PYROLYSIS OF BIOMASS TO LIQUID FUEL

A DISSERTATION

Submitted in partial fulfillment of the requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Computer Aided Process Plant Design)

By

SRIDHAR DALAI

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE - 247 667 (INDIA)
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CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in this dissertation entitled "**PYROLYSIS OF BIOMASS TO LIQUID FUEL**", in partial fulfillment of the requirement for the award of the degree of **Master of Technology** in **Chemical Engineering** with specialization in "**COMPUTER AIDED PROCESS PLANT DESIGN**", submitted in the **Department of Chemical Engineering** of **Indian Institute of Technology Roorkee**, Roorkee is an authentic record of my own work carried out during the period from June 2005 to June 2006 at Indian Institute of Petroleum, Dehradun, under supervision of Dr.H.B.Goyal, Scientist 'F', Dehradun, Dr.V.K.Agrawal, Associate Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

The matter embodied in this dissertation work has not been submitted for the award of any other degree.

Date: 13. June, 2006
Place: Roorkee.

D. Sridhar
(SRIDHAR DALAI)

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Dr.H.B.Goyal,
Scientist 'F',
(Chemical and Bio-technology Division)
Indian Institute of Petroleum,
Dehradun.

Agrawal
13.6.06

Dr.V.K.Agrawal
Associate Professor,
Dept. of Chemical Engg.
IIT Roorkee.
Roorkee.

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Place: Roorkee
Date: 14 June, 2006

D. Sridhar
(SRIDHAR DALAI)

ABSTRACT

Jatropha curcas seed cake was pyrolysed in a fixed-bed reactor. The effects of pyrolysis temperature, particle size and N_2 gas flow rates on the yields of the products were investigated. Pyrolysis runs were performed using pyrolysis temperatures between 400 and 600 ^{0}C with heating rates of 10^{0}C /min. The particle size and N_2 gas flow rate varied in the ranges -6+8 to -8+12 mesh number and 50–150 cm^3 /min respectively. The bio-oil obtained at 600°C was analysed and at this temperature the liquid product yield was the maximum. The various characteristics of bio-oil obtained under these conditions were identified on the basis of standard test methods. The empirical formula of the bio-oil with heating value of 37.3 MJ/kg was established as $CH_{1.39}O_{0.28}$. The chemical characterization showed that the bio-oil obtained from Jatropha curcas seed cake may be potentially valuable as a fuel and chemical feedstock. Liquid products obtained under the most suitable conditions were characterized by elemental analyses, FTIR and HNMR. Gas chromatography and mass spectroscopy was achieved on n-pentane fractions. The results show that it is possible to obtain liquid products similar to petroleum from Jatropha curcas seed cake residue if the pyrolysis conditions are chosen accordingly.

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Global use of energy has been growing faster than the world population. The development of energy sources is not keeping pace with spiraling consumption. In 1950 the production and consumption of energy were in virtual balance for the developed countries as a whole, but by 1973 production in the developed countries had virtually doubled but consumption was far more increased than production. The word reserves of petroleum, the most important fuel today, has been dropping and shows meager signs of recovery.

The world major energy demand is provided from the convectional energy sources such as coal, oil, natural gas etc. The life of all the convectional fuels is limited by the present and foreseeable future energy consumption of the world, e.g. the world's oil reserves are estimated to be depleted by 2050. Therefore, attention is being given to alternate and renewable sources, such as solar, wind, thermal, hydroelectric, biomass etc.

Energy production is one of the major sources of pollution in any developing country. It is well known that SO_2 emissions produced by burning fossil fuels are the major cause of acid rain. Globally, increase in the emissions rates of greenhouse gases i.e. CO_2 present a threat to the world climate. As an estimate in the year 2000, over 20 million metric tons of CO_2 were expected to be released in the atmosphere every year [10]. Over the last half century, there appeared a continuously increasing trend in the average temperature to the tune of a half degree centigrade. If this trend continues, some extreme natural calamities are expected such as excessive rainfall and consequent floods, droughts and local imbalances.

With increasing energy demand the emerging alternative and renewable energy resources are expected to take an increasing role in energy scenario of the future energy consumptions, at least in order to reduce the environmental concerns and impacts with regard to air and water quality, acid rain, global warming etc [11].

Renewable biomass is now being considered as an important energy resource all over the world. Biomass is used to meet a variety of energy needs, including generating electricity, fueling vehicles and providing process heat for industrial facilities. Among all the renewable sources of energy biomass is unique as it effectively store solar energy. It is the only renewable source of carbon that can be converted into convenient solid, liquid, and gaseous fuels through different conversion processes [14].

Biomass has a great potential by offering annually renewable sources to replace the liquid hydrocarbons used mainly for transportation. Thus both the developing world and industrialized nations require technologies that efficiently utilize the biomass resources. There are many conversion processes used to convert the biomass into higher value fuels. The different conversion processes are biochemical and thermo-chemical.

The thermo-chemical process includes combustion, gasification and pyrolysis. Among these, pyrolysis is an important thermo-chemical process. The pyrolysis is of particular interest since it may be stored and transported. The oil may be used directly as a liquid fuel added to petroleum refinery feed-tocks or catalytically upgraded to transport grade fuels [3-5, 15].

Biomass is a domestic resource, and is not subjected to world price fluctuations or the supply uncertainties like the imported fuels. In developing countries, in particular, the use of liquid bio fuels, such as bio-diesel and ethanol, reduces the economic pressures of petroleum products.

Biomass is a renewable environmental friendly source of energy. The substitution of fossil fuels for energy production with biomass will result in a net reduction in greenhouse gas emissions and the replacement of a non-renewable energy source. Burning fossil fuel produces CO_2, which contributes to green house effect while burning biomass, it emits roughly the same amount of CO_2 during conversion as it is taken up during plant growth and hence contributes no CO_2 to the atmosphere [7, 16].

