amount of water mass % remained in bio-oil still if any, after phase separation, it is determined by using Karl-Fisher's titration (KFT, Make: Metrohm, Model: 878 KF, Switzerland). It uses 99.99 % pure dry methanol as a KFT solvent and pyridine free KF reagent. Around 20 µl of the liquid sample is injected through the septum in the titration chamber and the obtained value of water in mass % is then recorded. Fuel potential of bio-oils is calculated as calorific value (CV) in MJ/kg on oxygen bomb calorimeter (Make: Toshniwal, Delhi, India).

After the physico-chemical and fuel analysis, bio-oils are further characterized by advanced characterization tools to study their chemical structure. Fourier transform infrared spectroscopy (FTIR) of bio-oils is done on FTIR spectrometer (Make: Shimadzu, Model: IRAffinity-1, Japan). FTIR spectrometer is equipped with attenuated total reflectance (ATR) assembly having diamond crystal as a sample holder. Analysis is carried out in room atmosphere as a background in the range of 400-4000 cm^{-1} wavenumber based on % transmittance mode and the data is recorded on IR solution software in 30 scans. IR spectrum generated through the analysis represents the presence of particular functional group at particular wavenumber. Further to the functional group analysis, bio-oils are subjected to analyze their chemical conformation by determining presence of chemical compounds and hydrocarbons with the help of gas chromatography and mass spectrometry (GCMS). GCMS analysis is carried out on gas chromatograph coupled with mass spectrometer (Make: Agilent, Model: 7890B GC 5977B MSD, United States). System is equipped with Agilent HP-5 DBMS capillary column having 30-meter length × 30 µm internal diameter × 0.25 µm film.

Oven of GC can withstand maximum temperature up-to 350 °C, where the bio-oil samples are analyzed following justified method. The analysis method has 80 °C as initial temperature for 2-minute hold-up and then first ramp is given till 140 °C as 8 °C/minute and second ramp is given till 210 °C as 4 °C/minute. The total running time of above method is 29 minutes which has solvent delay of 3 minutes. 2 μl of sample is injected in GC oven in 1:20 split ratio with acetone as a solvent as well as standard. Next to this, MS has high ionization capacity which ionizes the compound on mass to charge ratio and MS detector detects the compound. The list of compounds and hydrocarbons present in bio-oil is generated by National Institute of Standards and Technology (NIST) library which is stored in Agilent Mass Hunter Workstation software version B.0.7.00. For validation of obtained functional groups and chemical compounds, the bio-oils are then experimented in high frequency 600 MHz nuclear magnetic resonance (NMR) spectroscopy (Make: Bruker, Model: 600 MHz, United States). NMR operates in high vacuum and equipped with superconducting magnets which are kept cooled with helium and whole assembly is cooled with liquid nitrogen. For NMR study of all the bio-oils Chloroform-D ($CDCl_3$) is taken as solvent and the study of proton (^1H) assignments is carried out at 16 number of scans by ^1H NMR.

Bio-char yield is calculated on mass % basis by weighing the remained solid material inside of the reactor, after the reaction. The HHV of the char is calculated similarly as that of feed material using oxygen bomb calorimeter. Further to check the crystal behaviour of all bio-chars, they are tested under XRD, similar to that of raw material i.e., biomass and tube waste with all the conditions kept same as elaborated in materials characterization section. Lately, to know the pore size distribution and total surface area of the bio-chars, they are tested on Brunauer-Emmett-Teller (BET) instrument (Make: Micromeritics, Model: Tristar II, United States). The bio-char samples are kept for degasying at 120 °C for 4 hours in vacuum and then placed over a Dewar filled with liquid nitrogen, further covering the sample tubes. The analysis runs for twelve hours, then the data is generated and shown by Tristar software V 3.02. Surface morphology study of all the bio-chars is carried out on Field emission scanning electron microscope (FESEM), in same manner as previously done on raw materials.

CHAPTER 5

Results and Discussions

5.A Pyrolysis of Delonix Regia at Variable Temperatures Study

5.A.1 Biomass Quality

Table 5.1 presents proximate and ultimate analysis along with HHV of DR on “as received basis.” From the proximate analysis, it is clear that this biomass feedstock consists of 17.6 wt. % fixed carbon, 9 wt. % of moisture and only 1.2 wt. % of ash content which indicates a good potential of this biomass as a resource for biofuels production by pyrolysis. The ultimate analysis of DR reported in Table 5.1 indicate that a good wt. % of Carbon and moderately low wt. % of Oxygen is also an indication of a useful resource for biofuels production and easily be realized by comparison with other literature values [119]. This also shows the potential of DR as a good resource for biofuel production. The gross calorific value (GCV) or higher heating value (HHV) is a characteristic of any fuel. It is the amount of energy released by combusting it, and that measured in MJ/kg. For DR, the HHV estimated by Dulong formula [117] using its C, H, and O contents obtained by ultimate analysis; and is found to be 15.18 MJ/kg. According to review article by Gollakota et al. [119], a few biomass feedstock possesses HHV as low as < 10 MJ/kg and a few possess as high as 20 MJ/kg whereas the present feedstock (DR) is in the moderate range displaying approximately 15 MJ/kg calorific value. Thus, by comparing with existing literature values and as per the ultimate and proximate analyses followed by reported HHV of DR, it is clear that this biomass feedstock has a moderately high potential to use as feedstock to produce biofuels by thermochemical conversion processes.

Table 5.1. Ultimate analysis, proximate analysis, and higher heating value of *Delonix Regia* biomass on “as received basis.”

Biomass	Elemental Composition (wt. %)				Proximate Analysis (wt. %)				HHV (MJ/kg)
	C	H	N	O[a]	Moisture	Volatiles	Fixed Carbon	Ash	
Delonix Regia	45.4	5.9	1.2	47.5	9	72.2	17.6	1.2	15.18

[a] :calculated by the difference.

Figure 5.1 presented patterns of thermogravimetric and differential thermogravimetric analysis of DR biomass on “as received basis” and “dry basis.” From TGA, it is clear that the moisture content of the sample released until 190 ºC for DR of “as received basis,” whereas for “dry basis,” moisture content released until about 150 ºC. As the biomass on “as received basis” contains more amount of moisture content, it produces vapours for a longer duration with increasing temperature which then reacts with pyrolytic mists from primary reactions to form more oxygenated products. Thermal degradation of hemicellulose fraction of DR biomass started around 270 ºC – 280 ºC in both the cases of dry basis and as received basis, and is in line with other published results [36,81,120]. The cellulose and lignin fractions of DR started degradation after 300 ºC. To be specific, much of the cellulose fraction started degrading from 300 ºC to over 400 ºC, but lignin degradation of the DR sample took place till 700 ºC. As received basis and dry basis study interprets the degradation behavior, where weight % reaches almost zero after 700 °C for moisture free basis and for “as received basis” does not display complete degradation even at 750 °C. It is happening because the degradation of biomass is hindered by the presence of moisture content which collaborates in the intact structure of biomass. Thus, from the above results, it is advisable to use moisture-free dry biomass for pyrolysis study. From the DTG curve of “as received biomass” at around 180 °C to 230 °C, the biomass found to started gaining mass but it is just for a matter of time showing that the primary reactions are active. The maximum degradation temperature is 370 °C according to a “dry basis” and 380 °C in the case of “as received basis.” Around 690 °C, the DTG curve shows a small degradation that is nothing but the representation of the polymerization caused by the secondary reactions. Thus, it is inadvisable to use “as received basis” of the biomass for pyrolysis. Therefore, on the basis of these results, it is decided to use the biomass feedstock (DR) on dry basis to study its pyrolysis behaviour, and the operating temperature determined to investigate its effect in the range of 500 °C to 700 °C. Further, the TGA and DTG patterns of DR biomass are found to be similar to those reported in open literature by many other researchers [36,81,120,121].

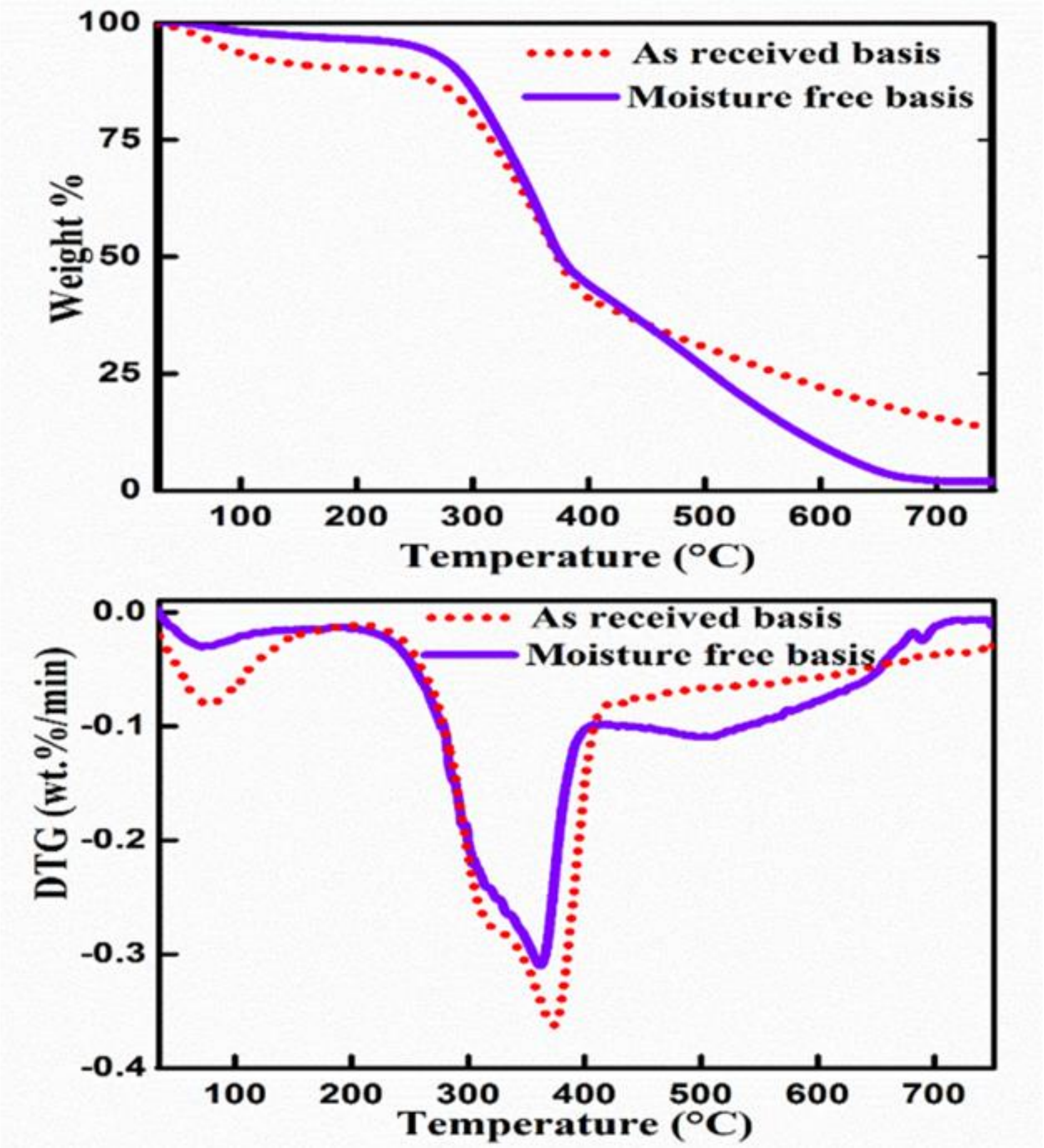

Figure 5.1. TGA and DTG patterns of DR biomass.

5.A.2 Pyrolysis Product Yield

Table 5.2 presented the yields of bio-oil, bio-char, and non-condensable gases along with their percentage difference by three repetition experiments for each pyrolysis temperature. At 500 °C, the bio-oil yield is approximately 38 wt. % with ± 2 % of difference, at 600 °C the bio-oil yield decreases to 32 wt. % with ± 2 % of difference, and at 700 ºC the yield is again increased to near about 36 wt. % that of the inlet feed material with ± 5 % of difference. The differences in repetition experiments are not at all uncommon in experimental studies of such kind and depend on variations in the size of feedstock, possible fluctuations in heating rate, inert gas flow rate, etc. But, here in this particular study the increased temperature of the pyrolysis reaction is supporting formation of more gaseous product in outlet stream whilst the elevated temperature of 700 ºC represnts the balanced product distribution over other cases.

Table 5.2. Overall distribution of pyrolysis products at different pyrolysis temperatures.

Temperature (°C)	500	600	700
Bio-oil (Wt. %)	37.8 ± 2	31.5 ± 2	35.2 ± 5
Bio-char (Wt. %)	34.7 ± 2	32.7 ± 1.4	30.7 ± 1.3
Non-condensable gases (Wt. %)[b]	25.5 ± 2	34.1 ± 1.7	30.95 ± 3.15

[b]: calculated by the difference.

5.A.3 Pyrolytic Bio-oil Characteristics

Table 5.3 presented ultimate analysis, pH value, moisture content, density, viscosity, and HHV of bio-oils obtained by pyrolysis of DR at three different temperatures. The pH of bio-oil is found to be acidic and is consistent with other reported literature [28,72,122–124]. In present study, the bio-oil is less acidic, i.e., 3.4 at 500 °C then at 600 °C its acidity increases, i.e., pH decreases to 3.3, and at 700 °C acidity remains same, i.e., 3.3. The increase in temperature increased the acidity of bio-oil because of the increase in carboxylic and phenolic components which are formed by the degradation of lignin at elevated temperatures. The weight percentage of water in the bio-oil is almost found to be unaffected by increasing the pyrolysis temperature from 500 °C to 700 °C displaying only a nominal change from 38.95 wt. % to 39.79 wt. %. This small or negligible increase in water content with increasing temperature may be because of secondary reactions coinciding during the reactions forming oxygenated compounds in the process of pyrolysis. The density of bio-oils at 500, 600 and 700 °C respectively are 0.95, 0.92, and 0.88 (kg/lit) whereas their corresponding viscosity values are 1.35, 1.24, and 1.22 (mPa.s). In other words, the density and viscosity of bio-oil are found to be decreasing with increasing the pyrolysis temperature which is a positive indicator in the context of bio-oil quality. Because producing bio-oils of less density and less viscosity is favourable prior to their upgrading by catalytic hydrodeoxygenation [125]. The ultimate elemental analysis presented in Table 5.3 indicates that the weight percentages of C and H increase with the pyrolysis temperature, whereas that of O decreases. This result is also favourable in the context of bio-oil, where it is preferred to have improved C/H ratio and decreased oxygenated components. The HHV of bio-oil samples obtained by Dulong formula [117] using elemental composition of C, H and O displayed increasing trend with increasing tempertaure (see Table 5.3). To be specific, calorific value of bio-oil at 500 °C is 20.88 MJ/kg, then at 600 °C it increased up to 23.28 MJ/kg, and at 700 °C it further increased to 25.70 MJ/kg. For non-catalytic pyrolysis, the obtained value of CV of DR bio-oil can be considered as an honest assessment and has more potential and energy value than that of reported similar kind of bio-oil from other biomass feedstocks [27,72,125,126].

Table 5.3. Ultimate analysis of bio-oil, bio-char with higher heating values on a dry basis, and physical properties of bio-oil on wet basis.

T (°C)	Sample	C %	H %	N%	O %	pH	Water (wt. %)	ρ (Kg/ lit)	μ (mPa.s)	HHV (MJ/kg) (Dulong)
500	bio-oil	50.62	6.96	1.06	41.34	3.4	38.95	0.95	1.35	20.88
600	bio-oil	55.62	6.93	1.28	36.15	3.3	39.33	0.92	1.24	23.28
700	bio-oil	58.32	7.65	1.26	32.75	3.3	39.79	0.88	1.22	25.70
500	biochar	68.40	10.9	3.66	16.98	-	-	-	-	36.04
600	biochar	78.09	8.10	3.15	10.65	-	-	-	-	36.18
700	biochar	81.51	8.59	2.98	6.90	-	-	-	-	36.25

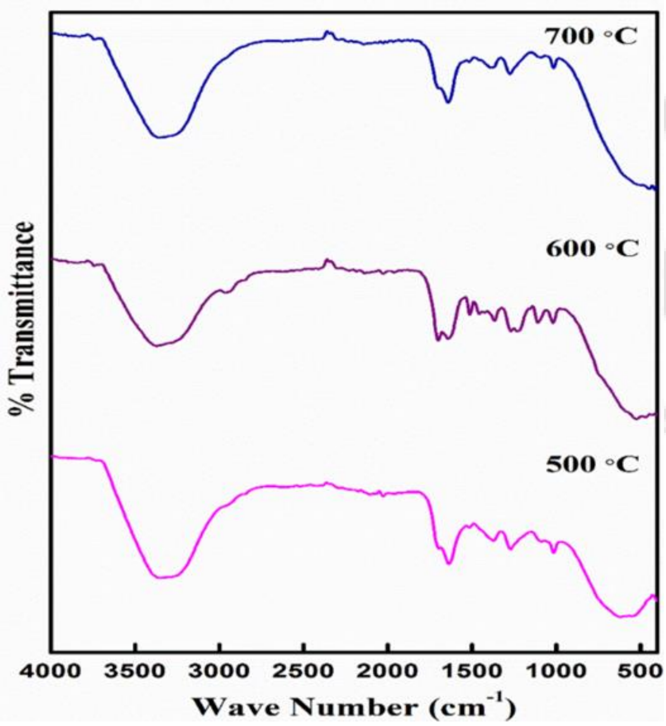

Figure 5.2. FTIR spectrogram of bio-oils obtained from DR biomass pyrolysis at variable temperatures.

FTIR spectrum of the bio-oils obtained at 500 °C, 600 °C, and 700 °C shown in Figure 5.2, and Table 5.4 illustrates the functional groups, their stretching, and bending present in obtained bio-oil samples over a frequency range of 4000 – 400 cm^{-1}. At 500 °C wave number 631 cm^{-1}, at 600 °C wave number 518 $cm^{-1,}$ and 700 °C wave number 450 cm^{-1} corresponds to aromatic compounds. Similarly, for all temperatures, 1018 cm^{-1} gives information about the presence of primary, secondary, tertiary alcohols, phenol, ester, and ether. 1375 cm^{-1} for 500 ºC case, 1364 cm^{-1} for 600 °C case, and 1398 cm^{-1} for 700 °C case represent the presence of alkanes in the bio-oil. Then 1636, 1642 and 1648 cm^{-1} show alkenes at 500, 600 and 700 °C cases respectively. From the plots, it is seen that the frequency at 1700, 1694 and again 1694 cm^{-1} at 500, 600 and 700 °C cases respectively gives functional group of ketones, aldehydes, and carboxylic acids. A prominent percent transmittance peak at around 3358 to 3376 cm^{-1} at all temperatures show the presence of polymeric OH or water impurities, which are present in the bio-oil samples. Thus, from the spectrum and analysed functional groups, it is confirming that the bio-oil obtained at each temperature contains broad range of alkanes, alkenes, ketones, aldehydes, carboxylic acids, primary alcohols, secondary alcohols, tertiary alcohols, phenol, ester and ether, aromatic compounds, naphthalene, ring in benzene derivative indefinite of the frequency range. The results of this FTIR study at all three temperatures show the similar functional groups present in the bio-oils. As all the bio-oils are obtained from the same source material, there is not much difference in their functional groups. Hence, it is uncertain about specifying the distinct difference between the three bio-oils at variable temperatures obtained from the same biomass feedstock (DR) as FTIR provides information on functional groups only but not about the composition of the sample.

Table 5.4. Functional groups present in pyrolytic bio-oil of *Delonix Regia* confirmed by their FTIR analysis.

Wavenumber (cm^{-1})	Group	Class of compound
3650-3100	O-H stretching	Polymeric O-H, water impurities
3000-2800	C-H stretching	Alkanes, Alkenes
1761-1676	C=O stretching	Ketones, Aldehydes, Carboxylic acids
1670-1550	C=C stretching	Alkenes
1400-1300	C-H stretching	Alkanes
1020-950	C-O stretching O-H bending	Primary, Secondary, Tertiary alcohols, Phenol, Ester and Ether
950-875	C-H bending	Aromatics
900-540	-	An aromatic compound, Naphthalene, ring in benzene derivative

Thus, to verify the effect of temperature on the bio-oil composition, these samples are further analysed by GCMS analysis. It is a qualitative and quantitative method to analyse the sample, where gas chromatograph separates the mixture of compounds and mass spectrometer detects the ionized compound to give a particular informative data of the components present in the bio-oil. Figure 5.3 displayed the GCMS chromatogram of bio-oil obtained at 500 °C, 600 °C, and 700 °C pyrolysis temperature. These chromatograms analysed with NIST library search which indicated the existence of hundreds of components in the bio-oil samples. The information about the major components present in bio-oils obtained by pyrolysis of DR at three different temperatures in terms of their retention time and area % are presented in Table 5.5. This information about components is further segregated as a collective sheet presenting 140 components which are present in all three bio-oil samples obtained at three different temperatures (see Table 5.6). This table also includes the information about their retention time according to GC-MS, molecular weight and chemical formula of those components.

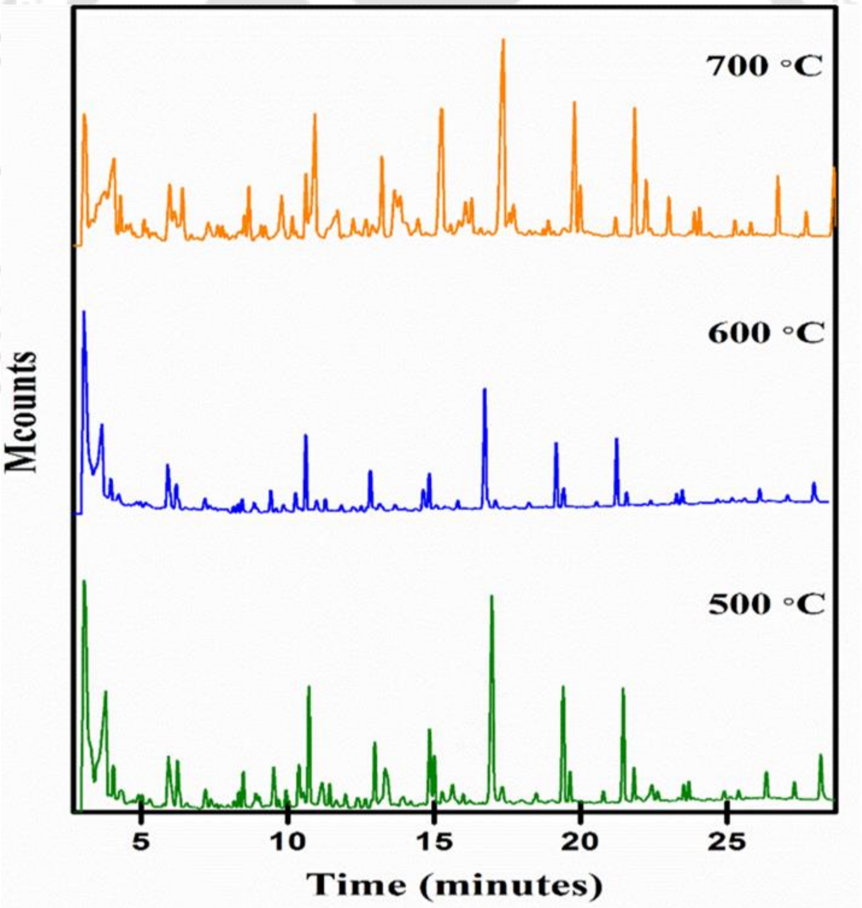

Figure 5.3. GCMS chromatogram of bio-oils obtained from DR biomass pyrolysis at 500 °C, 600 °C, and 700 °C.

Table 5.5. Major compounds in bio-oils obtained by pyrolysis of DR at 500 °C, 600 °C, and 700 °C recognized by GCMS.

Compounds	500 °C		600 °C		700 °C	
	RT (min.)	Area (%)	RT (min.)	Area (%)	RT (min.)	Area (%)
Benzene	3.9	13.5	3.8	14.6	-	-
1,2-Propandiol, 2-acetate	4.0	1.7	3.9	1.2	-	-
4-Penten-2-one, 4-methyl-	-	-	-	-	4.0	1.3
Acetohydroxamic acid	-	-	4.9	0.2	-	-
N,N,O-Triacetylhydroxylamine	4.9	0.4	-	-	-	-
Hexane, 2,2,4-trimethyl-	5.0	0.3	-	-	-	-
Pilocarpine	5.9	1.7	5.9	3.9	5.9	3.7
3-Furanmethanol	6.2	2.2	-	-	6.2	1.7
1H-Imidazole-4-methanol	-	-	6.2	2.2		
2,4-Dimethylfuran	-	-	-	-	7.2	0.7
Furan, 2-ethyl-5-methyl-	7.2	0.8	7.2	0.8	-	-
2-Furancarboxyaldehyde, 5-methyl-	8.2	0.4	8.2	0.2	-	-
2,4-Dimethylfuran	8.3	0.5	8.4	0.5	8.3	0.4
Phenol	8.5	0.9	8.5	1.3	8.5	0.9
Propanoic acid, 2-methyl-, anhydride	-	-	-	-	8.9	0.8
Furan, 2-butyltetrahydro-	9.0	0.8	9.0	0.5	-	-
1,2-Cyclopentanedione, 3-methyl-	9.5	1.5	9.6	1.5	9.6	1.3
2-Cyclopenten-1-one, 2,3-dimethyl-	9.7	0.2	-	-	-	-
Phenol, 2-methyl-	10.0	0.5	10.0	0.5	10.0	0.5
p-Cresol	10.4	1.2	10.5	1.6	-	-
Phenol, 2-methyl-	-	-	-	-	10.4	1.3
2-Octen-4-ol	-	-	10.6	0.6	-	-
Phenol, 2-methoxy-	10.8	4.7	10.8	4.4	10.8	4.2
Phenol, 2,3-dimethyl-	11.2	0.8	-	-	-	-
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	11.5	0.8	11.5	0.8	11.5	0.8
Phenol, 2-ethyl-	-	-	12.5	0.5	-	-
Creosol	-	-	12.8	0.4	-	-

Creosol	13.1	2.7	13.1	2.1	13.1	1.8
Resorcinol	-	-	13.5	2.7	13.4	0.7
1,2-Benzenediol, 3-methoxy-	14.9	1.5	15.0	3.2	14.9	1.7
Phenol, 4-ethyl-2-methoxy-	15.1	2.3	15.2	1.9	15.1	1.5
1,2-Benzenediol, 4-methyl	-	-	15.8	1.5	-	-
4-Hydroxy-2-methylacetophenone	-	-	-	-	16.1	0.4
Ethanone, 1-(2-hydroxy-5-methylphenyl)-	16.2	0.5	16.2	0.4	-	-
Phenol, 2,6-dimethoxy-	17.1	9.5	17.2	10.5	17.1	10.2
Phenol, 3,4-dimethoxy-	17.5	0.6	-	-	17.5	0.5
1,2,4 – Trimethoxybenzene	19.6	4.2	19.6	4.5	19.6	4.4
Phenol-2-methoxy-4-(1-proprnyl)-	19.9	1.2	19.9	1.1	19.8	0.7
Apocynin	-	-	21.0	0.4	21.0	0.3
4-Ethylbiphenyl	21.7	4.4	21.7	4.7	21.7	3.8
2-Propenone, 1-(4-hydroxy-3-methoxyphenyl)-	22.0	0.8	22.1	1.1	22.0	0.9
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	23.7	0.6	23.8	0.5	23.8	0.4
Benzene, 1,1'-propylidenebis-	23.9	0.9	23.9	0.7	23.9	0.4
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	26.6	0.9	26.6	0.9	26.6	0.5
Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	27.5	0.5	27.6	0.6	27.6	0.5
Unknown	28.4	1.6	28.5	2.1	28.4	1.9

From the GCMS analysis, it is clear that the variation in temperature affected only the percentage of the components; thus, their GCMS pattern is qualitatively similar to each other for different temperatures as shown in Figure 5 and the same is confirmed from Table 5.5 in terms of retention time (RT) and area %. However, quantitatively there is a slight difference in the retention time and peak intensities of the compounds at each temperature. In other words, from the list given in Table 5.5, it is clear that the bio-oil changes its composition slightly over an applied temperature range. According to this table, major compounds present in substantial area percentage (with more than 3 area %) at all temperatures are: Pilocarpine (3.9 %), Phenol, 2-methoxy- (4.7 %), 1,2-Benzenediol, 3-methoxy (3.2 %), Phenol, 2,6-dimethoxy- (10.5 %), 1,2,4 -Trimethoxybenzene (4.5 %), 4-Ethylbiphenyl (4.7 %). On the other hand, the benzene is present with the highest area % of 13.5, and 14.6 at 500 °C and 600 °C respectively. The peak shown in the figure 5.3 at RT 3.9 for 700 ºC doesn't represent any plausible compound that should be predicted by NIST library. By analysing the basic classes/catalogue/group of compounds shown in Table 5, it can be observed that the aromaticity of the bio-oil is increasing by increasing the pyrolysis temperature.

Table 5.6. List of plausible compounds existing in all three bio-oil samples obtained by pyrolysis of *Delonix Regia* biomass at 500 °C, 600 °C and 700 °C.

Sr. No.	Compound Name	Retention Time (min.)	Molecular Weight	Chemical Formula
1	Benzene	3.9	78	C_6H_6
2	4-Penten-2-one, 4-methyl-	4.0	98	$C_6H_{10}O$
3	1,4-Butanediol, diacetate	4.4	174	$C_8H_{14}O_4$
4	N,N,O-Triacetylhydroxylamine	4.5	159	$C_6H_6NO_4$
5	Pyridine	4.8	79	C_5H_5N
;6	Propanedinitrile, (acetyloxy)methyl-	4.9	138	$C_6H_6N_2O_2$
7	Acetohydroxamic acid	4.9	75	$C_2H_5NO_2$
8	Pentane,2,2,4,4-tetramethyl-	4.9	128	C_9H_20
9	Pentane, 2,4-dimethyl-	4.9	100	C_7H_{16}
10	Heptane, 2,2,4,6,6-pentamethyl-	4.9	170	$C_{12}H_{26}$
11	Butanoic acid	5.0	88	$C_4H_8O_2$
12	Hexane, 2,2,4-trimethyl-	5.0	128	C_9H_{20}
13	Butane, 2,2-dimethyl-	5.0	86	C_6H_{14}
14	Hexane, 2,3,5-trimethyl-	5.1	128	C_9H_{20}
15	Piperidine, 1-methyl-	5.1	99	$C_6H_{13}N$

16	Xylose	5.2	150	$C_5H_{10}O_5$
17	1-Penten, 3-ethyl-2-methyl-	5.3	112	C_8H_{16}
18	Cyclopentanone	5.3	84	C_5H_8O
19	n-Hexyl acrylate	5.3	156	$C_9H_{16}O_2$
20	Oxirane, tetramethyl-	5.4	100	$C_6H_{12}O$
21	Pilocarpine	5.6	208	$C_{11}H_{16}N_2O_2$
22	Pyridine, 3-methyl-	5.7	93	C_6H_7N
23	3,5-Dimethylpyrazol	5.8	96	$C_5H_8N_2$
24	Furfural	5.9	96	$C_5H_4O_2$
25	2-Furanmethanol	6.1	98	$C_5H_6O_2$
26	3-Furanmethanol	6.1	98	$C_5H_6O_2$
27	Propane-1, 1-diol diacetate	6.2	160	$C_7H_{12}O_4$
28	1H-Imidazole-4-methanol	6.3	98	$C_4H_6N_2O$
29	Acetic anhydride	6.3	102	C4H6O3
30	Furan, tetrahydro-2,5-dimethoxy-	6.4	132	$C_6H_{12}O_3$
31	Pyridine, 2,3-dimethyl-	6.7	107	C_7H_9N
32	2,6-Lutidine	6.8	107	C_7H_9N
33	1-Penten-3-ol, 2-methyl-	6.9	100	$C_6H_{12}O$
34	Dinocap	7.1	207	$C_{10}H_9NO_4$
35	2,4-Dimethylfuran	7.2	96	C_6H_8O
36	Furan, 2-ethyl-5-methyl-	7.2	110	$C_7H_{10}O$
37	2-Isopropylimidazole	7.2	110	$C_6H_{10}N_2$
38	2,5-Hexanedione	7.4	114	$C_6H_{10}O_2$
39	Cyclohexanone	7.6	98	$C_6H_{10}O$
40	Pyridine, 3,5-dimethyl-	7.7	107	C_7H_9N
41	2-Heptyne-4-one	7.9	110	$C_7H_{10}O$
42	Pyridine, 4-ethyl-	8.0	107	C_6H_7N
43	2-Furancarboxyaldehyde, 5-methyl-	8.2	110	$C_6H_6O_2$
44	Furan, 2,5-dimethyl-	8.3	96	C_6H_8O
45	Furyl hydroxymethyl ketone	8.4	126	$C_6H_6O_3$
46	Phenol	8.5	94	$C_6H_6O_2$
47	Cyclopentene, 1-(1-methylethyl)-	8.9	110	C_8H_{14}
48	1,3-Dimethyl-1-cyclohexene	8.9	110	C_8H_{14}
49	exo-2-Bromonorbornane	8.9	174	$C_7H_{11}Br$
50	2-Furanmethanol, tetrahydro-	8.9	102	$C_5H_{10}O_2$
51	Propanoic acid, 2-methyl-, anhydride	8.9	158	$C_8H_{14}O_3$
52	Furan, 2-butyltetrahydro-	9.0	128	$C_8H_{16}O$
53	Butanoic acid, 2-propenyl ester	9.0	128	$C_7H_{12}O_2$
54	2-Hydrazinopyridine	9.0	109	$C_5H_7N_3$
55	1H-Pyrrole-2-carboaldehyde, 1-methyl-	9.1	109	C_6H_7NO

56	1,2-Cyclopentanedione, 3-methyl-	9.5	112	$C_6H_8O_2$
57	2-Acetyl-5-methylfuran	9.6	124	$C_7H_8O_2$
58	Furan, 2-ethyl-5-methyl-	9.7	110	$C_7H_{10}O$
59	2-Cyclopenten-1-one, 2,3-dimethyl-	9.7	110	$C_7H_{10}O$
60	Benzene, (butoxymethyl)-	9.9	164	$C_{11}H_{16}O$
61	Toluene	9.9	92	C_7H_8
62	Phenol, 2-methyl-	10.0	108	C_7H_8O
63	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	10.1	126	$C_7H_{10}O_2$
64	2-Cyclopenten-1-one, 3,4,4-trimethyl-	10.2	124	$C_8H_{12}O$
65	1,2-Ethanediol, 1,2-diphenyl-	10.4	214	$C_4H_{14}O_2$
66	Phenol, 2-methyl-	10.4	108	C_7H_8O
67	p-Cresol	10.5	108	C_7H_8O
68	2-Cyclopenten-1-one, 3,4,5-trimethyl-	10.6	124	$C_8H_{12}O$
69	2-Octen-4-ol	10.6	128	$C_8H_{16}O$
70	Mequinol	10.7	124	$C_7H_8O_2$
71	Phenol, 2-methoxy-	10.8	124	$C_7H_8O_2$
72	Phenol, 2,3-dimethyl-	11.2	122	$C_8H_{10}O$
73	Maltol	11.4	126	$C_6H_6O_3$
74	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	11.5	126	$C_7H_{10}O_2$
75	Furyl hydroxymethyl ketone	11.5	126	$C_6H_6O_3$
76	5-Ethyl-2-furaldehyde	11.7	124	$C_7H_8O_2$
77	Phenol, 2-ethyl-	11.7	122	$C_8H_{10}O$
78	2(1H)-Pyridinone, 5-methyl-	11.8	109	C_6H_7NO
79	1,3-Benzenediol, 4-ethyl-	11.8	138	$C_8H_{10}O_2$
80	Phenol, 3,4-dimethyl-	12.0	122	$C_8H_{10}O$
81	Phenol, 3-ethyl-	12.5	122	$C_8H_{10}O$
82	Creosol	12.7	138	$C_8H_{10}O_2$
83	2-Methoxy-5-methylphenol	13.0	138	$C_8H_{10}O_2$
84	Creosol	13.1	138	$C_8H_{10}O_2$
85	Resorcinol	13.4	110	$C_6H_6O_2$
86	Catechol	13.4	110	$C_6H_6O_2$
87	2-Cyclohexen-1-one, 5-methyl-2-(1-methylethyl)-	14.0	152	$C_{10}H_{16}O$
88	Benzene, 1-ethyl-4-methoxy-	14.1	136	$C_9H_{12}O$
89	Phenol, 3,4-dimethoxy-	14.3	154	$C_8H_{10}O_3$
90	2-Cyclohexen-1-one, 4-(1-methylethyl)-	14.4	138	$C_9H_{14}O$
91	Phenol, 2-ethyl-4-methyl-	14.6	136	$C_9H_{12}O$
92	1,2 -Benzenediol, 3-methoxy	14.9	140	$C_7H_8O_3$
93	Phenol, 4-ethyl-2-methoxy-	15.1	152	$C_9H_{12}O_2$

94	1,4 -Benzenediol, 2,3,5-trimethyl-	15.2	152	$C_9H_{12}O_2$
95	3,4-Dihydroxyacetophenone	15.4	152	$C_8H_8O_3$
96	Ethanone, 1-(2,4-dihydroxyphenyl)-	15.4	152	$C_8H_8O_3$
97	Resorcinol, 2-acetyl-	15.4	152	$C_8H_8O_3$
98	2-Cyclohexene-1-one, 5-methyl-2-(1-methylethyl)-	15.4	152	$C_{10}H_{16}O$
99	Benzene, 1-methoxy-4-(1-methylethyl)-	15.6	150	$C_{10}H_{14}O$
100	1,2-Benzenediol, 4-methyl-	15.7	124	$C_7H_8O_2$
101	1H-Inden-1-one, 2,3-dihydro-	16.1	132	C_9H_8O
102	Ethanone, 1-(2-hydroxy-5-methylphenyl)-	16.1	150	$C_9H_{10}O_2$
103	4-Hydroxy-2-methylacetophenone	16.1	150	$C_9H_{10}O_2$
104	3-Methoxy-5-methylphenol	16.3	138	$C_8H_{10}O_2$
105	1,2,4 – Trimethoxybenzene	16.7	168	$C_9H_{12}O_3$
106	Ethanone, 1-(2,3,4-trihydroxyphenyl)-	16.7	168	$C_8H_8O_4$
107	Phenol, 2,6-dimethoxy-	17.1	154	$C_8H_{10}O_3$
108	Phenol, 2-methoxy-6-(2-propenyl)-	17.2	164	$C_{10}H_{12}O_2$
109	2-Propanone, 1-hydroxy-3-(4-hydroxy-3-methxyphenyl)-	17.4	196	$C_{10}H_{12}O_4$
110	Phenol, 3,4-dimethoxy-	17.5	154	$C_8H_{10}O_3$
111	2,5-Dihydroxypropiophenone	18.0	166	$C_9H_{10}O_3$
112	Benzene, 1,2,3-trimethoxy-5-methyl-	18.1	182	$C_{10}H_{14}O_3$
113	1,3 -Benzenediol, 4-ethyl-	18.2	138	$C_8H_{10}O_2$
114	Benzaldehyde, 3-hydroxy-4-methoxy-	18.6	152	$C_8H_8O_3$
115	Vanillin	18.7	152	$C_8H_8O_3$
116	3-Hydroxy-4-methoxybenzoic acid	19.6	168	$C_8H_8O_4$
117	Phenol, 2-methoxy-4-(1-propenyl)- (Z)-	19.6	164	$C_{10}H_{12}O_2$
118	Phenol, 2-methoxy-6-(2-propenyl)-	20.5	164	$C_{10}H_{12}O_2$
119	Apocynin	20.9	166	$C_9H_{10}O_3$
120	4-Acetoxy-3-methoxyacetophenon	21.0	208	$C_{11}H_{12}O_4$
121	4-Ethylbiphenyl	21.6	182	$C_{14}H_{14}$
122	Benzene, 1,2,3-trimethoxy-5-methyl-	21.7	182	$C_{10}H_{14}O_3$
123	Phenethylamine, 2,4,5-trimethoxy-.alpha.-methyl-	21.7	225	$C_{12}H_{19}NO_3$

124	2-Propanone, 1-(4-hydroxy-3-methxyphenyl)-	22.0	180	$C_{10}H_{12}O_3$
125	4-Methoxyphenol,TMS derivative	22.7	196	$C_{10}H_{16}O_2Si$
126	Hexadecanoic acid, methyl ester	22.7	270	$C_{17}H_{34}O_2$
127	2,5-Dimethoxy-4-ethylamphetamine	22.8	223	$C_{13}H_{21}NO_2$
128	2',4'-Dimethoxyacetophenone	22.8	180	$C_{10}H_{12}O_3$
129	4-Acetoxy-3-methoxyacetophenon	23.5	208	$C_{11}H_{12}O_4$
130	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	23.7	194	$C_{11}H_{14}O_3$
131	Benzene, 1,1'-propylidenebis-	23.9	196	$C_{15}H_{16}$
132	Benzene, 1,1',1",1'"-(1,2-ethanediylidene) tetrakis-	24.1	334	$C_{26}H_{22}$
133	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	25.1	194	$C_{11}H_{14}O_3$
134	2-Butanone, 4-(4-hydroxy-3-methoxyphenyl)-	25.2	194	$C_{11}H_{14}O_3$
135	Homovanillic acid	25.3	182	$C_9H_{10}O_4$
136	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	25.7	182	$C_9H_{10}O_4$
137	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	26.6	194	$C_{11}H_{14}O_3$
138	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	27.5	196	$C_{10}H_{12}O_4$
139	Xanthoxylin	27.6	196	$C_{10}H_{12}O_4$
140	Carbazole	28.4	167	$C_{12}H_9N$

The proton NMR describes the orientation of the hydrogen atom attached to the particular group or compound, and it provides a structural analysis of the group or compound by inducing spin state. Figure 5.4 shows the NMR spectra of bio-oils obtained by pyrolysis of DR at 500 °C, 600 °C, and 700 °C. In proton NMR spectra, the line at zero chemical shift (ppm) represents tetramethylsilane (TMS) and chloroform-D ($CDCl_3$) is used as a solvent for NMR sample preparation [127]. ^{1}H NMR data interpretation is carried out using ACDNMR software. These spectra presented up to chemical shift of 6 ppm only without the reference peak and after removal of TMS impurity at 0 ppm. The percentage amount 'H' present in a group of compounds determined by the area of the particular peak. A detailed list of chemical shifts (ppm) and the corresponding group with hydrogen % distribution presented in Table 5.7. The chemical shift at 0.5 - 1.5 ppm indicates the proton assignment of alkanes, 1.5 - 3.0 indicates aliphatics, wide range of 1.0 - 5.0 indicates the broad spectrum of alcohol. Similarly, chemical shift in the range of 4.5 - 6.0 ppm represents alkenes [128,129]. Thus, all the compounds listed by GCMS analysis verified and confirmed by ^{1}H NMR analysis as well. Therefore, this proton NMR investigation proved to be of vital importance in confirming the functional groups present and their structural orientation data. From the results presented in Table 5.7, it can be seen that the percentage of hydrogen due to aromatic compounds increasing with pyrolysis temperature.