Biomass fuels have negligible sulfur content and therefore do not contribute to the sulfur dioxide emissions, which causes acid rain. The combustion of biomass produces less ash than coal combustion. Moreover the ash produced can be used as soil additive on farms.

Presently, biomass contributes mainly only 3% of primary energy consumption in industrialized countries. However much of the rural population in developing countries which represents about 50% of the world's population, is dependent on biomass, mainly in the form of wood or fuel. Biomass accounts for 35 % of primary energy consumption in developing countries, raising the world total to 14% of primary energy consumption. One analysis provided by the United Nations Conference on Environment and Development (UNCED) estimates that biomass could potentially supply about half of the present world primary energy consumption by 2050 [4].

1.1 Definition of biomass

Biomass can generally be defined as any hydrocarbon material which mainly consists of carbon, hydrogen, oxygen and nitrogen. Sulfur is also present in less proportion. Some biomass types also carry significant proportions of inorganic species. The concentration of the ash arising from these inorganics changes from less than 1% in softwoods to 15% in herbaceous biomass and agricultural residues.

Biomass resources include various natural and derived materials, such as woody and herbaceous species, wood wastes, bagasse, agricultural and industrial residues, waste paper, municipal solid waste, sawdust, biosolids, grass, waste from food processing, animal wastes, aquatic plants and algae etc. [Pyrolysis of biomass to produce fuels and chemical feedstocks]

1.2 The chemical structure and the major components of biomass

The chemical structure and major organic components in biomass are extremely important in the development of processes for producing derived fuels and chemicals. The major organic components of biomass can be classified as cellulose, hemi cellulose and lignin. Alpha cellulose is a polysaccharide having the general formula $(C_6H_{10}O_5)_n$ and an average molecular weight range of 300,000–500,000. Cotton is almost pure a-cellulose, whereas wood cellulose, the raw material for the pulp and paper industry, always occurs in association with hemi cellulose and lignin's. Cellulose is insoluble in water, forms the skeletal structure of most terrestrial biomass and constitutes approximately 50% of the cell wall material.

Hemicelluloses are complex polysaccharides that take place in association with cellulose in the cell wall, but unlike cellulose, hemicelluloses are soluble in dilute alkali and consist of branched structures, which vary considerably among different woody and herbaceous biomass species. Many of them have the general formula $(C_5H_8O_4)_n$. Hemicelluloses usually carry 50–200 monomeric units and a few simple sugar residues. The most abundant one is xylan. The xylans exist in softwoods and hardwoods up to about 10% and 30% of the dry weight of the species, respectively.

The lignins are highly branched, substituted, mononuclear aromatic polymers in the cell walls of certain biomass, especially woody species, and are often bound to adjacent cellulose fibers to form a lignocellulosic complex. This complex and the lignins alone are often quite resistant to conversion by microbial systems and many chemical agents. The complex can be broken, and the lignin fraction separated, however, by treatment with strong sulfuric acid, in which the lignins are insoluble. The lignin contents on a dry basis in both softwoods and hardwoods generally range from 20% to 40% by weight and from 10% to 40% by weight in various herbaceous species, such as bagasse, corncobs, peanut shells, rice hulls and straws.

1.3 Importance of biomass

Biomass, mainly in the form of wood, is the oldest form of energy used by human. Traditionally, biomass has been utilized through direct combustion, and this process is widely used in many parts of the world. Biomass, mainly now represents only 3% of primary energy consumption in industrialized countries. Biomass accounts for the 35% of primary energy consumption in developing countries, raising the world total to 14% of primary energy consumption. The demand for energy is increasing at an exponential rate due to the exponential growth of world's population. This, combined with the widespread depletion of fossil fuels and gradually emerging consciousness about environmental degradation, suggests that the energy supply in the future has to come from renewable sources of energy[17].

Biomass has great potential as a renewable energy source, both for the richer countries and for the developing world. Biomass is used in similar way to fossil fuels, by burning it at a constant rate in a boiler furnace to heat water and produce steam. Liquid biofuels, such as wheat, sugar, root, rapeseed and sunflower oil, are currently being used in some member states of European Union, like Austria, Belgium, France, Germany, Italy and Spain.

Burning biomass produces some pollutants, including some dust and the acid rain gases sulfur dioxide and nitrogen oxides. Burning wood produces 90% less sulfur than coal. These can all be reduced before releasing the fuel gases into the atmosphere. At the present rate of use, the quantities of atmospheric pollution involved are insignificant compared with other pollution sources, but this would be a factor to consider if the use of biomass increased. Carbon dioxide, the green house gas is also released. However, as this originates from harvested or processed plants, which have absorbed it from the atmosphere, so no additional amounts are involved.

1.4 Resources of biomass

Biomass resources include wood and wood wastes, agricultural crops and their waste by products, municipal solid waste, animal wastes, wastes from food processing and aquatic plants and algae. The average majority of biomass energy is produced from wood and wood wastes (64%), followed by MSW (24%), agricultural waste (5%) and landfill gases. Biomass is the oldest known source of energy.

Biomass differs from other alternative energy sources in that the resource is varied, and it can be converted to energy through many conversion processes. Biomass resource can be divided into three categories[4,7]:

1. Wastes
2. Standing forests
3. Energy crops

Biomass resources that can be used for energy production cover a wide range of materials. Biomass energy can be separated into two categories, namely modern biomass and traditional biomass. Modern biomass usually involves large-scale uses and aims to substitute for conventional energy sources. It includes wood and agricultural residues, urban wastes and biofuels, such as biogas and energy crops. Traditional biomass is generally confined to developing countries and small scale uses. It includes fuelwood and charcoal for domestic use, rice husks and other plant residues and animal wastes. Examples of biomass energy resources are:

Wastes:

- Agricultural production wastes
- Agricultural processing wastes
- Crop residues
- Mill wood wastes
- Urban wood wastes
- Urban organic wastes

Forest products:

- Wood
- Logging residues
- Trees, shrubs and wood residues

- Sawdust, bark etc. from forest clearings

Energy crops:

- Short rotation woody crops
- Herbaceous woody crops
- Grasses
- Starch Crops (corn, wheat and barley)
- Sugar Crops (cane and beet)
- Oilseed crops (soybean, sunflower, safflower)
- Forage crops (grasses, alfalfa and clover)

1.5 Constraints to biomass

- In nature, biomass is not concentrated, and so, the use of naturally occuring biomass requires transportation, which increases the cost.
- Biomass has low bulk density, which makes transportation and handling difficult and costly.
- The incomplete combustion of fuelwood produces organic particulate matter, carbon dioxide and other organic gases. The health impact of air pollution inside buildings is a significant problem in developing countries, where fuelwood is burnt inefficiently in open fires for domestic cooking and space heating.
- There is the potential for widespread use of natural forests to cause deforestation and localized fuelwood scarcity.
- There is a potential conflict over the use of land and water resources for biomass energy and other uses such as food production.
- Some biomass applications are not fully competitive at this stage. However the economics of biomass energy production are improving and the growing concern about greenhouse gas emissions is making biomass energy more attractive.
- The production and processing of biomass can involve significant energy input, such as fuel for agricultural vehicles and fertilizers, resulting in a poor energy balance.
- The biofuels usually have only a modest thermal content compared with fossil fuels.

1.6 Biomass properties

It is the inherent properties of the biomass source that determines both the choice of conversion process and any subsequent processing difficulties that may arise. The main material properties of interest, during subsequent processing as an energy source are:

1.6.1 Moisture content

Two forms of moisture content are of interest in biomass:

- Intrinsic moisture: the moisture content of the material without the influence of weather effects.
- Extrinsic moisture: the influence of prevailing weather conditions during harvesting on the overall biomass moisture contents.

In practical terms, it is the extrinsic moisture content that is of concern, as the intrinsic moisture is applicable only in laboratory scale. In the conversion of biomass to gas/oil or alcohol, the relationship between biomass moisture content and appropriate bio-conversion technology is essentially straight forward, in that thermal conversion requires low moisture content feedstock, while bio-conversion can utilize high moisture content feedstocks.

1.6.2 Calorific value

The calorific value of a material is an expression of the energy content released when burnt in air. The actual amount of energy recovered will vary with the conversion technology and also with the form of that energy i.e. combustible gas, oil, steam etc. If any moisture content is present in the biomass, this reduces the calorific value proportional to the moisture content.

1.6.3 Proportions of fixed carbon and volatile matter

- Volatile matter: It is that portion of a solid fuel, which is driven off as a gas (including moisture) by heating (to 950 ^{0}C for 7 min).
- Fixed carbon: It is the mass remaining after the releases of volatiles, excluding the ash and moisture contents.

The significance of the volatile matter and fixed carbon contents is that they provide a measure of the ease with which the biomass can be ignited and subsequently gasified, or oxidized, depending on how biomass is to be utilized as energy source.

1.6.4 Alkali metal content

The alkali metal content of biomass i.e. Na, K, Mg, P and Ca, is especially important for any thermo-chemical conversion processes. The reaction of alkali metals with silica present in the ash produces a sticky, mobile liquid phase, which can lead to blockages of airways in the furnace and boiler plant.

1.7 Some methods are applied to biomass to make use of its energy

Direct combustion of biomass to take advantage of its heating value has been known for ages, but direct combustion of biomass is not favored any more because it has too high content of moisture to perform stable combustion. Thus, it has highly changeable combustion rates. On the other hand, the density for many kinds of biomass is lower than that of coal, leading to important economic limitations in transportation. In order to overcome these problems, briquetting of low density biomass species before combustion has been considered. It is also possible to blend biomass with coal in various proportions and then produce coal-biomass briquettes.

Other common methods applied to biomass to make use of its energy potential are biochemical and thermochemical conversion methods. Well known biochemical methods are the biochemical liquefaction and microbial gasification processes.

Biochemical conversion methods are based on the conversion of biomass into alcohols or oxygenated products by biological activity. Thermochemical processes involve the pyrolysis, liquefaction, gasification and supercritical fluid extraction methods.

The products of the thermochemical processes are divided into a volatile fraction consisting of gases, vapours and tar components and a carbon rich solid residue. The pyrolysis process consists of a very complex set of reactions involving the formation of radicals. The gasification of biomass is a thermal treatment, which results in a high proportion of gaseous products and small quantities of char (solid product) and ash. If the purpose is to maximize the liquid product yield, process conditions are selected as low temperature, high heating rate and short gas residence time. For high char yield, low temperature and low heating rate are required. In order to produce high yield of gas product, high temperature, low heating rate and long gas residence time should be applied.

Heating values of the chars obtained from pyrolysis are comparable with those of lignite and coke, and the heating values of liquids are comparable with those of oxygenated fuels, such as CH_3OH and C_2H_5OH, which are much lower than those of petroleum fuels. The heating value of gases is comparable with those of producer gas or coal gas and is much lower than that of natural gas. The heating values of the products are functions of the initial composition of the biomass. [Pyrolysis of biomass to produce fuels and chemical feedstocks].