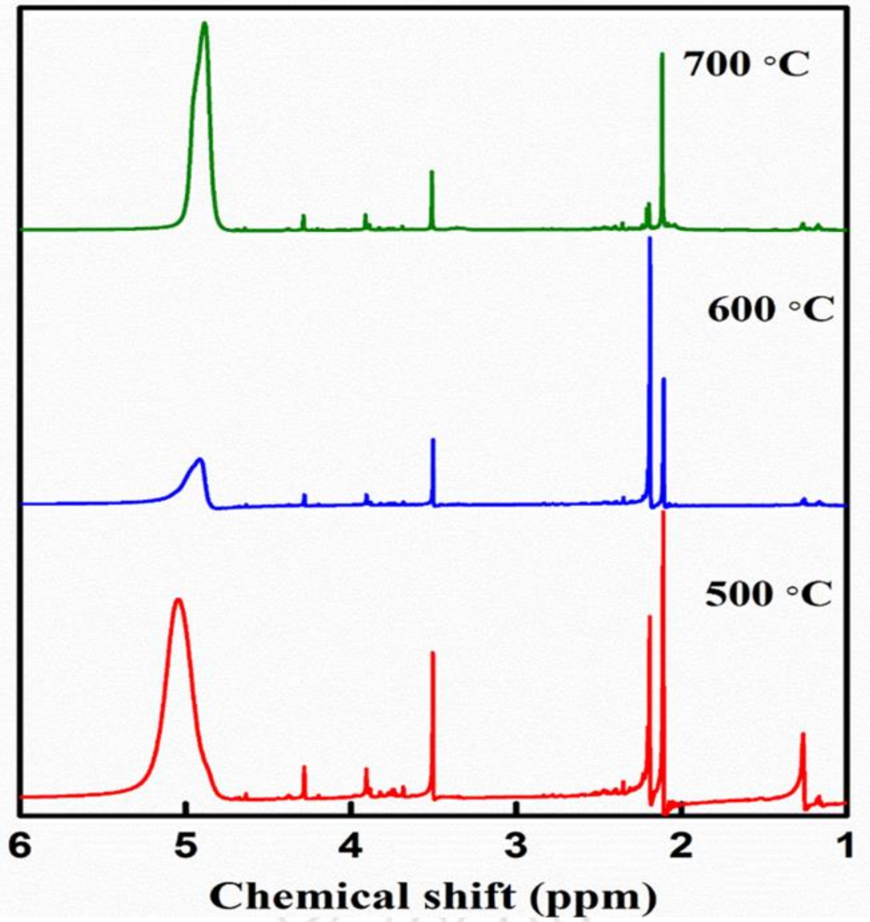

Figure 5.4. Proton NMR representation of the bio-oils obtained at 500 °C, 600 °C, and 700 °C.

Table 5.7. Hydrogen percentage at various temperatures in bio-oil samples by ^{1}H NMR.

Chemical Shift range (ppm)	Proton Assignments	500 °C (% H)	600 °C (% H)	700 °C (% H)
0.5-1.5	Alkanes (C-H)	3.9	2.5	6.9
1.5-3.0	Aliphatic	10	20.5	5.0
1.0-5.0	Alcohol (OH)	62	53	73
4.5-6.0	Alkenes (C=C)	18	13.5	9

5.A.4 Bio-char Properties

Table 5.2 presented the yield of biochar obtained after the pyrolysis of biomass feedstock (DR) at three different temperatures with possible percentage difference by three repetition experiments for each temperature; and found that it is slightly decreasing with increasing the temperature. It is around 35 wt. % at 500 °C, then reduced to approximately 33 wt. % at 600 °C and finally it is 31 wt. % at 700 °C. Table 5.3 presented the ultimate elemental analysis of bio-char obtained by pyrolysis of DR at three different temperatures and their HHV obtained by the Dulong formula [117]. The HHV of bio-char is found to be almost unaffected by increasing the pyrolysis temperature and it is approximately 36 MJ/kg. These results indicated that the temperature does not affect the biochar much in the perspective of HHV.

The X-ray Diffraction (XRD) pattern of biomass and its pyrolytic bio-char at three different temperatures presented in Figure 5.5. From the XRD graph, the biomass sample found to possess a crystalline structure at the 2θ value of 22.76°, 35° and 44°. From the literature data, the XRD peak at 22.76° corresponds to cellulose and peak at 44° matches to hexagonal ring structure present in biomass [130,131]. The effect of temperature apparent through the amorphous nature of the bio-chars is in decreasing order with the decreasing temperature, i.e., applying increased temperature producing slightly crystalline bio-char. From this particular study, it is clear that the biomass has its crystalline structure which is then breaking down at 500 °C and again at 600 °C the bio-char is gaining crystallinity, which is then increased further by increasing temperature to 700 °C. Thus, bio-chars are amorphous at lower pyrolytic temperatures, and crystalline at higher pyrolytic temperatures. These bio-chars can be considered as activated charcoal, which can be useful for carbon sequestration, contaminant remediation, and environmental sorbents after proper activation treatments [132,133].

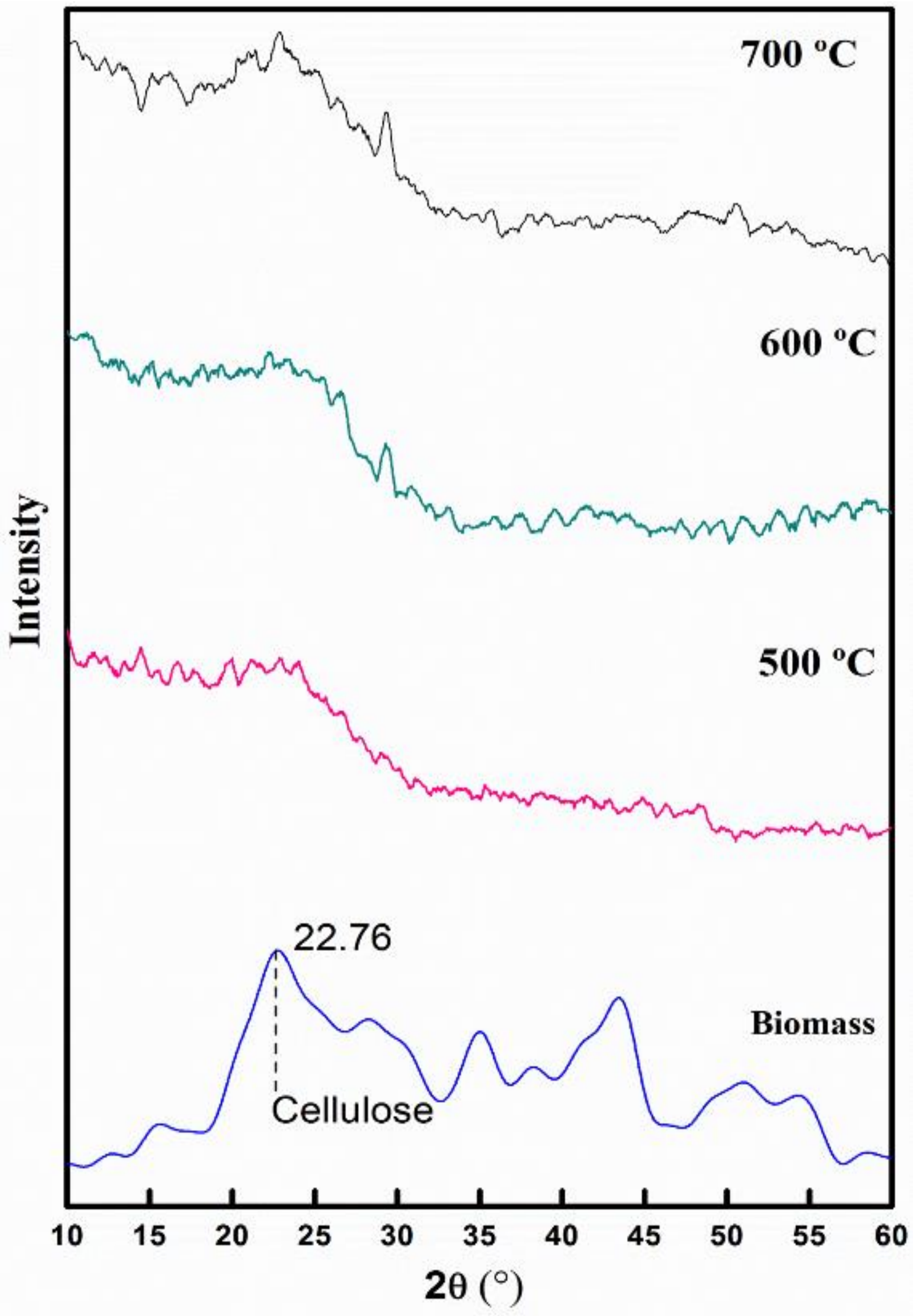

Figure 5.5. XRD diffractogram of DR biomass and respective bio-chars from 500 °C, 600 °C, and 700 °C.

5.A.5 Summary

Pyrolysis of a rarely researched biomass, *Delonix Regia*, has been conducted in a tubular reactor. The effects of pyrolysis temperature on physicochemical and fuel properties along with yield and functional variations of bio-oil compositions have been established over a range of 500 - 700 °C. The weight % of the bio-oil obtained from *DR* biomass feedstock is ranging between 31.52 - 37.84 % following mixed trends with the pyrolysis temperature, whereas the weight % of biochar decreased from 34.75 % to 30.65 % with the increasing temperature. The higher heating value of the bio-oil is ranging between 20.88 - 25.70 MJ/kg, indicating an increase in HHV values with the increasing pyrolysis temperature from 500 °C to 700 °C. The HHV of biochar is approximately 36 MJ/kg and is unaffected by the present range of pyrolysis temperature. The pH of bio-oil has shown a slight increase in acidity of bio-oil with the increasing pyrolysis temperature though the scale is limited to 3.3 - 3.4. The density and viscosity of the bio-oil found to be decreasing with the increasing pyrolysis temperature. Bio-oils produced at processed temperatures showed a number of functional groups as given by FTIR and detailed list of aromatics, aliphatic, etc. presented based on the GCMS analysis. The bio-oil displayed a broad spectrum of organics such as alkanes, alkenes, ketones, aldehydes, aromatics, esters, ethers, etc. However, the benzene fraction is found to be the highest among other compounds with 14.6 area % at 600 ºC and phenol fraction, phenol, 2,6-dimethoxy (Syringol) is found to be the second-largest area % occupying compound with 10.5 area % according to present GCMS results. Proton NMR confirmed the manifestation of the functional groups and different compounds. XRD showed the amorphous nature of bio-char at 500 °C and upsurge in crystallinity with the increasing temperature.

5.B. Non-catalytic, Catalytic, and Hydropyrolysis of Delonix Regia

5.B.1 Properties of Biomass

The elemental analysis of DR biomass is given in Table 5.8, and its proximate analysis with calorific value is shown in Table 5.9. From Table 5.8, the H/C ratio of biomass is calculated, and the biomass has H/C ratio of 1.56 which is slightly greater than coal (H/C of coal ranges between 1 – 1.4) and smaller than gasoline (H/C of gasoline is 1.8). This ratio signifies that the taken biomass for research has a good fuel property and will produce more numbers of hydrocarbons. From Table 5.9, CV represents the gross calorific value as the biomass is dried completely before the experiment and the higher heating value of 16.83 MJ/kg defines the capability of this biomass as a reliable source for biofuels production. Jenkins et al. [13] reviewed some biomasses of similar calorific value on which pyrolysis research is already done and they are alfalfa stems (18.67 MJ/kg), wheat straw (17.94 MJ/kg), rice straw (15.09 MJ/kg), sugarcane bagasse (18.99 MJ/kg), willow wood (19.59 MJ/kg), hybrid poplar (19.02 MJ/kg). A few biomasses are also researched by Demirbas [134] and found their HHV as softwood (20 MJ/kg), hardwood (18.8 MJ/kg), tea waste (17.1 MJ/kg), beech wood (19.2 MJ/kg), tobacco stalk (17.7 MJ/kg). Thus, in comparison to these literature values, the DR biomass could be treated as a great resource to produce a better pyrolytic bio-oil.

Table 5.8. Ultimate analysis of *Delonix Regia* biomass in mass % on dry basis.

Carbon	Hydrogen	Nitrogen	Oxygen[a]
45.43	5.95	1.25	47.37

[a]:calculated by the difference.

Table 5.9. Proximate analysis and CV of *Delonix Regia* biomass on mass % (dry basis).

Moisture (%)	Volatiles (%)	Ash Content (%)	Fixed Carbon (%)[b]	CV (MJ/kg)
9	72.2	1.2	17.6	16.83

[b]:calculated by the difference.

5.B.2 Catalyst Properties

The zeolite catalyst used in this study has some special properties according to its product specification and chemical properties which are presented in Table 5.10. The catalyst used has a high surface area of 900 m^2/g with silica to alumina ratio of 5.1:1. This catalyst provides Bronsted acid sites which donate protons and thus reduce oxygenates in the product stream. To make a compatible catalytic process for deoxygenation reaction in product line the zeolite, Y sodium is very much useful in current study.

Table 5.10. Properties of zeolite catalyst.

Catalyst	SiO_2:Al_2O_3	Arrangement	Na_2O (wt. %)	Surface Area (m^2/g)	Make
Zeolite Y, Sodium	5.1:1	Na^+	13	900	Alfa Aesar

5.B.3 Distribution of Pyrolysis Products and their Properties

This study on pyrolysis of particular biomass, *Delonix Regia*, reports the catalytic cracking of pyrolysis vapours at 600 °C, over a zeolite Y, sodium alongside the non-catalytic and hydropyrolysis at 600 ºC. This particular temperature is chosen for all the experiments in this case with constant pressure of 1 bar to understand the effect of various atmospheres over qualitative and quantitative product variation. The catalyst activity increases the product yield due to the high conversion rate of the catalyst and decreases the oxygenated compounds by converting heavy fractions of oxygen into carbon monoxide, carbon dioxide, and water content. The product distribution of pyrolysis products is given in Table 5.11 from which it can be seen that the yield of bio-oil is 37.83 % by catalytic and hydropyrolysis, whereas it is 33.52 % by non-catalytic pyrolysis, i.e. the catalytic activity is increasing bio-oil yield. The calorific value of bio-oil is in increasing order as non-catalytic pyrolysis < catalytic pyrolysis < hydropyrolysis, i.e., 16.5 MJ/kg, 18.14 MJ/kg and 20.65 MJ/kg respectively, thus, the catalyst is responsible for increasing CV of bio-oil. On the other hand, pH is decreasing, i.e. acidity is increasing in the same order (see Table 5.11). The trends shown here by the pyrolytic oil are qualitatively similar to the other studies reported in the literature [135,136].

Table 5.11. Distribution of pyrolytic products obtained by pyrolysis of DR in three different reaction atmospheres and their properties.

Pyrolysis	Bio-oil (wt. %)	CV of bio-oil (MJ/kg)	pH of bio-oil	Bio-char (wt. %)	CV of bio-char (MJ/kg)
Non-catalytic	33.52	16.5	3.32	33.35	29.22
Catalytic	37.83	18.14	3.30	36.48	22.45
Catalytic hydro	37.83	20.65	3.25	34.03	24.28

Apart from this, bio-char shows a mixed trend having a yield of 33.35 wt.% at the non-catalytic condition, which has a calorific value of 29.22 MJ/kg and contributing as blackish charcoal. But the bio-char obtained by catalytic pyrolysis contains coke [66,70] along with spent catalyst which eventually decreases the calorific value of biochar. This spent catalyst can be recovered from biochar by calcination at 600 °C - 800 °C in a furnace for 3 – 4 hours. The calcination will result in activated bio-char and regenerated catalyst for further purposes. Additionally, its physical appearance is not same as in the one obtained by non-catalytic pyrolysis, but brownish because of the presence of spent catalyst. The biochar yield in the catalytic pyrolysis case is increased than that of non-catalytic pyrolysis, i.e., it is 36.48 wt. % having a calorific value of 22.45 MJ/kg which is substantially lower than of the bio-char obtained by non-catalytic pyrolysis. In catalytic hydropyrolysis case, the yield is decreased than that of catalytic case, i.e., 34.03 wt. % but with an increased calorific value of 24.28 MJ/kg compared to catalytic pyrolysis and decreased CV compared to bio-char obtained by non-catalytic pyrolysis. This difference in both the catalytic processes is because of the hydrogen used in hydropyrolysis which reduces coke formation but increases hydrocarbon amount in the final products. The basic chemistry between Sodium, Y zeolite and hydrogen is responsible for getting high calorific value bio-oil even though the reaction is carried out at atmospheric pressure. This catalyst has more numbers of Bronsted acid sites than that of Lewis acid sites thus in the catalytic pyrolysis experiments proton is donated and the process which is occurring at the very moment is called as protonation of hydrocarbons. Whilst in catalytic hydropyrolysis when hydrogen is introduced in reaction, the Sodium, Y zeolite slightly changes its form where hydrogen replaces sodium to give H, Y zeolite but the extent of this exchange of hydrogen over sodium is much lesser and can be neglected. Thus, it affects the quality of product to give high calorific value bio-oil. The effect of change in operating atmosphere also shows mixed trends of the non-condensable gas production because of aforementioned reasons. Figure 5.6 gives overall product distribution of all three cases. Thus, from this product outline, it can be observed that the hydropyrolysis is most suitable process for conversion of biomass into biofuels which results in higher calorific value products. Though the hydrogen is costly the best alternative is to use bio-hydrogen which is obtained by thermal degradation of biomass using pressure swing adsorption.

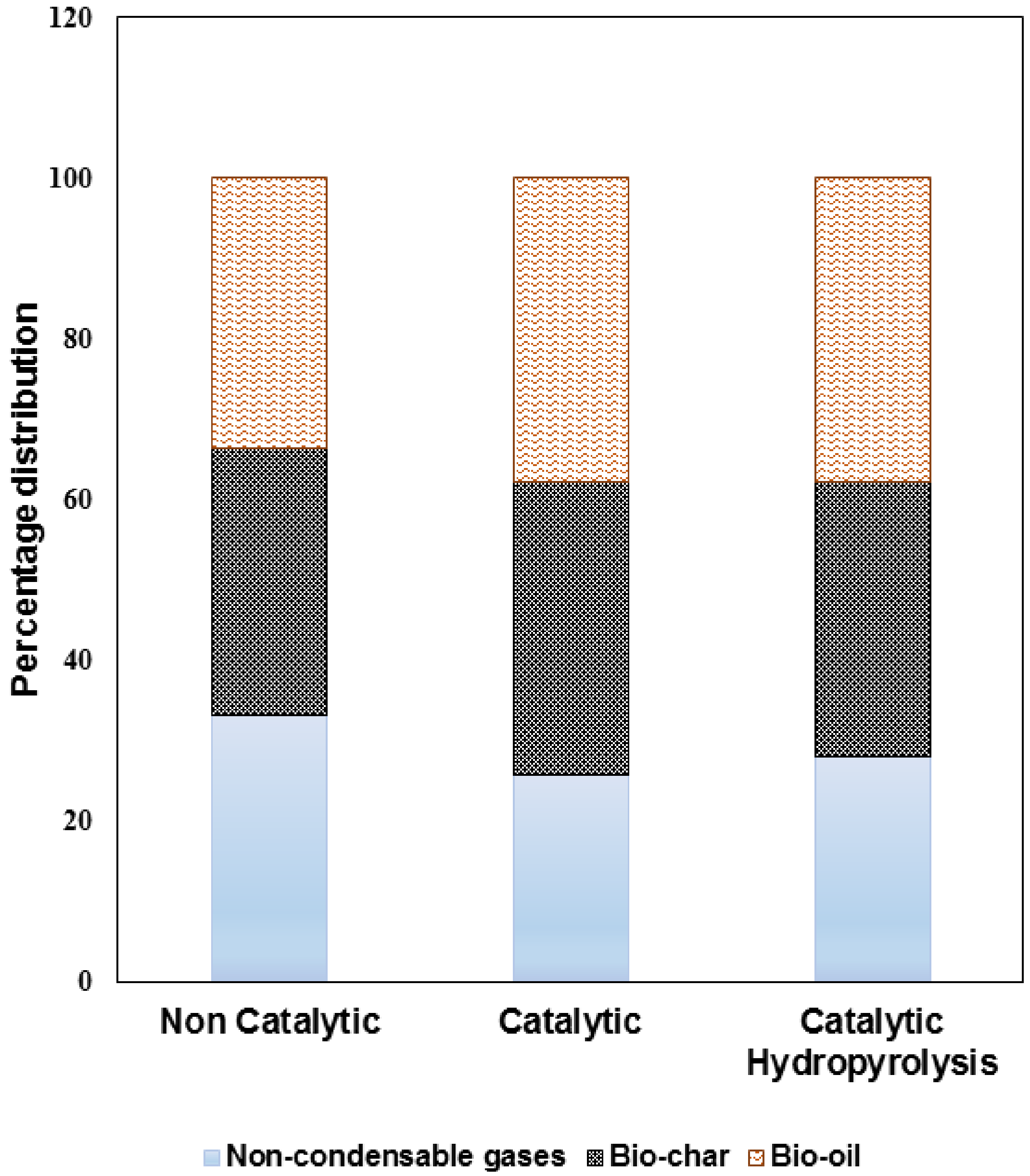

Figure 5.6. Distribution of pyrolytic products (in mass %) obtained by pyrolysis of *Delonix Regia* biomass in three different reaction atmospheres.

5.B.4 Qualitative Analysis of Bio-oil

The bio-oil samples are then subjected to the FTIR analysis. Figure 5.7 shows the variation in functional groups over different types of pyrolysis atmosphere, viz. non-catalytic, catalytic and hydropyrolysis and Table 5.12 gives the corresponding detailed information of the group of compounds associated with each functional group at each peak. The wave numbers 3738.86, 3365.96 and 3355.8 cm^{-1} represents O-H stretching with strong interaction, which can contribute to water impurities and more likely due to higher contents of phenols present in the bio-oil.

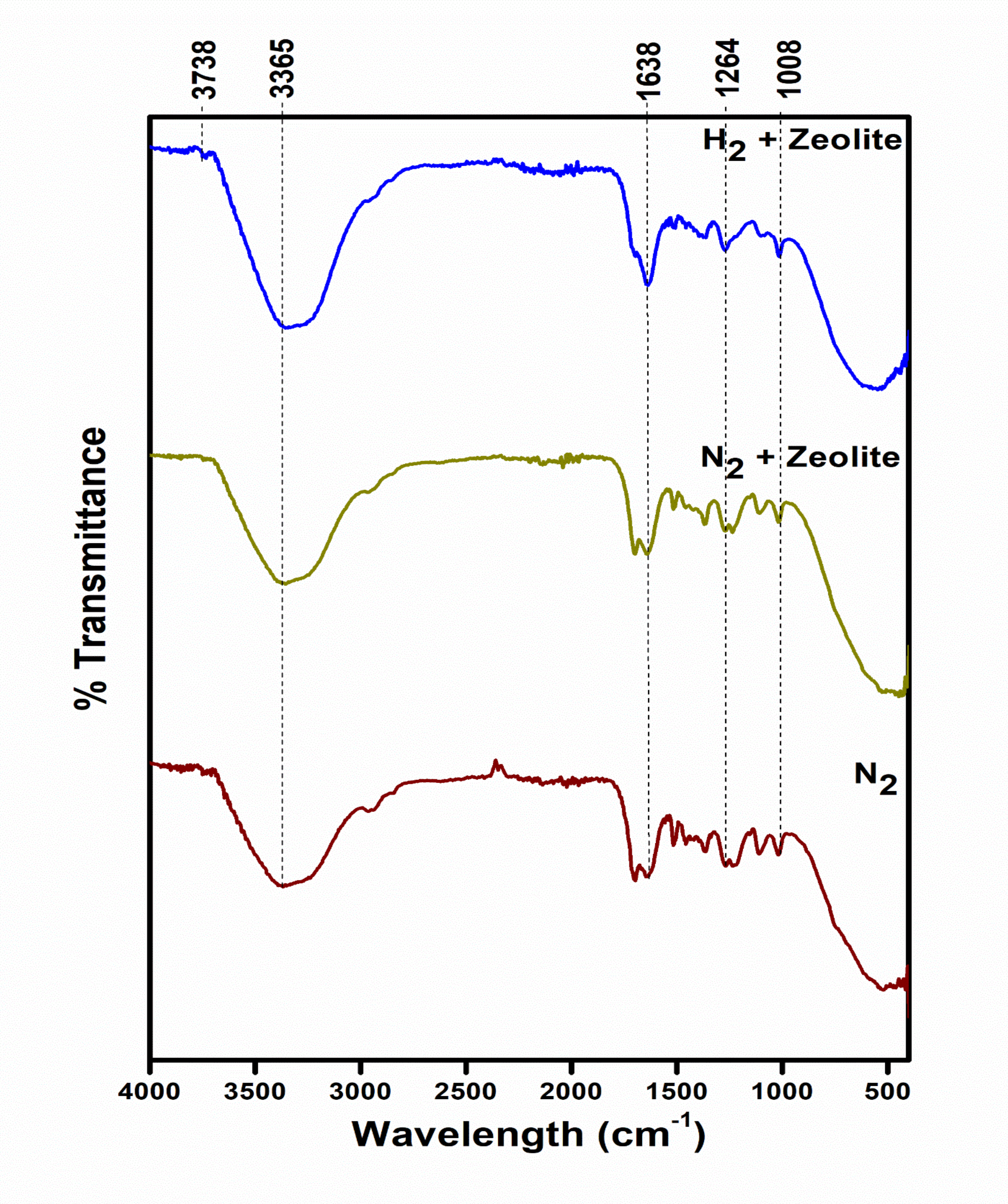

Figure 5.7. FTIR analysis of three different bio-oils showing the variation in functional groups over the reaction atmosphere.

Table 5.12. Variation of functional groups present in each case based on FT-IR analysis of all three bio-oils.

Non-catalytic	Catalytic	Catalytic hydropyrolysis	Wave number (cm^{-1})	Group	Class of compound
3738.86, 3365.96	3365.96	3355.8	3750-3100	O-H stretching	Polymeric O-H, water impurities
2943.26	-	-	3000-2800	C-H stretching	Alkanes
1697.54	1697.54	1697.54	1761-1676	C=O stretching	Ketones, aldehydes, carboxylic acids
1638.61	1638.61	1638.61	1670-1550	C=C stretching	Alkenes
1510.58	1510.58	1500.42	1515-1490	-	Benzene ring in aromatic compounds
1451.65	-	-	1465-1440	CH$_3$	In Aliphatic compounds
1353.09	1363.25	-	1400-1300	C-H stretching	Alkanes
1264.69	1264.69	1274.85	1280-1150	C-O-C	Esters
1226.07, 1108.21	1236.24, 1108.21	-	1240-1070	C-O-C	Ethers
1009.65	1009.65	1009.65	1020-950	C-O stretching O-H bending	Primary, Secondary, Tertiary alcohols, Phenol, Ester and Ether
754.61	-	-	900-650	-	o-Benzenes

Non-catalytic pyrolysis bio-oil consists more no. of functional groups which are likely to exist because of the presence of a large number of oxygenated compounds in it. At 2943.26 cm^{-1}**,** peak indicates C-H stretching due to alkanes group whereas at 1451.65 cm^{-1} it represents –CH$_3$ group of aliphatic compounds and at 754.61 cm^{-1} it is of an o-benzenes class of compound. Catalytic pyrolysis bio-oil contains a little less number of functional groups than that of non-catalytic pyrolysis oil. C-H stretching of alkanes at 1363.25 cm^{-1} in the catalytic atmosphere is in the place of 2943.26 cm^{-1} peaks in non-catalytic case. Similarly,1236.24 and 1108.21 cm^{-1} in the catalytic atmosphere and 1226.07 and 1108.21 cm^{-1} in the non-catalytic atmosphere represents C-O-C group of ethers with very strong interaction. The catalytic hydropyrolysis bio-oil contains further less number of functional groups than that of non-catalytic and catalytic pyrolysis bio-oil samples. The common groups present in all three cases are as follows: (a) 1697.54 cm^{-1} attributes C=O stretching of carboxylic acids, ketones and aldehydes, (b) 1638.61 cm^{-1} due to C=C stretch with strong interaction representing alkenes, (c) 1510.58 cm^{-1} in catalytic and non-catalytic condition and 1500.42 cm^{-1} in catalytic hydropyrolysis condition represents the benzene ring of aromatic compounds, (d) 1264.69 and 1274.85 cm^{-1} represents string interaction of C-O-C ester group, (e) the common group of C-O stretching and O-H bending of primary, secondary, tertiary alcohols, phenol, ester, and ether is present in all the cases at 1009.65 cm^{-1}. Thus, from this FT-IR results, it can be elaborated that the bio-oil in catalytic hydropyrolysis suppresses a few functional groups which are responsible for the degradation of bio-oil quality. Finally, it is not an exaggeration to state that the hydropyrolysis is a refined approach to obtain better quality fuel from biomass. A few similar studies [137–139] on biomass pyrolysis reported the trends of bio-oil functional groups, which are reported in the present study.

Figure 5.8 represents the GCMS peak intensities of each type of pyrolysis bio-oil of the present study, and it can be seen that the chromatogram shows peaks at same retention time but the intensity of peak is in increasing order of non-catalytic < catalytic < hydropyrolysis. There are thirteen common compounds which are present in the bio-oil of three types of researched cases, as shown in Table 5.13. These are 1,2-Propandiol, 2-acetate; Phenol; p-Cresol; 2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-; Catechol; 1,2-Benzenediol, 3-methoxy-; Ethanone, 1-(2-hydroxy-5-methylphenyl)-; 1,2,4 – Trimethoxybenzene; Apocynin; 4-Ethylbiphenyl; 2-Propenone, 1-(4-hydroxy-3-methoxyphenyl)-; Phenol, 2,6-dimethoxy-4-(2-propenyl)-; Benzene, 1,1'-propylidenebis. Among the verified compounds, the major components present in non-catalytic pyrolysis with more than 3 area % of the total area are viz. 1,2,4-Trimethoxybenzene (4.59), 4-Ethylbiphenyl (4.72), Pilocarpine (3.96), 1,2-Benzenediol, 3-methoxy- (3.25), Phenol, 2,6-dimethoxy- (10.59) showing highest area %. The compounds present at area more than 3 area % in catalytic bio-oil are Phenol, 2,6-dimethoxy- (7.68), 1,2-Propandiol, 2-acetate (3.51), Furfural (3.78), Phenol, 2-methoxy- (3.51), 1,2,4-Trimethoxybenzene (3.05), 4-Ethylbiphenyl (3.03). The bio-oil from catalytic hydropyrolysis process exclusively contains value-added model compounds such as Mequinol (3.7 %), 2-

Methoxy-5-methylphenol (Isocreosol-2.23 %), Catechol (4.38 %), Resorcinol (1.81 %), 1,2-Benzenediol, 3-methoxy- (6.3 %), at highest area percentage it contains, 4-Ethylbiphenyl (6.47 %), Phenol, 2,6-dimethoxy-, acetate (14.69 %), 1,2,4-Trimethoxybenzene (6.78 %), Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- (4 %) are a few amongst other compounds present with more than 3 area %. On the other hand, some other chemicals follow a different trend of percentage present in bio-oil, which is, catalytic < non-catalytic < hydropyrolysis. These are, 2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-; Catechol; 1,2-Benzenediol, 3-methoxy-; 1,2,4-Trimethoxybenzene; Apocynin; 4-Ethylbiphenyl; 2-Propenone, 1-(4-hydroxy-3-methoxyphenyl)-; and Benzene, 1,1'-propylidenebis-. Agblevor et al. [66] conducted fractional catalytic pyrolysis of hybrid poplar wood and found similar aromatic hydrocarbons. The results are also comparable with the catalytic flash pyrolysis of biomass using different types of zeolite studied by Imran et al. [29] where zeolite, Y sodium showed a similar type of significant amount of deoxygenation which converts secondary pyrolysis vapours in gas form and reduces the number of undesirable ketones and aldehydes.

Table 5.14 is showing the classification of compounds present in all three cases of bio-oils based on the performed GC-MS analysis and obtained results with the help of the NIST library. The area % is taken from Table 5.13 by the functional classification of groups of compounds based on the possibilities of their existence. From Table 5.14, it can be seen that the amount of acids is increasing in catalytic pyrolysis and then in hydropyrolysis and it is happening so because of the acid sites of the catalyst leading to the protonation of hydrocarbons present in the vapour phase before condensation. Furans are in the stable zone to indicate the basic formulation of the biomass-derived bio-oil. Aldehydes are showing mix trends, one possibility of the hydropyrolysis reaction is that the catalyst H^+ ions may be responsible here for Claisen - Schmidt condensation reaction. The area % of phenols shows that the lignin degradation is decreasing by employing catalyst in the catalytic pyrolysis reaction, but again increasing by introducing hydrogen in hydropyrolysis reaction. Similarly, the class of other aromatics represents the degradation of cellulose, which is decreasing in catalytic pyrolysis and increasing in hydropyrolysis. The overall unidentified compounds of bio-oil can also contribute to the mentioned classes of Table 5.14. This particular classification throws the light on the bio-oils composition by explaining its chemistry, and to use this particular biomass for bio-oil production as a new renewable energy source.

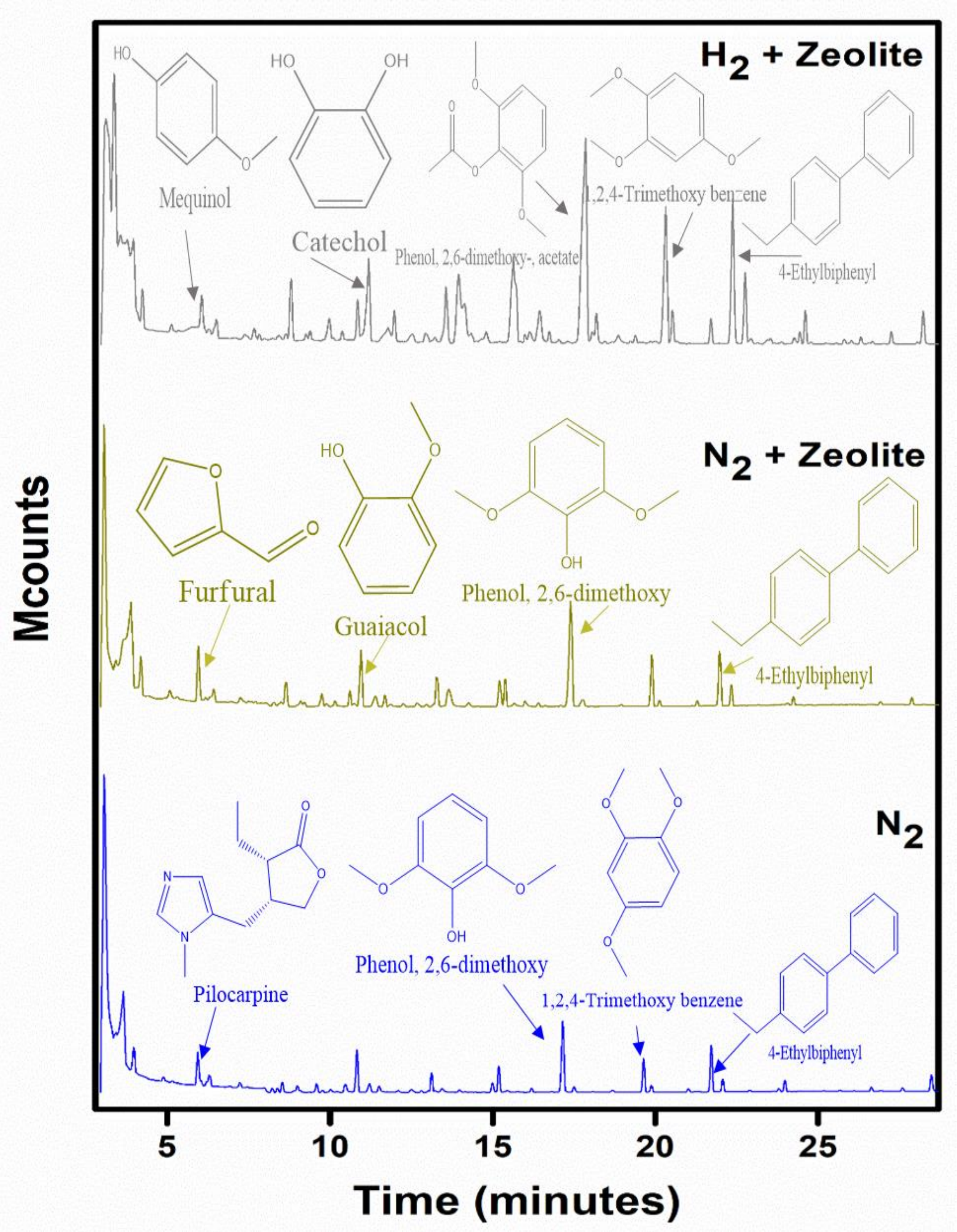

Figure 5.8. The GCMS intensity difference of three pyrolytic bio-oils showing variation in plausible hydrocarbons in N_2, N_2 + Zeolite, H_2 + Zeolite atmospheres.

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Table 5.13. GC-MS verified compounds majorly present in bio-oils obtained from pyrolysis of DR under three different atmospheres.