1.8 Outlines of biomass pyrolysis

Pyrolysis of biomass can be described as the direct thermal decomposition of the organic matrix in the absence of oxygen to obtain an array of solid, liquid and gas products. The pyrolysis method has been used for commercial production of a wide range of fuels, solvents, chemicals and other products from biomass feedstock's. Conventional pyrolysis consists of the slow, irreversible, thermal decomposition of the organic components in biomass. Slow pyrolysis has traditionally been used for the production of charcoal. Short residence time pyrolysis (fast, flash, rapid, ultrapyrolysis) of biomass at moderate temperatures has generally been used to obtain high yield of liquid products. Fast pyrolysis is characterized by high heating rates and rapid quenching of the liquid products to terminate the secondary conversion of the products. [Pyrolysis of biomass to produce fuels and chemical feedstocks].

Fast pyrolysis (more accurately defined as thermolysis) is a process in which a material, such as biomass, is rapidly heated to high temperatures in the absence of air (specifically oxygen). The biomass decomposes into a combination of solid char, gas, vapors and aerosols. When cooled, most volatiles condense to a liquid referred to as 'Bio-Oil'. The remaining gases comprise a medium calorific value non-condensable gas. Bio-Oil is a liquid mixture of oxygenated compounds containing various chemical functional groups, such as carbonyl, carboxyl and phenolic. Bio-Oil is made up of the following constituents: 20-25% water, 25-30% water insoluble pyrolytic lignin, 5-12% organic acids, 5-10% non-polar hydrocarbons, 5-10% anhydrosugars and 10- 25% other oxygenated compounds.

1.9 Fast pyrolysis Process description

Feed stock

crop residues , debarking waste ,forage grasses , forest residues , hulls , municipal solid waste, pomace, scrap and spoilage (fruit & vegetable processing) , sawdust, spent grains, spent hops, spent yeast ,switchgrass, waste woodchips, woodchips[www.wisbiorefine.org]

Feedstock Restrictions

Solid or liquid feed stocks must be processed to a small particle or droplet size to assure high heat transfer rate in the process (less than 6 mm or ¼ inch, but 1 to 2 mm is preferred). Feedstock should be dried to less than 10 percent moisture content. [www.wisbiorefine.org]

The following figure gives a schematic for bio-oil production. The major components are drying, grinding, the fast pyrolysis reactor itself, char removal, and vapor quench to separate condensable liquids from light gases.

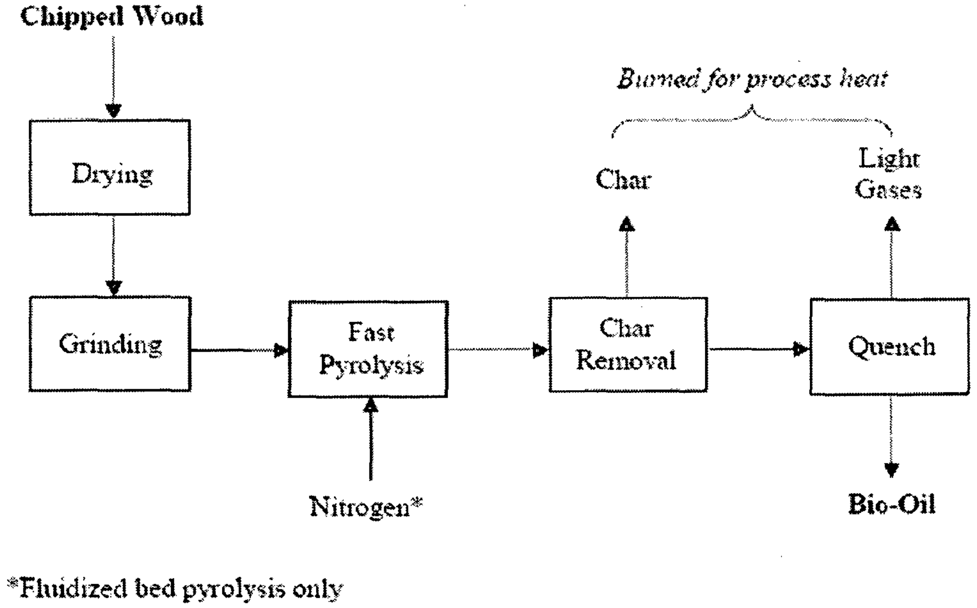


Fig 1.1 [Overview of Potential Conversion Technologies for Forest Thinnings Brian L. Polagye and Philip C. MalteDepartment of Mechanical Engineering, University of Washington]

The maximum feedstock moisture content allowable for fast pyrolysis is 10-15% by weight. The moisture content of bio-oil (15-30%) is a combination of moisture present in the feedstock and moisture generated by condensation reactions during fast pyrolysis. If feedstock moisture is higher than 10-15%, the final water content of the bio-oil will be high enough to result in rapid phase separation, rendering the bio-oil of little commercial value. Additional grinding in a hammer-mill and screen filtration is also necessary to reduce feedstock to a size amenable for fast pyrolysis. For bubbling fluidized bed reactors this is 2 mm or less. For ablative reactors this may be larger, up to 6 mm.

Once fed into the reactor, wood temperature is rapidly elevated (>100°C/s), bringing wood to pyrolysis conditions (450-550°C). In fast pyrolysis, wood decomposes to yield condensable organic vapors (70%), char (15%), and light gases (15%). Two approaches are used to minimize time spent below 500°C, where char formation is kinetically favored. In fluidized bed reactors, the particles of biomass are small enough that the entire particle is rapidly, uniformly brought to pyrolysis temperature. In ablative reactors, the feedstock surface is brought to reaction temperature, then mechanically removed (ablated) by friction, exposing the next layer directly to the high temperature environment. This is accomplished rapidly enough so that the bulk of the biomass stays below 100°C and does not thermally decompose. Vapor residence time in reactors is normally less than one second in order to discourage secondary reactions.