Compound Name	Molecular Mass	Chemical formula	N_2		N_2 + Zeolite		H_2 + Zeolite	
			Retention time (min.)	Area (%)	Retention time (min.)	Area (%)	Retention time (min.)	Area (%)
1,2-Propandiol, 2-acetate	118	$C_5H_{10}O_3$	3.97	1.23	4.18	3.5	4.07	1.65
Acetohydroxamic acid	75	$C_2H_5NO_2$	4.93	0.25	-	-	4.22	1.13
Propane-1, 1-diol diacetate	160	$C_7H_{12}O_4$	-	-	5.08	0.59	-	-
Pilocarpine	208	$C_{11}H_{16}N_2O_2$	5.93	3.96	-	-	6.02	1.29
Furfural	96	$C_5H_4O_2$	-	-	5.95	3.7	-	-
3-Furanmethanol	98	$C_5H_6O_2$	-	-	6.23	2.2	-	-
Furan, 2-ethyl-5-methyl-	110	$C_7H_{10}O$	-	-	7.23	0.84	-	-
2-Furancarboxyaldehyde, 5-methyl-	110	$C_6H_6O_2$	8.22	0.25	8.25	0.23	-	-
Furyl hydroxymethyl ketone	126	$C_6H_6O_3$	8.4	0.56	-	-	-	-
2,4-Dimethylfuran	96	C_6H_8O	-	-	8.45	0.3	-	-
Phenol	94	$C_6H_6O_2$	8.54	1.36	8.60	1.4	8.60	2.15
p-Cresol	108	C_7H_8O	10.47	1.64	10.52	0.9	10.57	1.29
Phenol, 2-methoxy- (Guaiacol)	124	$C_7H_8O_2$	10.81	0.63	10.85	3.51	-	-
Mequinol	124	$C_7H_8O_2$	-	-	-	-	10.9	3.71
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	126	$C_7H_{10}O_2$	11.51	0.81	11.56	0.59	11.64	0.89
Creosol	138	$C_8H_{10}O_2$	12.80	0.49	12.82	0.13	-	-
Creosol	138	$C_8H_{10}O_2$	13.13	2.10	13.13	1.76	-	-
2-Methoxy-5-methylphenol	138	$C_8H_{10}O_2$	-	-	-	-	13.17	2.23
Phenol, 2,3-dimethyl-	122	$C_8H_{10}O$	-	-	13.23	0.84	-	-
Catechol	110	$C_6H_6O_2$	13.45	2.76	13.50	1.79	13.55	4.38

Resorcinol	110	$C_6H_6O_2$	-	-	-	-	13.72	1.81
2-Methyl-4-pentenoic acid	114	$C_6H_{10}O_2$	-	-	-	-	14.38	0.35
1,2-Benzenediol, 3-methoxy-	140	$C_7H_8O_3$	14.98	3.25	15.04	1.57	15.17	6.30
Phenol, 4-ethyl-2-methoxy-	152	$C_9H_{12}O_2$	15.18	1.95	15.21	1.53	-	-
3,4-Dihydroxyacetophenone	152	$C_8H_8O_3$	15.49	1.59	-	-	-	-
Resorcinol	110	$C_6H_6O_2$	-	-	-	-	15.66	0.41
1,2-Benzenediol, 3-methyl-	124	$C_7H_8O_2$	-	-	15.82	0.42	15.96	1.80
Ethanone, 1-(2-hydroxy-5-methylphenyl)-	150	$C_9H_{10}O_2$	16.21	0.42	16.22	0.19	16.24	0.36
3-Methoxy-5-methylphenol	138	$C_8H_{10}O_2$	-	-	16.43	0.35	-	-
Phenol, 2,6-dimethoxy-	154	$C_8H_{10}O_3$	17.14	10.59	17.20	7.68	-	-
Phenol, 2,6-dimethoxy-, acetate	196	$C_{10}H_{12}O_4$	-	-	-	-	17.34	14.69
Phenol, 3,4-dimethoxy-	154	$C_8H_{10}O_3$	-	-	17.55	0.53	17.66	0.71
1,2,4 - Trimethoxybenzene	168	$C_9H_{12}O_3$	19.62	4.59	19.66	3.05	19.76	6.78
Phenol-2-methoxy-6-(2-propenyl)-	164	$C_{10}H_{12}O_2$	-	-	19.90	0.31	-	-
Phenol-2-methoxy-4-(1-propenyl)-, (Z)-	164	$C_{10}H_{12}O_2$	19.90	1.13	-	-	-	-
Apocynin	166	$C_9H_{10}O_3$	21.02	0.47	21.06	0.27	21.13	0.90
4-Ethylbiphenyl	182	$C_{14}H_{14}$	21.72	4.72	21.74	3.03	21.80	6.47
2-Propenone, 1-(4-hydroxy-3-methoxyphenyl)-	180	$C_{10}H_{12}O_3$	22.07	1.18	22.10	1.12	22.12	2.74
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	194	$C_{11}H_{14}O_3$	23.79	0.55	23.81	0.08	23.84	0.36
Benzene, 1,1'-propylidenebis-	196	$C_{15}H_{16}$	23.97	0.79	23.99	0.42	24.01	1.14
Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	182	$C_9H_{10}O_4$	25.70	0.98	-	-	-	-

Phenol, 2,6-dimethoxy-4-(2-propenyl)-	194	$C_{11}H_{14}O_3$	26.65	0.67	26.65	0.13	26.66	0.44
[1,1'-Biphenyl]-3,3'-diol	186	$C_{12}H_{10}O_2$	-	-	-	-	27.46	1.27
Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	196	$C_{10}H_{12}O_4$	27.59	2.14	-	-	27.64	4.00
Carbazole	167	$C_{12}H_9N$	-	-	28.50	1.46	-	-

Table 5.14. Class of compounds present (in area %) in all three bio-oils based on GC-MS analysis.

Class of Compound	Non-catalytic Pyrolysis	Catalytic Pyrolysis	Catalytic Hydropyrolysis
Acids	1.48	3.5	3.13
Aliphatics	0.81	1.18	0.89
Furans	4.77	3.57	1.29
Aldehydes	0.98	3.7	-
Phenols	36.34	26.45	53.61
Other Aromatics	6.69	6.04	10.35
Others	48.93	55.55	30.73

Thus, from above results, it is clear that the bio-oil obtained through non-catalytic condition contains more oxygenated compounds than that of catalytic bio-oil and the chemicals obtained through GC-MS analysis confirms the possibilities of functional groups suggested by FT-IR. The major conclusion from this result is that the pyrolytic vapours of DR biomass pyrolysis are partially upgraded (in terms of partial deoxygenation by hydrotreatment) by the catalytic activity in the presence of hydrogen as reacting medium. The upgraded bio-oil hence has less phenolic compounds, and the bio-oil from hydropyrolysis is rich in aromatic hydrocarbons which eventually increases the energy value of the bio-oil.

The positioning of hydrogen attached to a particular group is described by ^{1}H NMR as a structural analysis of a compound and it is shown here in Figure 5.9 for all three bio-oil samples obtained by non-catalytic, catalytic, and hydropyrolysis. From the figure, it can be seen that the bio-oil in each case consists the same group over the described range of chemical shift, but the percentage of proton assignment differs in the order of non-catalytic < catalytic < hydropyrolysis. All bio-oil samples containing proton assignments at a given chemical shift range in ppm are discussed here. From 0.5 to 1.5 ppm bio-oil consists of alkane (C-H) group, at 2.5 ppm it contains alkyne (C≡H) proton assignment from 1.5 to 3.0 ppm it contains aliphatic hydrocarbon assignment. Further, the bio-oils contain alcoholic proton assignments in the chemical shift range of 3.0 to 4.4 ppm; they also include lignin-derived methoxyphenols in the range of 4.4 to 6.0 ppm. Aromatics such as benzene are identified in the range of 6.0 to 8.5 ppm and the region of 9.0 to 10.0 ppm comprises aldehyde (-CHO) assignments as well as carboxylic acids. From the proton NMR data analysis, it is found that the proton assignments present in all bio-oil samples eventually confirms the results shown by the FT-IR and GC-MS analysis and also in accordance with Mullen et al. [128] who performed catalytic fast pyrolysis of white oak wood in a fluidized bed reactor. However, the intensity of peaks at 7 – 8 ppm and 2 – 2.5 ppm decreased in the order of non-catalytic, catalytic, and hydropyrolysis. Further, the intensity of various peaks in the case of hydropyrolysis substantially increased compared to their catalytic counterparts except at 0 – 0.5 ppm chemical shift.

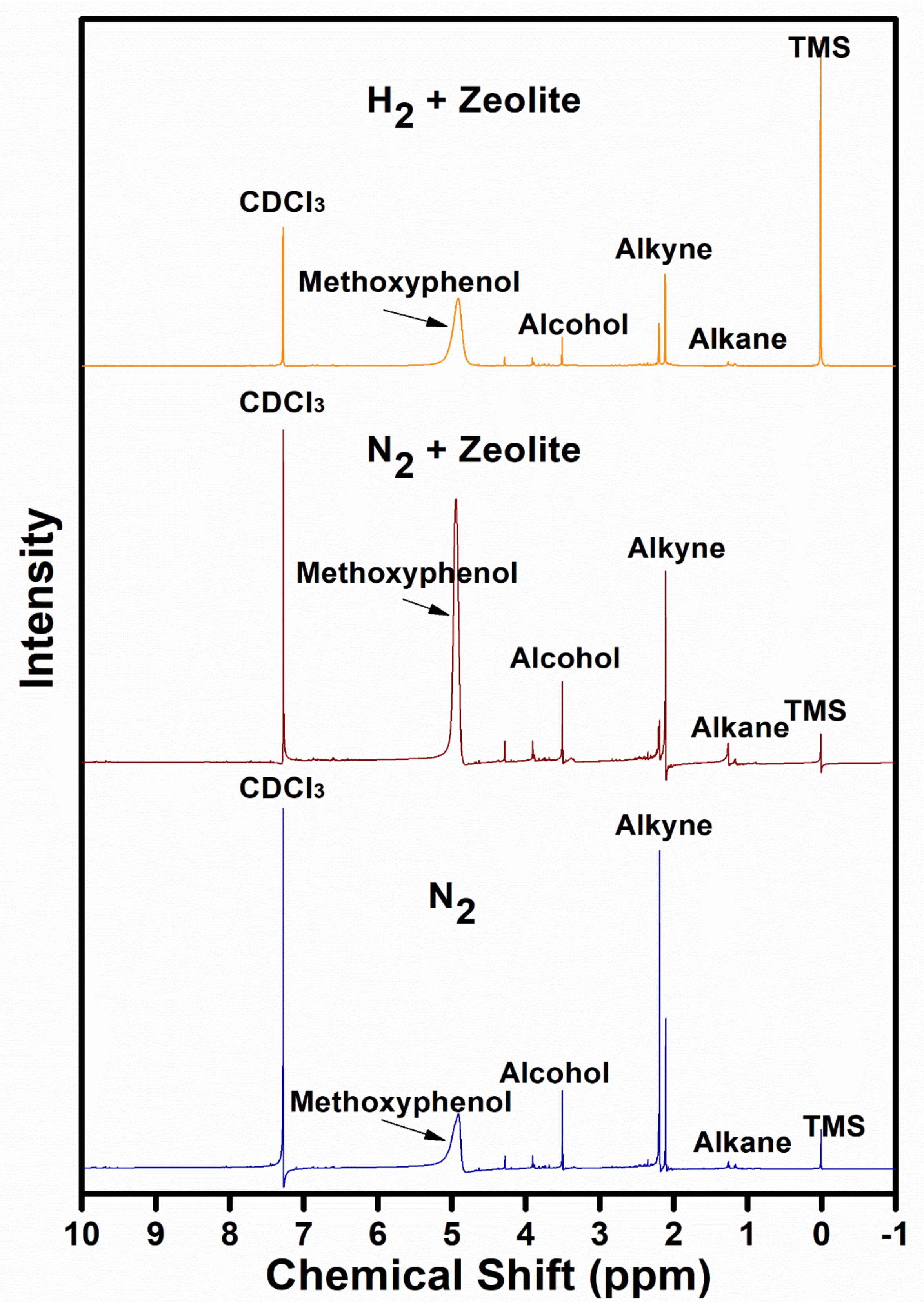

Figure 5.9. ^{1}H NMR spectra of three different bio-oils for comparative study of three pyrolysis atmospheres.

5.B.5 XRD of Biomass and Bio-char

Figure 5.10 represents XRD patterns of raw biomass and biochar obtained by each case viz. non-catalytic, catalytic, and hydropyrolysis of DR biomass at 600°C and 1 bar pressure in a tubular reactor. Raw biomass showing a peak at the 2θ value of 22.89° represents the cellulose, and 44° represents a hexagonal ring structure of the biomass material [131]. However, after pyrolysis, biomass crystallinity breaks down and shows amorphous nature to represent the carbonized structure of biochar from non-catalytic pyrolysis. Even though the crystal structure of the biochar is distorted, it shows the peaks of zeolite in each catalytic case. Both the cases, i.e., catalytic pyrolysis and hydropyrolysis, these are showing the presence of zeolite Y, sodium in high intensity. In catalytic pyrolysis, the peak at a 2θ value of 23° represents the structure of Faujasite, and the complete XRD pattern signifies Faujasite framework [29,140]. In catalytic hydropyrolysis, though the pattern differs by showing the highest peak at a 2θ value of 17° which represents an alteration in crystal structure due to hydrogen atmosphere, i.e., zeolite Y, sodium is actually a Faujasite framework only. In general, this Faujasite framework of zeolite Y, sodium is used for catalytic cracking of crude petroleum vapours into high-grade gasoline product.

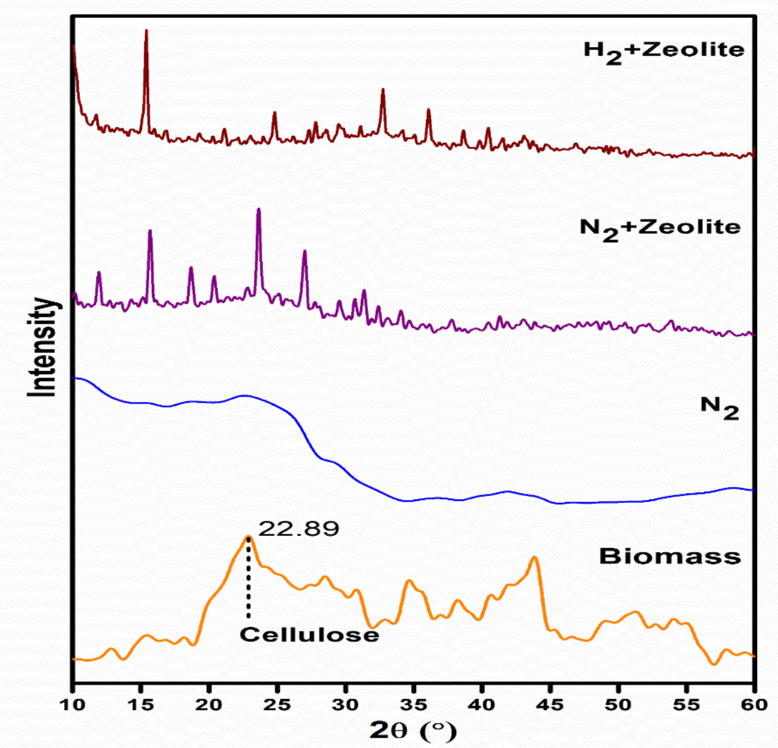

Figure 5.10. X-ray diffractogram of DR biomass and biochars obtained by its pyrolysis in three different reaction atmospheres.

5.B.6 Summary

The catalytic pyrolysis and hydro-pyrolysis of a rarely researched biomass, *Delonix Regia* (DR), resulted a yield of 37.83 mass % bio-oils having a calorific value of 18.14 MJ/kg and 20.65 MJ/kg, respectively, whereas the bio-oil yield by non-catalytic pyrolysis is 33.52 mass % with HHV of 16.50 MJ/kg. FTIR results indicated that the number of bio-oil functional groups decreased from non-catalytic to catalytic, followed by hydro-pyrolysis at identical temperature and pressure conditions. GCMS results depicted several peaks at the same retention time for all three types of bio-oils of the present study. However, the peak intensities increased gradually as the pyrolysis type changed from non-catalytic to catalytic, followed by hydro-pyrolysis maintaining rest all conditions the same. It is also found from GCMS that a greater number of value-added chemicals are present in bio-oil of hydro-pyrolysis. The fraction of aromatics with 10.35 area % is largest in hydro-pyrolysis bio-oil compared to two other cases. Further, the presence of oxygenated compounds such as furans decreases in the zeolite catalytic atmosphere whereas it further decreases in the catalytic hydro-pyrolysis atmosphere. In addition, the bio-oil obtained from *Delonix Regia* biomass mostly contain C_5 to C_{12} cut organic fractions. ^{1}H NMR results displayed that the bio-oils in each case consist of the same groups over a chemical shift range. However, the percentage of proton assignment differs in the order of non-catalytic < catalytic < hydropyrolysis. Finally, liquid bio-oil products obtained from *Delonix Regia* biomass by different pyrolysis environments have energy value and a combination of valuable hydrocarbons that can be directly used as furnace oil, heating oil, or co-feeded with the upstream crude oil processing apart from being a good source of value-added green chemicals.

5.C Non-catalytic, Catalytic, and Hydropyrolysis of *Oscillatoria*

5.C.1 Algal Biomass

Algal Biomass *Oscillatoria* is physically characterized to determine its quality before processing it for bio-fuels production. The proximate analysis of biomass gives a brief idea about the quality of biomass and tells whether the biomass is suitable for biofuels production or not. Table 5.15 represents the proximate analysis of Oscillatoria on a dry basis and its higher heating value (HHV).

Table 5.15. Proximate Analysis of *Oscillatoria* and its HHV on dry basis.

Moisture content (wt. %)	Volatile matter (wt. %)	Ash Content (wt. %)	Fixed carbon (wt. %)	HHV (MJ/kg)
22.30	58.20	2.40	17.10	14.26

From the obtained values, it clear that this biomass contains high moisture content of 22.30 wt. % which eventually reduces the amount of volatile matter and results in 58.20 wt. %. It has 2.40 wt. % of inorganic material which is given by ash content in the biomass sample. Subtracting above all three contents from the total biomass weight results in fixed carbon and thus it comes 17.10 wt. %. These values thus define that this biomass can be processed for hydrocarbons production. The higher heating value of 14.26 MJ/kg on dry basis shows that the biomass is quite good for studying its fuel characteristics also. Further to the speculation of compositional study, the ultimate analysis has been carried out on CHNS elemental analyzer, the result is shown in Table 5.16 and according to the basis of biomass, it contains more amount of oxygen i.e., 54.784 wt. % with 36.393 wt. % carbon, 5.784 wt. % hydrogen, 2.608 wt. % nitrogen and 0.511 wt. % sulfur. The H/C ratio of *Oscillatoria* is 1.893 which signifies its deliberate property as solid fuel and can be considered for further studies.

Table 5.16. Ultimate Analysis of *Oscillatoria* on dry basis.

Sample	Carbon (wt. %)	Hydrogen (wt. %)	Nitrogen (wt. %)	Sulphur (wt. %)	Oxygen[a] (wt. %)	H/C
Oscillatoria	36.393	5.784	2.608	0.511	54.704	1.893

[a]: calculated as a difference.

5.C.2 Catalyst study

For the study of pyrolytic behavior of Oscillatoria simple photo-catalyst nanopowder is used. The titanium dioxide is well-known catalyst for benzene, toluene and xylene separation in petroleum industry to take out these hydrocarbons from refinery wastewater. To investigate the phenomenon of separation of hydrocarbons zinc oxide in the reaction is added. Thus, the catalytic pyrolysis and hydropyrolysis are carried out at the molar ratio 0.5 of TiO_2: ZnO. The physical properties of these two catalyst are given in Table 5.17. The main aim of this study is to extract hydrocarbons from the biomass as much as possible.

Table 5.17. Catalysts properties.

Catalyst	Molecular Weight	Avg. Particle Size (nm)	Assay (%)	Make
TiO_2	79.87	50	98	Sisco Research Laboratories
ZnO	81.38	30	99.9	

5.C.3 Final product outcome

Table 5.18 gives a brief about the pyrolysis product distribution from the pyrolysis, catalytic pyrolysis and hydropyrolysis of algal biomass *Oscillatoria*. From the table, it is clear that non-catalytic pyrolysis gives more bio-oil yield than catalytic and hydropyrolysis. It can be seen that as the atmosphere changes from pyrolysis to catalytic pyrolysis and catalytic pyrolysis to hydropyrolysis, overall bio-oil yield decreases whereas bio-char yield increases and the gas yield is more in pyrolysis condition whilst it is almost similar in both catalytic and hydropyrolysis. It can be seen that as the atmosphere changes from pyrolysis to catalytic pyrolysis and catalytic pyrolysis to hydropyrolysis, overall bio-oil yield decreases whereas biochar yield increases and the gas yield is more in pyrolysis condition whilst it is almost similar in both catalytic and hydropyrolysis. The maximum bio-oil yield obtained among all three conditions is 36.25 wt. % by pyrolysis and maximum bio-char yield is 44.14 wt. %.

Table 5.18. *Oscillatoria* pyrolysis product yield distribution at 550 ºC.

Atmosphere	Pyrolysis	Catalytic Pyrolysis	Hydropyrolysis
Bio-Oil (wt. %)	36.25	33.33	31.94
Bio-Char (wt. %)	37.5	43.05	44.14
Non-Condensable gas (wt. %)	26.25	23.62	23.92

As incorporation of catalyst brings bio-oil yield down it improves the quality of product. Figure 5.11 represents the product distribution graph.

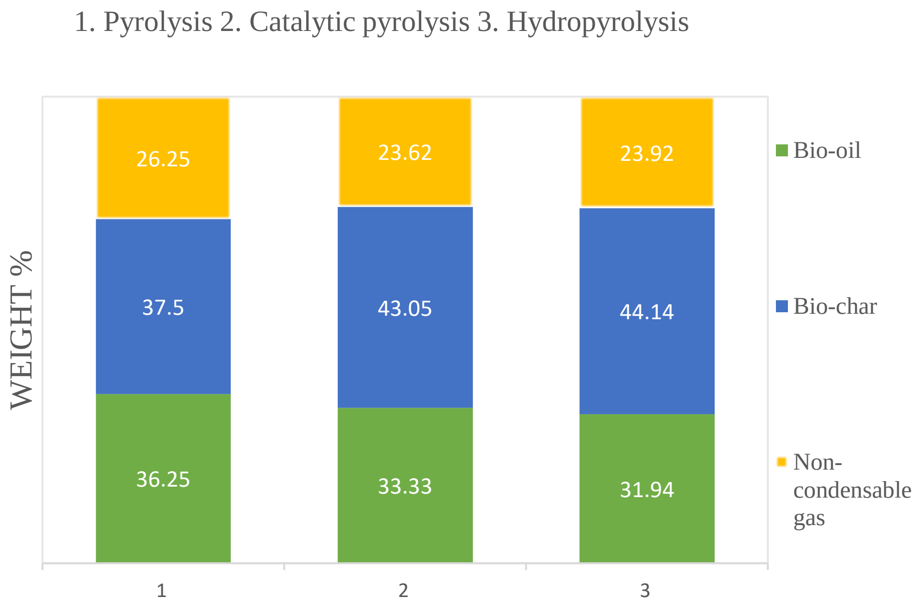

Figure 5.11. *Oscillatoria* pyrolysis product distribution chart in various atmospheres at 550 ºC.

5.C.4 Bio-oil

Pyrolytic bio-oil is the main product of this experimental research work, as it comprehends fuel characteristics with presence of value-added chemicals. The physical characteristics of bio-oil on wet basis are presented in Table 5.19. The density and viscosity of bio-oil are showing mix trends with respect to the applied experimental conditions. Bio-oil from pyrolysis results in density of 1.01 g/ml with viscosity of 2.5 mPa.s, whereas the density of bio-oil from catalytic pyrolysis decreases to 0.987 g/ml and viscosity is increases to 2.96 mPa.s. The density of bio-oil from hydropyrolysis is just exceeding the density of pyrolytic bio-oil i.e., 1.02 g/ml with lowest viscosity of 2.22 mPa.s among all three cases. The difference between densities and viscosities of all three bio-oils is in the considerable range described elsewhere [141]. Hydropyrolysis and catalytic pyrolysis delivers the purpose of improvisation in the quality of bio-oil. The pH of bio-oil goes from basicity 8.25 for pyrolytic bio-oil and catalytic pyrolytic bio-oil 8.02 down to acidity 6.07 in case of hydropyrolysis, this change in the pH comprises of the upgraded quality of bio-oil over catalytic pyrolysis and hydropyrolysis. It also suggests that the hydrogen atmosphere improves the quality of bio-oil procured. On the other hand, water percentage present in the bio-oil samples decreases in the order of pyrolysis, catalytic pyrolysis, and hydropyrolysis thus to signify the degradation of moisture from bio-oil. Pyrolytic bio-oil contains 27.5 wt. % water, bio-oil from catalytic pyrolysis contains 25.5 wt. % water, and bio-oil from hydropyrolysis contains 24.5 wt. % water. Inversely to that of water percentage, the higher heating value (HHV) of bio-oil increases from 16.59 MJ/kg from pyrolysis to 16.61 MJ/kg in catalytic pyrolysis, and 16.66 MJ/kg in hydropyrolysis. This significant rise in calorific value in the bio-oil from different atmospheres conclude that the effect of catalyst and hydrogen plays a vital role for production of upgraded bio-oil. This physical characteristics of bio-oil implies the qualitative enhancement in the bio-oil samples from catalytic pyrolysis and hydropyrolysis than non-catalytic pyrolysis.

Table 5.19. Physical characteristics of pyrolytic bio-oil on wet basis and HHV of bio-char from *Oscillatoria.*

Condition	Pyrolysis	Catalytic Pyrolysis	Hydropyrolysis
Density (g/ml)	1.01955	0.987279	1.020079
Viscosity (mPa.s)	2.50481	2.96832	2.22879
pH	8.25	8.02	6.07
Water % (KFT)	27.5	25.5	24.5
HHV (MJ/kg)	16.597	16.61	16.664
HHV of bio-char (MJ/kg)	19.59	16.06	16.14

Further to the quality analysis of bio-oil, it is taken for FTIR analysis to determine the functional groups present in the bio-oil. Functional groups are those which represents the class of compounds available in the sample. The class of compounds are the building blocks of any material and thus the FTIR analysis is referred as fingerprint analysis of any sample. The FTIR analysis plot is shown in Figure 5.12 and corresponding class of compounds are shown in Table 5.20. FTIR analysis of bio-oil from pyrolysis exhibits the wave numbers in cm^{-1} are 3303, 2963, 1641, 1555, 1465, 1413, 1306, 1126, 946 which corresponds to various group and class of compounds i.e., polymeric and oximes OH group, aliphatic, imines and oximes, aliphatic nitro, aliphatic, primary amides, Azoxy, amines, vinyl compounds respectively. Similarly, bio-oil from catalytic pyrolysis exhibits wave number (cm^{-1}) as 3300, 2977,1641,1549, 1461, 1412, 1303, 1126, 1105, 1016, 945 corresponding to polymeric and oximes OH group, aliphatic, imines and oximes, aliphatic nitro, aliphatic, primary amides, isopropyl, Azoxy, amines, ethers, cyclic alcohols, vinyl compounds respectively.

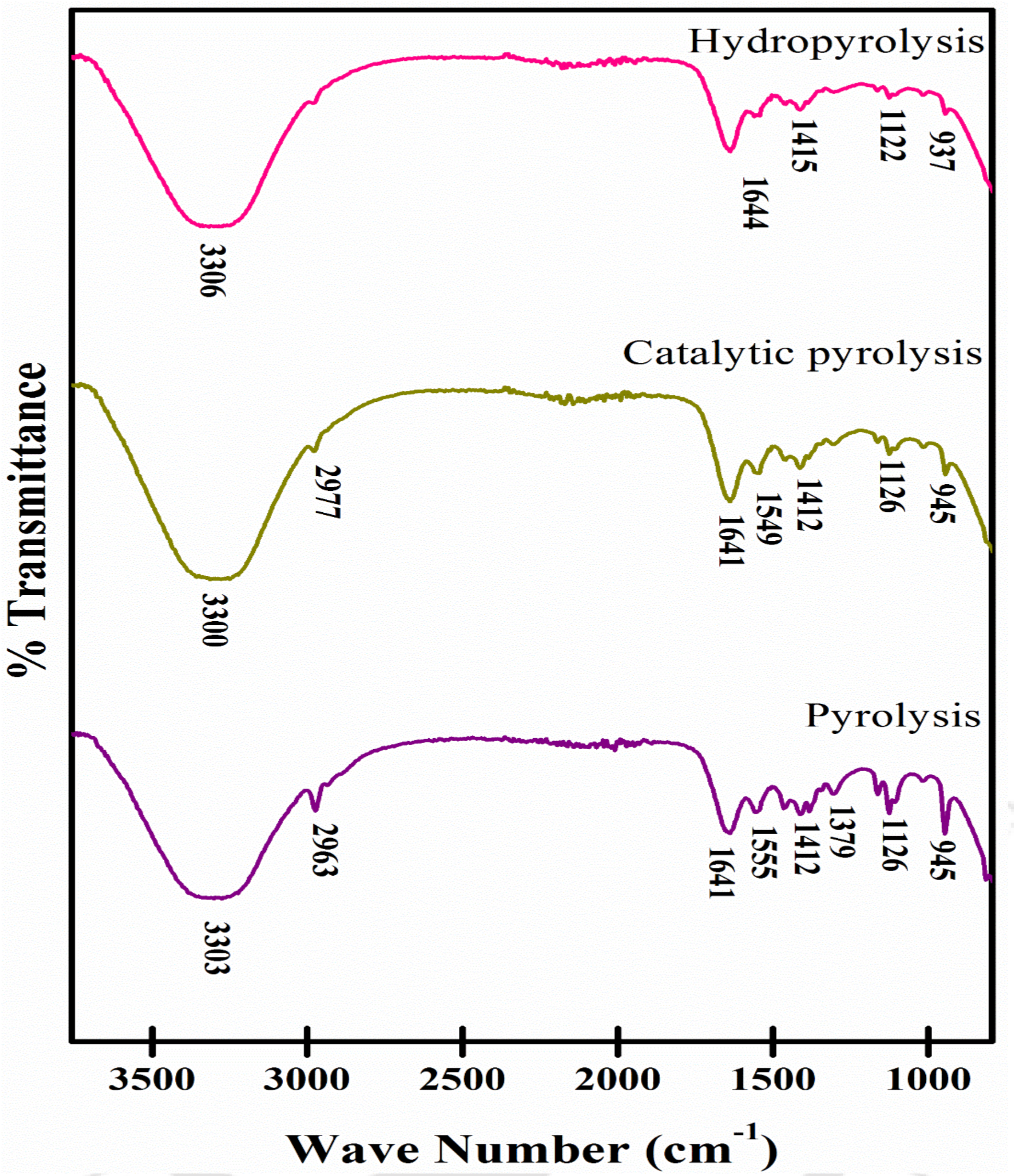

Figure 5.12. Presence of functional groups in bio-oil obtained from pyrolysis in different atmospheres.

The bio-oil from hydropyrolysis exhibits less no. of functional groups to show the upgraded quality which includes, wave number (cm^{-1}) from 3306 for polymeric OH, water impurity or OH in oximes, 1644 for imines and oximes, 1415 for primary amides, 1379 for isopropyl group, 1122 for amines, 937 for vinyl compounds. This analysis clarifies the quality check of bio-oils and shows the variation in the functional groups over different atmosphere. Auxiliary to this qualitative analysis, the qualitative and quantitative analysis of bio-oils has been done on compound level by GCMS.

Table 5.20. Presence of various functional groups in different cases based on FT-IR analysis.

Pyrolysis	Catalytic Pyrolysis	Hydropyrolysis	Wave number (cm^{-1})	Group	Class of compound
3303	3300	3306	3320-3250	-OH	Polymeric OH, water impurities, oximes
2963	2977	-	2990-2850	$-CH_3$ and $-CH_2$	Aliphatic compounds
1641	1641	1644	1690-1640	C=C	Imines and oximes
1555	1549	-	1575-1545	NO_2	Aliphatic nitro compound
1465	1461	-	1465-1440	$-CH_3$	Aliphatic compounds
1413	1412	1415	1420-1400	C-N	Primary amides
-	-	1379	1380-1360	-	Isopropyl group
1306	1303	-	1350-1280	N=N-O	Azoxy compounds
1126	1126	1122	1230-1100	C-C-N	Amines
-	1105	-	1240-1070	C-O-C	Ethers
-	1016		1065-1015	CH-O-H	Cyclic alcohol
946	945	937	950-900	$CH=CH_2$	Vinyl compound

To discover the amount and structure of hydrocarbons all three bio-oils are injected in gas chromatograph one by one. The breaking of bio-oil takes place inside the oven and then the complex mixture of bio-oil gets separated in no. of compounds. Mass spectroscopy ionizes the molecules to generate a peak on chromatogram. Depending on the concentration bio-oil the elution of compounds takes place at different retention time. Thus different mixtures result in different chromatogram. The GCMS analysis tells about the compound present in the fraction of bio-oil and it also projects the presence of compound quantitatively on specific area %. Figure 5.13 represents the GCMS chromatogram of bio-oils from different reaction mediums, the peaks are analyzed and the list of probable compounds present in bio-oil sample is given by NIST (National Institute for Standards and Technology) library present in the database of the system. The compound data of hydrocarbons obtained from the bio-oils with possible area % is shown in Table 5.21. From the table, on an overlook we can see significant amount and quality of bio-oil compounds. In detail, the common compounds available in all three cases are (i) Phenol, 4-ethyl-4-methyl- having 2.51 area % in pyrolysis case, 0.434 area % in catalytic case, and 0.956 area % in hydropyrolysis; (ii) Phenol, 2,6-dimethoxy- with area % of 1.7, 1.19, and 1.746 respectively for pyrolysis, catalytic pyrolysis and hydropyrolysis; (iii) 3,5-Dimethoxy-4-hydroxytoluene having area % of 0.81, 0.28, and 0.42 for pyrolysis, catalytic pyrolysis and hydropyrolysis respectively. Five major compounds with highest area % obtained in the bio-oils from all three cases are mentioned below: (A) Pyrolysis: 3,7,11,15-Tetramethyl-2-hexadecen-1-ol (7.027); Tetracontane, 3,5,24-trimethyl (6.386); p-Cresol (5.33); Carbonic acid, tetradecyl vinyl ester (3.22); Phenol, 2-ethyl (3.15). (B) Catalytic pyrolysis: 3-Methoxy-1H-pyrazol-5-ylacetamide (8.7121); p-Cresol (6.555); 2,4-Dimethyl furan (5.159); 2,5-Dimethyl hex-5-en-3-yn-2-ol (4.95); Phosphonic acid, (p-hydroxyphenyl)- (4.146). (C) Hydropyrolysis: 2-Propen-1-amine-N, N-bis(1-methylethyl) (8.588); 3-Cyclopent-1-enyl-3-hydroxy-2-methylpropionic acid, methyl (4.735); 3-Fluoro-o-xylene (4.451); 2-Cyclopenten-1-one, 2-hydroxy-3-methyl- (4.192); 4,4,6-Trimethyl-2-methylamino-5,6-dihydro-4H-1,3-Oxazine (4.072). From these obtained compounds it is now confirmed that the performed FTIR analysis on bio-oil samples represented exact functional groups of compounds as the compounds belongs to the FTIR mentioned groups. It is really an accountable fact that the bio-oils from *Oscillatoria* contains formative compounds of most popular hydrocarbons i.e., Benzene, Toluene, and Xylene (BTX). Furans, phenols, benzaldehydes, guaiacol (Mequinol), caprolactum, styrene, oximes, acids are present in all the bio-oil samples. These are very affirmative results for focusing on the research with the algal biomass of *Oscillatoria*.

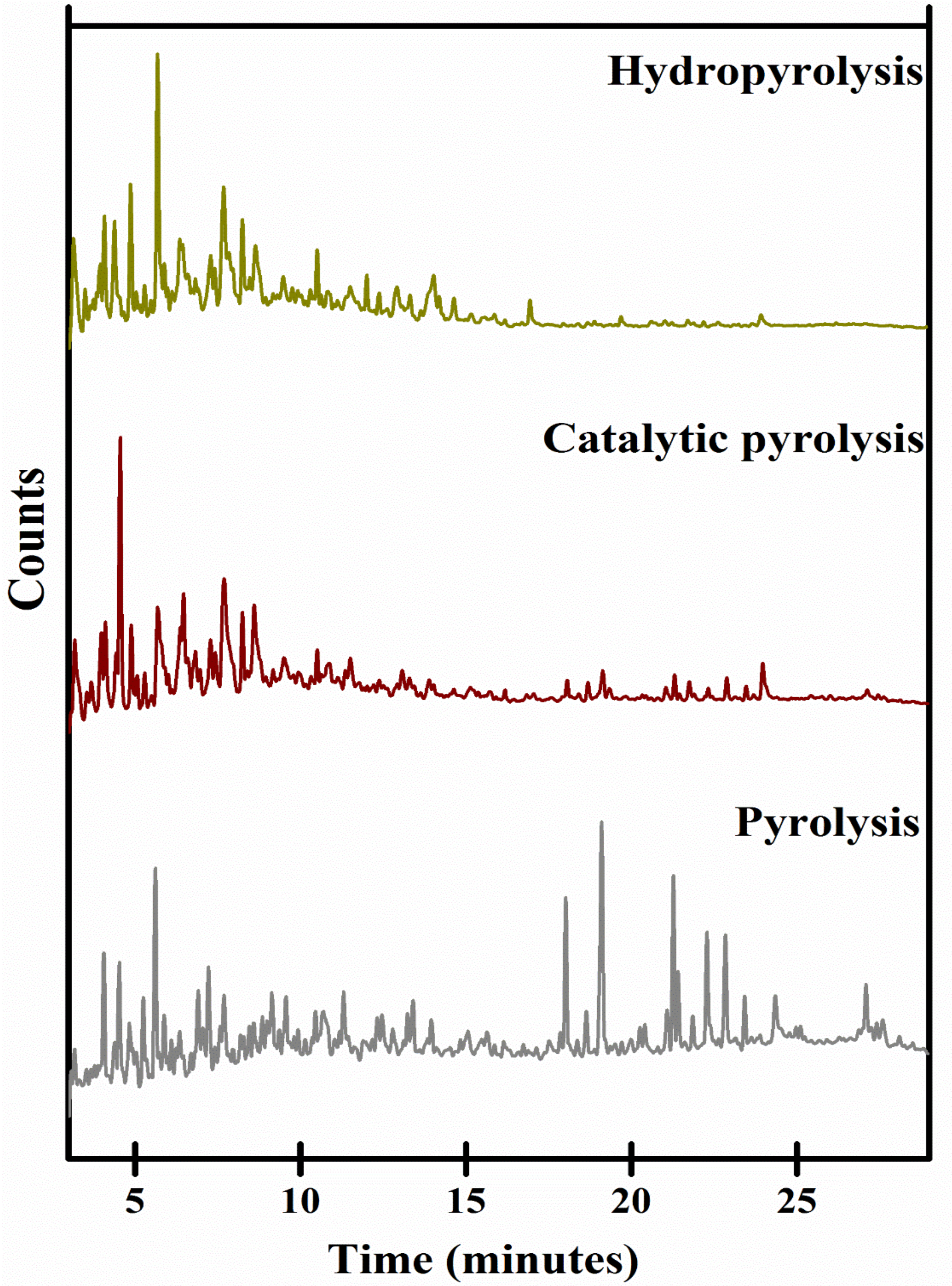

Figure 5.13. GCMS chromatogram of bio-oils from different reaction conditions.

Table 5.21. Valuable hydrocarbons obtained from pyrolysis of *Oscillatoria* in different reaction atmospheres.

Compound Name	Pyrolysis		Catalytic pyrolysis		Hydropyrolysis	
	Retention Time	Area %	Retention Time	Area %	Retention Time	Area %
3-Cyclopent-1-enyl-3-hydroxy-2-methylpropionic acid, methyl	-	-	-	-	3.135	4.735
2,4-Dimethylfuran	3.174	1.108	3.177	5.159	-	-
Pyridine, 3,5-dimethyl-	-	-	3.536	1.132	3.478	1.578
Pyridine, 2,4-dimethyl-	-	-	-	-	3.651	0.877
Tetraacetyl-d-xylonic nitrile	-	-	3.691	1.973	-	-
Pentanoic acid, 1,1-dimethylethyl ester	-	-	-	-	3.739	0.877
2-Furancarboxaldehyde, 5-methyl-	-	-	-	-	3.845	0.987
2-Cyclopenten-1-one, 3-methyl-	-	-	-	-	3.929	1.897
2,4-Dimethylfuran	-	-	3.965	3.064	-	-
Phosphonic acid, (p-hydroxyphenyl)-	4.059	3.013	4.095	4.146	-	-
Allophanic acid, phenyl ester	-	-	-	-	4.061	3.81
4,4,6-Trimethyl-2-methylamino-5,6-dihydro-4H-1,3-Oxazine	-	-	-	-	4.368	4.072
Benzene, 1-ethyl-3-methyl-	4.381	1.323	-	-	-	-
Unknown	-	-	4.424	2.74	-	-
2(1H)-Pyridinone, 4-hydroxy-1,6-dimethyl	4.516	3.259	-	-	-	-
N-Fluoro-2,4,6-trimethylpyridinium trifluoromethanesulfonate	-	-	-	-	4.527	0.774
3-Methoxy-1H-pyrazol-5-ylacetamide	-	-	4.541	8.7121	-	-
2(1H)-Pyridinone, 1-ethenyl-	-	-	-	-	4.642	0.658
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-			4.881	2.969	4.861	4.192
(-)-trans-Isopiperitenol	4.84	1.977	-	-	-	-
2-Cyclopenten-1-one, 2,3-dimethyl-	5.061	0.979	5.054	1.51	5.02	1.22
L-Proline, 1-acetyl-, methyl ester	-	-	-	-	5.101	0.609
Phenol, 2-methyl-	5.25	2.1	5.274	1.396	-	-
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	-	-	-	-	5.282	1.552

3-Acetyl-1H-pyrroline	-	-	-	-	5.476	1.055
Ethanone, 1-(1H-pyrrol-2-yl)-	-	-	-	-	5.507	0.618
p-Cresol	5.608	5.33	5.633	6.555	-	-
2-Propen-1-amine, N,N-bis(1-methylethyl)	-	-	-	-	5.658	8.588
Phenol, 2-methoxy-	-	-	-	-	5.861	1.566
Mequinol	5.885	1.87	5.89	1.127	-	-
Caprolactam	-	-	5.983	0.966	5.958	1.006
(2,5-Dimethylpyrazol-3-yl)methanamine	-	-	-	-	6.094	1.312
Bicyclo[2.2.1]heptane, 2-ethyl-	6.097	1.05	-	-	-	-
Phenol, 2,3-dimethyl	6.243	0.817	-	-	-	-
Tridecanoic acid, thiophen-2-ylmethylene	-	-	-	-	6.329	3.597
3-Methyl-2-[2-nitroprop-1-en-1-yl]thiophene	6.348	1.55	-	-	-	-
3,6-Pyridazinedione, 1,2-dihydro-4-methy	-	-	6.355	3.775	-	-
1,2-Cyclohexanedimethanol	-	-	-	-	6.406	2.465
4-Piperidinone, 2,2,6,6-tetramethyl-	-	-	6.448	3.798	-	-
benzenamine, 3-[(tetrahydro-2H-pyran-2-yl)oxy]-	-	-	-	-	6.571	1.575
3-Pyridinol, 2-methyl-	-	-	6.596	1.63	-	-
Phenol, 3,4-dimethyl-	6.899	0.699	-	-	-	-
4-Aminostyrene	-	-	-	-	6.696	1.034
3,4-Dimethyl-3-pyrrolin-2-one	-	-	6.786	2.66	-	-
5H-5-Methyl-6,7-dihydrocyclopentapyrazin	-	-	-	-	6.852	1.192
2H-Pyran-2-one, 4-methoxy-6-methyl-3-nitro-	-	-	-	-	6.892	1.268
Phenol, 2,3-dimethyl-	-	-	6.933	1.015	-	-
3-Pyridinol, 6-methyl-	7.033	1.67	-	-	-	-
Phenol, 2-ethyl-	7.21	3.15	-	-	-	-
3-Butyn-2-one, 4-[3,3-dimethyl-2-(1-methylethyl)oxiranyl]-	-	-	7.26	2.723	-	-
4a-Acetyl-hexahydrobenzo[1,3]dioxin-4-one	-	-	-	-	7.275	3.61
2(1H)-Pyridinone, 1,5-dimethyl-	-	-	7.399	1.942	7.376	1.448

Phenol, 2,3-dimethyl	7.419	0.756	-	-	-	-
1H-Pyrazole, 1,3,5-trimethyl-	-	-	-	-	7.669	1.796
1H-Imidazole-4-ethanamine, 1,5-dimethyl-	-	-	7.681	9.557	-	-
Creosol	7.684	1.24	-	-	-	-
Cyclohexanone, 4-hydroxy-4-methyl-	7.743	2.56	-	-	-	-
unknown	-	-	-	-	7.812	2.398
2-Acetonyl-9-[3-deoxy-.beta.-d-ribouranol]hypoxanthine	-	-	-	-	7.909	1.846
Oxalic acid, heptyl 2-isopropylphenyl ester	7.961	1.06	-	-	-	-
1,4:3,6-Dianhydro-.alpha.-d-glucopyranos	-	-	8.216	2.381	8.202	3.195
Phenol, 2-ethyl-4-methyl	8.278	0.804	-	-	-	-
2,5-Dimethyl-1-propylpyrrole	-	-	8.344	0.3737	-	-
3,6-Dimethyl-3,6-dihydro-pyran-2-one oxime	-	-	8.408	0.358	8.445	1.732
Benzene, 1-ethyl-4-methoxy	8.466	1.29	-	-	-	-
2,5-Dimethylhex-5-en-3-yn-2-ol	-	-	8.576	4.95	-	-
Benzenepropanenitrile	8.586	1.24	-	-	-	-
3-Fluoro-o-xylene	-	-	-	-	8.599	4.451
Phenol, 2-ethyl-4-methyl-	8.838	2.14	-	-	-	-
1-Naphthol, 1,2,3,4-tetrahydro-2-methyl-	8.976	1.24	-	-	-	-
Phenol, 4-ethyl-2-methoxy-	9.157	2.51	9.157	0.434	9.149	0.956
Cyclopentane, 1-pentyl-2-propyl-	9.352	1.18	-	-	-	-
3-Isobutyldihydropyrazin-2-one	-	-	-	-	9.431	2.144
2-(2-Hydroxyhex-1-enyl)-3-methyl-5,6-dihydropyrazine	-	-	9.463	1.248	-	-
Indole	9.556	2.35	9.57	0.646	-	-
Oxazole, 2,4-dimethyl-	-	-	-	-	9.994	0.504
Dodecalactone	-	-	-	-	10.258	1.003
Phenol, 2,6-dimethoxy-	10.458	1.7	10.466	1.19	10.464	1.746
2-Ethyl-5-undecyl-5-pyrroline	-	-	-	-	10.584	0.43
3-Amino-1-chloro-4-phenyl-2-butanone	-	-	-	-	10.764	0.596

trans-2-methyl-4-n-pentylthiane, S,S-dioxide	11.181	0.358	-	-	-	-
Indole, 3-methyl-	11.288	1.934	-	-	-	-
.alpha.-D-Galactopyranoside, methyl	-	-	10.768	1.74	11.458	1.111
1H-Azepine, 1-acetylhexahydro-	-	-	10.84	0.83	-	-
1H-Indole, 4-methyl-	-	-	11.302	0.579	-	-
4-[[3-(3,5-Dimethyl-pyrazol-1-yl)-[1,2,4]triazol-4	-	-	-	-	11.948	0.728
3,5-Dimethoxy-4-hydroxytoluene	12.312	0.812	12.318	0.283	12.315	0.429
1,2,3,4,5-Cyclopentanepentol	-	-	-	-	12.863	0.983
7-Heptadecene, 17-chloro-	13.236	0.728	-	-	-	-
t-Butylhydroquinone	-	-	-	-	13.268	0.367
9-methylheptadecane	13.404	1.29	-	-	-	-
Trimethoxyamphetamine, 2,3,5	13.956	0.568	-	-	-	-
2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	-	-	-	-	14.137	0.403
Idosan triacetate	-	-	-	-	14.583	0.651
Carbonic acid, tetradecyl vinyl ester	18.016	3.222	-	-	-	-
Hydroxylamine, O-decyl-	-	-	18.01	0.442	-	-
1-Dodecanol, 3,7,11-trimethyl-	18.647	1.096	-	-	-	-
Heptadecane	-	-	19.109	1.063	-	-
Tetracontane, 3,5,24-trimethyl-	19.117	6.386	-	-	-	-
2-Hexadecene, 3,7,11,15-tetramethyl-, [R-[R*,R*-(E)]]-	21.092	2.842	-	-	-	-
3,7,11,15-Tetramethyl-2-hexadecen-1-ol	21.201	7.027	-	-	-	-
Hexadecanenitrile	22.846	3.013	22.847	0.722	-	-
Pentadecanoic acid, 14-methyl-, methyl ester	23.418	1.165	-	-	-	-
Hexadecanoic acid, 1-(hydroxymethyl)-1,2-ethanediyl ester	24.346	1.153	23.924	1.707	-	-

To verify the structural hydrocarbon compounds with their concentration and for further upgradation of bio-oil as transportation fuel and to check the chemical functionalities of obtained compounds and compound mixture it is recommended to perform proton NMR study on obtained bio-oils. Thus at 600 MHz intensity with 16 scans for all bio-oil samples ^{1}H NMR is performed. 1H NMR spectra of bio-oils from pyrolysis, catalytic pyrolysis and hydropyrolysis is drawn as Figure 5.14. Common chemical shift shown by all three bio-oil samples at same chemical shifts represent that the basic constituent of bio-oil is same in all the three cases. But the variation in the intensity, broadness, and multiplicity of the peaks varies in each case which emphasizes the fact that all bio-oils have slightly different formation. The peak at chemical shift of 0 ppm represents Tetramethylsilane (TMS) showing singlet because all 12 hydrogen atoms are equivalent. Common structural formations in pyrolysis, catalytic pyrolysis, and hydropyrolysis bio-oils are at Chemical shifts of 1.3 ppm with singlet, 2.1-2.2 ppm with doublet, 3.5 ppm singlet, 4 ppm doublet, 4.2 ppm singlet, around 4.9 to 5.1 ppm the broadening, and singlet at 7.2 ppm. These peaks respectively indicate alkyl chain, aliphatic, vinyl ester, oximes, methyl benzenes, alcohol for broad peak area, and aromatics. Whilst around 8.5 ppm there is a singlet which also represents aromatic assignments and available in catalytic and hydropyrolysis bio-oil. Hydropyrolysis bio-oil consists the proton assignment of aldehyde at chemical shift of 9.8 ppm. Therefore, from the proton assignments present in bio-oil it confirms the structural configuration of bio-oil. It also approves that the functional groups given by FTIR are correct and at the same time the compound list generated by GCMS is also correct.

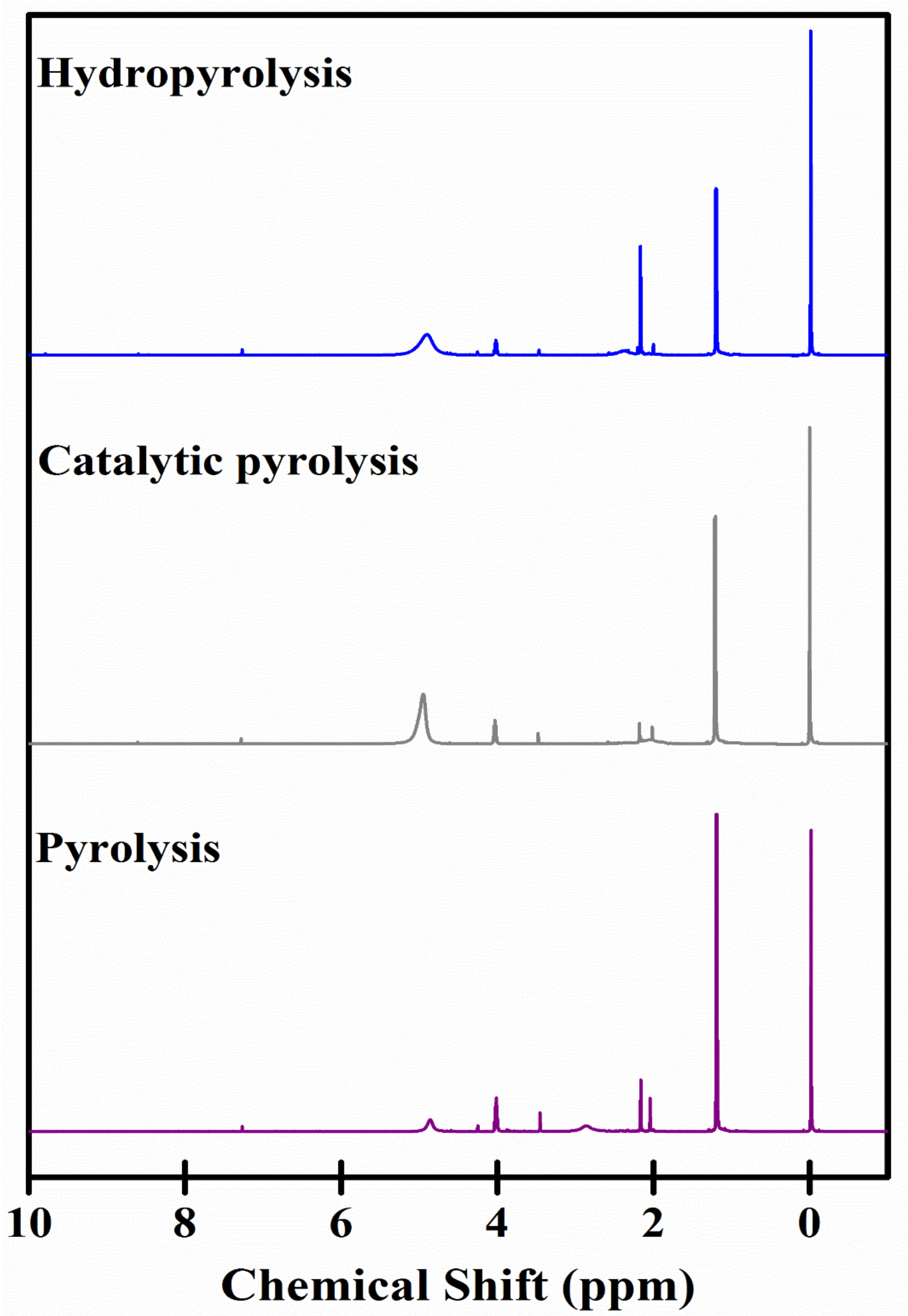

Figure 5.14: Proton NMR spectra of bio-oils from pyrolysis, catalytic pyrolysis and hydropyrolysis.

5.C.5 Bio-char

After the completion of pyrolysis reaction, the leftover residue inside the batch reactor corresponds to black char material which is termed as bio-char. From figure 5.11, it can be seen that the bio-char yield is increased in the catalytic pyrolysis and hydro-catalytic pyrolysis study, it is so, because of the presence of catalyst activity, the catalyst leads to $C_{(s)}$ formation. This bio-char has direct application as in fertilizer industry, combined heat and power plants, wastewater treatment plants and many more. Higher heating value of bio-char as shown in Table 5.19 from which it can be seen that the bio-char from pyrolysis of algal biomass *Oscillatoria* result in HHV of 19.59 MJ/kg which is as good as high ash coal. The calorific values of bio-chars from catalytic pyrolysis and hydropyrolysis decreases because of the intervention of catalyst activity in the reaction, and results in 16.06 MJ/kg for catalytic bio-char and 16.14 MJ/kg for hydropyrolysis bio-char. Figure 5.15 shows the field emission scanning electron microscope (FESEM) images for algal biomass Oscillatoria and the bio-char from different reaction medium. Image (a) represent the surface morphology of biomass, from the image it is clear that the structure of biomass is strong, tight, and bonded having no pores at all. Image (b) represent the surface of bio-char from pyrolysis at 550 °C, the bio-char tells the story of complete breakage of bond where the structure of bio-char has gaps with voids and pores and the bio-char is broken into structural layers of the material. Image (c) characterizes the bio-char of catalytic pyrolysis which is in similar structural appearance of pyrolytic bio-char but the catalyst particles can be seen on the surface. In Image (d) which is surface of bio-char from hydropyrolysis the lens is mainly focused on the upper part of void space present in the bio-char material. It is done so to check the effect of hydrogen environment on catalyst and bio-char. The spherical structures on the surface corresponds to ZnO and the tetragonal structures corresponds to TiO_2.

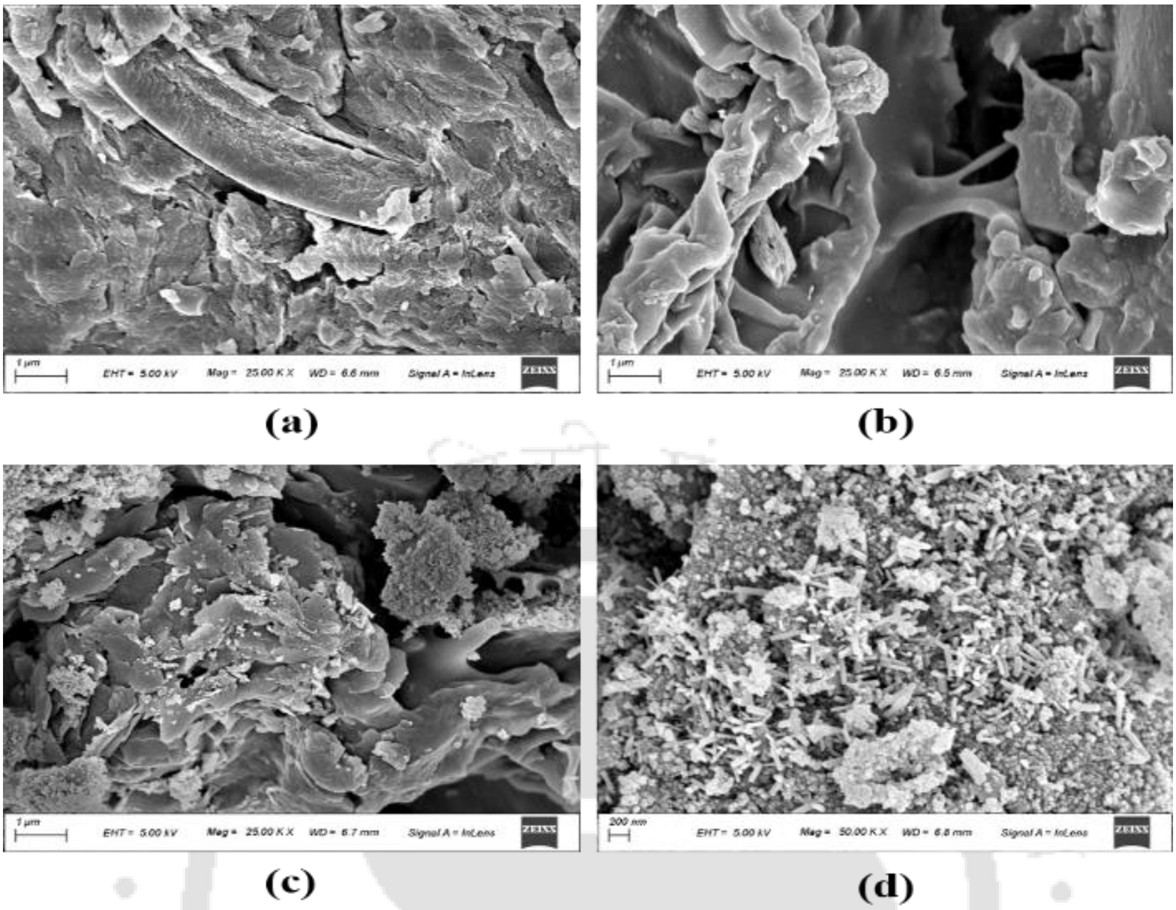

Figure 5.15. FESEM images of (a) *Oscillatoria*, (b) pyrolysis bio-char, (c) catalytic pyrolysis bio-char, and (d) hydropyrolysis bio-char.

Figure 5.16 is the XRD diffractogram of *Oscillatoria* biomass and obtained bio-chars from experimented conditions. The 2θ values at 21° and 26° defines the crystallographic structure of biomass which is present in all three bio-char samples at different intensities. But, the pattern of biomass graph has bulging at the start which is devastated after the pyrolysis reactions at each case. The graphs from pyrolysis and catalytic pyrolysis doesn't show a much difference in the pattern but hydropyrolysis completely changed the structure along with the increased pore size. As seen in FESEM analysis the bio-char from hydropyrolysis acquires special property, and change in structure with focus on identity of used catalysts. Hence, these advanced technologies of FESEM and XRD shows the structural identity of biomass and bio-chars. From the analyzed data, it is clear that the bio-char has more voids and pores which can be useful for water remediation purpose. After activation of these bio-chars at high temperatures they can be used as activated carbon and used for carbon capture and storage.

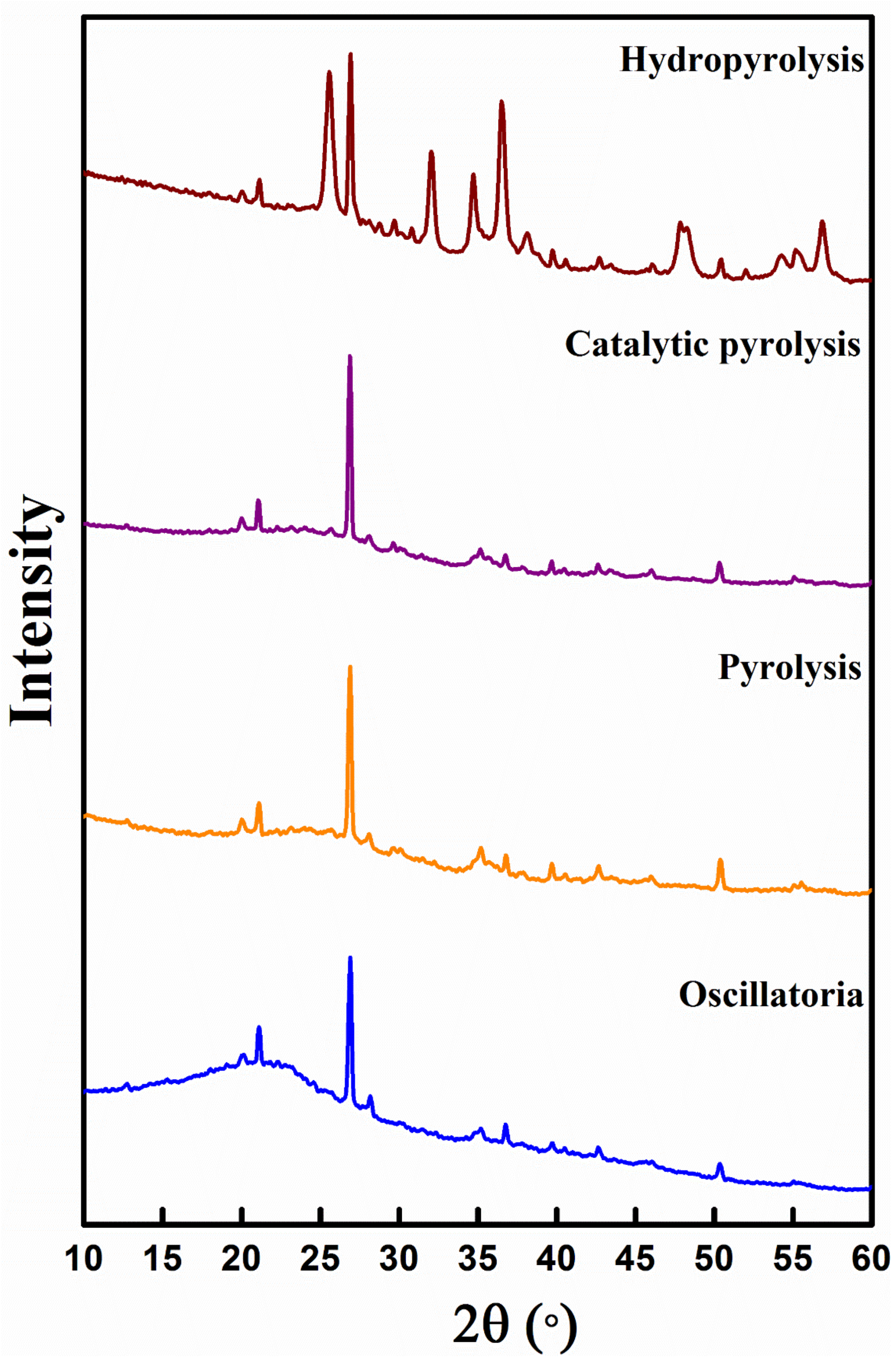

Figure 5.16. XRD diffractogram of algal biomass *Oscillatoria* and the bio-chars obtained in investigated conditions.

5.C.6 Summary

The study of non-catalytic pyrolysis, catalytic pyrolysis, and hydropyrolysis is conducted on algal biomass of *Oscillatoria* for the first time. The biomass has HHV of 14.26 MJ/kg which resulted in bio-oil of significant HHV of 16.66 MJ/kg from hydropyrolysis and 19.59 MJ/kg HHV of bio-char from non-catalytic pyrolysis. In general pH of pyrolytic bio-oils obtained from other biomass feedstock is in the range of 3 – 3.5 which is very low and those bio-oils are corrosive. However, the present pyrolytic bio-oils have the pH range 6 - 8 is really an encouraging results and indicate that the bio-oil obtained from *Oscillatoria* biomass feedstock has a less number of oxy-functional compounds compared to the other bio-oils reported in the open literature. It also suggests that the hydrogen atmosphere improves the quality of bio-oil produced. It is really an accountable fact that the bio-oils from *Oscillatoria* contains formative compounds of most popular hydrocarbons i.e., Benzene, Toluene, and Xylene (BTX). Furans, phenols, benzaldehydes, guaiacol (Mequinol), caprolactam, styrene, oximes, acids are present in all the bio-oil samples. These are very affirmative results for focusing on the research with the algal biomass of *Oscillatoria*. Further it is clear that the bio-chars obtained from pyrolysis of *Oscillatoria* biomass has more voids and pores which can be useful for water remediation purpose.

5.D Co-feed Pyrolysis of Delonix Regia and Pinewood Sawdust

5.D.1 Properties of Biomass materials

Delonix Regia and Pinewood sawdust are characterized on 'as received basis' for their calorific value. The calorific value (CV) of Pinewood biomass and Delonix Regia biomass doesn't have much difference i.e., the pinewood biomass has 18.684 MJ/kg of CV and Delonix Regia biomass has 18.564 MJ/kg of CV. Similar kind of biomass studies reported by other researchers can give us awareness about the fuel potential of Delonix Regia. Braz et al. [142] studied coffee husk, tucuma seed, sugar cane, peanut shell, rice husk, pine sawdust which has 16.79, 20.77, 17.46, 16.52, 15.39, 17.03 MJ/kg of calorific value respectively. Demirbas [143] stated the higher heating value of olive husk, cotton cocoon shell, tea factory waste as 19.0, 18.3 and 17.1 MJ/kg respectively. Wang et al. [144] reported calorific value of chlorella vulgaris as 22.05 MJ/kg which is an algal biomass. Thus, according to the relevant literature data, it is clear that the Delonix Regia is not a solid waste but it's a solid fuel and we can generate good revenue by focusing on more research in it and discovering its fuel perspective. Proximate analysis and higher heating value of both the biomass materials are presented in Table 5.22.

Table 5.22. Proximate analysis with higher heating value (HHV) of Pinewood and Delonix Regia biomass.

Biomass	Moisture Content (%)	Volatiles (%)	Ash Content (%)	Fixed Carbon (%)	HHV (MJ/kg)
Pinewood	6	79	0.6	14.4	18.684
Delonix Regia	9	72.2	1.2	17.6	18.564

According to this analysis from volatile matter content, it can be concluded that the DR biomass has similar kind of fuel potential despite of the fact that it has more moisture and ash content than that of PW biomass. The ultimate analysis of both the biomass materials showing elemental composition with C/H ratio is presented in Table 5.23.

Table 5.23. Elemental composition of Pinewood and Delonix Regia in wt. % on 'as received basis' with its C/H ratio.

Biomass	Carbon	Hydrogen	Nitrogen	Oxygen[a]	C/H
Pinewood	50.62	6.08	0.73	42.57	0.698
Delonix Regia	45.43	5.95	1.25	47.37	0.640

[a]:calculated using difference.

From the data, it is clear that the DR biomass exhibits similar elemental composition as PW biomass but obviously PW biomass has more good quality which will definitely result in good quality product than that of DR biomass. C/H ratio of DR biomass is 0.64 whereas it is 0.698 for PW biomass. From this analysis it can be seen that the quality of PW biomass is more efficient than that of DR biomass. Thus, to improve the quality of products obtained from DR biomass it is extensively recommended to pyrolyze it with the biomass having more C/H ratio. So, in accordance with this discussion the synergistic effects of DR biomass with PW biomass to deliver improved quality products are studied.

For analyzing the complete thermal degradation pattern and obtaining maximum degradation temperature, both the biomass materials are analyzed on Thermogravimetric analyzer. Figure 5.17 represents the thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) plots.

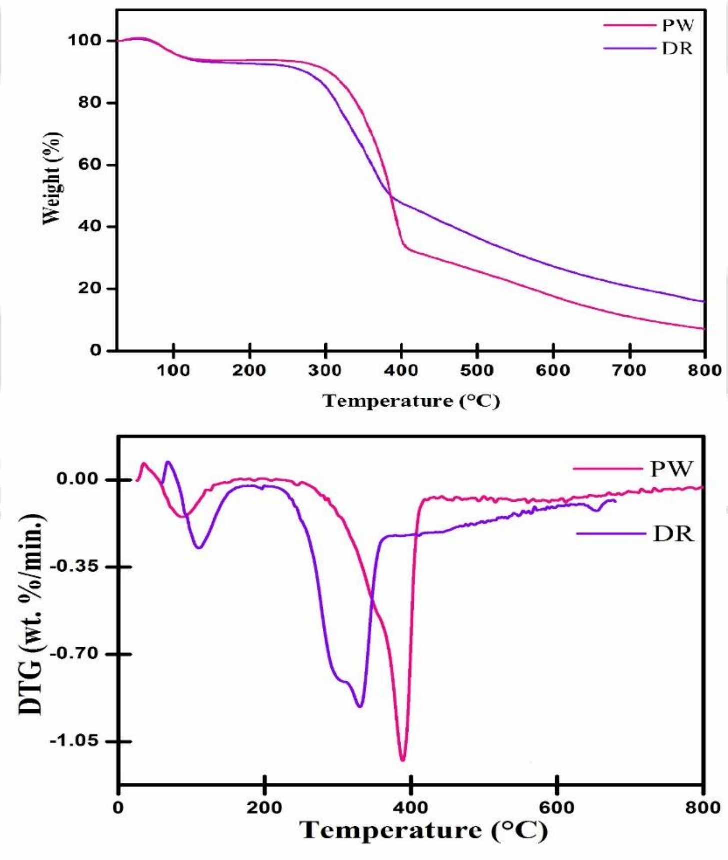

Figure 5.17. Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) of DR and PW biomass.

The experiments are performed at the heating rate of 20 °C/min, the initial temperature is 30 °C and the final temperature is 800 °C, Nitrogen gas is used as a carrier gas for the study. The sample mass taken in the crucible is 11.16 mg for Pinewood saw dust (PW) and 14.53 mg for Delonix Regia biomass. In the figure from first plot it can be observed that the moisture content degradation takes place below 150 °C for Pinewood biomass and that for Delonix Regia biomass it takes place below 180 °C. After that the degradation of hemicellulose and cellulose has been taken place such that hemicellulose degrades for PW in the temperature range of 300 - 340 °C and for DR in the temperature range of 280 - 320 °C. Cellulose degradation for PW biomass starts at 340 °C and degrades till 400 °C whilst for DR biomass it starts at 320 °C and degrades till 390 °C. After maximum degradation of cellulose, the degradation of lignin goes on in both the biomass materials till the final temperature of 800 °C. Second plot in figure 9 shows the differential thermogravimetric analysis which results in the maximum thermal degradation of biomass. For PW biomass the maximum thermal degradation temperature is 390 °C and that for DR biomass is 370 °C. Thus, from TGA and DTG plots we can extract the information of possible pyrolysis reaction temperature range and thermal degradation behaviour for available biomass material. In addition, to study the maximum pyrolytic conversion of biomass into biofuels, the chosen temperature for all the experiments is 625 °C.

5.D.2 Pyrolysis Product Distribution

Figure 5.18 represents the pyrolysis product distribution of each case of performed pyrolysis experiments showing the weight percentage of each product in terms of solid, liquid, and gas.

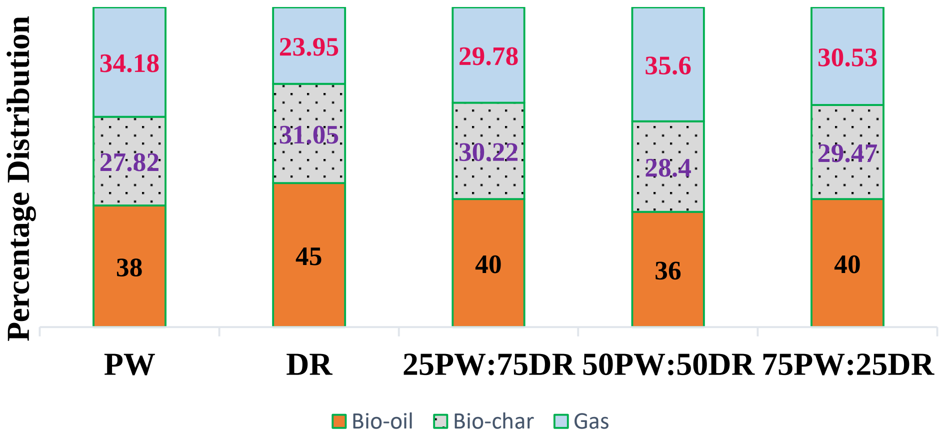

Figure 5.18. Distribution of bio-oil, bio-char, and non-condensable gas (in weight %) obtained by single and cofeed pyrolysis of DR and PW in different weight ratios.

Table 5.24 consists of the data for product distribution from pyrolysis experiment of Pinewood (PW) biomass, Delonix Regia (DR) biomass, 25 % PW: 75 % DR, 50 % PW: 50 % DR, and 75 % PW: 25 % DR. The maximum yield of bio-oil obtained among these performed experiments is of Delonix Regia biomass with 45 wt. % and the minimum obtained yield is from the ratio of 50:50 of PW: DR with 36 wt. %. Whilst maximum yield of bio-char obtained is also from DR biomass pyrolysis with 31.05 wt. %, and the minimum yield of bio-char obtained is from PW biomass with 27.82 wt. %. The product distribution thus confirms that the DR biomass results in good quantity of usable products than that of pinewood biomass. But as per concern of producer gas having captivating energy value from each pyrolysis experiment the maximum yield is obtained of 35.6 wt. % from 50:50 ratio of PW: DR biomass mixture and the minimum yield obtained is of 23.95 wt. % from pure DR biomass pyrolysis. Overall, it is clear that the various proportions or ratios of both the biomass result in different quantity of products which eventually force us to study the products qualitatively.

Table 5.24. Distribution of bio-oil, biochar and pyrolytic gases (in wt. %) obtained by single and co-feed pyrolysis of DR and PW.

Biomass	Bio-oil (wt. %)	Bio-char (wt. %)	Gases[a] (wt. %)
PW	38	27.82	34.18
DR	45	31.05	23.95
25PW:75DR	40	30.22	29.78
50PW:50DR	36	28.4	35.6
75PW:25DR	40	29.47	30.53

[a] calculated by difference {100-[Bio-oil(wt.%) + Bio-char(wt.%)]}.

5.D.3 Properties of Bio-oil

Fuel and physical properties of the bio-oil are determined by various methods and the properties are listed in Table 5.25. The calorific values of bio-oils are obtained on Toshniwal Bomb Calorimeter. The bio-oil from the source of PW biomass has calorific value of 19.4 MJ/kg whilst it is 18.88 MJ/kg from DR biomass. The highest calorific value bio-oil is obtained from co-feed pyrolysis of PW and DR with ratio of 50: 50 resulting in 20.29 MJ/kg of energy content which is as good as half of the gasoline. This bio-oil can be further processed for enhancing its energy value to meet the gasoline range and for production of valuable green chemicals. To check the acidity level of bio-oil pH analysis is carried out and resulted in overall acidic nature of bio-oil. Bio-oil from PW biomass has pH of 4.06 and bio-oil from DR biomass has pH of 4.05, with 25: 75 (PW: DR) ratio bio-oil shows pH of 4.20. Among all bio-oils the pH of bio-oil from 75: 25 (PW: DR) ratio has more acidic pH i.e., 3.99 and less acidic pH of

4.55 from 50: 50 (PW: DR) ratio. This pH determination represents that the blending of both the biomass at 50: 50 ratios is a promising practice for processing of biomass conversion to biofuels in co-feed pyrolysis. Cracking of acetic acid from hemicellulose and levullinic acid from cellulose leads to the increase in acidity of product bio-oil. Moisture content on weight % present in the bio-oil is characterized by Karl-Fisher Titrator using pyridine free KFT solution and dry methanol as a dry solvent. Highest moisture content is present in pure DR bio-oil with 21.92 wt. % and the lowest moisture content is present in co-feed ratio of 50PW: 50DR with 14.35 wt. %. The density in kg/lit. is obtained using pycnometer for all the bio-oils and the obtained values shows that the bio-oils are having density similar to that of water at room temperature. The table also demonstrates the viscosity of bio-oils obtained by Ostwald's viscometer and measured in mPa.s. bio-oil from 50: 50 ratio of co-feed has highest viscosity of 3.609 mPa.s whereas the bio-oil from pinewood biomass has lowest viscosity of 2.073 mPa.s.

Table 5.25. Fuel and physical properties of bio-oil and calorific value (CV) of bio-char.

Bio-oil	CV of bio-oil (MJ/kg)	pH	Moisture (Wt. %)	Density (kg/lit.)	Viscosity (mPa.s)	CV of bio-char (MJ/kg)
PW	19.4	4.0	15.4	0.984	2.073	32.2
DR	18.8	4.0	21.9	0.998	2.127	31.3
25PW:75DR	18.0	4.2	19.8	0.996	2.081	30.1
50PW:50DR	20.3	4.5	14.3	0.966	3.609	29.8
75PW:25DR	19.2	3.9	21.1	1.008	2.147	30.3

Figure 5.19 represents the FT-IR spectrum of bio-oil generated by ATR from single feed and co-feed pyrolysis of Pinewood (PW) sawdust and Delonix Regia (DR) biomass. From the figure it can be seen that the bio-oil from each case contributes to the similar kind of functionality. But, after analyzing the % transmittance against the wave number given by each in IR radiation, they show the difference which is presented in Table 5.26. Common functional groups present in all samples of pyrolytic bio-oil are in the range of wave numbers 3750-3100 cm^{-1}, 3000-2800 cm^{-1}, 1761-1676 cm^{-1}, 1670-1550 cm^{-1}, 1515-1490 cm^{-1}, 1400-1300 cm^{-1}, 1280-1150 cm^{-1}, 1240-1070 cm^{-1},1020-950 cm^{-1}, 950-875 cm^{-1}; which represents O-H (Polymeric O-H or water impurities), C=O (Ketones, aldehydes, carboxylic acids), C=C (Alkenes), Benzene ring in aromatic compounds, C-H (Alkanes), C-O-OR bio-oil. (Esters), C-O-C (Ether), C-O (Primary, Secondary, Tertiary alcohols, Phenol, Ester and Ether), C-H (Alkanes) respectively.

Co-pyrolytic bio-oil solely consists of additional functional groups than that of single feed pyrolytic bio-oil. These are, C-H stretching of alkanes at 3000-2800 cm^{-1}, O-H stretching of carboxylic acids at 3400-2400 cm^{-1}, methyl group in aliphatic compounds at 1465-1440 cm^{-1}, C-O-C group of ethers at 1240-1070 cm^{-1} and C-H stretching of alkanes at 950-875 cm^{-1}. These results state that the co-pyrolysis of Pinewood sawdust with Delonix Regia biomass produces more value-added product and thus it has a promising potential after upgrading to be used as a renewable and sustainable alternative to the fossil fuels. Wang et al. [144] and Stankovikj et al. [138] enlisted similar type of results for pyrolysis.

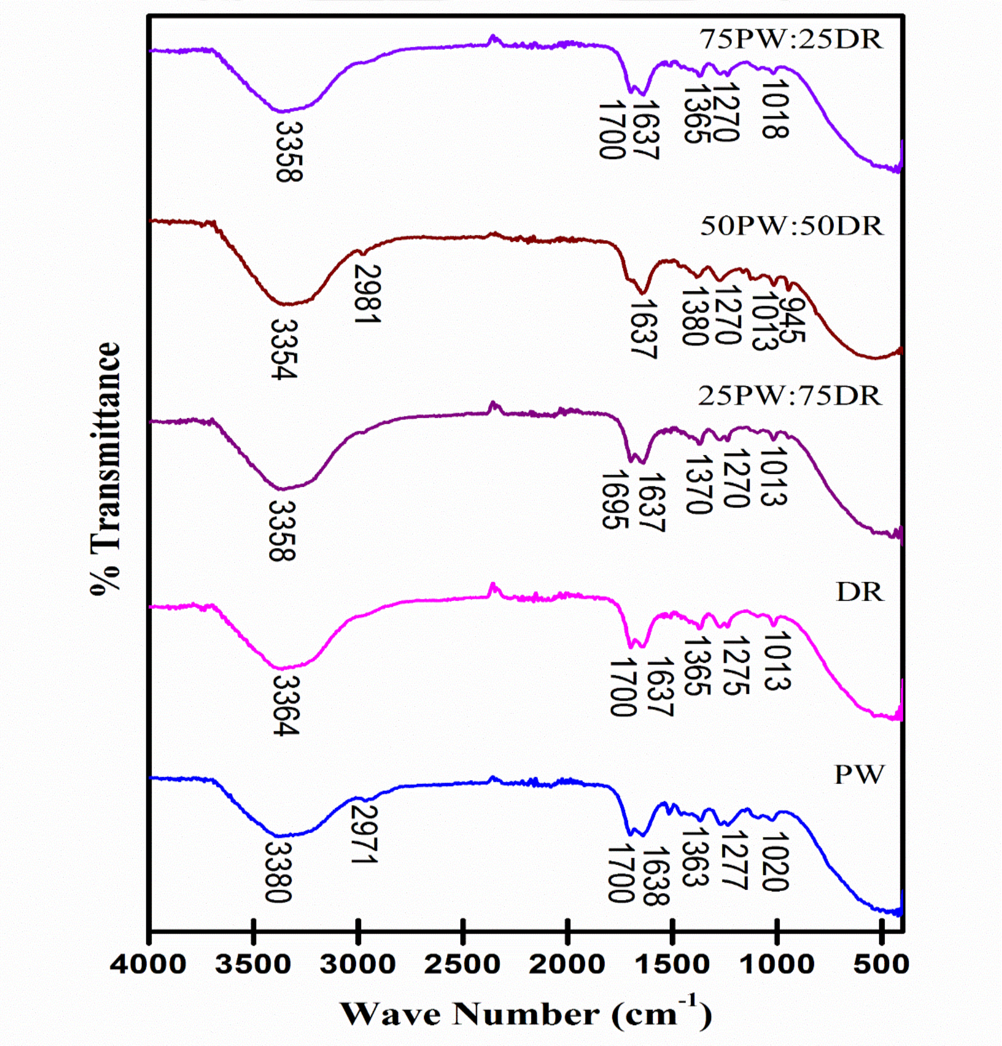

Figure 5.19. Availability of various functional groups in the bio-oils from the pyrolysis of PW and DR as single feed and as co-feed in different ratios.

Table 5.26. Variation of functional groups present in each case of pyrolytic bio-oil.