Char exits the reactor along with light gases and condensable vapors and must be rapidly filtered out for two reasons. First, at pyrolysis temperature, the char particles will crack the condensable vapors to light gases, reducing bio-oil yield. Second, if char fines are entrained in the condensed bio-oil they will accelerate "aging" as discussed later. Char removal is accomplished either through cyclone separation or hot gas filtration. Hot gas filtration is more effective at removing char, but char build-up on the filter effectively creates a vapor cracking bed that reduces bio-oil yield by 10-20%.

The quench stage rapidly cools bio-oil to ambient temperature (200°C/s), condensing the volatile organic fraction to a liquid oil. However, the components of quenched bio-oil continue to react with each other at a slow, temperature sensitive rate. Over several months of storage, bio-oil viscosity increases, flammability decreases, and water content increases. This effect is known as "aging" and is an impediment to storing unstabilized bio-oil for extended periods of time.

1.10 Applications

1. Bio-oil can substitute for fuel oil or diesel in many static applications including boilers, furnaces, engines and turbines.
2. There are range of chemicals that can be extracted or derived including food flavorings, specialties, resins, agrichemicals, fertilizers, and emission control agents.
3. The char produced during the fast pyrolysis can be used as media for scrubbing pollutants from emissions of coal fired plants and also excellent soil amendment.

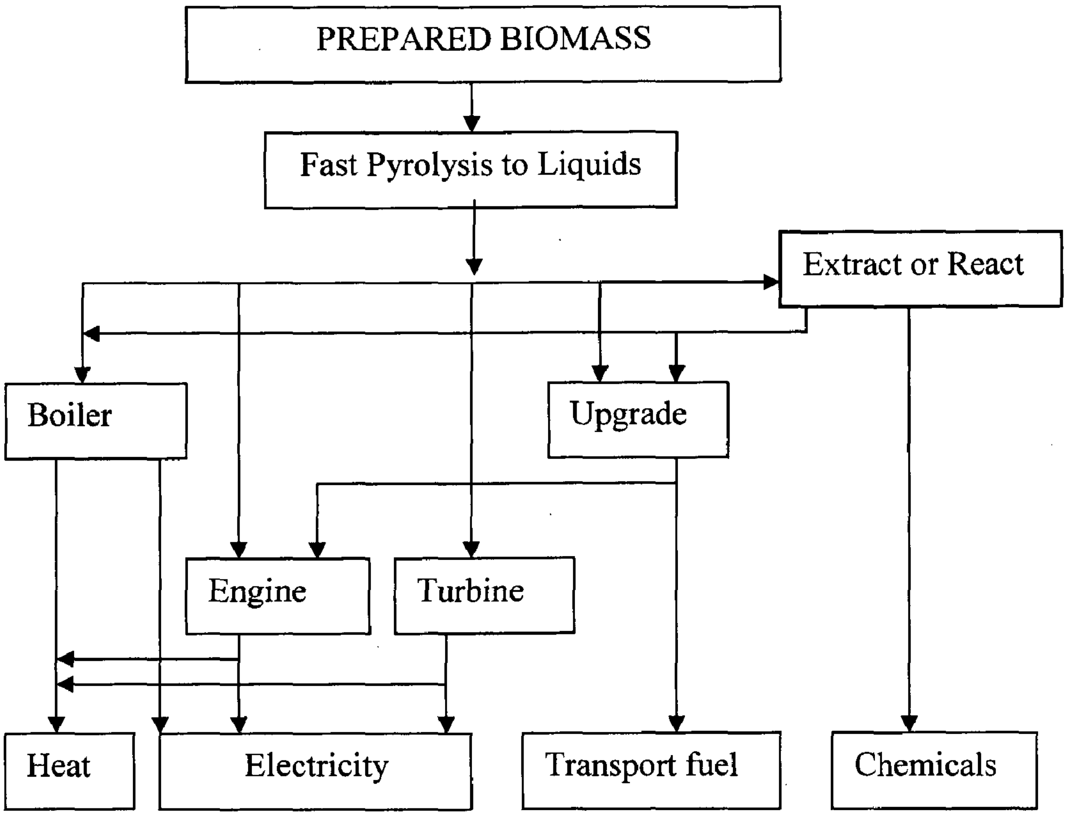


Figure 1.2 Processes and products from fast pyrolysis of biomass. [Fast pyrolysis processes for biomass A.V. Bridgwater, G.V.C. Peacocke2000]

1.11 Pyrolysis product composition

Pyrolysis oil composition

Oil obtained from the pyrolysis of biomass contains several organic as well as Inorganic species. Some of the organic groups present in the bio-oil are:

Acids: Formic, Acetic, Propanoic, Hexanoic, Benzoic, etc.

Esters: Methyl formate, Methyl propionate, Butyrolactone, Methyl n-butyrate, Velerolactone, etc.

Alcohols: Methanol, Ethanol, 2-Propene-1-ol, Isobutanol etc.

Ketones: Acetone, 2-Butanone, 2-Butanone , 2-Pentanone, 2-Cyclopentanone, 2,3 Pentenedione, 2-Hexanone, Cyclo hexanone, etc.

Aldehydes: Formaldehyde, Acetaldehyde, 2-Butenal, Pentanal, Ethanedial etc.

Phenols: Phenol, Methyl substituted phenols).

Alkenes: 2-Methyl Propene, Dimethylcyclopentene, Alpha-pinene, etc.

Aromatics: Benzene, Toluene, Xylenes, Nphthalenes, Phenanthrene, Fluoranthrene, Chrysene etc.

Nitrogen compounds: Ammonia, Methylamine, Pyridine, MethylPyridine etc.

Furans: Furan, 2-Methyl furan, 2-Furanone, Furfural, Furfural alcohol, etc.

Guaiacols: 2-Methoxy phenol, 4-Methyl guaiacol, Ethyl guaiacol, Eugenol, etc.

Syringols: Methyl syringol, 4-Ethyl syringol, Propyl syringol etc.