PW	DR	25PW:75DR	50PW:50DR	75PW:25DR	Wave number (cm^{-1})	Group	Class of compound
3380	3364	3358	3354	3358	3750-3100	O-H stretching	Polymeric O-H, water impurities
2971	-	-	2981	-	3000-2800	C-H stretching	Alkanes
1706	1700	1695	-	1700	1761-1676	C=O stretching	Ketones, aldehydes, carboxylic acids
1638	1637	1637	1637	1637	1670-1550	C=C stretching	Alkenes
1510	1506	-	-	1512	1515-1490	-	Benzene ring in aromatic compounds
1363	1365	1370	1380	1365	1400-1300	C-H stretching	Alkanes
1277	1275	1270	1270	1270	1280-1150	C-O-OR	Esters
1226	1234	1238	1160, 1120	1234, 1092	1240-1070	C-O-C	Ethers
1020	1013	1013	1013	1018	1020-950	C-O stretching O-H bending	Primary, Secondary, Tertiary alcohols, Phenol, Ester and Ether
-	-	-	945	-	950-875	C-H stretching	Alkanes

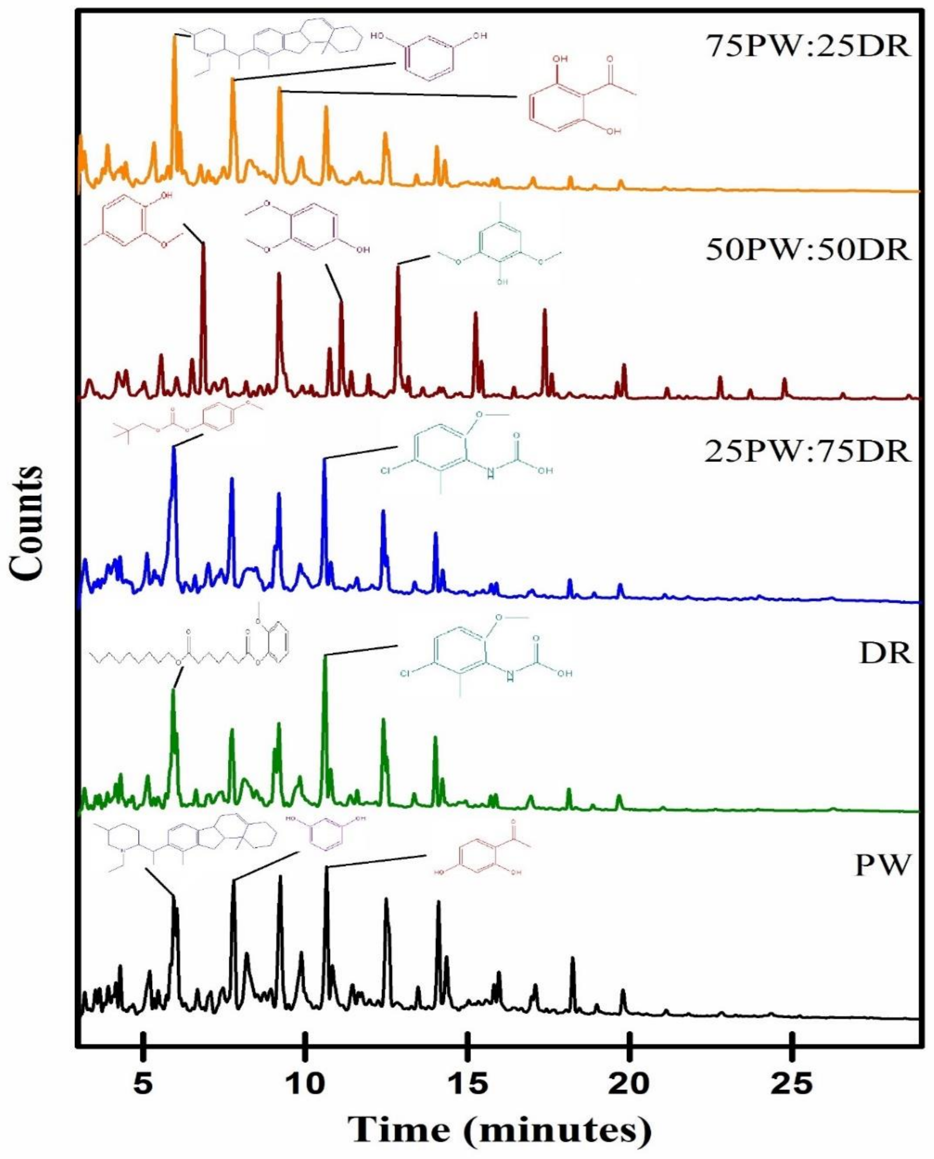

Figure 5.20. GCMS of bio-oils obtained by single and co-feed pyrolysis of DR and PW in different weight ratios.

GC-MS analysis of all bio-oil samples is carried out on VF-5ms capillary column having dimension 30m x 0.25m x 0.25µm. The method exhibits the total run time of 29.00 minutes and the entire task is operated by Varian VS software. The main principle of GC-MS is that; the GC separate out the mixture of bio-oil by breaking the components whereas the MS ionizes the molecules to identify the compound at that particular retention time. National Institute of Standards and Technology (NIST) generates the database library of possible compounds from which MS detects the most probable chemical compound and reports it.

Figure 5.20 represents the chromatogram of the bio-oil analysis in each case, from figure it is clear that the intensity of the co-pyrolytic oil is more. To know the components, present in the particular bio-oil sample, the chromatogram is studied with the help of software and NIST library search which resulted in the hundreds of the components.

The major components present in all the bio-oil samples are shown in Table 5.27. The Major findings of the GC-MS analysis of Co-pyrolytic bio-oil of Pinewood sawdust and Delonix Regia biomass at co-feed ratio of 50: 50 are described as (A) more than 3 %: Benzene, 1-fluoro-3-methyl- (3.169), Cyclopenten-1-one, 2,3 (3.52), p-Cresol (3.33), Creosol (10.117), Resorcinol (4.933), 1,2-Benzenediol, 3-methoxy- (3.286), Phenol, 4-ethyl-2-methoxy- (5.676), Phenol, 3,4-dimethoxy- (9.617), 3,5-Dimethoxy-4-hydroxytoluene (5.248). (B) between 1-3 %: Furan, 2-ethyl-5-methyl- (2.606), 3,4,5-Trimethylpyrazole (2.529), 4-Heptanone (2.47), Carbamic acid, methyl- (2.179), Mequinol (1.669),9 1H-Imidazole-carboxylic acid (1.132), 2-Cyclopenten-1-one, 3-ethyl (1.133), Phenol, 2,4-dimethyl- (1.142), Phenol, 3,4-dimethyl- (1.135), Arbutin (1.872), 2-Methyl-4-pentenoic acid (1.082), 1,2-Benzenediol, 4-methyl (1.54), Phenol, 3-methyl-5-(1-methyl) (1.024), 1,2,5-Oxadiazole-3-carboxamide, 4-amino-N (1.027), trans-Isoeugenol (1.961), 2-Propanone, 1-(4-hydroxy-3-methoxy-) (1.128), Phenol, 2,6-dimethoxy-4-(2-propenyl)- (1.274), 4-Propyl-1,1’-diphenyl (2.002), and 1-Butanone, 1,-(2,4,6-trihydroxy-3-methylphenyl)- (1.008). Other probable elements present in the bio-oil sample of co-feed ratio 50: 50 along with the bio-oil samples from PW, DR, 25PW: 75DR, and 75PW: 25DR are presented in table 5.27. From this GC-MS result, it is clear that all the bio-oil samples qualify the test to provide class of compounds given by FT-IR analysis and thus, resulted in number of value-added chemicals. The above results state that the bio-oil obtained from co-pyrolysis of Pinewood sawdust and Delonix Regia has a tremendous potential as an energy source as well as it has quality of precursor material to the green chemicals or bio-based petrochemicals. Thus, the GC-MS analysis reveals the actual chemical composition of the bio-oil and it varies in all cases. Few similar kinds of results are obtained by Kumar et al. [136].

Table 5.27. Enlist of compounds present in bio-oil obtained from each case predicted by the NIST library.

Chemical Compound	PW		DR		25PW:75DR		50PW:50DR		75PW:25DR	
	RT	Area %	RT	Area %	RT	Area %	RT	Area %	RT	Area %
Furan, 2-hexyl-	-	-	-	-	-	-	-	-	3.0	2.0
Ethanone, 1,2-di-2-furanyl-2	-	-	-	-	3.2	5.6	-	-	-	-
Furan, 2-ethyl-5-methyl-	-	-	-	-	-	-	3.2	2.6	-	-
2-Oxabicyclo[3.2.1]nonan-7-one, 1,5-dimethyl-	-	-	3.2	1.6	-	-	-	-	-	-
2-Butenoic acid, 4-hydroxy-,methyl ester	-	-	-	-	3.5	1.1	-	-	-	-
Pyridine, 2,3-dimethyl-	-	-	3.7	0.3	-	-	-	-	-	-
Acetic acid, (3-allyloxy-1,1-dimethylbutyl) ester	3.5	0.9	-	-	-	-	-	-	-	-
2-Butenoic acid, 4-hydroxy-, methyl ester	-	-	3.5	0.8	-	-	-	-	-	-
4-Decyl methylphosphonofluoridate	-	-	-	-	3.6	0.9	-	-	-	-
d-Galactano-1,4-lactone, 5,6-O-(ethylboranediyl)-2	3.6	0.9	-	-	-	-	3.6	0.7	-	-
Carbonochloridic acid, 2-bromoethyl ester	-	-	-	-	3.7	0.8	-	-	-	-
Acetic acid, (3-allyloxy-1,1-dimethylbutyl) ester	-	-	-	-	-	-	-	-	3.7	1.165
5-([(4-Fluorophenyl)amino]methyl)-	-	-	-	-	-	-	-	-	3.9	3.6
Benzene, 1-fluoro-3-methyl-	-	-	-	-	-	-	3.9	3.1	-	-
(3-Fluorophenyl) methanol,isopropyl ether	4.0	0.4	-	-	3.9	2.3	-	-	-	-
2-Furancarboxaldehyde, 5-methyl-	3.9	0.8	3.9	1.1	-	-	-	-	-	-
2-Vinylfuran	-	-	-	-	4.2	1.4	-	-	-	-
3,4,5-Trimethylpyrazole	-	-	-	-	-	-	4.1	2.5	-	-
3-Butene-1,2-diol, 1-(2-furanyl)-	-	-	-	-	-	-	-	-	4.1	0.8
3,5-O-Furylidene-d-xylofuranose	4.1	1.0	4.1	2.7	4.1	1.4	-	-	4.3	1.0
Allophanic acid, phenyl ester	4.3	1.6	4.3	2.2	-	-	-	-	-	-
1 Hexanoic acid, phenyl ester	-	-	-	-	-	-	-	-	4.4	2.0
4-Heptanone	-	-	-	-	-	-	4.5	2.4	-	-
Octadecylamine, N,N-di(allyl)-	-	-	4.6	0.7	-	-	-	-	-	-
2-Cyclopenten-1-one, 2,3	-	-	-	-	-	-	4.9	3.5	-	-
Phenyl 2,2-dimethyl-propane-thiosulfonate	-	-	-	-	4.6	0.2	-	-	-	-

Propanoic acid, 2-methyl-, anhydride	-	-	-	-	-	-	-	-	4.7	0.2
Carbamic acid, methyl-	-	-	-	-	-	-	5.3	2.1	-	-
Mequinol	-	-	-	-	-	-	5.9	1.6	-	-
3-Buten-2-ol	-	-	-	-	-	-	6.2	0.8	-	-
Pyrazole-4-carboxaldehyde, 1-methyl-	-	-	-	-	-	-	-	-	4.8	0.1
1-Propanesulfonyl chloride,3-bromo-	-	-	-	-	4.8	0.2	-	-	-	-
Silane, 1-butynyltrimethyl-	5.2	2.6	-	-	-	-	-	-	-	-
Phosphonofluoridic acid, ethyl-, decyl ester	-	-	5.1	2.7	-	-	-	-	-	-
10,11-Dioxatricyclo[6.2.2.0(1,6)]dodecane-7,7,8-tr	-	-	-	-	5.1	3.3	-	-	5.3	4.0
Acetamide (N-B)tris(trifluoromethyl)borane	-	-	-	-	5.3	1.5	-	-	-	-
Phenol, 3-methyl-	5.4	0.4	5.3	0.4	5.4	1.1	-	-	-	-
3-Cyclopentylpropionic acid,	-	-	5.4	0.8	-	-	-	-	-	-
2-Furanethanol, .alpha.-methyl-, acetate	-	-	-	-	-	-	-	-	5.5	0.5
p-Cresol	5.7	0.9	5.7	0.8	-	-	5.7	3.3	5.7	1.3
2-Furancarboxylic acid, 2-tetrahydrofurylmethyl ester	-	-	4.5	0.7	-	-	-	-	-	-
Pimelic acid, 2-methoxyphenyl nonyl ester	-	-	5.9	9.9	-	-	-	-	-	-
Fumaric acid, 4-methoxyphenyl 2-ethylhexyl ester	-	-	6.0	4.1	-	-	-	-	-	-
2-Methyl-4-pyridinamine 1-oxide	-	-	-	-	5.8	6.8	-	-	-	-
N-Ethyl-desoxy-veratramine	5.9	6.9	-	-	-	-	-	-	5.9	10.4
Myristic acid, 4-methoxyphenyl ester	6.0	3.0	-	-	-	-	-	-	-	-
Carbonic acid, neopentyl 4-methoxyphenyl ester	-	-	-	-	5.9	12.6	-	-	-	-
2-Methylvaleric acid, 4-methoxyphenyl ester	-	-	-	-	-	-	-	-	6.1	3.1
Propanoic acid, 2-methyl-, anhydride	-	-	6.1	0.6	-	-	-	-	6.2	1.2
1,3,5-Triazin-2(1H)-one, 4,6-diamino-	-	-	-	-	6.6	0.9	-	-	-	-
9 1H-Imidazole-4-carboxylic acid	-	-	-	-	-	-	6.4	1.1	-	-
2-Cyclopenten-1-one, 3-ethyl	-	-	-	-	-	-	6.4	1.1	-	-
1H-Imidazole, 1-methyl-5-nitro-	-	-	6.6	1.0	-	-	-	-	6.7	1.8
Phenol, 2,4-dimethyl-	-	-	6.9	1.1	7.0	2.5	6.9	1.1	7.0	1.1

Phenol, 3,5-dimethyl-	-	-	-	-	6.7	0.3	7.3	1.1	7.1	0.4
1,3-Butadiene, 1-(ethylthio)	-	-	-	-	-	-	7.1	0.4	-	-
2-Methoxy-5-methylphenol	-	-	-	-	-	-	7.4	0.9	-	-
Creosol	-	-	-	-	7.2	1.3	7.7	10.1	-	-
Phenol, 3-ethyl-	7.4	1.8	-	-	-	-	-	-	-	-
(6S,11R,12aR)-6'-Hydroxy-2,2	-	-	-	-	-	-	7.5	0.3	-	-
(3S,9aR)-3-Butyloctahydro-1H-pyrrolo[1,2-a]azepine	7.8	8.4	7.7	5.9	7.7	8.3	-	-	-	-
Arbutin	-	-	-	-	-	-	7.8	1.8	-	-
2-Methyl-4-pentenoic acid	-	-	-	-	-	-	8.3	1.0	-	-
3,4-Dimethoxytoluene	-	-	-	-	-	-	8.5	0.6	-	-
1-Azabicyclo[2.2.2]octane-4-methanol	-	-	8.1	5.9	-	-	-	-	-	-
Resorcinol	8.2	6.3	-	-	-	-	8.6	4.9	8.2	4.6
1,2-Benzenediol, 3-methoxy-	-	-	-	-	-	-	8.9	3.2	-	-
Phenol, 4-ethyl-2-methoxy-	-	-	-	-	-	-	9.2	5.6	-	-
1,2-Benzenediol, 4-methyl-	-	-	-	-	-	-	9.4	1.5	-	-
Phenol, 3-methyl-5-(1-methoxy)-	-	-	-	-			9.8	1.0	-	-
Resorcinol, 2-acetyl-	-	-	9.4	0.1	9.1	5.9	-	-	9.2	8.2
Ethanone, 1-(2,4-dihydroxyphenyl)-	9.2	8.7	9.2	6.1	-	-	-	-	-	-
2-Fluoro-5-dimethylaminopyrimidine	-	-	9.0	4.0	-	-	-	-	-	-
5-Isopropyl-2-methylphenyl heptanoate	-	-	9.8	2.8	-	-	-	-	-	-
8-Azidoadenosine	-	-	-	-	9.8	2.2	-	-	-	-
4-Amino-3,5-diethylpyridine	9.8	4.6	-	-	-	-	-	-	9.8	3.3
Phenol, 3,4-dimethoxy-	-	-	-	-	-	-	10.5	9.6	-	-
(5-Chloro-2-methoxyphenyl)carbamic acid, 2,6-dimethyl	10.6	8.2	10.6	12.2	10.5	6.9	-	-	10.6	6.0
1,4-benzenediol, 2-(1-methylpropyl)-	-	-	-	-	-	-	-	-	10.8	1.1
1,2,5-Oxadiazole-3-carboxamide, 4-amino-N-	-	-	-	-	-	-	10.8	1.0	10.9	1.2
Ethyl Vanillin	10.8	3.8	-	-	-	-	-	-	-	-
Benzene, 2-fluoro-1,3,5-trimethyl-	11.4	1.6	-	-	-	-	-	-	-	-
Benzaldehyde, 2-hydroxy-4-methoxy-	11.7	0.6	-	-	-	-	-	-	-	-

4-Ethylcatechol	-	-	-	-	-	-	11.1	0.5	-	-
Phenol, 2-methoxy-4-(1-propenyl-)	-	-	-	-	-	-	11.6	0.5	-	-
Pyridine, 3-methyl-2-phenyl-	-	-	-	-	12.4	4.0	-	-	-	-
Cyclopropanecarboxylic acid, 2,2-dimethyl-3-(2-methyl-)	-	-	11.3	0.9	-	-	-	-	-	-
N-(3,5-Diisopropyl-4-oxo-cyclohexadienylidene)-N'	12.4	8.2	12.4	5.9	-	-	-	-	12.4	3.6
trans-Isoeugenol	11.6	0.6	12.5	2.4	12.5	1.6	12.5	1.9	-	-
3,5-Dimethoxy-4-hydroxytoluene	-	-	-	-	-	-	12.9	5.2	-	-
Ethanone, 1-(3-hydroxy-4-metoxy-)	-	-	-	-	-	-	13.3	0.5	-	-
2-Propanone, 1-(4-hydroxy-3-methoxy-)	-	-	-	-	-	-	14.1	1.1	-	-
Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	-	-	-	-	-	-	-	-	12.5	1.7
4-Acetoxy-3-methoxyacetophenone	-	-	-	-	-	-	-	-	13.4	0.8
Apocynin	13.4	0.9	-	-	-	-	-	-	-	-
Phenethylamine, 2,4,5-trimethoxy-.alpha.-methyl-	14.1	5.5	14.0	4.1	14.0	2.7	-	-	14.0	2.6
Propan-2-one, 1-(4-isopropoxy-3-methoxyphenyl)-	14.3	3.7	14.2	1.8	-	-	-	-	14.2	1.7
Benzene, 1-acetoxy-2,3-dimethoxy-5-(2-propenyl)-	15.8	0.8	-	-	-	-	-	-	-	-
(+)-s-2-Phenethanamine, 1-methyl-N-vanillyl-	-	-	-	-	14.2	1.2	-	-	-	-
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	-	-	15.7	0.6	15.7	0.5	15.1	1.2	15.7	0.4
4-Propyl-1,1'-diphenyl	15.9	1.7	15.8	0.7	15.8	0.5	15.9	2.0	15.9	0.5
2-Butanone, 4-(4-hydroxy-3-methoxy-)	-	-	-	-	-	-	16.9	0.6	-	-
Benzenepropanol, 4-hydroxy-3-methoxy-	17.0	1.4	-	-	-	-	-	-	-	-
6-Methoxyeugenyl isovalerate	16.9	0.7	18.1	1.2	18.1	0.8	-	-	18.1	0.7
1-Butanone, 1-(2,4,6-trihydroxy-3-methylphenyl)-	19.8	1.4	-	-	19.7	0.8	19.7	1.0	19.7	0.7

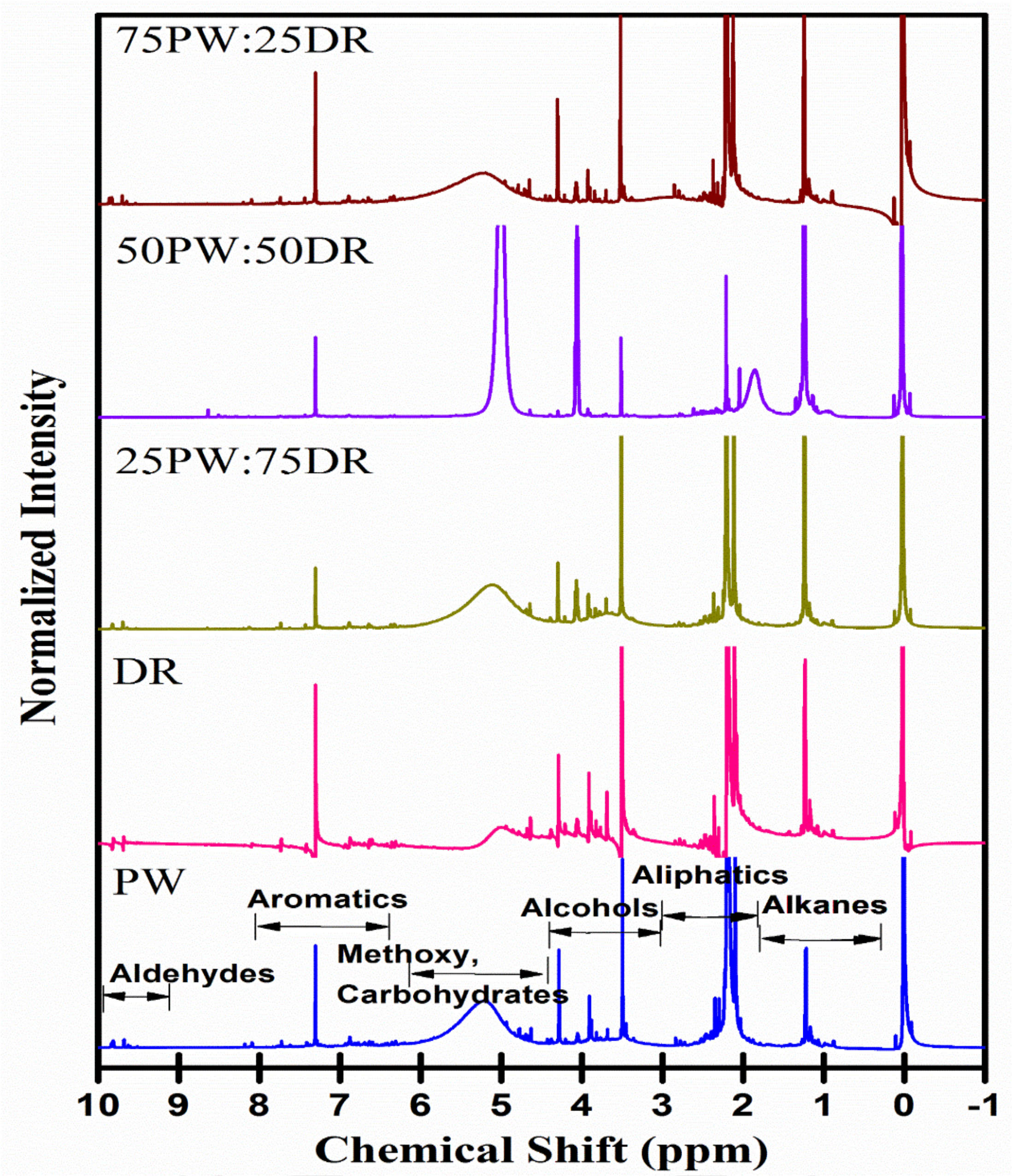

Figure 5.21. ^{1}H Nuclear Magnetic Resonance Spectroscopy of bio-oils obtained by single and co-feed pyrolysis of DR and PW in different weight ratios.

To confirm the orientation of class of compounds present in the bio-oil samples, all bio-oils are subjected to the proton NMR analysis. Figure 5.21 represents the ^{1}H NMR interpretation of the bio-oils given by various proton assignments. The proton NMR is done at 16 scans in 600 MHz NMR spectrometer and the solvent used for all the bio-oil samples is $CDCl_3$ (Chloroform-D) which is showing pick at chemical shift of 7.26 ppm. The pick at 0 ppm stands for water impurity of Tetramethylsilane (TMS). All the bio-oils contains similar percentage of Alkanes (0.5-1.5 ppm), Aliphatic α to heteroatom or unsaturation (1.5-3.0 ppm), Alcohols, methylene-dibenzene (3.0-4.4 ppm), Methoxy, carbohydrates (4.4- 6.0 ppm), (hetero-) Aromatics (6.0-8.5 ppm), and Aldehydes (9.5-10 ppm). Among these bio-oils the bio-oil from co-feed ratio of 50PW:50DR contains high amount of Methoxy, carbohydrate group at the chemical shift of 4.4-6.0 ppm and heavy aromatics in the chemical shift range of 6.0-8.5 ppm. Therefore, this qualitative analysis describes the overall composition of bio-oils and confirm that, each bio-oil exhibits the functional groups given by FTIR analysis and composition given by GCMS in form of chemical compounds. It also verifies that the bio-oil from co-feed pyrolysis of ratio 50PW:50DR has good quality over other bio-oils.

5.D.4 Properties of Bio-char

Bio-char yield is reported in Table 5.24 and the amount of yield obtained is really creating interest to study its behaviour. Delonix Regia biomass has a maximum amount of bio-char yield i.e., 31.05 wt. % and it is correlated with the ash content which is 1.2 wt. %. The Pinewood sawdust has lowest yield of bio-char i.e., 27.82 wt. % and it also correlates with the ash content of 0.6 wt. %. From above two statements, it is clear that the Delonix Regia is producing more bio-char than that of Pinewood which eventually states that the Pinewood is giving more fine liquid products than Delonix Regia. But at the same time, it is also clear that the Delonix Regia is a good sustainable biomass material in comparison with the Pinewood to produce activated charcoal or briquettes. Co-pyrolysis of these two competitive biomasses resulted in a minimum amount of bio-char in the ratio of 50PW: 50DR yielding 28.4 wt. %. The Higher heating value of Pinewood bio-char is maximum among all the cases with 32.23 MJ/kg followed by Delonix Regia bio-char with 31.30 MJ/kg. The co-pyrolytic bio-chars in the co-feed ratio of 25PW: 75DR, and 75PW: 25DR have nearly equal heating value i.e., 30.18, and 30.32 MJ/kg respectively. The bio-char from co-feed ratio of 50PW: 50DR has minimum CV among all bio-chars i.e., 29.84 MJ/kg. All the calorific values are obtained by Toshniwal bomb calorimeter and reported in Table 5.25. In total this much energy containing bio-chars can be utilized as bio-coal the value also opens up the scope for bio-char research in detail.

Figure 5.22 represents the FESEM images of pure Pinewood biomass and pure Delonix Regia biomass and their respective bio-chars. The images are taken at 500X zoom, and from these images it is clear that both the biomass materials have strong and smooth surface with high interlinkage bonding between the molecules. On the other hand, the bio-chars from both the biomass materials are showing same property of swelling nature on surface with distorted structure having voids and space. This FESEM analysis gives idea about the physical nature of bio-chars.

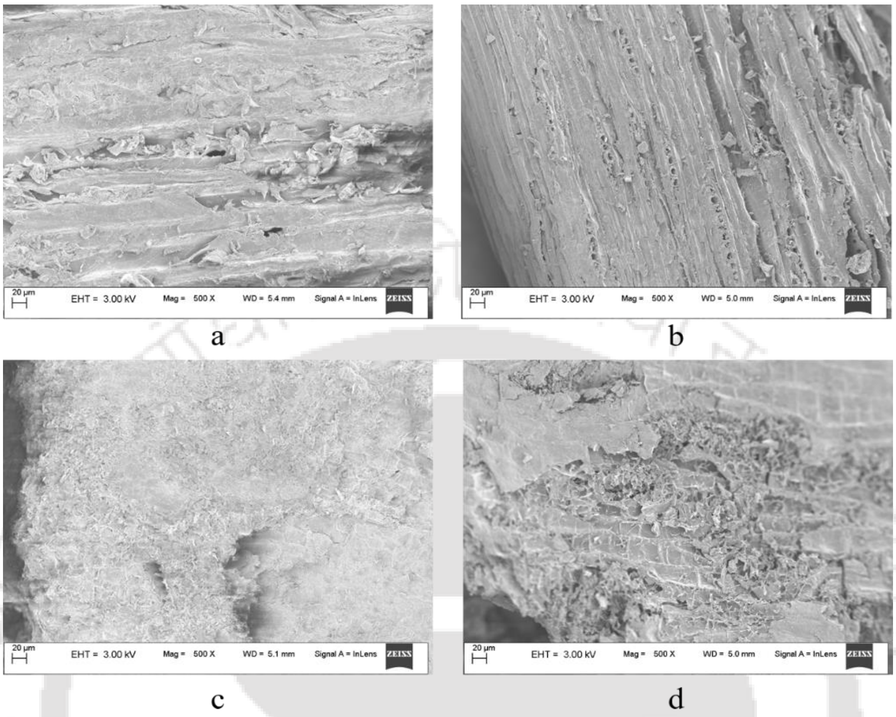

Figure 5.22. Field Emission Scanning Electron Microscope images of biomass and biochar: a) PW b) Biochar of PW c) DR and d) Biochar of DR.

Figure 5.23 represents the X-ray diffractogram of both the biomass materials and their bio-chars having different feed ratios in the range of 2θ value of 10 to 80°.Pinewood biomass and Delonix Regia biomass has crystalline structure at 2θ value of 23°, which is common peak present in all lignocellulosic biomass materials. The bio-chars from all the cases are not showing any crystalline peak on the diffractogram as they are completely degraded except the one bio-char with co-feed ratio of 50:50. The bio-char with 50:50 co-feed ratio shows a small peak at 23° which means this bio-char still contains some amount of cellulosic material left in it and it can be further processed. It also interprets that the bio-char contains some organic matters because of possible secondary reaction as both the primary reactions of both the biomass leads to high volatile compounds. Overall, the bio-chars from all the cases have good quality as a solid fuel and can be used for different application oriented technologies.

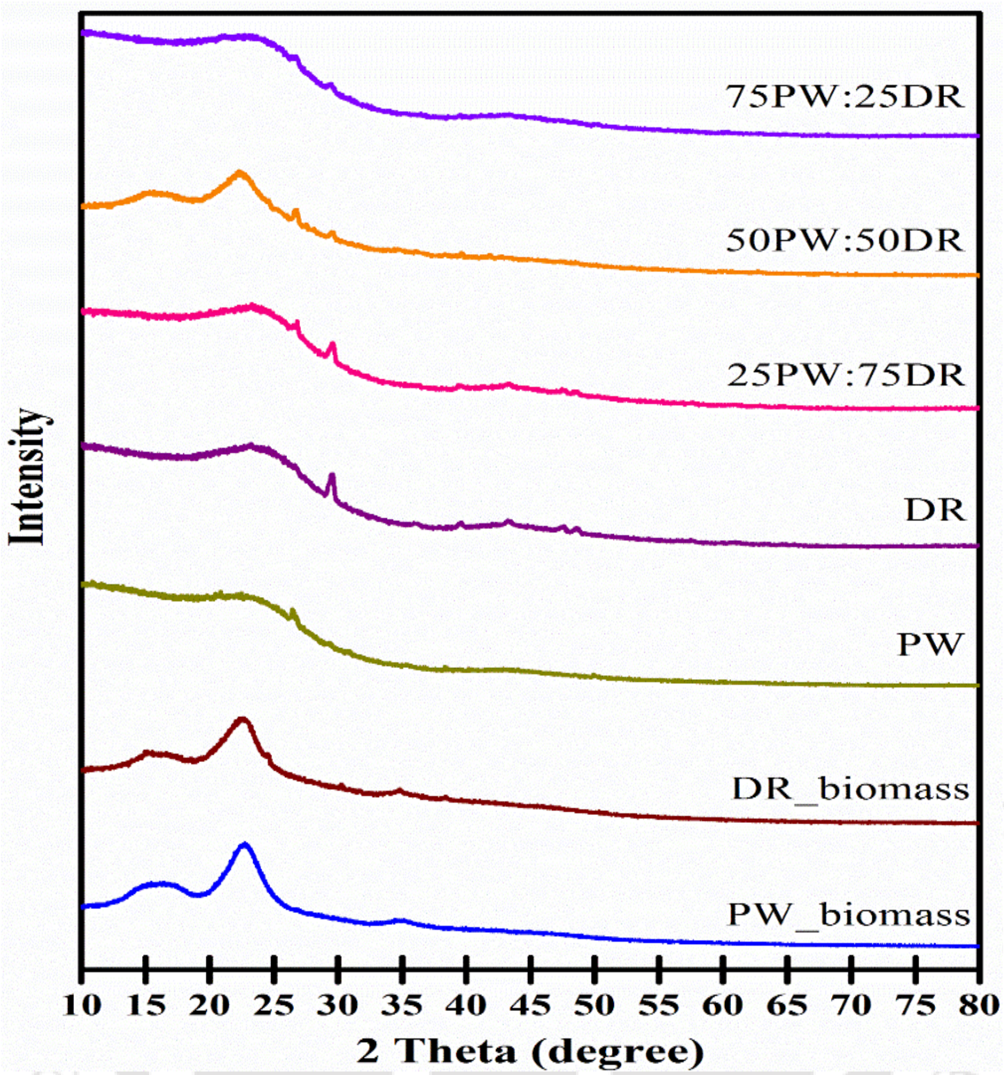

Figure 5.23. X-ray Diffractogram of biomass and biochar obtained by single and co-feed pyrolysis of DR and PW.

5.D.5 Non-condensable Gases

Non-condensable gases are collected in tedler bags, and the amount of total gas coming out of the system is calculated by the material balance of the overall product stream, and the yield is given in Table 5.24. It is observed that the Delonix Regia pyrolysis has less amount of gas with 23.95 wt. %, Pinewood pyrolysis has 34.18 wt. % gas, and the maximum amount of gas is obtained from the co-pyrolysis experiment at the ratio of 50:50 having 35.6 wt. %. The gas yield from 25:75 and 75:25 ratios is almost same with 29.78 wt. %, and 30.53 wt. % respectively. This suggests that the non-condensable gases coming out from pyrolysis, and the co-pyrolysis of Delonix Regia and Pinewood sawdust in different ratios have a remarkable amount of energy.

5.D.6 Summary

The experiments on single feed pyrolysis and co-pyrolysis of DR with PW are conducted at the temperature of 625 °C and pressure of 1 bar in a tubular reactor. The product analysis is compared with the conventional single feed pyrolysis of these biomass materials. From the comparative data, it is clear that the scarcely researched DR biomass has a similar kind of fuel and energy potential with that of broadly researched PW biomass. The bio-oil obtained from the co-feed ratio of 50:50 has the highest calorific value of 20.3 MJ/kg on average, among other bio-oils. Its moisture content is also minimum amongst all cases, with only 14.3 wt. % on average. However, the yield of biochar obtained by 50:50 co-feed is minimum with 28.4 wt. % on average, whereas the yield of non-condensable gases by 50:50 co-feed pyrolysis is maximum amongst all cases with 35.6 wt. % on average. The densities of all bio-oils produced in this work are close to that of water (~ 1g/cc) at room temperature, whereas their viscosity varies in the range 2.07 – 3.61 mPa.s on average. The pH of bio-oil obtained with 50:50 co-feed is highest amongst all cases indicating decreased acidity by co-pyrolysis. Further, the total area % of acids in bio-oil obtained by 50:50 co-feed pyrolysis is only 5.1 which is an encouraging result to experiment more on co-pyrolysis of various biomasses or materials combined with DR. The major product groups obtained in this bio-oil are phenolic and methoxyphenol groups where creosol is present in the highest fraction of 10.1 area % in the case of 50:50 co-feed pyrolytic bio-oil. The non-condensable gases which are around 35 wt. % can be directly used to generate energy in the form of electricity. Thus, the selection of mass ratio for co-pyrolysis plays an important role and in the present study it is found that 50:50 co-feed is optimum in terms of HHV, pH, density and moisture content.

5.E Co-feed Pyrolysis of Delonix Regia and Tube Waste

5.E.1 Co-feed Material Properties

Lignocellulosic biomass Delonix regia (DR) and rubber tube waste (TW) are taken here as co-feed at variable ratio of 95DR:5TW, 85DR:15TW, 75DR:25TW, 65DR:35TW and 50DR:50TW. Proximate and ultimate analysis along with calorific value determination of both the feeds are tested in identical conditions to determine actual difference between both solid waste materials. All the characterizations of feed materials are carried out on dry basis.

Table 5.28. Proximate Analysis and HHV of Delonix Regia, and Tube waste on dry basis (mass %).

Sample	Moisture	Volatiles	Ash	Fixed Carbon[a]	HHV (MJ/kg)
DR	9	72.2	1.2	17.6	16.83
TW	0	56.4	10	33.5	22.07

[a]: calculated by difference

Table 5.28 presents the proximate analysis of DR and TW in mass % on dry basis, representing moisture, volatiles, ash and fixed carbon content along with HHV in MJ/kg. The moisture content of DR is 9 mass % that is very less thus, suitable for the purpose of bio-oil generation, besides TW has no moisture in it, which is an encouraging factor for co-feed study. Whilst, the moisture confirms the presence of oxygenates in obtained bio-oil. The volatile matter which is a key measure to know about the combustion characteristics of solid fuel is high for DR i.e., 72.2 mass % than TW i.e., 56.4 mass %. This indicates the presence of lighter components in the biomass that are useful for bio-oil and heavier components in rubber to result in lower hydrocarbons. In general, volatile matter contributes to the condensable hydrocarbons coming from the feed materials. Ash content of DR is 1.2 mass % which is very less as compared to the ash content of TW i.e., 10 mass %. It signifies that, the increase in the presence of TW in co-feed will increase the biochar yield. The fixed carbon relates to non-condensable gases and solid char, thus in accordance with ash content it is also responsible for the increase in solid product with increase in mass of TW in co-feed. The presence of 17.6 mass % and 33.5 mass % fixed carbon content for DR and TW respectively indicate the ability of the biomass and tube waste material to be used for possible hydrocarbons production. HHV of DR biomass is 16.83 MJ/kg which is best suitable for any biomass considered for co-feed study. The relevant literature data for HHV is available elsewhere [92,142,145,146] showing the potential of various biomass materials considered for thermochemical conversion studies. Apart from this, the energy potential of waste rubber tubes is also estimable with 22.07 MJ/kg of HHV.

Table 5.29. Ultimate Analysis of Delonix Regia, and Tube waste on dry basis (mass %).

Sample	C	H	N	S	O^b	H/C
DR	45.43	5.95	1.25	-	47.37	1.57
TW	57.73	5.96	-	0.84	-	1.23

^{b}: calculated by difference

Table 5.29 is showing ultimate analysis of DR and TW on mass percentage along with their H/C atomic ratio on dry basis. From the ultimate analysis it can be seen that, both the materials have versatile elemental analysis. TW has more carbon content with 57.73 mass % than that of DR which has 45.43 mass % of carbon. It signifies that the amount of carbon plays an important role in basic structure of any material. Thus, this distinct amounts of carbon in both the materials will surely contribute together to the advanced carbonaceous materials as products. DR and TW almost have same amount of hydrogen content with 5.95 and 5.96 mass %, respectively. This will surely affect the formation reactions of lower hydrocarbons in order to supress oxygen content of the product streams. 1.25 mass % of nitrogen is present in DR biomass whereas TW doesn't have any nitrogen in it. Similarly, 0.84 mass % sulfur is present in TW but DR biomass has no sulfur content and it's a good factor for any biomass. So, from these results it is clear that the nitrogen content in biomass will result in amines and other nitrogen containing compounds whereas little amount sulfur can be taken out of the system in form of sulfur oxides (SOx) in a permissible limit of parts per million (ppm). While a high H/C atomic ratio of 1.57 and 1.23 for DR and TW indicates its deliberate properties as a solid fuel and paves the path for its consideration for further studies. This H/C atomic ratio itself clears that the biomass has competitive intervene for biofuels production as compared with popular biomass pinewood, which has H/C ratio of 1.6 [110]. TW also has more H/C ratio in comparison with mostly researched rubber waste i.e., tyre waste (styrene-butadiene rubber) having H/C ratio of 1.14 [102]. From the obtained H/C atomic ratios of both the materials and their comparison with the present literature it is oblivious to state that, both the materials are competitive enough to study their co-feed synergy.

To decide the temperature of thermal degradation/pyrolysis of both the co-feed materials, they are tested with thermogravimetric analysis. Figure 5.24 represents the thermogravimetric and differential thermogravimetric analysis of DR and TW. In figure, the line with single dash and dot chain represents the TGA study of DR biomass. From the graph, it can be seen that the first sharp curve till around 140 °C represents the removal of whatsoever moisture present in the biomass. In the same drift the degradation of hemicellulose content of biomass is taking place till 240 °C. Forward to that, up-to 490 °C the degradation of cellulosic material is taking place. From 500 °C onwards a clear degradation pattern of lignin can be seen which is showing degradation till 800 °C. Lignin is a very complex compound thus, it requires very high temperature to break it down into lower hydrocarbons. After the degradation of whole biomass in parts according to its constituents, some amount of residue is remaining and that is nothing but an ash content and carbon present in biomass resulting in char. TGA curve for butadiene rubber/IIR is represented by the short dash and two dots line in the graph. A slight degradation pattern of the TGA plot of TW till 350 °C is due to the decomposition of plasticizers which is corresponding to around the mass loss 5 percent. But, from 350 °C onwards till 500 °C, there is sharp degradation curve resulting in huge mass loss of almost 45 percent of the whole material representing the decomposition of isobutylene polymer. Next to that, around 5 mass % of degradation till 750 °C is due to isoprene polymer can be seen. 45 mass % of rubber stays undecomposed due to secondary reactions happening between IIR co-polymer and hence resulting in solid char. Maximum thermal degradation behaviour of both the co-feed materials is given by DTG curves. The DTG curve for DR is represented by small dash line, which is showing two sharp downward peaks i.e., one small peak at 70 °C and another large peak at 335 °C. Respectively, these two peaks are representing the maximum thermal degradation point of moisture in the biomass material and its combined structure mainly consisting holocellulose (cellulose and hemicellulose) [147]. The DTG curve for TW is represented by dot line in the graph, which is also showing two sharp downward peaks respectively at 380 °C and 740 °C. Maximum degradation of IIR is taking place at 380 °C and it is due to decomposition of the main constituent of IIR i.e., isobutylene polymer. The degradation peak at 740 °C represents the degradation of secondary compounds formed during the reaction. The results obtained from TGA in present study are analogous with the study reported by Martinez et al. [103] for co-pyrolysis of biomass with waste tyres. Thus, to avoid exposure of more secondary reaction, to allow the radicle interaction and to attain maximum degradation of both the feeds by co-feeding, it is advisable to perform co-pyrolysis in 550 °C to 700 °C temperature window. Based on this TGA and DTG results 600 °C temperature is chosen as optimum temperature for all the co-feed experiments based on performed experiments.

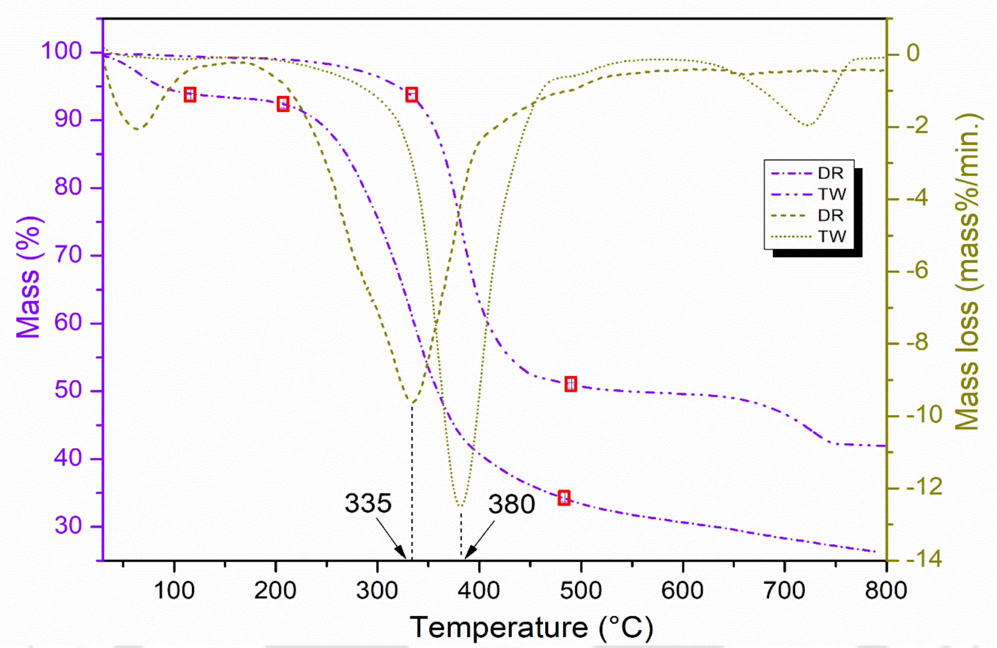

Figure 5.24. Thermogravimetric and differential thermogravimetric analysis of Delonix regia and Tube waste.

5.E.2 Co-pyrolysis Product Distribution

Co-pyrolysis of DR and TW resulted in condensed liquid as bio-oil, solid black char (bio-char) and some non-condensable vapours. This study reports actual mass % of liquid and solid products as they are main products for fulfilling the objective of work. Table 5.30 represents the overall product distribution of co-feed pyrolysis of DR and TW at variable ratios (95DR:5TW, 85DR:15TW, 75DR:25TW, 65DR:35TW and 50DR:50TW). From table in general it can be seen that, with increase in TW amount in co-feed ratio there is an increase in both solid and liquid products by decreasing gas product. Bio-oil having two phases i.e., organic phase and aqueous phase and both are contributing whole to 22.67, 24.00, 24.34, 25.00 and 36.67 mass %, respectively for 95DR:5TW (DT 5), 85DR:15TW (DT 15), 75DR:25TW (DT 25), 65DR:35TW (DT 35) and 50DR:50TW (DT 50). The organic phase of bio-oil showing very interesting rise in product yield with the increasing butyl rubber tube waste. For bio-oil, from DT 5 to DT 35 the pace of increase in bio-oil yield is very slow whereas from DT 35 to DT 50 there is a sudden rise in bio-oil yield.

Table 5.30. Co-feed pyrolysis product yield distribution of all the cases.

Sample	Bio-oil (mass %)		Bio-char (mass %)	Gases (mass %)^c
	Organic	Aqueous		
95 %DR+5 %TW (DT 5)	4.00	18.67	37.00	40.33
85 %DR+15 %TW (DT 15)	5.33	18.67	43.77	32.23
75 %DR+25 %TW (DT 25)	5.67	18.67	44.67	27.33
65 %DR+35 %TW (DT 35)	11.67	13.33	45.33	29.67
50 %DR+50 %TW (DT 50)	18.00	18.67	49.52	13.81

^{c}: calculated by difference

This result is showing that, though the bio-oil yield is increasing with the increasing tube waste percentage in co-feed, its optimum result is obtained at DT 50 i.e., the 1:1 ratio. So, to obtained high quantity of bio-oil yield from co-feed pyrolysis of DR and TW, it is recommended to opt for 1:1 co-feed ratio. In accordance with this the organic phase bio-oil is showing rise in order of DT 5, DT 15, DT 25, DT 35 and DT 50 as 4.00, 5.33, 5.67, 11.67, 18.00 mass %, respectively. Similarly, the char yield is also increasing as 37.00, 43.77, 44.67, 45.33 and 49.52 mass % with increasing TW content as DT 5, DT 15, DT 25, DT 35 and DT 50, the rise in char content is having near to parallel stretch of upsurge. Similar to that of bio-oil, bio-char is also resulting in optimum yield at 1:1 co-feed ratio in this study.

5.E.3 Qualitative Interpretation of Bio-oil

Organic phase bio-oil has been characterized to qualitatively examine its fuel potential as well as its chemical behaviour. Table 5.31 represents the physico-chemical properties of the bio-oil from each case with respect to petrol and diesel. The density of bio-oil is in general decreasing with increasing TW ratio in co-feed pyrolysis study. At ratio DT 5 the density of bio-oil is maximum with 1.11 g/ml and eventually it is decreasing to 1.01 g/ml at DT 15 ratio. The density at DT 25 is slightly increased to 1.02 g/ml and then decreased to 0.97 g/ml and 0.94 g/ml, respectively for DT 35 and DT 50. Whilst petrol has 0.75 g/ml density and diesel has 0.83 g/ml density. The density of bio-oil from DT 50 i.e., 1:1 ratio is the lowest among bio-oils from all the co-feed ratio studied and nearer to the density of diesel. Viscosity of the bio-oils from all the co-feed ratios is showing mixed trends, where it's in the range of 1.05 – 1.93 mPa.s. the lowest viscosity bio-oil is from DT 5 whereas with TW co-feed ratio DT 15 it is increased to 1.17 mPa.s and again decreased to 1.06 mPa.s for DT 25 co-feed ratio. The viscosity of the bio-oil from DT 35 is the highest among all the bio-oils with 1.93 mPa.s whereas it is again decreased for DT 50 co-feed ratio to 1.32 mPa.s. Petrol is very less viscosity of 0.28 mPa.s and diesel has viscosity of 1.14 mPa.s. The bio-oil from 1:1 ratio has the better fuel quality and can be upgraded to diesel grade fuel as compared from the density and viscosity values.

Table 5.31. Physico-chemical properties of the organic phase bio-oils from all co-feed cases.

Sample	Density, ρ (g/ml)	Viscosity, μ (mPa.s)	pH	Water mass % (KFT)	CV of liquid fuels (MJ/kg)	CV of bio-char (MJ/kg)
DT 5	1.11	1.05	4.05	0.87	20.55	23.01
DT 15	1.01	1.17	4.28	0.86	26.56	22.94
DT 25	1.02	1.06	3.60	0.85	29.15	22.26
DT 35	0.97	1.93	4.25	0.85	30.24	20.77
DT 50	0.94	1.32	4.58	0.84	32.61	13.61
Petrol	0.75	0.28	6.60	-	39.05	-
Diesel	0.83	1.14	7.60	-	41.09	-

The pH is showing mixed trends as the pH of 4.05 is at DT 5 i.e., the bio-oil is acidic in nature for this case. The pH rises to 4.28 for DT 15 but decreases to 3.60 for DT 25 which is the minimum pH recorded among all the bio-oils. It again increased to 4.25 and then to 4.58 in DT 35 and DT 50 co-feed ratio. The less is the pH, the bio-oil is more acidic and the more is the pH, the bio-oil is basic. Thus, from above results, it is found that the pH of bio-oil at 1:1 ratio is greater than other bio-oils and less than the pH values of petrol and diesel which are 6.60 and 7.60 respectively. In contrast to above properties, the most defining element of bio-oil property i.e., water mass % is showing unblemished vision of the bio-oil composition. With increasing TW amount in co-feed ratio the water content is decreased, though the range is from 0.84 – 0.87. The maximum possible water content in mass % is 0.87 for DT 5 co-feed ratio whereas the least possible water content is 0.84 mass % for DT 50 co-feed ratio. This water % is indicating the presence of water molecule in organic phase of bio-oil after separating the bio-oil in organic and aqueous phase. The calorific value (CV) is the most deciding element when defining the fuel properties of bio-oil. Table 5 also represents the CV of liquid fuels in MJ/kg. The CV of bio-oil is in perfect increasing order with respect to the increasing TW amount in co-feed ratio. The minimum CV is 20.55 MJ/kg of DT 5 co-feed ratio among all bio-oils, whereas it is increasing as 26.56, 29.15, 30.24 and maximum 32.61 MJ/kg for DT 15, DT 25, DT 35 and DT 50 co-feed conditions respectively. The CV of bio-oil procured from pure DR biomass is reported 18.8 MJ/kg in previous work [99]. The automobile/transportation fuel procured from nearby fuel station has CV of 39.05 MJ/kg and 41.09 MJ/kg for petrol and diesel, correspondingly. From the studied physico-chemical and fuel properties of the bio-oils from all the co-feed ratios, the bio-oil from 1:1 co-feed ratio is exhibiting the best quality with respect to that of existing transportation fuels in the market.

Further, the bio-oils are characterized by FTIR analysis for the determination of their functional groups. Figure 5.25 is the representation of the FTIR analysis, where common functional groups are represented according to the % transmission at the particular wavenumber in cm^{-1}. From the figure it can be seen that, the bio-oils from all co-feed ratios are showing similar downward peaks but the intensity of the % transmission is differing in all cases. Table 5.32 is stating the interpretation of obtained FTIR spectrogram with common functional groups present in all the bio-oils from various co-feed ratios. The wavenumbers displaying common functional groups are 3749, 2923, 1716, 1512, 1441, 1363, 1215, 1108, 1029, 882, 814, 735 and 520 cm^{-1}. These functional groups are correspondingly representing the class compounds, which are OH in alcohols and phenols, CH_3 and CH_2 in aliphatic compounds, ketones, benzene rings in aromatic compounds, NH in secondary amides, CH_3 in aliphatic compounds, CH_2 in aliphatic compounds, NO_2 in aromatic nitro compounds, vinyl ethers, thiocarbonyl compounds, aliphatic ethers, cyclic compounds, 1,2,4-trisubst benzenes, vinyl compounds Monosubst benzenes and ring in cycloalkanes. The intensity of maximum functional groups is very strong because of the exact interpretation of the FTIR data. On the other hand, the presence of almost all functional groups in all co-feed pyrolytic bio-oil is due to the basic materials, which are DR and TW, similar results are reported by Wang et al. [144].

Table 5.32. Common functional groups present in all the bio-oils.

Wavenumber (cm^{-1})	Wavenumber range (cm^{-1})	Class of Compound
3749	3760-3600 (s)	OH in alcohols and phenols
2923	2990-2850 (m-s)	$-CH_3$ and $–CH_2$ in aliphatic compounds
1716	1720-1700 (s)	C=O in ketones
1512	1515-1485 (m)	Benzene ring in aromatic compounds
	1565-1475 (vs)	NH in secondary amides
1441	1465-1440 (vs)	$-CH_3$ in aliphatic compounds
	1475-1450 (vs)	$-CH_2$ in aliphatic compounds
1363	1370-1350 (vs)	NO_2 in aromatic nitro compounds
1215	1225-1200 (vs)	C-O-C in vinyl ethers
1108	1160-1100 (m)	C=S in thiocarbonyl compounds
	1150-1070 (vs)	C-O-C in aliphatic ethers
1029	1035-950 (w)	Carbon ring in cyclic compounds
882	890-805 (vs)	1,2,4-trisubst benzenes
814	815-810 (vs)	$CH=CH_2$ in vinyl compounds
735	770-690 (vs)	Monosubst benzenes
529	580-430 (s)	Ring in cycloalkanes

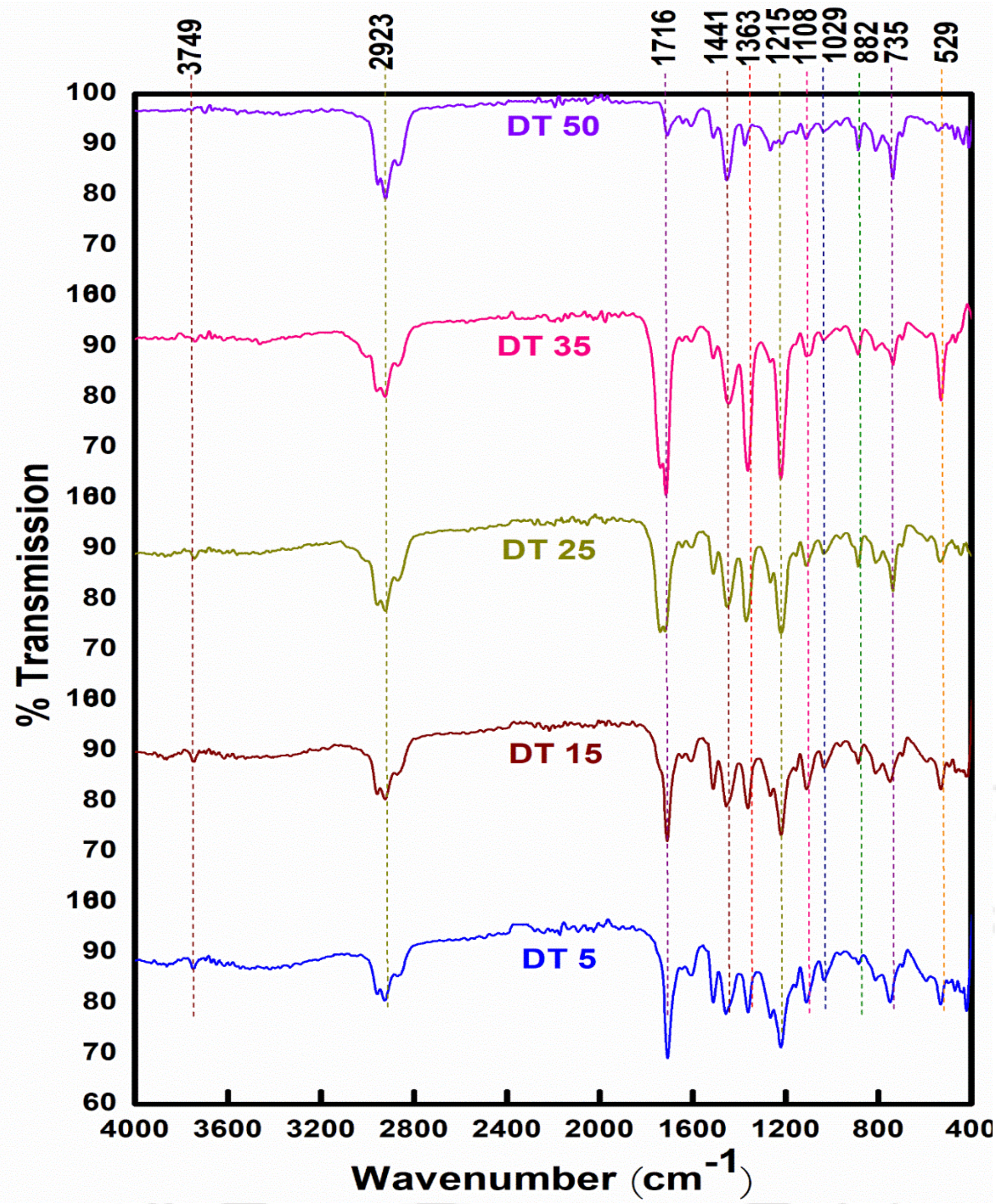

Figure 5.25. FT-IR spectrogram of bio-oils from all the studied cases.

Figure 5.26 is showing GCMS chromatogram of bio-oils obtained from all the co-feed conditions and the major three components in area % are drawn for each co-feed case. DT 5 contains D-Limonene, Phenol-2-methoxy-, and Phenol, 4-ethyl-2-methoxy- as highest area % occupying compounds. In co-feed conditions DT 15, DT 25 and DT 35 the highest area % occupying components are same, which are Benzene, 1,4-diethyl-, D-Limonene, and Phenol, 2-methoxy-. Co-feed condition DT 50 contains Benzene, 1-ethyl-2-methyl, D-Limonene, and Phenol, 2-methoxy- as highest area % occupying compounds. D-Limonene is present in highest amount in 1:1 co-feed ratio with 22.29 area %, another study by Kan et al. [148] based on natural rubber also reports high amount of D-Limonene. The detailed compound list is given as Table 5.33, which is showing all the compounds and hydrocarbons obtained through the variation in co-feed pyrolysis.

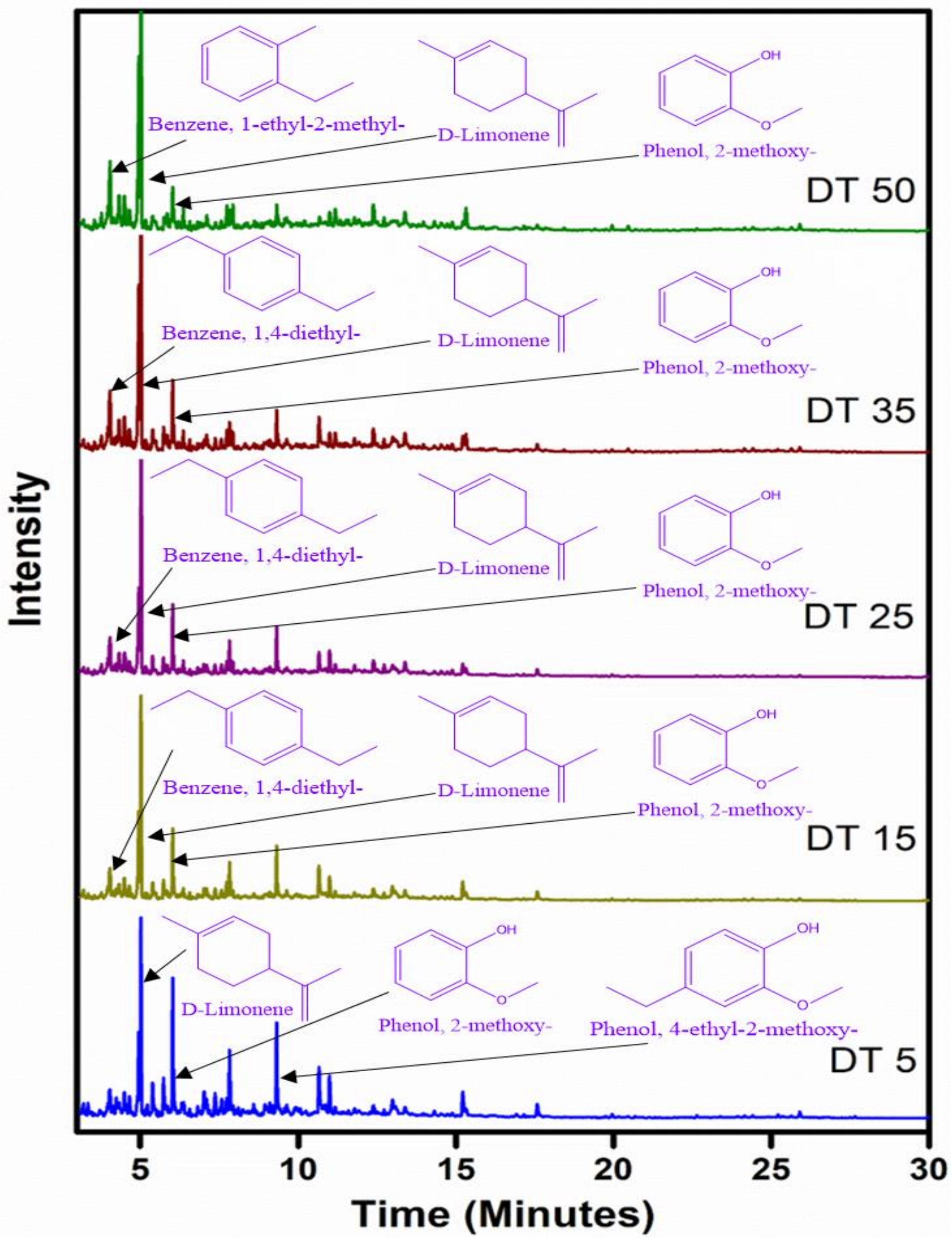

Figure 5.26. GCMS chromatogram of all the co-feed bio-oils.

The significance of this datasheet is that, it is classifying C_5-C_{12} hydrocarbons (petrol range) present in the bio-oil contributing to the major fraction in all the obtained bio-oils, whilst it is increasing with increasing TW ratio. As well as some fraction is contributing to C_{12}+ (Diesel range) hydrocarbons. Some major compounds are highlighted in Table A1 that are, Benzene, 1-ethyl-2-methyl-(C_9H_{12}); Phenol (C_6H_5OH); Benzene, 1,2,4-trimethyl (C_9H_{12}); Benzene, 1,4-diethyl- ($C_{10}H_{14}$); D-limonene ($C_{10}H_{16}$); p-Cresol (C_7H_8O); Benzene, 4-ethyl-1-2-dimethyl- ($C_{10}H_{14}$); Benzene, 1-methyl-4-(1-methylpropyl)- ($C_{11}H_{16}$); 2,2-dimethylindene,2,3-dihydro ($C_{11}H_{14}$); Naphthalene ($C_{10}H_8$); 2-Methoxy-5-methylphenol ($C_8H_{10}O_2$); Naphthalene, 1,2-dihydro-4-methyl- ($C_{11}H_{12}$); Phenol, 4-ethyl-2-methoxy- ($C_9H_{12}O_2$); Tridecane ($C_{13}H_{28}$); Phenol, 2,6-dimethoxy- ($C_8H_{10}O$); Phenol, 2-methoxy-4-propyl- ($C_{10}H_{14}O_2$); 1H-indene, 1,1,3-trimethyl- ($C_{12}H_{14}$); 3,5 – Dimethoxy-4-hydroxytoluene ($C_9H_{12}O_3$); Pentadecane ($C_{15}H_{32}$); 6,10-Dimethyl-3-(1-methylethylidene)-1-cyclodecane ($C_{15}H_{26}$); Benzene, 1,2,3 – trimethoxy-5-methyl ($C_{10}H_{14}O_3$); Naphtalene, 1,6,7-trimetyl ($C_{13}H_{14}$).

Based on Table A1, a concise compound classification in area % is done and reported here as Table 5.33. The classification is based on the compounds present in the list and their orientation, thus divided in the classes of aliphatics, aromatic, phenols, acid, ester, ether, ketone, furan, amine and aldehyde. The results are clear enough to state that the increasing amount of TW in co-feed ratio is directly affecting and improving the quality of bio-oil. The amount of aliphatics is increasing with the increase in TW proportion. As it can be seen that, 95 mass % of DR biomass in DT 5 case, is resulting in aliphatic compounds comprising of 20.73 area %, which is increasing in DT 15 to 31.49 area %. Similarly, for other co-feed ratios of DT 25, DT 35 and DT 50, the amount of aliphatic compounds are increased with 38.98, 39.81 and 42.99 area %, respectively. In co-feed ratio 1:1 i.e., in DT 50 the aliphatic compounds are more, which emphasis on the primary reactions occurred during the co-feed devolatilization of both the co-feed materials. The results out-coming from the GCMS analysis are very positive in aspect of increasing aromatic hydrocarbons. One objective of this study was to obtained valuable popular hydrocarbons, and the GCMS results are showing an effective rise in quality of the bio-oil with increasing TW ratio in co-feed by increasing amount of aromatics in the bio-oil. At DT 5 the amount of aromatics obtained are 30.43 area %, the amount is increased to 34.76 area % for DT 15 case. But, for DT 25 case, the aromatics in area % are decreasing whilst the probable reason for this to happen is because of the MS compound detection.

Table 5.33. Compound Classifications in Area % present in each co-feed based on GCMS analysis.

Class	DT 5	DT 15	DT 25	DT 35	DT 50
Aliphatic	20.73	31.49	38.98	39.81	42.99
Aromatic	30.43	34.76	31.37	37.41	42.66
Phenols	38.78	25.47	19.98	17.24	6.72
Acid	3.34	1.38	1.64	1.10	1.24
Ester	0.32	2.14	0.62	1.15	0.82
Ether	0.0	0.0	0.0	0.0	0.38
Ketone	4.48	2.65	2.71	1.69	0.80
Furan	1.45	0.73	1.07	0.24	0.34
Amine	0.41	0.25	0.48	0.59	0.36
Aldehyde	0.0	0.0	0.0	0.74	0.0

On the other hand, for DT 35 and DT 50, the aromatics in the corresponding bio-oils are increasing as 37.41 area % and 42.66 area %. The production of this huge amount of aromatics in co-feed ratio 1:1, itself signifies the value of that particular bio-oil. In terms of interesting results, the amount of phenolic compounds is decreasing with the increasing TW in co-feed ratio. A clearer picture can be seen from the Table 5.33, as the phenol content is highest with 38.78 area % at 95 mass % DR and 5 mass % TW co-feed case. The phenolic compounds are decreasing with very faster rate for increasing TW in co-feed ratio, where DT 15 has 25.47 area % phenolic compounds, phenols decreased to 19.98 and 17.24 area % correspondingly for DT 25 and DT 35. Most captivating result, is obtained from 1:1 co-feed ratio of DR:TW i.e., in DT 50, the total amount of phenolic compound decreased to 6.72 area %. From this obtained result, it is worth stating that the obtained bio-oil from the 1:1 co-feed ratio of tested materials is upgrading the bio-oil quality in every aspect. The phenolic compounds are the most unstable oxygen containing compounds, which leads to the increase in overall acidity of bio-oil and decreases its durability with degrading other physico-chemical properties. Thus, this co-feed pyrolysis is resulting in deoxygenation of bio-oil which eventually leads to the alternative fuel. Next to this, the acidic compounds present in area % are also showing decrease in acidic nature of the bio-oil but it has some up and down results. DT 5 bio-oil contains highest acid amount with 3.34 area %, which decreased in DT 15 case to 1.38 area %, then increased a little to 1.64 area %in DT 25 case, and again decreased to the lowest of all with 1.10 area % in DT 35 case, and finally increased a little to 1.24 area % which is very near to the least amount of acidic compounds present among the bio-oils from all the co-feed ratios studied. The amount of ester in area % is also showing mixed results whereas the presence of ether is only reported in DT 50 co-feed condition. The ketones, which are also oxygen containing compounds showing decrease in area % with increasing TW amount in the co-feed. It is maximum in DT 5 with 4.48 area % and minimum in DT 50 with 0.80 area %. Furans also showing similar type of constructive results by decreasing the overall area %, whereas DT 5 bio-oil has 1.45 area %, which is highest among all and DT 35 and DT 50 bio-oils are correspondingly showing least area % of furans with 0.24 and 0.34 area %. Amines in the bio-oils are coming from the nitrogen present in biomass and resulting in mixed amounts in bio-oils from all tested co-feed ratios. Only DT 35 co-feed condition is showing significant amount of aldehyde in it with 0.74 area %. From, these GCMS results, it will be not an exaggeration here, if it's state that this co-feed study found an alternative contender with existing resources. The co-feed ratios are more overly decreasing the adverse effects of secondary and post-secondary reactions during the formation of vapours inside the reactor.

Figure 5.27 is representing the NMR spectrogram obtained from proton analysis, the graph shows normalized intensity against chemical shift in ppm. From the figure, it can be seen that the presence of proton assignments in all the cases are similar but there is difference in intensity of the peaks with respect to the experimented co-feed condition. The change in peak's orientation is reported in and as Table 5.34 based on the obtained absolute values.

Table 5.34. Variation in proton assignments based on absolute values of peaks in ^{1}H-NMR.

Chemical Shift (ppm)	Assignments	DT 5	DT 15	DT 25	DT 35	DT 50
0.5-1.5	Alkanes	22.03	9.02	17.25	6.11	6.18
1.5-3.0	Aliphatic α to heteroatom or unsaturation	33.28	21.00	21.32	15.92	18.83
3.0-4.5	Alcohol (OH), methylene-dibenzene	23.05	21.84	15.07	21.72	13.41
4.5-6.0	Alkenes (C=C), methoxy, carbohydrates	15.05	14.48	15.12	20.26	21.04
6.0-8.5	Aromatics (hetero-)	4.28	26.92	22.07	35.15	34.01
9.5-10.0	Aldehydes	2.28	6.71	9.14	0.82	6.49

A brief overview of the obtained results is given here as the chemical shift from 0.5 – 1.5 ppm represents presence of alkanes, 1.5-3.0 ppm are aliphatic heteroatoms, 3.0-4.5 ppm shows alcohol and methylene–dibenzene, 4.5-6.0 ppm reports alkenes, methoxy and carbohydrates, 6.0-8.5 ppm results in hetero-aromatics and 9.5-10.0 ppm results in aldehydes. The proton assignments in the same range are also reported by Mullen et al. [128]. Thus, the proton NMR reports the variability of the bio-oil based on the structural orientation, where protons are distributed in saturated and unsaturated compounds. The bio-oil structures are very complex to understand and hence proton NMR study reveals the proper representation of the compound mixtures present in those bio-oils. From Table 5.34 it is perceivable that, the OH containing groups are getting decreased and aromatics are increased more-overly with increasing TW in co-feed ratio. Thus, this result signifies the improved quality of bio-oil over the corresponding increasing co-feed ratio. Also, the obtained results are quite analogues to the results obtained from GCMS analysis and thus it proves that, co-feeding both the tested materials in same proportion is leading to the upgraded quality of bio-oil.

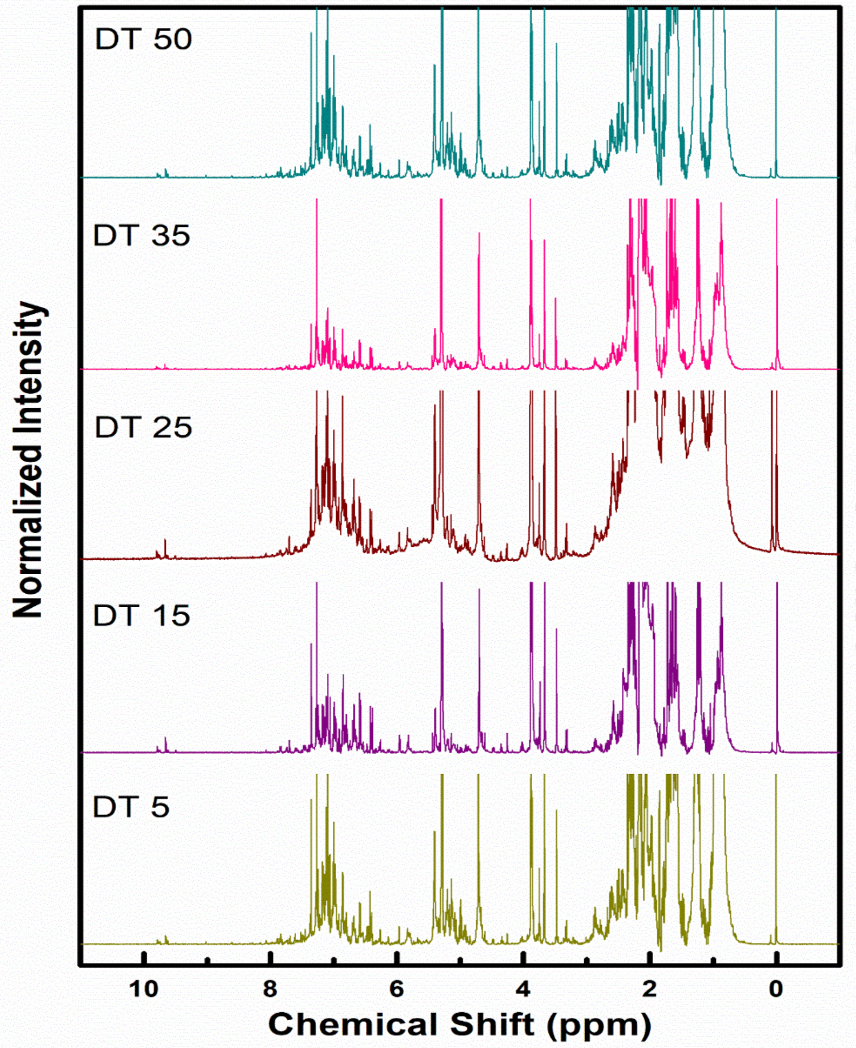

Figure 5.27. ^{1}H-NMR of all the bio-oils.

5.E.4 Char Properties

The actual numerical values of obtained CV results of the chars are displayed in Table 5.31. The CV of char from DT 5 is maximum with 23.01 MJ/kg and minimum from DT 50 with 13.61 MJ/kg. Such result corroborates that, not only primary vapours of the co-feed are reacting but also the physical structure of char forming due to the high temperature is resulting in altered properties. XRD results of chars are evident of above statement that are shown as Figure 5.28 and discussed in detail here.

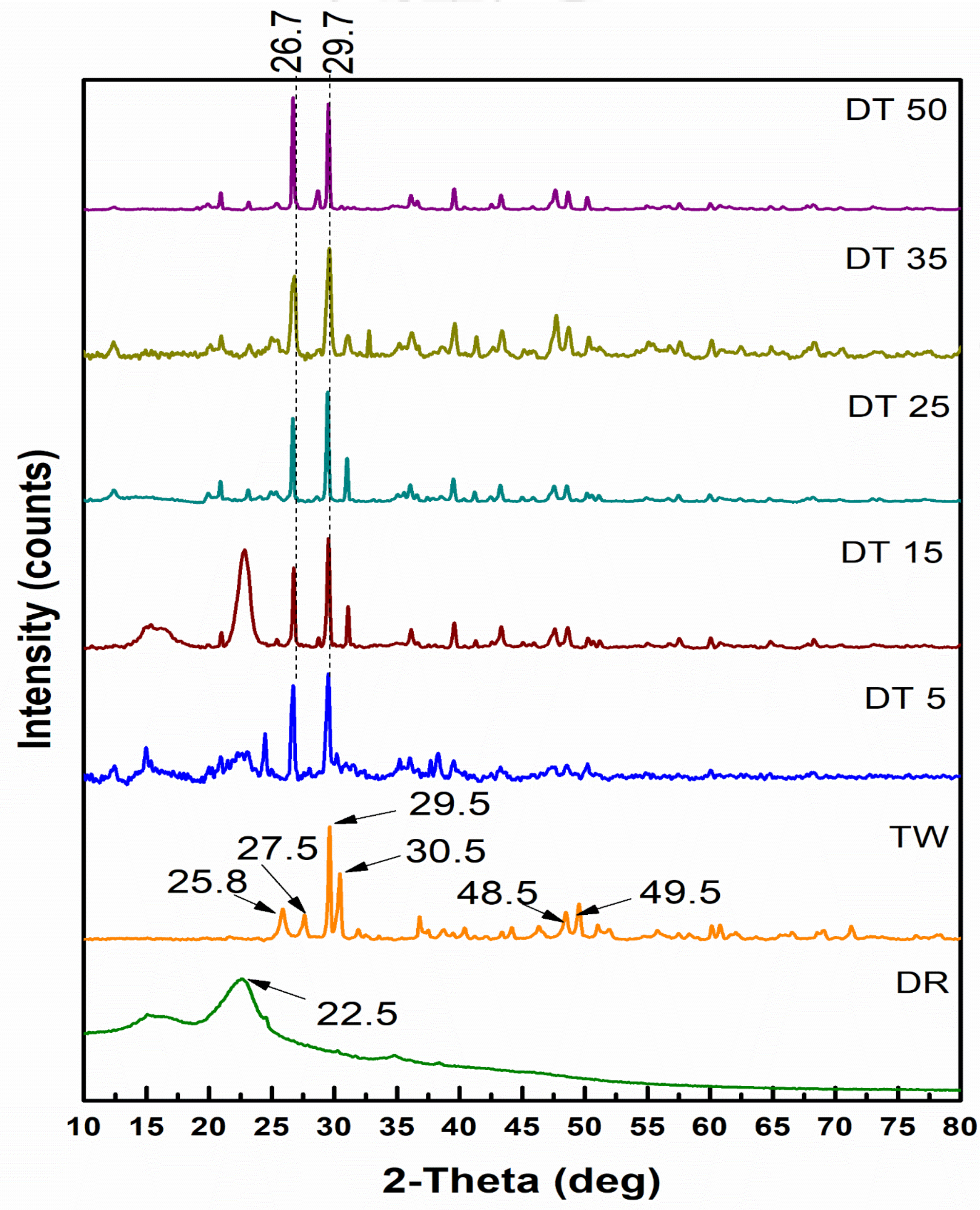

Figure 5.28. XRD diffractogram of DR, TW and their bio-chars from variable conditions.

Basic structure of the DR biomass shows a broad peak ranging from 20° to 24° at 2θ value of 22.5° representing crystal structure due to cellulose [149]. The basic structure of TW material is showing heavy crystallographic nature compared to that of the biomass by showing peaks at 2θ values of 25.8°, 27.5°, 29.5°, 30.5°, 48.5° and 49.5°. The obtained bio-chars from these co-feed materials are exhibiting the similar crystallographic structure, which is only possible when both the materials are thermally degraded to form transformed single product. The difference in all the bio-chars is in their responding intensities and the intensities are varying with the variation in co-feed ratio. Procured bio-chars are having common peaks at 31°, 36.5°, 40°, 41°, 43°, 47.5°, 48.8° and 50°. From these results it is worth stating that the quality of bio-chars is worth exploring for different purposes like fertilizer, water remediation and carbon sequestration.

Figure 5.29 is showing a graph of increasing total surface area of bio-chars obtained from BET analysis in m^2/g to that of increasing co-feed ratio, the corresponding values are 6.87, 11.67, 11.69, 15.34 and 18.63 m^2/g, respectively for DT 5, DT 15, DT 25, DT 35 and DT 50. Figure 5.30 is a typical plot showing N_2 adsorption-desorption isotherms (77K) for various chars obtained from the co-pyrolysis of DR+TW at 600°C. According to International Union of Pure and Applied Chemistry (IUPAC) classification of sorption isotherms, obtained isotherms are of type II. This type of isotherm is a characteristic of non-porous and macro porous adsorbents. The 'sharp knee' of isotherms correspond to multilayer formation after the monolayer formation of adsorbed molecules are complete. The desorption curve traces the adsorption curve resulting in hysteresis loop associated with slit shaped pores or wide capillaries [150]. Type II isotherm associated with capillary condensation in mesoporous structure [151] was observed in various co-pyrolysis researches [152]. These biochars of co-pyrolysis process without further activation step involved resulting in blockage of the initial porosity of the chars by some residual volatile matter [151]. BET surface areas of non-activated chars as low as 0.65 – 112.4 m^2/g were reported by Liu et al. [153] while performing pyrolysis of pine biomass.

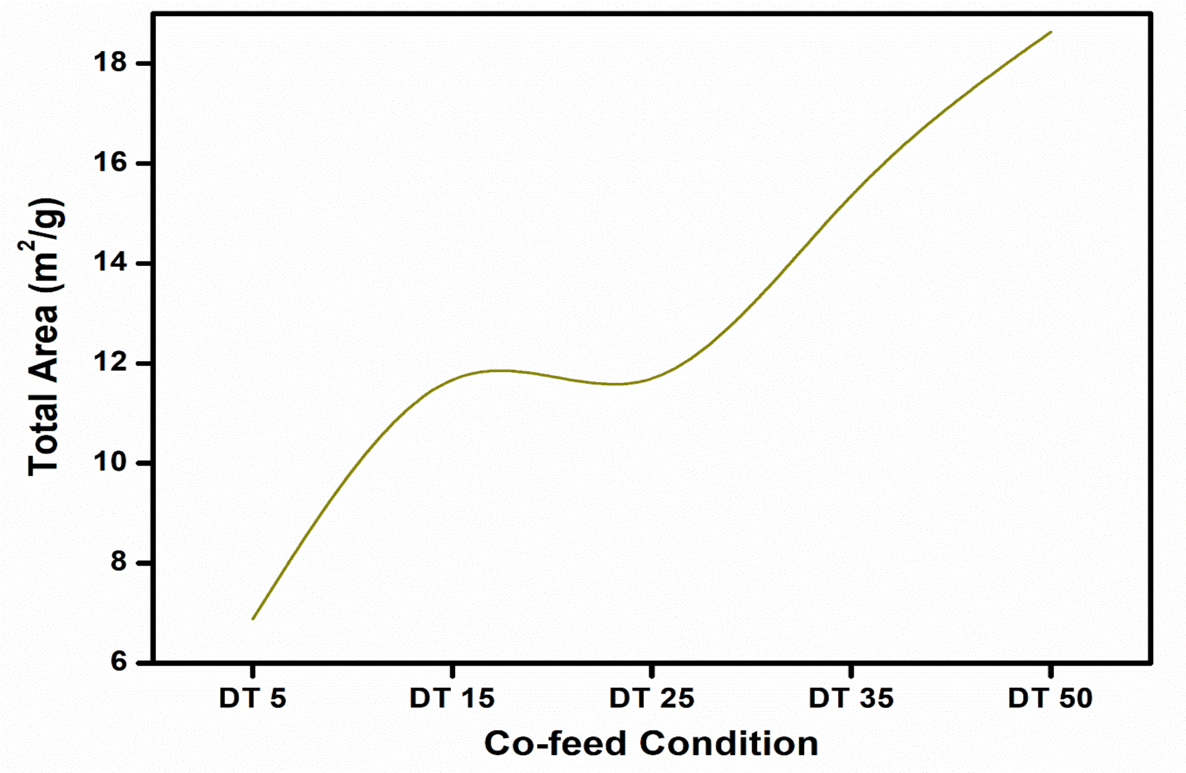

Figure 5.29. Total surface area of bio-char respected to the co-feed condition.