Sugars : Levoglucosan, Glucose, Fructose, D-xylose, D-Arabinose, etc.

Miscellaneous Oxygenates : Hydroxyacetaldehyde, Hydroxyacetone, Dimethyl acetal, Acetal, Methyl cyclopentenolone, etc.)

Inorganics are present in following forms in the bio-oil:

- Associated with counter ions.
- Connected to organic acids.
- Related to various enzymatic compounds.

Inorganics present in the bio oil comprises of Ca, Si, K, Fe, Al, Na, S, P Mg, Ni, Cr, Zn, Li, Ti, Mn, Ln, Ba, V, Cl etc.

Pyrolysis gas composition

Pyrolysis gas comprises of CO, CO_2 and CH_4. With these other components present are H_2, propane, propylene, butane, butenes, C_5, ethane etc.

Pyrolysis char composition

Char contains elemental carbon along with hydrogen.

1.12 Objective of project report

- The objective of present work is set as analysis of biomass, characterization of bio-oil and analysis of gas product.
- Thereafter a detailed work to study the effect of various parameters on pyrolysis of biomass to liquid fuel for maximum yield of liquid fuel.
- Finally, with reference to above mentioned analysis and parameter studies, we need to develop various experimental results such as Fourier Transform Infra-Red (FTIR) spectrophotometer, H-NMR and Gas chromatography/Mass spectroscopy.

The experimental works (Bench scale experiment) needed for the completion of present project work is carried out at Indian Institute of Petroleum (IIP), Dehradun.

Biomass-Derived Oil

2.1 Production of BDO via pyrolysis of biomass

The pyrolysis of biomass is a thermal treatment which results in the production of char, liquid and gaseous products. Pyrolysis is the general term to describe the process whereby organic material is heated essentially in the absence of oxidizing agents. Biomass conversion into oil and gas has been achieved by thermo-chemical technologies such as vacuum pyrolysis, fast pyrolysis, flash pyrolysis and gasification.

Fast pyrolysis has made significant advances in the past 20 years. It requires rapid heating of biomass to temperatures between 450 and 550°C and short residence times of 0.5 to 1 second of the volatile vapors in the reaction zone in order to prevent secondary cracking. In such conditions the yield of the liquid product (BDO) can reach up to 80 wt%.

Fluidized bed technology appears to be the most potential in fast pyrolysis of biomass for bio-oil, as it offers a high heating rate, rapid devolatilization, easy control, convenient char collection, low cost and so on.

Sevgi sensoz et al, [2005]

Olive bagasse (Olea europea L) pyrolysis

Olive bagasse is the solid residue obtained from pressuring the olives. Its pyrolysis was conducted under different conditions in a fixed-bed reactor. Olive bagasse was found to consist of 12.81% oil, 31.1% cellulose and 10.5%protein.

The results showed that both the temperature and heating rate had a significant effect on yields of oils, char and gas resulting from pyrolysis of olive wastes. From this paper concluded that higher treatment temperature led to lower bio oil yields and higher gas yields. Below figure-4.1 shows the Maximum liquid yield of 37.7 % was obtained at a final temperature of 500°C with a particle size of 0.425–0.60 mm, a heating rate of 10°C min^{-1} and a nitrogen flow rate of $150 cm^3 min^{-1}$. As is consistent with the literature, the maximum conversion attained at 400–450°C is considered to be the consequence of the rapid devolatilization of cellulose and hemicellulose at this temperature. The bio-oil was a mixture of aliphatic and aromatic hydrocarbons having an empirical formula of $CH_{1.65}O_{0.25}N_{0.03}$, H/C molar ratio 1.65, O/C molar ratio 0.25 and a heating value of 31.8 MJ/kg. Comparison of the H/C ratios with those of conventional fuels indicates that the bio-oils obtained in this work lay between light and heavy petroleum products.

The bio-oil was characterized by lower oxygen content than that of the original feedstock. The decrease in the oxygen content of the bio-oil (21.9%) compared to the original feedstock (37.5%) is important because the high oxygen content is not attractive for the production of transport fuels.

The FTIR spectral data showed that alcohol, ketone, ester and carboxylic acid groups are also major oxygen functions present in the polar fractions. The O–H stretching vibrations between 3300 and 3600 cm^{-1} for the bio-oil and toluene soluble fraction indicate the presence of phenols and alcohols. Also, the presence of the above mentioned peaks, together with the presence of C=O stretching vibrations between 1680 and 1718 cm^{-1}, is compatible with the presence of ketone, quinone, aldehyde groups, etc.

The hydrogen distribution of H-NMR is also listed in Table 4.1.Resonances between 7 and 9 ppm were assigned to aromatic structures. Resonances between 5 and 7 ppm have been attributed to non-conjugated olefins, mainly between 5 and 6.5 ppm. Aromatic ring-joining methylene protons were observed in the bio-oil and their characteristic peaks are in the range of 3.2–4.5 ppm. The naphthenic protons (β to CH and CH_2), and β -CH_3, CH_2, CHγ (centered at 1.25 ppm) protons were indicated as the majority in the bio-oil but in different amounts. $CH_{3\gamma}$, i.e. CH_3 at γ position or further from an aromatic ring and paraffinic CH_3 protons were also observed in the bio-oil. The data indicated that the olive bagasse biooil had a larger H_β fraction than pine chips bio-oil, poplar wood chips and eucalyptus wood waste oils.