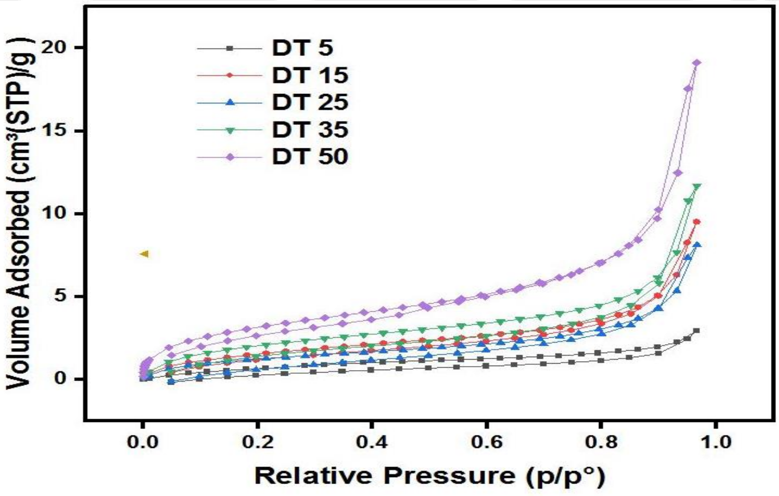

Figure 5.30. N_2 adsorption-desorption isotherms of biochars from all co-feed ratios at 77K.

Figure 5.31 is demonstrating the structural morphology of the feed materials along with the chars obtained from co-feeding them in various ratios based on FESEM results. The structure of DR biomass is intact and the orientation shows a uniform binding of the biomass.

Whilst the TW material displays a layered and little cracked structure with having very small circular bubbles on the surface. The bio-char obtained from DT 5 a distorted structure in terms of consecutive holes placed in specific distance. The structural view is of TW material and the sparkling substance seen around and over the hole containing material is actually the bio-char due to biomass. On the other hand, DT 15 bio-char shows a completely bound structure which is evident of binding of both the feeds tighter due to effect of heat at such a high temperature. DT 25 co-feed bio-char is showing clearer vision, where specifically arranged pores structure of the material taking down the small particles. This result discovers oneness of the bio-char obtained from co-feeding DR and TW at 3:1 ratio. Bio-char from DT 35 co-feed ratio delivers an image showing, cracked layer surrounded by tiny organic frameworks. Similar to previous results the bio-char from DT 50 is also showing pores structure having voids and space stacked with very small intact particles. Structural morphology of various bio-chars by FESEM analysis is also studied by Bourke et al. [131]. Thus, the acquired structural analysis data reports the overall quality of the bio-chars from DR and TW at variable co-feed ratios, which can be further activated to charcoal and can be used as support for catalyst preparation [154].

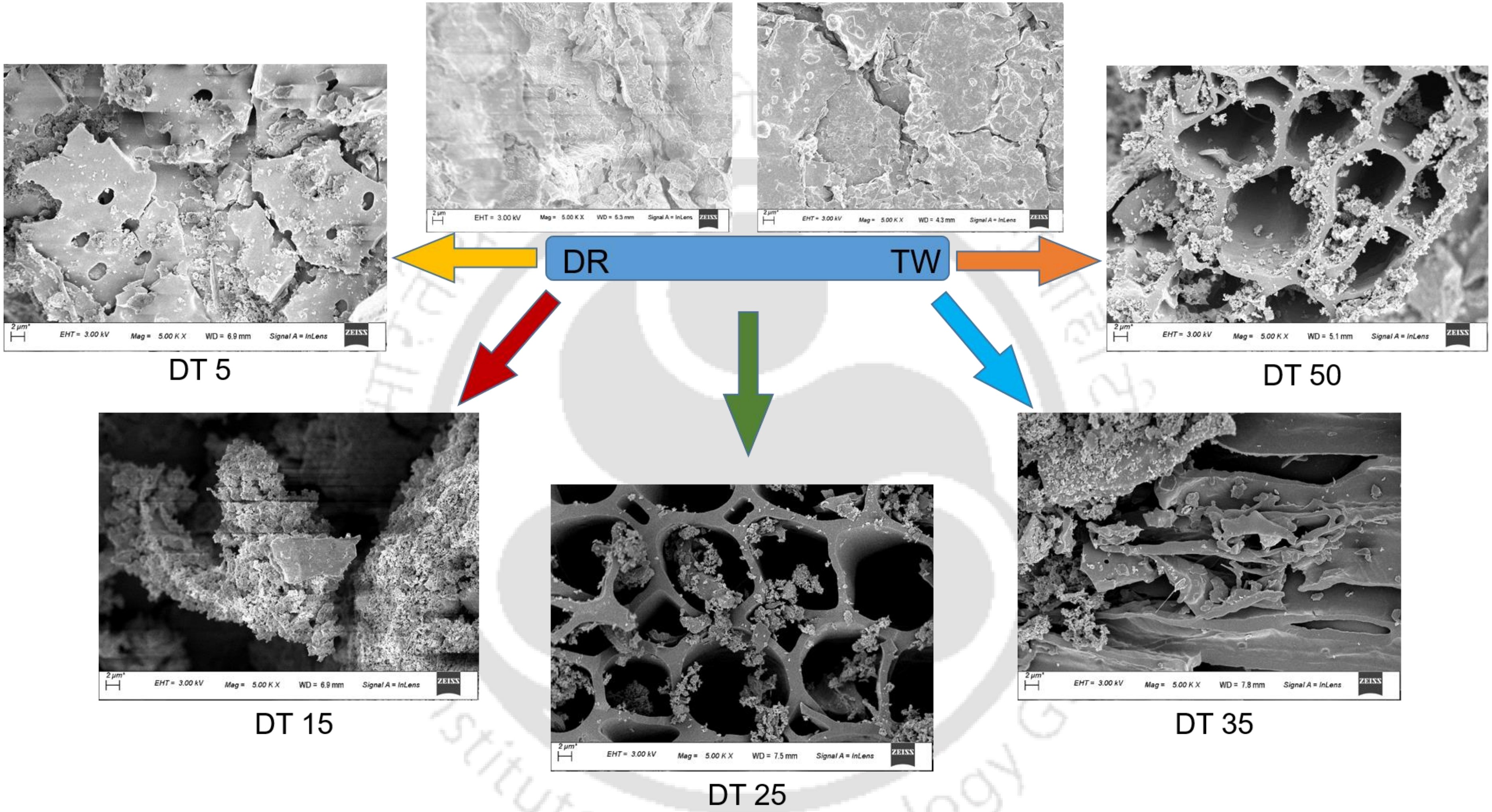

Figure 5.31. FESEM images of DR, TW and their co-feed biochars at 5 KX zoom.

5.E.5 Summary

The co-feed pyrolysis experiments of two potential solid waste materials i.e., Delonix regia biomass and butyl rubber tube wastes are conducted at their variable weight ratios. The ratios include 95DR:5TW (DT 5), 85DR:15TW (DT 15), 75DR:25TW (DT 25), 65DR:35TW (DT 35) and 50DR:50TW (DT 50). The study is focused on co-feed chemistry of biomass with petrochemical based rubber wastes and it is totally energy centric. The calorific values of bio-oils obtained from the increasing tube waste content in co-feed, is in increasing order and the highest CV bio-oil is obtained from DT 50 co-feed ratio with an average value of 32.61 MJ/kg. Also, bio-oil obtained by pyrolysis of the co-feed ratio DT 50 is displaying the improved physicochemical properties in terms of density (0.94 g/lt), viscosity (1.32 mPa.s), pH (4.58) and moisture content (only 0.84 mass %). It also results in less oxygenated compounds amongst all other tested co-feed ratios. The presence of popular hydrocarbons such as benzene oriented compounds, p-xylene and styrene display the worth of the bio-oil. An aliphatic hydrocarbon D-Limonene is present in highest area % in all the co-feed bio-oils, but the highest among all is 22.29 area % from DT 50 co-feed ratio case. The bio-char is also showing improvement with increasing co-feed ratio, the highest total BET surface area of 18.63 m^2/g is obtained from DT 50 co-feed case. The aliphatic and aromatic fractions are occupying more than 85 area % of bio-oil in the case of DT50; and individually contributing to 42.99 area % and 42.66 area % respectively. On the other hand, phenols and acids occupying only 6.72 area % and 1.24 area % respectively. For a fuel to be suitable to transportation vehicles, high fraction of aromatics and aliphatic compounds with lower fraction of phenols and acids are very important characteristics along with negligible moisture content, low density and pH close 6 – 7; and all of these are found in close proximity in this study by 1:1 co-feed pyrolysis of DR and TW. Thus, 50:50 mass % co-feed ratio of DR and TW is recommended for the production of green fuels which also provide a platform for waste minimization and management.

CHAPTER 6

Conclusions

The objectives based on knowledge gaps in the field of experimental pyrolysis are fulfilled with this thesis work. The extensive research on Delonix Regia biomass is conducted with the help of pyrolysis technology and its fuel potential is discovered. This thesis work covered pyrolysis at variable temperature, catalytic pyrolysis, catalytic hydropyrolysis and co-feed pyrolysis. With these various pyrolysis reaction environment, the vast range of materials are successfully tested. The scarcely researched lignocellulosic biomass of Delonix Regia is extensively researched in this work along with it green algal biomass *Oscillatoria* of good product quality has also been researched. Other than this, two different lignocellulosic biomass materials viz., Delonix Regia and Pinewood saw dust are tested to reveal their synergistic effects. The Co-feed pyrolysis study of Delonix Regia with Butyl rubber tube waste material at variable ratios has also been researched. Inclusively, this thesis work explored the fuel potential of lignocellulosic biomass waste, algal biomass waste and rubber tube waste. This work thus follows waste minimization and management, energy conversion from waste to biofuels and renewable energy resources approach. The results obtained from these studies are captivating and industry oriented as well as practical. The lignocellulosic biomass of Delonix Regia at variable temperature resulted in increasing HHV bio-oil with increasing temperature and highest HHV bio-oil is obtained at 25.27 MJ/kg at 700 °C. The bio-oil from catalytic hydropyrolysis of the lignocellulosic biomass resulted in bio-oil of 20.65 MJ/kg HHV. The catalytic pyrolysis and hydropyrolysis of algal biomass of *Oscillatoria* resulted in 16.61 MJ/kg and 16.66 MJ/kg HHV bio-oils respectively. The co-feed study of two lignocellulosic biomass of Delonix Regia and Pinewood Sawdust resulted in the upgraded quality product than single feed pyrolysis of any of both the materials, where the bio-oil from co-feed of 1:1 ratio has 20.29 MJ/kg of HHV. Next to that, the co-feed pyrolysis of lignocellulosic biomass and butyl rubber tube waste showed that the addition of tube waste amount in co-feed increases the product quality. The 1:1 co-feed ratio of Delonix Regia biomass and Tube waste material resulted in average calorific value of 32.61 MJ/kg, which is highest among all other studies. Thus, the bio-oils obtained from this thesis work are ready to serve as heating furnace oil or blend to crude oil and upon upgradation they can serve as transportation fuel as well.

CHAPTER 7

Future Scope of Work

- More novel biomass materials can be taken for energy conversion, production of bio-fuels and value added chemicals.
- Upgradation of bio-oil to the transportation fuel can be carried out using Catalytic Hydrodeoxygenation.
- Catalytic co-pyrolysis approach can also be explored for same biomass and materials as tested in this thesis work.
- The study on production of novel catalysts for catalytic HDO, catalytic pyrolysis and catalytic co-feed pyrolysis is also necessary in this area of work.
- Kinetic study of all the objectives will definitely give better understanding about the pyrolysis process on micro to large scale.
- Some characterizations such as, flash point, fire point, carbon residue test, total acid number and ASTM distillation and rheology will give more insights into the fuel quality of bio-oil.

Research Output

In International Referred Journals

Published

1) Kawale HD, Kishore N, "Comprehensive study on thermochemical putrefaction of *Delonix Regia* in non-catalytic, catalytic and hydro-catalytic pyrolysis atmospheres", *Renewable Energy*. **173**, 223-236 (2021). (doi.org/10.1016/j.renene.2021.03.139)
2) Kawale HD, Kishore N, "Thermochemical putrefaction of *Delonix regia* biomass and tube waste to produce high-quality pyrolytic bio-oil", *Journal of Thermal Analysis and Calorimetry*. (2021). (doi.org/10.1007/s10973-021-10725-2)
3) H. D. Kawale and N. Kishore, "Comparative study on pyrolysis of Delonix Regia, Pinewood sawdust and their co-feed for plausible bio-fuels production", *Energy*, **203**, 117921-1 to 117921-14 (2020). (doi.org/10.1016/j.energy.2020.117921)
4) H. D. Kawale and N. Kishore, "Pyrolysis of Delonix Regia and Characterization of its Pyrolytic Products: Effect of Pyrolysis Temperature", *Journal of Energy Resources Technology*, **142**, 082306-1 – 082306-11 (2020). (doi.org/10.1115/1.4046226)
5) H. D. Kawale and N. Kishore, "Production of hydrocarbons from a green algae (Oscillatoria) with exploration of its fuel characteristics over different reaction atmospheres", *Energy*, **178**, 344-355 (2019). (doi.org/10.1016/j.energy.2019.04.103)
6) H. D. Kawale and N. Kishore, "Bio-oil Production from a Lignocellulosic Biomass and its Fuel Characteristics", *Journal of Physics*, **1276** (2019) 012073. (doi:10.1088/1742-6596/1276/1/012073)

In National/International Conference Presentations

Presented

1) **H. D. Kawale**, N. Kishore *"Comparative Study on Waste Valorization of Lignocellulosic Biomass, E-Waste and Rubber Tube* Waste to Produce High Quality Bio-oil using Single and Co-Feed Pyrolysis*"* 2nd International Symposium on Analytical and Applied Pyrolysis, PYRO ASIA 2020, E-SYMPOSIUM, 11 - 13 December (2020).

2) **H. D. Kawale** and N. Kishore *"*Synergistic Study of Delonix regia with Tube Waste for Production of Valuable Products*"*, *Proceedings of 4th International Conference on Sustainable Energy & Environmental Challenges (IV SEEC 2019)*, CSIR-NEERI, Nagpur, INDIA, 27 - 29 November (2019).
3) Sneha Acharya, Gaffer Ahmed, **H. D. Kawale**, and N. Kishore, "Co-pyrolysis of *Delonix regia* (Gulmohar) with Tube waste for production of bio-oil and biochar", *Proceedings of Thirty-fifth National Convention of Chemical Engineers on The Food-Energy-Water Nexus-Challenges for Chemical Engineers*, Guwahati, Assam, India, 6 - 7 September (2019).
4) **H. D. Kawale**, Sneha Acharya, Gaffer Ahmed and N. Kishore, *"*Co-pyrolysis of Waste Gulmohar Biomass with Tube Waste*"*, *Annual Symposium of Chemical Engineering – REFLUX 7.0,* IIT Guwahati, INDIA, 28 - 29 September (2019).
5) **H. D. Kawale**, Abhishek Singh and N. Kishore, *"*Bio-oil Generation and Characterization from an Algal Biomass as Sustainable and Renewable Energy Resource*"*, *RESEARCH CONCLAVE 2019*, IIT Guwahati, INDIA, 14 - 17 March (2019).
6) **H. D. Kawale** and N. Kishore, "Bio-oil production from a lignocellulosic biomass and its fuel characteristics", *International Conference on Recent Advances in Fluid and Thermal Sciences (iCRAFT 2018)*, Dubai, UAE, 5 - 7 December (2018).
7) **H. D. Kawale** and N. Kishore, "Pyrolytic Bio-oil Derived from A Lignocellulosic Biomass and its Characterization", *71st Annual Session of Indian Institute of Chemical Engineers* (CHEMCON – 2018), NIT Jalandhar, Punjab, India, 27 - 30 December (2018).

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Table A1. GCMS analysis of bio-oils obtained from each co-feed pyrolysis condition of DR with TW.

Chemical Compound	DT 5			DT 15			DT 25			DT 35			DT 50		
	m/z	RT	Area %	m/z	RT	Area %	m/z	RT	Area %	m/z	RT	Area %	m/z	RT	Area %
6-Decen-5-one	-	-	-	-	-	-	97	3.15	0.29	-	-	-	-	-	-
1-Hexene-3,5-dione	-	-	-	-	-	-	-	-	-	97	3.15	0.33	-	-	-
Undecane, 5-methyl-	-	-	-	-	-	-		-	-	-	-	-	57	3.17	0.27
Butanoic acid, 2-methyl-, octyl ester	-	-	-	-	-	-	104	3.18	0.25	-	-	-	-	-	-
Styrene	104	3.18	0.31	-	-	-	-	-	-		-	-	-	-	-
Benzene, 1,3-dimethyl-	91	3.20	0.64	91	3.20	0.72	91	3.20	0.55						
p-Xylene										91	3.20	0.70	91	3.20	0.63
Cyclohexanone	55	3.23	0.25	-	-	-	-	-	-		-	-	-	-	-

6,6-Dimethylhepta-2,4-diene	-	-	-	-	-	-	109	3.25	0.25	-	-	-	-	-	-
2-Acetyl-5-methylfuran	109	3.28	0.18	109	3.28	0.17	-	-	-	-	-	-	-	-	-
2-Cyclopenten-1-one, 2-methyl-	96	3.35	0.82	96	3.35	0.53	96	3.35	0.56	96	3.36	0.45	-	-	-
2,4-Dimethylfuran	-	-	-	-	-	-		-	-	-	-	-	67	3.35	0.34
Ethanone, 1-(2-furanyl)-	95	3.41	0.43	-	-	-	95	3.41	0.21	-	-	-	-	-	-
1,4-Cyclohexadiene, 3,3,6,6-tetramethyl-	-	-	-	95	3.44	0.36	-	-	-	121	3.45	0.31	121	3.45	0.24
1,3-Cyclopentadiene, 1,2,3,4,5-pentamethyl-	-	-	-	-	-	-	121	3.45	0.23	-	-	-	-	-	-

Pyrazine, 2-methyl-5-propyl-	121	3.46	0.31	-	-	-	-	-	-		-	-	-	-	-
(1-Oxa-2-aza-spiro[2.5]oct-2-yl)-phenylmethanone	105	3.55	0.15	-	-	-	-	-	-		-	-	-	-	-
E-2-Hexenyl benzoate	-	-	-	105	3.55	0.37	-	-	-	-	-	-	-	-	-
3-Hexen-1-ol, benzoate, (Z)-	-	-	-	-	-	-	-	-	-	105	3.55	0.48	105	3.55	0.52
1,3-Hexadiene, 3-ethyl-2-methyl-	-	-	-	-	-	-	105	3.55	0.48	-	-	-	-	-	-
N-Propionylimidazole	-	-	-	68	3.69	0.16	-	-	-	-	-	-	-	-	-
Isobutyl 3-methylbut-3-enyl carbonate	-	-	-	-	-	-		-	-	-	-	-	67	3.69	0.30

3,7-Dimethyloct-6-en-1-yl propyl carbonate	-	-	-	-	-	-	-	-	-	95	3.70	0.46	-	-	-
2-Cyclohexen-1-one, 3,4,4-trimethyl-	-	-	-	95	3.72	0.37	-	-	-	-	-	-	-	-	-
Bicyclo[3.1.0]hexan-2-one, 3,3,6-trimethyl-	-	-	-	-	-	-	95	3.72	0.48	-	-	-	-	-	-
Bicyclo[2.2.1]hept-2-ene, 1,7,7-trimethyl-	-	-	-	121	3.78	0.60	-	-	-	-	-	-	-	-	-
1,3,6-Heptatriene, 2,5,6-trimethyl-	121	3.78	0.24	-	-	-	-	-	-	121	3.78	0.94	121	3.78	0.94
Cyclohexene, 1,5,5-trimethyl-3-methylene-	-	-	-	-	-	-	121	3.78	0.84	-	-	-	-	-	-
Bicyclo[3.2.1]octane	67	3.81	0.25	-	-	-	-	-	-		-	-	-	-	-

1-Pentanone, 1-(1H-imidazol-4-yl)-	-	-	-	-	-	-	67	3.82	0.21	-	-	-	-	-	-
Phenol, 4-propyl-	107	3.88	0.12	-	-	-	-	-	-	107	3.89	0.25	-	-	-
Ethyltetrafluorophosphorane	-	-	-	107	3.89	0.19	-	-	-	-	-	-	-	-	-
N-Benzyl-2-phenethylamine	-	-	-	91	3.92	0.25	-	-	-	-	-	-	-	-	-
Benzene, propyl-	91	3.93	0.27	-	-	-	-	-	-	-	-	-	-	-	-
Furfurylmethylamphetamine	-	-	-	-	-	-	-	-	-	91	3.93	0.32	91	3.93	0.36
Furan, 2-pentyl-	-	-	-	-	-	-	91	3.93	0.37	-	-	-	-	-	-
Ethanone, 1-(3-thienyl)-	-	-	-	111	4.02	0.45	111	4.02	0.50	111	4.03	0.47	111	4.03	0.38
Benzene, 1-ethyl-2-methyl-	105	4.04	1.65	105	4.04	2.84	105	4.05	3.11	-	-	-	105	4.05	4.17
Mesitylene	105	4.12	0.45	-	-	-	-	-	-	-	-	-	-	-	-
Cyclopenta[c]pyran-1,3-dione, 4,4a,5,6-	-	-	-	96	4.16	0.36	-	-	-	-	-	-	-	-	-

tetrahydro-4,7-dimethyl-															
Bicyclo[2.2.1]heptane, 7,7-dimethyl-2-methylene-	-	-	-	-	-	-	107	4.16	0.46	107	4.16	0.55	109	4.16	0.50
1,6-Octadiene, 2,6-dimethyl-, (Z)-	-	-	-	-	-	-	-	-	-	67	4.22	0.39	-	-	-
Cyclohexane, methylene-	-	-	-	-	-	-		-	-	-	-	-	67	4.22	0.43
Bicyclo[2.2.1]heptane, 2-ethyl-	-	-	-	-	-	-	95	4.22	0.65	-	-	-	-	-	-
Phenol	94	4.24	1.46	94	4.24	1.14	94	4.23	0.71	94	4.24	1.03	94	4.25	0.68
Benzene, 1,2,3-trimethyl-	-	-	-	-	-	-	-	-	-	105	4.30	0.29	-	-	-
Benzene, (1-methylethyl)-	105	4.30	0.37	105	4.30	0.30	105	4.30	0.31	-	-	-	-	-	-
Benzene, 1-ethyl-4-methyl-	-	-	-	-	-	-	-	-	-	-	-	-	105	4.30	0.30

6-Octen-1-ol, 3,7-dimethyl-, acetate	-	-	-	69	4.33	1.28	-	-	-	-	-	-	-	-	-
Bicyclo[4.1.0]heptane, 3,7,7-trimethyl-, [1S-(1.alpha.,3.beta.,6.alpha.)]-	-	-	-	-	-	-	-	-	-	-	-	-	69	4.33	2.08
1,5-Heptadiene, 3,3,6-trimethyl-	69	4.33	0.52	-	-	-	-	-	-		-	-	-	-	-
Cyclohexane, 1-methyl-3-(1-methylethenyl)-, cis-	-	-	-	-	-	-	-	-	-	69	4.33	1.87	-	-	-
1,5-Heptadiene, 3,3,5-trimethyl-	-	-	-	-	-	-	69	4.33	1.80	-	-	-	-	-	-
1,3-Cyclopentadiene, 5,5-dimethyl-1-propyl-	107	4.44	0.27	-	-	-	-	-	-	107	4.44	0.23	-	-	-

Cyclohexane, butylidene-	67	4.39	0.35	-	-	-	-	-	-	-	-	-	-	-	-
1,6-Octadiene, 2,5-dimethyl-, (E)-	-	-	-	67	4.39	0.47	67	4.39	0.61	67	4.39	0.54	67	4.39	0.54
2-Furanmethanol, acetate	81	4.44	0.24	81	4.44	0.26	81	4.44	0.25	-	-	-	-	-	-
Benzene, 1,2,4-trimethyl-	105	4.49	1.03	105	4.49	1.76	105	4.50	1.53	105	4.50	1.71	105	4.50	1.65
2,6-Dimethyl-2-trans-6-octadiene	69	4.52	0.54	69	4.52	0.83	69	4.53	1.15	-	-	-	-	-	-
2-Amino-3-hydroxypyridine	-	-	-	-	-	-	110	4.57	0.29	-	-	-	-	-	-
Noratropine	-	-	-	67	4.57	0.49	-	-	-	-	-	-	-	-	-
7-Propylidene-bicyclo[4.1.0]heptane	-	-	-	-	-	-	-	-	-	67	4.57	0.44	-	-	-
Bicyclo[4.3.0]nonane, 2-methylene-, cis-	-	-	-	-	-	-	-	-	-	-	-	-	79	4.58	0.35

2-Purinol	-	-	-	-	-	-	67	4.62	0.21	-	-	-	-	-	-
Benzaldehyde, 3-amino-, oxime	-	-	-	-	-	-	-	-	-	93	4.63	0.30	-	-	-
.alpha.-Phellandrene, dimer	-	-	-	-	-	-	-	-	-	-	-	-	93	4.64	0.44
Pentane, 3-bromo-	-	-	-	71	4.66	0.94	71	4.66	0.67	71	4.66	0.88	71	4.66	0.77
Propanoic acid, 2-methyl-, anhydride	71	4.66	0.99	-	-	-	-	-	-	-	-	-	-	-	-
1,3-Cyclopentadiene, 5,5-dimethyl-1-ethyl-	-	-	-	-	-	-	107	4.68	0.53	-	-	-	-	-	-
Spiro[2.4]heptane, 1,5-dimethyl-6-methylene-	-	-	-	107	4.75	0.83	-	-	-	-	-	-	-	-	-
1,3-Cyclopentadiene,	-	-	-	-	-	-	107	4.75	0.53	107	4.75	0.52	107	4.75	0.31

5,5-dimethyl-2-propyl-															
Thiophene, 3-(1,1-dimethylethyl)-	-	-	-	125	4.86	0.19	-	-	-	125	4.86	0.32	-	-	-
2-Acetyl-5-methylthiophene	125	4.86	0.14	-	-	-	125	4.87	0.29	-	-	-	125	4.87	0.31
Benzene, 1-methoxy-4-methyl-	122	4.89	0.39	-	-	-	-	-	-	-	-	-	-	-	-
Bicyclo[2.2.1]heptane, 1,7,7-trimethyl-	95	4.92	0.47	95	4.92	0.81	-	-	-	95	4.92	1.20	95	4.92	1.61
Cyclohexane, 1-methyl-4-(1-methylethenyl)-, cis-	-	-	-	-	-	-	95	4.92	1.25	-	-	-	-	-	-
Benzene, 1,4-diethyl-	119	4.95	4.41	119	4.96	6.92	119	4.96	6.57	119	4.96	8.79	119	4.96	9.13
D-Limonene	68	5.03	11.39	68	5.03	17.79	68	5.03	20.16	68	5.03	21.45	68	5.03	22.29

Cyclohexene, 4-methyl-1-(1-methylethenyl)-	93	5.11	0.16	-	-	-	-	-	-	-	-	-	-	-	-
Cyclohexene, 4-methylene-1-(1-methylethyl)-	-	-	-	-	-	-	-	-	-	93	5.12	0.41	-	-	-
Cycloheptene, 5-ethylidene-1-methyl-	-	-	-	-	-	-	93	5.12	0.41	-	-	-	93	5.12	0.38
1-(2-Methylphenyl)ethanol	117	5.18	0.38	117	5.18	0.41	-	-	-	-	-	-	-	-	-
Benzyl alcohol, 2,3-dimethyl-	-	-	-	-	-	-	117	5.18	0.48	93	5.18	0.53	93	5.18	0.43
2-Cyclopenten-1-one, 2,3-dimethyl-	67	5.23	1.77	67	5.23	0.50	67	5.23	0.44	110	5.23	0.44	-	-	-
Indene	116	5.33	0.18	-	-	-	-	-	-	-	-	-	-	-	-
Phenol, 2-methyl-	108	5.39	2.04	-	-	-	108	5.39	1.23	108	5.40	1.23	108	5.41	0.80

Benzene, 1-methyl-4-propyl-	-	-	-	105	5.44	0.59	105	5.44	0.68	105	5.44	0.75	105	5.45	0.85
Benzeneethanol, .beta.-methyl-	105	5.44	0.17	-	-	-	-	-	-	-	-	-	-	-	-
2-Cyclopenten-1-one, 3,4,5-trimethyl-	109	5.60	0.63	-	-	-	-	-	-	-	-	-	-	-	-
p-Cresol	107	5.74	3.05	107	5.74	3.71	107	5.73	1.73	107	5.74	1.92	107	5.75	1.13
o-Cymene				119	5.85	0.53	-	-	-	-	-	-	119	5.85	0.22
p-Cymene	119	5.85	0.52	-	-	-	-	-	-	-	-	-	-	-	-
Benzene, 1-ethyl-2,4-dimethyl-	-	-	-	-	-	-	119	5.85	0.83	119	5.85	0.75	119	5.85	0.78
Benzene, 1-methyl-3-(1-methylethenyl)-	119	5.96	0.29	91	5.91	0.48	-	-	-	-	-	-	91	5.91	1.38
Benzene, (1-ethylpropyl)-	91	5.91	0.22	-	-	-	-	-	-	-	-	-	-	-	-
Benzene, 1-ethyl-3,5-dimethyl-	-	-	-	-	-	-	-	-	-	119	5.96	0.27	119	5.96	0.29

Benzene, 4-ethenyl-1,2-dimethyl-	117	6.02	1.25	117	6.02	1.77	117	6.02	2.03	117	6.02	2.02	117	6.02	0.35
Phenol, 2-methoxy-	109	6.03	6.98	109	6.03	4.96	109	6.03	4.16	109	6.04	3.10	-	-	-
Mequinol	-	-	-	-	-	-	-	-	-	-	-	-	109	6.04	1.87
Undecane	57	6.11	0.20	57	6.11	0.18	57	6.11	0.20	-	-	-	57	6.11	0.25
(E)-2,6-Dimethylocta-3,7-diene-2,6-diol	-	-	-	-	-	-	-	-	-	82	6.12	0.21	-	-	-
Benzoic acid, hydrazide	105	6.15	0.20	-	-	-	-	-	-	-	-	-	-	-	-
Benzene, (1,2-dimethylpropyl)-	105	6.21	0.22	105	6.22	0.28	105	6.22	0.35	105	6.22	0.36	-	-	-
Benzene, (1-methylbutyl)-	-	-	-	-	-	-	-	-	-	-	-	-	105	6.22	0.39
2-Cyclopenten-1-one, 2,3,4-trimethyl-	131	6.29	0.38	131	6.29	0.44	124	6.29	0.30	-	-	-	81	6.29	0.42

4-Ethylphenyl acetate	-	-	-	-	-	-	122	6.33	0.29	-	-	-	-	-	-
Phenol, 4-ethyl-	-	-	-	122	6.33	0.37	-	-	-	-	-	-	-	-	-
2,4,6-Octatriene, 2,6-dimethyl-	-	-	-	-	-	-	-	-	-	121	6.34	0.37	121	6.34	0.31
Benzene, 1-methyl-4-(1-methylpropyl)-	119	6.37	0.37	119	6.37	0.62	119	6.37	0.86	119	6.37	0.85	119	6.37	0.96
Benzofuran, 2-methyl-	131	6.39	0.46	131	6.39	0.30	131	6.39	0.26	-	-	-	-	-	-
(1R,5R)-1,8-Dimethyl-4-(propan-2-ylidene)spiro[4.5]dec-7-ene	121	6.45	0.17	-	-	-	-	-	-	-	-	-	-	-	-
Benzene, 2-ethyl-1,4-dimethyl-	-	-	-	119	6.49	0.18	-	-	-	-	-	-	-	-	-
1-o-Tolylprop-2-en-1-one	-	-	-	-	-	-	119	6.49	0.20	-	-	-	-	-	-

Benzene, 1,2,3,5-tetramethyl-	119	6.57	0.86	119	6.57	0.79	119	6.57	0.48	119	6.57	0.46	119	6.57	0.36
Benzene, (2-methyl-1-butenyl)-	131	6.67	0.16	-	-	-	-	-	-	-	-	-	-	-	-
Furan, 2-hexyl-	-	-	-	-	-	-	-	-	-	95	6.70	0.24	-	-	-
Bicyclo[5.4.0]undecane (trans)	-	-	-	-	-	-	-	-	-	-	-	-	95	6.70	0.23
Benzene, 1,4-dimethyl-2-(1-methylethyl)-	-	-	-	133	6.81	0.33	133	6.81	0.33	-	-	-	-	-	-
Benzene, pentamethyl-	-	-	-	-	-	-	-	-	-	133	6.81	0.29	-	-	-
3,4-Dimethylcumene	-	-	-	-	-	-	-	-	-	-	-	-	133	6.81	0.33
Phenol, 2-ethyl-	107	6.83	0.49	-	-	-	-	-	-	-	-	-	-	-	-
2,4,6-Octatriene, 2,6-dimethyl-, (E,Z)-	121	6.88	0.19	121	6.88	0.28	121	6.88	0.33	121	6.88	0.28	121	6.88	0.25

1-Propanone, 1-(4-fluorophenyl)-	95	6.69	0.14	-	-	-	-	-	-	-	-	-	-	-	-
Benzene, 1-ethyl-4-(1-methylethyl)-	133	6.96	0.22	133	6.96	0.18	133	6.96	0.21	133	6.96	0.25	133	6.96	0.31
Succinic acid, 3-chlorophenyl 4-methoxybenzyl ester	121	7.02	0.43	-	-	-	-	-	-	-	-	-	-	-	-
(2S,6R,7S,8E)-(+)-2,7-Epoxy-4,8-megastigmadiene	-	-	-	-	-	-	122	7.02	0.97	-	-	-	-	-	-
Phenol, 2,4-dimethyl-	122	7.03	3.10	122	7.03	1.45	-	-	-	122	7.03	1.08	122	7.04	0.62
2-Methylindene	115	7.10	0.86	115	7.10	0.87	115	7.10	0.22	-	-	-	-	-	-
Benzene, (methylenecyclopropyl)-	-	-	-	-	-	-	-	-	-	115	7.10	0.59	-	-	-

Benzene,1-methyl-1,2-propadienyl-	-	-	-	-	-	-	115	7.10	0.39	-	-	-	-	-	-
Benzene, (2-methyl-2-propenyl)-	-	-	-	117	7.11	0.38	-	-	-	-	-	-	-	-	-
Benzene, 1-methyl-2-(2-propenyl)-	-	-	-	-	-	-	-	-	-	-	-	-	117	7.11	0.66
Indan, 1-methyl-	-	-	-	-	-	-	117	7.11	0.47	-	-	-	-	-	-
trans-Verbenyl laureate	119	7.14	0.19	-	-	-	-	-	-	-	-	-	-	-	-
3-Buten-2-ol, 4-phenyl-	-	-	-	-	-	-	-	-	-	-	-	-	105	7.20	0.24
Cycloprop[a]indene, 1,1a,6,6a-tetrahydro-	-	-	-	-	-	-	-	-	-	130	7.21	0.27	-	-	-
Phenol, 3,5-dimethyl-	107	7.37	2.42	107	7.37	1.34	107	7.37	1.33	107	7.38	0.98	-	-	-

4-(2-Ethylhexoxy)ethylbenzene	-	-	-	107	7.54	0.31	-	-	-	107	7.54	0.47	-	-	-
2,2-Dimethylindene, 2,3-dihydro-	131	7.57	0.47	131	7.57	1.21	131	7.57	1.59	131	7.57	1.73	131	7.57	1.80
Phenol, 4-methoxy-3-methyl-	-	-	-	-	-	-	123	7.58	0.39	123	7.59	0.22	-	-	-
Benzene, (3-iodo-1-methoxybutyl)-	-	-	-	121	7.67	0.21	-	-	-	-	-	-	-	-	-
Phenol, 2-(1-methylethyl)-	121	7.67	0.26	-	-	-	-	-	-	-	-	-	-	-	-
Naphthalene	128	7.74	0.55	128	7.74	1.05	128	7.74	0.47	128	7.74	0.60	128	7.74	0.68
2-Methoxy-5-methylphenol	138	7.83	4.70	138	7.83	3.58	138	7.83	2.52	138	7.83	1.62	138	7.84	0.98
Dodecane	57	7.85	0.30	107	7.85	0.35	57	7.85	0.24	-	-	-	57	7.85	0.50
Benzene, 1-methyl-2-(1-	-	-	-	131	7.94	0.48	-	-	-	131	7.94	0.21	131	7.94	1.06

methyl-2-propenyl)-															
Benzene, 1-methyl-4-(1-methyl-2-propenyl)-	131	7.94	0.38	-	-	-	131	7.94	0.75	131	7.94	0.73	-	-	-
Phenol, 2,4,6-trimethyl-	121	8.02	0.84	121	8.02	0.27	121	8.02	0.25	-	-	-	-	-	-
5-Isopropyl-2-methylphenyl carbanilate	150	8.06	0.14	-	-	-	-	-	-	-	-	-	-	-	-
1H-Benzimidazole, 5,6-dimethyl-	146	8.11	0.38	146	8.11	0.24	146	8.11	0.21	-	-	-	-	-	-
Benzofuran, 4,7-dimethyl-	145	8.25	0.57	-	-	-	-	-	-	-	-	-	-	-	-
1,2-Dimethylbenzimidazole	-	-	-	145	8.25	0.34	145	8.25	0.31	-	-	-	-	-	-

Naphthalene, decahydro-1,6-dimethyl-	-	-	-	-	-	-	-	-	-	95	8.29	0.20	-	-	-
trans,trans-1,7-Dimethylspiro[4.5]decane	-	-	-	95	8.29	0.19	95	8.29	0.24	-	-	-	95	8.29	0.24
1H-Indazole, 5,7-dimethyl-	146	8.36	0.26	-	-	-	-	-	-	-	-	-	-	-	-
1H-Indene, 2,3-dihydro-1,1,4-trimethyl-	-	-	-	-	-	-	-	-	-	145	8.40	0.24	145	8.39	0.57
(1R,5S)-1,8-Dimethyl-4-(propan-2-ylidene)spiro[4.5]dec-7-ene	-	-	-	-	-	-	121	8.40	0.27	-	-	-	-	-	-
Phenol, 2-(1-methylethyl)-, methylcarbamate	121	8.41	0.27	121	8.41	0.57	-	-	-	-	-	-	-	-	-

Phenol, 3-ethyl-5-methyl-	121	8.52	0.84	121	8.53	0.20	-	-	-	-	-	-	-	-	-
2-(4-Methoxyphenyl)ethanol	-	-	-	121	8.60	0.52	121	8.60	0.42	-	-	-	-	-	-
4-Methoxybenzyl alcohol, methyl ether	121	8.60	0.74	-	-	-	-	-	-	-	-	-	-	-	-
Benzene, 1-ethyl-4-methoxy-	121	8.47	0.23	-	-	-	121	8.67	0.21	-	-	-	-	-	-
2H-1-Benzopyran, 2,2-dimethyl-	145	8.61	0.21	-	-	-	-	-	-	145	8.61	0.41	-	-	-
Fenazaquin	-	-	-	-	-	-	-	-	-	145	8.70	0.23	-	-	-
Benzene, 1-(1,1-dimethylethyl)-4-ethenyl-	-	-	-	-	-	-	-	-	-	-	-	-	145	8.70	0.32
Ethaneperoxoic acid, 1-cyano-1-phenylbutyl ester	-	-	-	-	-	-	-	-	-	131	8.83	0.21	-	-	-

Phenol, 2-ethyl-4-methyl-	121	8.68	0.29	121	8.68	0.53	-	-	-	121	8.96	0.40	-	-	-
Phenol, 3-(1-methylethyl)-	121	8.96	0.83	-	-	-	121	8.96	0.38	-	-	-	-	-	-
Silane, methyltripropynyl-	-	-	-	-	-	-	-	-	-	-	-	-	145	8.99	0.31
Naphthalene, 1,2-dihydro-4-methyl-	129	8.93	0.89	129	9.04	0.86	129	9.04	0.57	129	9.04	1.82	129	9.04	1.56
Phenol, 3,4,5-trimethyl-	-	-	-	129	9.11	0.50	121	9.18	0.64	-	-	-	-	-	-
Benzene, 1-methyl-3,5-bis(1-methylethyl)-	-	-	-	-	-	-	-	-	-	-	-	-	133	9.26	0.33
D-Alanine, N-(4-ethylbenzoyl)-, pentyl ester	133	9.26	0.13	-	-	-	133	9.25	0.22	133	9.25	0.21	-	-	-