Type of hydrogen	Chemical shift (ppm)
Aromatic	7.0–9.0
Phenolic (OH) or olefinic proton	5.0–6.5
Ring-join methylene ($Ar-CH_2-Ar$)	3.2–4.5
CH_3, CH_2 and CH_α to an aromatic ring	1.6–2.0
CH_2 and CH_β to an aromatic ring (naphthenic)	1.6–3.2
β-CH_3, CH_2 and CHγ or further from an aromatic ring	1.0–1.6
$CH_{3\gamma}$ or further from an aromatic ring and paraffinic CH_3	0.5–1.0

Table-2.1 H-NMR results of biooil

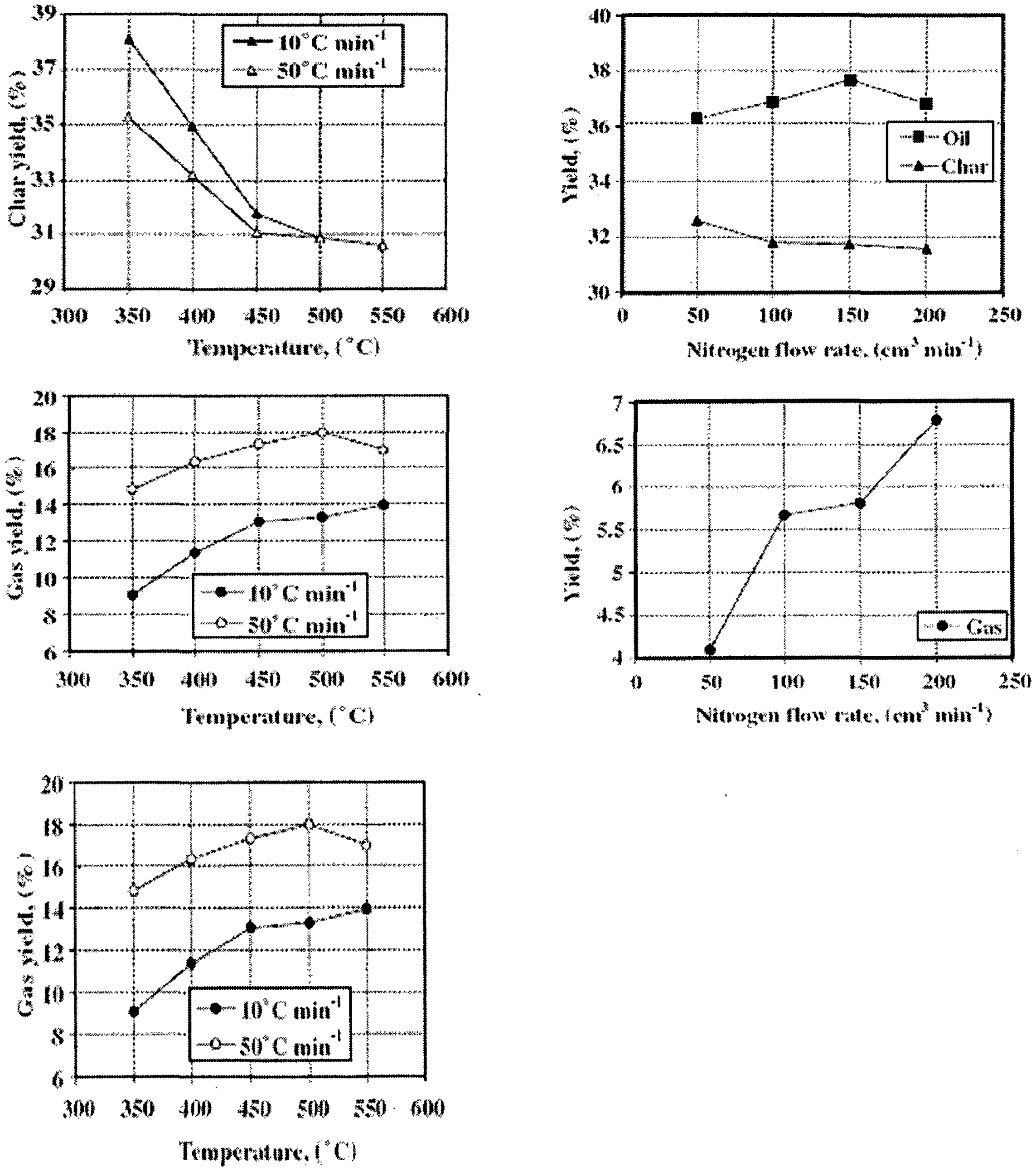


Fig 2.1 yields of Pyrolysis products at different pyrolysis temperatures, nitrogen flow rates and heating rates (particle size: 0.425–0.60 mm)

Sevgi et al, [2005]

Bio-oil production from soybean; fuel properties of Bio-oil

The pyrolysis experiments were performed in a fixed-bed reactor with a length of 104mm and internal diameter 70 mm; heated externally by an electric furnace with the temperature being controlled by a thermocouple inside in the bed.

In this study, the maximum bio-oil yield of 25.81 wt.% was obtained at a final pyrolysis temperature of 400 ^{0}C, a heating rate of 50 ^{0}C/min and a particle size range of 0.425–0.600 mm. The higher treatment temperature has led to lower bio-oil yields and higher gas yields. The higher heating rate favours also the decrease of char yield. The char yield is comprised between 22 and 24 wt. %. This solid fuel could be used in boilers where cake is presently burned. It also represents a good feedstock for the production of activated carbon. The bio-oil is a mixture of aliphatic and aromatic hydrocarbons having an empirical formula of $CH_{1.37}O_{0.15}N_{0.14}$ and an H/C atomic ratio of 1.37 at optimum conditions. The higher calorific value of the bio-oil is 33.6 MJ/kg, which is very close to those of petroleum fractions.

Ayse E. Putun et al,[2004]

Bio-oil from olive oil industry wastes: Pyrolysis of olive residue under different conditions.

This study deals with the fixed-bed pyrolysis of a biomass sample, olive residue, under different atmospheres in order to obtain synthetic liquid fuels. The experimental studies showed that pyrolysis temperature and atmosphere have important roles on the bio-oil yield and composition.