Benzene, 1,3,5-trimethyl-2-propyl-	-	-	-	133	9.26	0.17	-	-	-	-	-	-	-	-	-
Phenol, 4-ethyl-2-methoxy-	137	9.32	4.77	137	9.32	3.90	137	9.32	3.16	137	9.32	2.13	137	9.33	1.36
Benzene, 1,4-bis(1-methylethenyl)-	-	-	-	-	-	-	-	-	-	-	-	-	143	9.38	0.33
1,7-Diazabicyclo[2.2.0]heptane, 7-chloro-	132	9.44	0.25	132	9.44	0.18	-	-	-	-	-	-	-	-	-
Tridecane	57	9.57	0.24	57	9.57	0.26	57	9.57	0.20	57	9.58	0.22	57	9.58	0.30
1H-Indene, 2,3-dihydro-1,1,3-trimethyl-	-	-	-	145	9.60	0.52	145	9.60	0.74	145	9.47	1.08	159	9.47	1.40
1H-Indene, 1-ethylidene-	142	9.64	0.54	142	9.64	0.97	142	9.64	0.66	-	-	-	142	9.64	0.78
Hexestrol dimethyl ether	-	-	-	-	-	-	-	-	-	-	-	-	121	9.69	0.38

Phthalic acid, di(2,4,5-trifluorobenzyl) ester	-	-	-	145	9.69	0.18	149	9.69	0.21	-	-	-	-	-	-
Benzothiazole, 2-methyl-	-	-	-	-	-	-	-	-	-	149	9.69	0.25	-	-	-
Benzene, 1,3,5-trimethyl-2-(1,2-propadienyl)-	121	9.82	0.11	-	-	-	-	-	-	-	-	-	-	-	-
Naphthalene, 1,2,3,4-tetrahydro-1,6,8-trimethyl-	-	-	-	-	-	-	-	-	-	-	-	-	159	9.84	0.22
1,2,3-Trimethoxybenzene	160	9.89	0.37	-	-	-	160	9.90	0.20	-	-	-	-	-	-
1H-Pyrrolo[2,3-b]pyridine, 2-(1-methylethyl)-	-	-	-	145	9.90	0.36	-	-	-	-	-	-	-	-	-

Naphthalene, 2-methyl-	142	9.95	0.38	-	-	-	-	-	-	142	9.64	0.76	-	-	-
1H-Indene, 2,3-dihydro-4,5,7-trimethyl-	151	10.07	0.44	-	-	-	145	10.07	0.50	-	-	-	145	10.07	0.25
Phenol, 4-(1-methylpropyl)-	121	10.17	0.31	-	-	-	-	-	-	-	-	-	-	-	-
(3aR,6R,8aS)-7,7-Dimethyl-8-methyleneoctahydro-1H-3a,6-methanoazulene	-	-	-	-	-	-	-	-	-	121	10.18	0.20	107	10.18	0.21
Dibenzo[a,i]biphenylene, 5,6,6a,6b,7,8,12b,12c-octahydro-2,11-dimethoxy-	160	10.25	0.26	-	-	-	-	-	-	-	-	-	-	-	-
Phenol, 2-chloro-4-methoxy-	159	10.42	0.11	-	-	-	-	-	-	-	-	-	-	-	-

Cycloocta-1,3,6-triene, 2,3,5,5,8,8-hexamethyl-	-	-	-	-	-	-	107	10.42	0.21	-	-	-	107	10.42	0.23
4-Ethylbenzoic acid, 6-chlorohexyl ester	135	10.50	0.21	-	-	-	-	-	-	-	-	-	-	-	-
Naphthalene, 1,2,3,4-tetrahydro-1,5-dimethyl-	-	-	-	-	-	-	-	-	-	145	10.56	0.22	-	-	-
Phenol, 4-(methoxymethyl)-2,6-dimethyl-	135	10.59	0.16	-	-	-	-	-	-	-	-	-	-	-	-
Phenol, 2,6-dimethoxy-	154	10.66	3.35	154	10.66	3.25	154	10.66	1.85	154	10.67	2.32	154	10.68	0.96
Eugenol	164	10.80	0.25	164	10.80	0.56	164	10.80	0.25	164	10.80	0.51	-	-	-
Ethanone, 1-(2-hydroxy-6-methoxyphenyl)-	-	-	-	151	10.85	0.33	-	-	-	-	-	-	-	-	-

2'-Hydroxy-6'-methoxyacetophenone, acetate	-	-	-	-	-	-	-	-	-	151	10.85	0.32	-	-	-
Ethanone, 1-(3-hydroxy-4-methoxyphenyl)-	151	10.74	0.54	-	-	-	151	10.85	0.33	-	-	-	-	-	-
2-Methyl-2-adamantanol	-	-	-	-	-	-	-	-	-	-	-	-	151	10.85	0.29
Phenol, 2-methoxy-4-propyl-	137	11.00	2.07	137	11.00	1.73	137	11.00	1.62	137	11.00	0.90	137	11.00	0.88
1H-Indene, 1,1,3-trimethyl-	143	11.18	0.74	143	11.18	0.74	143	11.18	1.13	143	11.18	1.75	143	11.18	1.44
2,3,4-Trifluorobenzoic acid, cyclobutyl ester	-	-	-	-	-	-	-	-	-	-	-	-	159	11.25	0.21
trans-.alpha.-Bergamotene	93	11.44	0.17	93	11.44	0.59	-	-	-	-	-	-	-	-	-

Boron, diethyl[3-imino-2-(1-iminoethyl)butanenitrilato-N2,N3]-, (t-4)-	162	11.52	0.18	-	-	-	-	-	-	-	-	-	-	-	-
Benzo[b]thiophene, 3,5-dimethyl-	-	-	-	162	11.53	0.19	162	11.53	0.21	162	11.53	0.31	162	11.53	0.38
Tetradecane	57	11.60	0.27	-	-	-	57	11.60	0.25	-	-	-	57	11.60	0.40
Naphthalene, 6-(1-ethylpropyl)-1,2,3,4-tetrahydro-	-	-	-	-	-	-	173	11.77	0.23	-	-	-	-	-	-
6,8-Nonadien-2-one, 6-methyl-5-(1-methylethylidene)-	119	11.79	0.45	-	-	-	-	-	-	-	-	-	-	-	-
(Z)-1-Methyl-4-(6-methylhept-5-en-2-	-	-	-	93	11.44	0.19	119	11.79	0.96	119	11.79	0.59	119	11.79	0.59

ylidene)cyclohex-1-ene															
.beta.-Elemenone	-	-	-	-	-	-	107	11.87	0.22	-	-	-	-	-	-
Naphthalene, 1,4-dimethyl-	156	11.93	0.41	156	11.93	0.38	156	11.93	0.36	156	11.93	0.58	156	11.93	0.64
Ethane, 1,1-dibromo-	-	-	-	-	-	-	172	11.99	0.20	-	-	-	-	-	-
Benzaldehyde, 2-chloro-3,4-dihydroxy-	-	-	-	-	-	-	-	-	-	172	11.99	0.21	-	-	-
1,3,2-Dioxaborolane-4,5-dimethanol, 2-phenyl-, dibenzoate, trans-	-	-	-	164	11.99	0.17	-	-	-	-	-	-	-	-	-
Cycloheptane, 4-methylene-1-methyl-2-(2-methyl-1-propen-1-yl)-1-vinyl-	-	-	-	-	-	-	-	-	-	81	12.10	0.35	-	-	-

Cyclohexane, 1-ethenyl-1-methyl-2,4-bis(1-methylethenyl)-, [1S-(1.alpha.,2.beta.,4.beta.)]-	-	-	-	81	12.10	0.27	-	-	-	-	-	-	-	-	-
2,3-Diazabicyclo[2.2.1]hept-2-ene, 4-methyl-1-(pent-4-en-1-yl)-	-	-	-	-	-	-	-	-	-	-	-	-	81	12.10	0.26
3,7,11,Trimethyl-8,10-dodecedienylacetate	-	-	-	-	-	-	81	12.10	0.35	-	-	-	-	-	-
Fenchone	81	12.10	0.14	-	-	-	-	-	-	-	-	-	-	-	-
Silane, trimethyl(2-phenylethenyl)-	159	12.17	0.15	-	-	-	-	-	-	-	-	-	-	-	-

2,4,8-Trimethyl-1,2,3,4-tetrahydroquinoline	-	-	-	-	-	-	-	-	-	107	12.18	0.27	-	-	-
Myrtene acid chloride	-	-	-	-	-	-	107	12.19	0.22	-	-	-	-	-	-
Naphthalene, 1,2,3,4-tetrahydro-5,6,7,8-tetramethyl-	-	-	-	-	-	-	-	-	-	-	-	-	160	12.20	0.26
Naphthalene, 1,6-dimethyl-	156	12.29	0.39	156	12.29	0.26	156	12.29	0.20	156	12.29	0.53	156	12.29	0.57
Naphthalene, 2,6-dimethyl-	156	12.39	0.65	156	12.39	1.12	156	12.39	0.81	156	12.38	1.12	156	12.38	1.39
1,5-Cyclodecadiene, 1,5-dimethyl-8-(1-	-	-	-	107	12.50	0.31	-	-	-	107	12.50	0.35	-	-	-

methylethenyl)-, [S-(Z,E)]-															
(1S,2E,6E,10R)-3,7,11,11-Tetramethylbicyclo[8.1.0]undeca-2,6-diene	107	12.50	0.27	-	-	-	-	-	-	-	-	-	-	-	-
1,5-Cyclodecadiene, 1,5-dimethyl-8-(1-methylethylidene)-, (E,E)-	-	-	-	-	-	-	107	12.51	0.44	-	-	-	107	12.51	0.42
m-Cresol	165	12.59	0.18	-	-	-	-	-	-	-	-	-	-	-	-
1,5,9-Undecatriene, 2,6,10-trimethyl-, (Z)-	-	-	-	69	12.72	0.50	69	12.73	0.73	69	12.72	0.61	-	-	-

1,5,9-Decatriene, 2,3,5,8-tetramethyl-	-	-	-	-	-	-	69	12.75	0.60	-	-	-	69	12.75	0.59
2H-imidazole-2-thione, 1,3-dihydro-1-methyl-5-(1-methylethyl)-	-	-	-	-	-	-	81	12.82	0.19	-	-	-	-	-	-
2,6-Diisopropylanisole	119	12.93	0.21	-	-	-	-	-	-	-	-	-	-	-	-
Benzene, 1-(1,5-dimethylhexyl)-4-methyl-	-	-	-	-	-	-	-	-	-	119	12.95	0.28	119	12.95	0.35
Benzoic acid, 3-methyl-, methyl ester	-	-	-	-	-	-	119	12.95	0.31	-	-	-	-	-	-
3,5-Dimethoxy-4-hydroxytoluene	168	12.99	1.49	168	12.99	1.63	168	12.99	0.82	168	13.00	0.95	168	13.01	0.44
Geranylformate	-	-	-	-	-	-	69	13.06	0.40	-	-	-	-	-	-

4,8,12-Tetradecatrienal, 5,9,13-trimethyl-	-	-	-	-	-	-	-	-	-	-	-	-	69	13.07	0.43
2,6-Octadiene, 1-(2-bromophenoxy)-3,7-dimethyl-, (E)-	-	-	-	-	-	-	-	-	-	69	13.07	0.54	-	-	-
Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	164	13.09	0.46	164	13.09	0.30	81	13.09	0.34	-	-	-	-	-	-
.alpha.-Cuprenene	-	-	-	119	13.15	0.23	-	-	-	-	-	-	-	-	-
Cubenene	-	-	-	-	-	-	-	-	-	119	13.15	0.28	-	-	-
1H-Benzocycloheptene, 2,4a,5,6,7,8-hexahydro-3,5,5,9-tetramethyl-, (R)-	-	-	-	-	-	-	119	13.15	0.28	-	-	-	-	-	-

(1R,4R,4aS,8aR)-4,7-Dimethyl-1-(prop-1-en-2-yl)-1,2,3,4,4a,5,6,8a-octahydronaphthalene	69	13.39	0.71	119	13.39	0.94	119	13.40	0.95	119	13.39	1.10	119	13.39	1.05
Cyclobutaneacetonitrile, 1-methyl-2-(1-methylethylidene)-	-	-	-	107	13.47	0.17	-	-	-	-	-	-	-	-	-
Cis-8-thiabicyclo[4.3.0]nonane S,S-dioxide	107	13.43	0.21	-	-	-	-	-	-	-	-	-	-	-	-
Ethane, 1,2-dibromo-	107	13.47	0.11	-	-	-	107	13.47	0.20	107	13.47	0.22	-	-	-
2-Phenyl-4-methyl-oxadiazol-1,3,4-one-5	119	13.61	0.16	-	-	-	-	-	-	-	-	-	-	-	-

Benzene, 1-(1,5-dimethyl-4-hexenyl)-4-methyl-	132	13.97	0.16	132	13.97	0.22	119	13.97	0.34	119	13.97	0.34	119	13.97	0.45
Piperidine, 1-[[(1,1-dimethylethyl)imino]methyl]-	168	14.09	0.14	-	-	-	-	-	-	-	-	-	-	-	-
Acetamide, N-cycloheptyl-2,2-diphenyl-	107	12.50	0.27	-	-	-	-	-	-	-	-	-	-	-	-
Pentadecane	57	14.32	0.34	57	14.32	0.23	57	14.32	0.27	71	14.32	0.21	57	14.32	0.44
6a-Ethyl-2,5-dioxohexahydrofuro[2,3-b]furan	-	-	-	-	-	-	57	14.32	0.19	-	-	-	-	-	-
1,3,4-Trimethyl-2-thiabicyclo[2.2.2]octane	121	14.53	0.22	-	-	-	-	-	-	-	-	-	-	-	-

Tetradecahydro-1-methylphenanthrene	-	-	-	-	-	-	121	14.53	0.42	-	-	-	-	-	-
trans-8-Isopropylbicyclo[4.3.0]non-3-ene	-	-	-	121	14.54	0.30	-	-	-	-	-	-	-	-	-
anti-10-Methyl-endo-tricyclo[5.2.1.0(2.6)]decane	-	-	-	-	-	-	-	-	-	-	-	-	121	14.54	0.46
Diphosphine, tetramethyl-, 1,2-disulfide	93	14.72	0.13	-	-	-	-	-	-	-	-	-	-	-	-
1,5,9-Decatriene, 1-phenyl-	-	-	-	-	-	-	93	14.73	0.39	-	-	-	-	-	-
Benzene, [(tetramethylcyclopropylidene)methyl]-	-	-	-	-	-	-	-	-	-	-	-	-	171	14.73	0.41

Benzene, (2-ethyl-4-methyl-1,3-pentadienyl)-, (E)-	-	-	-	-	-	-	-	-	-	93	14.74	0.38	-	-	-
6,10-Dimethyl-3-(1-methylethylidene)-1-cyclodecene	121	14.88	0.27	121	14.88	0.67	121	14.89	0.58	121	14.88	1.11	121	14.88	0.61
Indane, 2-methoxy-3-(2-methyl-1-propenyl-1)-	-	-	-	-	-	-	-	-	-	155	14.60	0.21	-	-	-
Benzene, 1,2,3-trimethoxy-5-methyl-	167	15.22	2.02	167	15.22	2.02	167	15.22	1.14	167	15.22	1.15	167	15.22	0.65
Naphthalene, 1,6,7-trimethyl-	170	15.32	0.40	170	15.32	0.87	170	15.32	0.61	170	15.32	1.17	170	15.32	1.76
Naphthalene, 2,3,6-trimethyl-	170	15.33	0.46	170	15.76	0.15	-	-	-	170	15.77	0.20	170	15.77	0.24
4-Bromoguaiacol	-	-	-	-	-	-	-	-	-	155	16.23	0.20	-	-	-

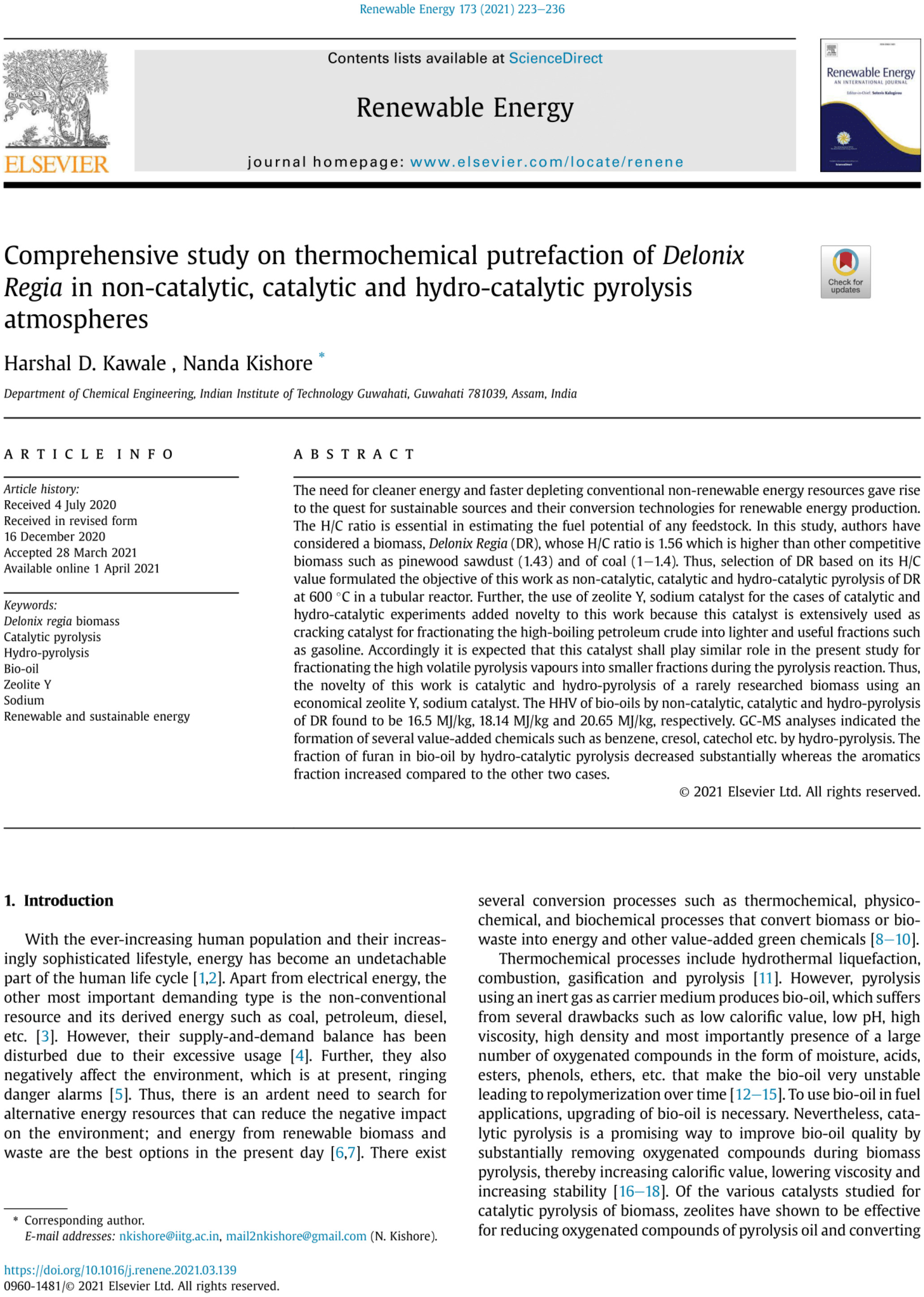
Tridecane, 3-methyl-	57	17.16	0.18	-	-	-	-	-	-	-	-	-	-	-	-
Hexadecane	-	-	-	-	-	-	-	-	-	-	-	-	57	17.16	0.27
2-(Methylmercapto) benzothiazole	-	-	-	-	-	-	-	-	-	-	-	-	181	17.35	0.21
2,4-Hexadienedioic acid, 3,4-diethyl-, dimethyl ester, (E,Z)-	-	-	-	-	-	-	-	-	-	167	17.59	0.56	167	17.59	0.37
N,N-Diphenylcarbamic acid, pentafluorophenyl ester	167	17.59	1.04	167	17.59	0.97	167	17.58	0.65	-	-	-	-	-	-
Dodecane, 2,7,10-trimethyl-	-	-	-	57	19.95	0.17	-	-	-	-	-	-	-	-	-
Undecane, 3,8-dimethyl-	57	19.96	0.26	-	-	-	-	-	-	-	-	-	-	-	-

Heptadecane	-	-	-	-	-	-	-	-	-	-	-	-	57	19.96	0.34
1,4,5,8-Tetramethylnaphthalene	169	20.47	0.11	-	-	-	-	-	-	169	20.47	0.26	169	20.47	0.38
phenol, 2-[(ethylamino)methyl]-4-nitro-	196	21.94	0.24	-	-	-	-	-	-	-	-	-	-	-	-
5,7-Dimethylpyrimido-[3,4-a]-indole	44	22.21	0.17	-	-	-	-	-	-	-	-	-	-	-	-
Undecane, 4,7-dimethyl-	57	22.64	0.15	57	22.64	0.22	-	-	-	-	-	-	-	-	-
Squalene	81	24.15	0.33	-	-	-	-	-	-	81	24.15	0.41	-	-	-
Benzene 1,2,4,5-tetrafluoro-3,6-dimethoxy-	44	24.83	0.16	-	-	-	-	-	-	-	-	-	-	-	-
Nonadecane	57	25.21	0.15	-	-	-	-	-	-	-	-	-	-	-	-
Cyclohexane, 1-ethenyl-1-methyl-2-(1-	-	-	-	-	-	-	-	-	-	-	-	-	121	25.64	0.33

methylethenyl)-4-(1-methylethylidene)-															
Elemene isomer	-	-	-	-	-	-	-	-	-	121	25.64	0.31	-	-	-
Hexadecanoic acid, methyl ester	74	25.90	0.47	74	25.90	0.23	-	-	-	74	25.90	0.34	74	25.90	0.45
Phenyl-pentamethyl-disiloxane	-	-	-	-	-	-	-	-	-	-	-	-	209	26.94	0.23

Appendix II

Front Page of Papers Published in Various International Journals



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Comprehensive study on thermochemical putrefaction of *Delonix Regia* in non-catalytic, catalytic and hydro-catalytic pyrolysis atmospheres

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ABSTRACT

The need for cleaner energy and faster depleting conventional non-renewable energy resources gave rise to the quest for sustainable sources and their conversion technologies for renewable energy production. The H/C ratio is essential in estimating the fuel potential of any feedstock. In this study, authors have considered a biomass, *Delonix Regia* (DR), whose H/C ratio is 1.56 which is higher than other competitive biomass such as pinewood sawdust (1.43) and of coal (1–1.4). Thus, selection of DR based on its H/C value formulated the objective of this work as non-catalytic, catalytic and hydro-catalytic pyrolysis of DR at 600 °C in a tubular reactor. Further, the use of zeolite Y, sodium catalyst for the cases of catalytic and hydro-catalytic experiments added novelty to this work because this catalyst is extensively used as cracking catalyst for fractionating the high-boiling petroleum crude into lighter and useful fractions such as gasoline. Accordingly it is expected that this catalyst shall play similar role in the present study for fractionating the high volatile pyrolysis vapours into smaller fractions during the pyrolysis reaction. Thus, the novelty of this work is catalytic and hydro-pyrolysis of a rarely researched biomass using an economical zeolite Y, sodium catalyst. The HHV of bio-oils by non-catalytic, catalytic and hydro-pyrolysis of DR found to be 16.5 MJ/kg, 18.14 MJ/kg and 20.65 MJ/kg, respectively. GC-MS analyses indicated the formation of several value-added chemicals such as benzene, cresol, catechol etc. by hydro-pyrolysis. The fraction of furan in bio-oil by hydro-catalytic pyrolysis decreased substantially whereas the aromatics fraction increased compared to the other two cases.

1. Introduction

With the ever-increasing human population and their increasingly sophisticated lifestyle, energy has become an undetachable part of the human life cycle [1,2]. Apart from electrical energy, the other most important demanding type is the non-conventional resource and its derived energy such as coal, petroleum, diesel, etc. [3]. However, their supply-and-demand balance has been disturbed due to their excessive usage [4]. Further, they also negatively affect the environment, which is at present, ringing danger alarms [5]. Thus, there is an ardent need to search for alternative energy resources that can reduce the negative impact on the environment; and energy from renewable biomass and waste are the best options in the present day [6,7]. There exist several conversion processes such as thermochemical, physico-chemical, and biochemical processes that convert biomass or bio-waste into energy and other value-added green chemicals [8–10].

Thermochemical processes include hydrothermal liquefaction, combustion, gasification and pyrolysis [11]. However, pyrolysis using an inert gas as carrier medium produces bio-oil, which suffers from several drawbacks such as low calorific value, low pH, high viscosity, high density and most importantly presence of a large number of oxygenated compounds in the form of moisture, acids, esters, phenols, ethers, etc. that make the bio-oil very unstable leading to repolymerization over time [12–15]. To use bio-oil in fuel applications, upgrading of bio-oil is necessary. Nevertheless, catalytic pyrolysis is a promising way to improve bio-oil quality by substantially removing oxygenated compounds during biomass pyrolysis, thereby increasing calorific value, lowering viscosity and increasing stability [16–18]. Of the various catalysts studied for catalytic pyrolysis of biomass, zeolites have shown to be effective for reducing oxygenated compounds of pyrolysis oil and converting

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Thermochemical putrefaction of *Delonix regia* biomass and tube waste to produce high-quality pyrolytic bio-oil

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Abstract
In this study, the authors have reported pyrolysis of two different waste materials, lignocellulosic biomass, *Delonix regia* (DR), and butyl rubber tube waste, (TW), at 600 °C temperature and 1 bar pressure using nitrogen inert atmosphere. In pursuit of obtaining high-quality products, the thermochemical reaction between 95, 85, 75, 65 and 50 mass % of DR is tested with 5, 15, 25, 35 and 50 mass % of TW, respectively. The co-feed ratio 95:5, 85:15, 75:25, 65:35 and 50:50 of DR/TW correspondingly resulted in the bio-oil yield of 22.67, 24.00, 24.34, 25.00 and 36.67 mass % and bio-char yield of 37.00, 43.77, 44.67, 45.33 and 49.52 mass %. The higher heating values (HHV) of all bio-oils are in increasing order to that of the increasing fraction of TW in co-feed where 50:50 ratio resulted in bio-oil of maximum HHV with 32.61 MJ kg^{-1}. Further increased mass % of tube waste may increase the energy content of the final liquid product; however, the present work focuses on co-feeding and management of both these two wastes and accordingly the mass % of tube waste has been limited to maximum of 50%. The bio-oil consists of more than 85 area % of aliphatic and aromatics, whereas phenols and acids occupy only 6.72 area % and 1.24 area %, respectively. Thus, this study provides waste minimization approach along with sustainable production of bio-oil that can be upgraded to transportation fuel, or utilized as furnace oil and for process heat purposes. The co-pyrolysis of these two waste materials resulted in popular hydrocarbons such as benzene, toluene, xylene, styrene and bigger fraction of C_{10} cut D-limonene.

Keywords *Delonix regia* · Tube waste · Pyrolysis · Thermogravimetry · GC–MS · FESEM · Proton NMR

Introduction

The ever-increasing consumption of fossil fuels has led to their faster depletion, which in turn increased pollution concerns, and a steep increase in prices of fossil fuels over the years [1–4]. In addition, waste minimization and management has also become inevitable to solve several present-day environmental issues [5]. Thus, it has become mandatory for the scientific community to explore more reliable renewable energy resources such as biomass to produce biofuels and bio-based chemicals [6]. The biomass can be treated in several ways to extract the stored energy within them [7, 8]. For the conversion of biomass to biofuels as transportation fuels, several techniques are being used, which are classified as thermochemical conversion, biochemical conversion and oil extraction [9]. The commonly used thermochemical processes are direct combustion that produces heat, gasification that produces fuel gas and pyrolysis that produces liquid fuel [10–12]. Among these processes, pyrolysis has got a much upper hand in research in recent times because its liquid product can be upgraded to transportation grade fuel [3, 13–15]. It also has the potential that can be added to petroleum refinery feedstock for the recovery of high-value chemicals [16]. Moreover, liquid products are easier to handle, store and transport [17].

The production of biofuels from biomass alone cannot replace the need for tremendous energy because of their low calorific value and more oxygen content; thus, it requires an alternative hydrogen and carbon source to improve its quality and durability [18]. Butyl rubber is used in various applications such as vehicles' inner tubes, rubber stoppers and automobile parts [19], and the huge amount of waste generated by them is treated by various ways which are environmentally hostile such as incineration and direct combustion. Thus, the proper mechanism for the utilization of waste

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Comparative study on pyrolysis of *Delonix Regia*, Pinewood sawdust and their co-feed for plausible bio-fuels production

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ABSTRACT

Individual and co-feed pyrolysis of various weight percentages of two solid waste biomasses, have been carried out in a tubular reactor at 625 °C and 1 bar. Both biomasses considered herein are having average calorific values of 18.33 MJ/kg and 18.5 MJ/kg. Experiments are performed individually on both the biomasses and then the co-feed in the ratio of 25:75, 50:50, and 75:25 taken for co-pyrolysis study. Further to be noted that pyrolysis experiments of each case and their product analyses in addition to feed characterization have been done thrice. These results are presented individually for each run in addition to their average and standard deviation values. The biomass feedstock, bio-oil, and biochar are thoroughly characterized by extensive advanced characterization techniques such as thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), gas chromatography-mass spectroscopy (GCMS), nuclear magnetic resonance (NMR), field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD) appropriately, as applicable for each case. The highest heating value of obtained pyrolytic bio-oil is from a co-feed ratio of 50:50 with an average HHV of 20.3 MJ/kg and having only 14.3 wt % of moisture content on average of three repetition experiments. The density of bio-oil obtained in all cases is approximately close to 1 g/cc, whereas their average viscosity varies between 2.07 and 3.61 mPa s. Thus, this study delivers that the rarely researched biomass considered for this study has almost similar potential to produce biofuels as that of extensively researched other biomass and their co-feed (1:1) pyrolysis is optimum for production of improved quality of pyrolytic bio-oil in terms of HHV, pH, density and moisture content.

1. Introduction

Day by day the consumption of fossil fuel is increasing as the increase in population is continuing to rise, with that the demand for such fuels is also growing. The excessive use of fossil fuels are degrading environmental quality by causing severe damage [1–4] and hence, it is a need of hour to look for cleaner alternative renewable energy resources [5]. Accordingly many institutions and governments have encouraged their researchers to find new routes or invent renewable and sustainable fuel [6–8]. In the last few decades, many efforts have been made to find alternative energy resources and develop technology which are energy-efficient and environment-friendly at the same time [9,10]. In the recent past, a large number of global researchers investigated biomass as an alternative source of energy [8,11] due to its high availability of feedstock, i.e., it is approximately estimated as 220 billion dry tons of feedstock of biomass available each year [7,12]. Moreover, energy production via thermochemical conversion routes from biomass is considered as minimal carbon emission technology [13–17]. The commonly used thermochemical processes for biofuels from biomass are, combustion (produces heat), gasification (produces fuel gas), and pyrolysis (provides liquid fuel) [18,19]. Among these processes, pyrolysis has received a much upper hand in research in recent times because of its liquid product which attains high energy density on upgrading by hydrotreatment [8,20–22]. Further, liquid products have ease in handling, storage, and transportation [23]. In addition to the pyrolysis oil, this process also produces char (solid product) and gaseous product [22,24–27]. Moreover, according to review by Abnisa and Wan [28], to achieve a good quality bio-oil, it is worthwhile to use co-pyrolysis of two or more biomass feedstocks of appropriate ratio at a time [28].

In other words, co-pyrolysis of lignocellulosic biomass with different sources such as coal, plastics, and other biomasses is

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Pyrolysis of *Delonix Regia* and Characterization of Its Pyrolytic Products: Effect of Pyrolysis Temperature

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Pyrolysis of a rarely researched biomass feedstock, Delonix regia (DR), at different pyrolysis temperatures carried out in a tubular reactor at an atmospheric pressure of one bar. In addition to the fuel and physical properties of produced bio-oil and bio-char, extensive advanced characterization of these products, viz. Fourier transformation infrared (FTIR), GC-MS, proton (^{1}H) nuclear magnetic resonance (^{1}H NMR), X-ray diffraction (XRD), etc. is also performed as applicable to different products. The main emphasis of this work is on both quantitative and qualitative analysis of pyrolytic bio-oil and bio-char obtained from DR at 500–700 °C. In this range of temperature, higher heating value (HHV) of bio-oil found to be varying between 20.88 MJ/kg and 25.70 MJ/kg following increasing trend with the temperature. However, HHV of bio-char observed to be almost unaffected by pyrolysis temperature, and it is approximately 36 MJ/kg. The density of bio-oil found to be decreasing from 0.95 g/cc to 0.88 g/cc as the pyrolysis temperature increases from 500 to 700 °C; however, pH is found to be almost unaffected by the pyrolysis temperature changing only slightly from 3.4 to 3.3. Furthermore, the moisture content of bio-oil is also found to be unaffected by the temperature variations. From the GC-MS chromatograms of bio-oils, it is found that benzene is highest area % (with 14.6%) and phenol, 2,6-dimethoxy is the second-highest area % occupying component (with 10.5%) in bio-oil obtained at 600 °C of pyrolysis temperature. This result indicates that the DR feedstock is also an excellent resource for producing value-added green chemicals.

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Keywords: Delonix regia, pyrolysis, bio-oil, bio-char, green chemicals, hydrocarbons, alternative energy sources, energy from biomass

1 Introduction

Globally faster depletion of petroleum resources is a primary concern of the energy sector due to their excessive consumption rate compared to their natural production rate. This excessive use also has a dangerous drawback of environment pollution [1–3]. Therefore, there is an urgent necessity of suitable feedstock for the production of energy, which can replace fossil fuels partially or completely and can also reduce environmental pollution risks simultaneously. In search of such feedstock, researchers found that lignocellulosic biomass waste is a suitable resource fulfilling the waste-to-wealth criteria of advancing countries [4,5] without disturbing the food chain. The lignocellulosic biomass contains lignin, cellulose, and hemicellulose. The lignocellulosic biomass waste can be converted into bioenergy by several thermochemical approaches such as pyrolysis, gasification, and liquefaction. However, pyrolysis and liquefaction are the only routes to obtain liquid biofuels [2,4–8].

Pyrolysis of biomass is thermal decomposition of material in an inert atmosphere producing liquid bio-oil, solid bio-char, and noncondensable gases. Bio-char produced from pyrolysis can be further used as activated charcoal after proper treatment [9,10]. Pyrolytic oil or bio-oil is the main pyrolysis product, which after upgrading, may be used as a transportation fuel, and it is also a source for value-added chemicals such as bio-based petrochemicals [11,12]. Noncondensable gases are of high calorific value and utilized directly for energy production [12]. Besides this, pyrolysis is an economical process compared to liquefaction because of less severe operating conditions [1]. In general, in pyrolysis of lignocellulosic biomass, the cellulose degrades over a temperature range of 240–350 °C, hemicellulose decomposes between 180 °C and 200 °C and lignin degrades at a range of temperature above 400 °C [11–13]. Finally, both yield and quality of bio-oil obtained from pyrolysis are strongly influenced by the nature of feedstock, pyrolysis temperature, and pressure along with heating rate, inert gas flowrate and the reactor type. Thus, this work aimed to delineate the effect of pyrolysis temperature on the yield and quality of bio-oil obtained by pyrolysis of a rarely researched biomass feedstock, *Delonix regia* (DR), at 500–700 °C in a tubular reactor.

2 Literature Review

Williams and Besler [14] studied slow pyrolysis of pinewood biomass at a temperature range of 300–720 °C with a heating rate of 5–80 K/min. The duration of the pyrolysis reaction is 2 h and carried out in a static bed batch reactor. The authors studied the effect of temperature and found that as the temperature and heating rate increased, the yield of the bio-oil product also increased. Li et al. [15] used legume straw and apricot stone biomass as feedstock and carried out pyrolysis at a temperature range of 500–800 °C with a heating rate of 10–40 °C/min in a free-fall reactor. The authors found that the yield and composition of hydrogen-rich gas as a product from fast pyrolysis depends on the composition of biomass. They reported that cellulose and hemicellulose produce more hydrogen-rich gas than lignin. Sun et al. [16]

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Production of hydrocarbons from a green algae (*Oscillatoria*) with exploration of its fuel characteristics over different reaction atmospheres

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A B S T R A C T

Authors conducted non-catalytic, catalytic, and hydropyrolysis at 550 °C temperature and 1 bar pressure to produce biofuels from an ignored algal biomass of *Oscillatoria* by thermo-chemical degradation study in a tubular reactor having an internal diameter of 25 mm and 300 mm of active length covered by a furnace of a single heating zone. The catalysts used for the catalytic pyrolysis and hydropyrolysis study are TiO_2: ZnO on 1:1 basis. Characterization of bio-oils by Fourier Transform Infrared Spectroscopy (FTIR) shows substantial variation in functional groups of all three types of bio-oils. Gas Chromatography-Mass Spectroscopy (GCMS) gives a detailed list of available hydrocarbons in bio-oil samples and proton NMR confirms the functionality of bio-oil by available proton assignments. Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD) shows morphology and the structural analogy of biochars with respect to biomass. Calorific values of three types of bio-oils ranges from 16.597 to 16.664 MJ/kg; and revealed that this particular biomass has potential as a resource of feedstock with an approximate yield of one-third of biomass on the dry weight basis. The pH of these bio-oils obtained from green algae varies in the range of 8.25 to 6.07 that indicates the less number of oxygenated compounds unlike very low pH bio-oils obtained from other types of biomass feedstock. Additionally, present results revealed that these bio-oils include formative compounds of most popular hydrocarbons, i.e., benzene, toluene and xylene (BTX). Further, they also include furans, phenols, benzaldehyde, guaiacol, caprolactam, styrene, oximes, etc. which can be used as green chemicals.

1. Introduction

The significant rise in oil prices, faster depleting crude-oil reserves, increasing energy consumption with the ever increasing population and the growing concern over the environment pollution has recently brought the need of improved utilization of renewable energy resources [1–3]. Non-renewable energy resources, like petroleum, coal, and natural gas meets about seventy-six percent of the world's main energy demand and supply, each analogous to about 33, 24, and 19%, respectively [4]. As the precursor of fossil feedstock, biomass which is rich in carbon appears to be one of the best choices for the substitution of fossil resources in many applications [5,6]. The term biomass refers to all organic material which has an origin of plants (counting algae), trees, and crops whilst they collect and store sun's energy via photosynthesis [5,7,8]. Biomass is recognized as the third largest renewable energy resource and it accounts for 12–15% of total world energy supply [4,5,9,10]. "National policy on biofuels India 2018" categorically describes biofuels as "Basic Biofuels" and "Advanced biofuels". This policy allows use of surplus food grains for the manufacture of biofuels to reduce the financial risk of farmer during surplus production of the crops. Producing energy from biomass has the lead of low emissions in form of gases like sulphur oxides (SO_X), nitrogen oxides (NO_X) which are environmentally detrimental in comparison with that of fossil fuels, on the basis of plants carbon cycle [4,7,8]. Typically, biomass contains organic matters such as lipids, proteins, sugars, starches, cellulose, hemicellulose, lignin with some inorganic matters and water [11,12]. For typical biomass, carbon and oxygen together constitute over 90% of dry weight of the biomass [11]. The biomass-based renewable energy will anticipate in a chief role of global energy demand and supply in near future. The diminution of fossil-based fuels and at the same

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Bio-oil production from a lignocellulosic biomass and its fuel characteristics

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Abstract. A wide research is going on in the field of renewable energy resources to shelter the scarcity of conventional fossil fuels. As we look back, from the beginning of Earths formation, a tremendous amount of the energy stored inside the earth. Until the start of 19th century man was unaware of this treasure and used lignocellulosic biomass / wood biomass as an energy source of which people unaware of its true potential. But, as fossil fuel sources were discovered, the excavation started to meet the energy demand which obviously replaced the biomass. Then from the petroleum crude oil, petrochemicals took birth and the industrial revolution changed the prospective of entire world. Now, in this first quarter of the 21st century when the population is gigantic and demand for energy sources has increased to the enormous level, fossil fuels are being consumed like never before and now they are diminishing with very fast rate leading towards the energy crisis. So, to overcome this problem; need for the replacements, blends of fossil fuels arises and as a result we are going back in time to utilize another huge source of energy i.e. Biomass. Lignocellulosic biomass can be thermally converted into biofuels by various technologies. One of such most effective and lucrative technology is pyrolysis. Pyrolysis of lignocellulosic biomass convert it into bio-oil, bio-char and pyrolysis gas, these all have high energy content and potential in them. In this deliberated work, authors conducted a pyrolysis experiment on a lignocellulosic biomass which is available as a solid waste on long and far terrestrial region though barely investigated. Temperature of the reaction was set at 500 ºC at which the bio-oil resulted its highest heating value of 17.093 MJ/kg and that of bio-char is 30.768 MJ/kg. Fourier Transform Infrared Spectroscopy (FTIR) showed number of functional groups present and Gas Chromatography-Mass Spectroscopy (GCMS) resulted in huge number of chemical compounds present in the bio-oil. Then we studied flow behaviour of bio-oil by Interfacial Rheometer and it demonstrated Shear-thinning behaviour. Thus, the study reveals fuel potential of untouched biomass in terms of bio-oil and its transport phenomenon.

1. Introduction

Petroleum depletion over a period of time, climate change and other environmental concerns triggered by consumption of fossil fuels and the need of value added petrochemicals drives a force to develop fruitful technologies [1]. For production of fuel grade chemicals and precursors to the specialty grade chemicals within a cost effective and environment friendly frame, biomass as a renewable feedstock plays a dynamic role. Mainly two routes are popular i.e., thermochemical conversion and biological conversion which produce biofuel in the form of solid, liquid (bio-oil) and gas from biomass which can be consumed as fuel and source for manufacturing of value added chemicals [2–5]. In thermochemical conversion process various technologies are developed to transform biomass into bio-fuels such as pyrolysis, gasification, hydrothermal gasification, hydrothermal liquefaction, chemical looping