As it is consistent with the literature, final temperature of the pyrolysis reactions has a great influence on the product yields. The oil yield was found to be 27.26% at a final pyrolysis temperature of 500 °C with a heating rate of 7 °C/min.

Bio-oil yield increased by 19.13 wt. % when nitrogen with a flow rate of 100 cm^3/min was used as the inert gas to sweep the products from hot zone. It is known that the presence of steam increases the oil yields significantly while char and gas product yields decrease. The maximum bio-oil yield, 42.12%, was reached under steam atmosphere when steam velocity was 1.3 cm/s.

Suping Zhang et al, [2004]

Upgrading of liquid fuel from the pyrolysis of biomass

The upgrading of biomass to liquid fuel is a two-step process. The first step is upgrading of biomass to liquid product.

Fast pyrolysis is regarded as one of the most reasonable and promising technologies for high yield of liquid product from biomass. The second step, i.e., upgrading of the bio-oil before use, is desirable to give a liquid product that can be used in a wider variety of applications. Two main routes to upgrading of bio-oil have been investigated: catalytic cracking and catalytic hydro treatment. Catalytic cracking is regarded as a cheaper route, by converting oxygenated feedstock to lighter fractions that fall particularly in the gasoline boiling range, but the results are not so encouraging due to high coking (8–25 wt.%) and the low quality of the fuels obtained . Hydro treatment is a good technology to improve the stability of the bio-oil by removing the oxygen.

In this paper, a fluidized bed unit was used to investigate optimal conditions for obtaining the maximum liquid yield. Liquid product was separated with a simple approach in separating the hydrophilic and hydrophobic fractions by adding water that eventually effected an induced phase separation. Most of the water in the liquid product could be removed by concentration in the separated hydrophilic phase and meanwhile recovery of some water-soluble chemicals more valuable than fuel itself could be realized. Investigations were made on the effects of reaction temperature, reaction time, cold hydrogen pressure and catalyst on product distribution and the optimal conditions were concluded.

Pyrolysis of biomass was carried out in a fluidized bed unit. The effect of reaction temperature and residence time, cold hydrogen pressure, solvent on production was studied.

Sawdust was been pyrolysed in a fluidized bed unit (5 kg/h) to produce a high liquid yield (70%) under conditions of medium temperature (470 °C) and short residence time (2 s). The liquid product was separated into two phases: water phase and oil phase. The water phase contained some chemicals, such as acetic acid and hydroxyacetone, which could be recovered as useful chemicals. The oil phase was upgraded into liquid fuel by hydro treatment using sulfided Co–Mo–P in an autoclave with tetralin as solvent. The optimum conditions were: temperature 360 °C, reaction time 30 min and cold hydrogen pressure 2 Mpa. The raw bio-oil was methanol-soluble and the upgraded oil was oil-soluble for the dehydroxy.

Funda Ates etal,[2004]

Fixed bed pyrolysis of Euphorbia rigida with different catalysts.

Euphorbia rigida is a celluloid plant with low fat content; the oil yields of previous fixed bed pyrolysis studies were low. In order to increase the oil yield, biomass pyrolysis experiments were performed in a fixed bed reactor with two selected commercial catalysts, namely Criterion-534 and activated alumina, and natural zeolite (klinoptilolite). Experiments were conducted in a static atmosphere with a heating rate of 7 ^{o}Cmin^{-1}, pyrolysis temperature of 550°C and mean particle size of 0.55 mm. In the experiments, all the catalysts were used with various percentages, and the effects of the variable catalysts on the yields and chemical composition of the oils obtained were investigated.

	Without catalyst	5%	10%	20%	25%
Char	22.21	21.04	21.01	21.61	21.43
Oil	21.65	23.39	25.32	27.55	27.26
Water	22.32	23.20	23.48	24.87	25.90
Gas	33.82	32.37	30.19	26.97	25.41

Table 2.2 The dependence of product yields of Euphorbia rigida on the natural zeolite percentages.

	With out catalyst	5%	10%	20%	25%
Char	22.21	22.54	22.37	21.38	22.21
Oil	21.65	29.38	29.14	30.98	30.11
Water	22.32	27.07	27.90	26.79	26.24
Gas	33.82	21.01	20.59	20.85	21.44

Table 2.3 The dependence of product yields of Euphorbia rigida on the Criterion-534 percentages.

	With out catalyst	5%	10%	20%	25%
Char	22.21	21.16	19.90	19.35	18.95
Oil	21.65	25.88	28.15	27.66	27.28
Water	22.32	28.72	26.15	26.52	27.17
Gas	33.82	24.24	25.80	26.47	26.60

Table 2.4 The dependence of product yields of Euphorbia rigida on the activated alumina percentages.

From above tables, it was established that the pyrolysis oil yield rises in conjunction with increasing catalyst percentage and reaches its maximum with using 20% by weight natural zeolite and Criterion-534 and 10% by weight activated alumina. The greatest increase in oil product yield was obtained by using the catalyst Criterion-534. The oil yield, which was 21.65% without catalyst, reached the maximum value of 30.98% by using this commercial catalyst at 20% by weight. This means an increase of 5%, when compared to utilization of the same catalyst at 5% by weight. While looking at the gaseous product yield, we see that the 33.82% gaseous product without catalyst reduces to 20.85% with use of this commercial catalyst.

The tests results obtained with activated alumina, another commercial catalyst, shows that the highest oil yield is 28.15%. An increase of 8.8% was achieved when compared to the usage of 5% by weight activated alumina. The gaseous product yield was reduced when compared to the non-catalyst test with this commercial catalyst also. It was reduced to 25.8%

in tests conducted with 10% by weight, a decrease of 23.7% from tests performed with no catalyst. The change in catalyst percentage has a small but positive effect on the pyrolysis oil yield for both commercial catalysts.

When we look at the results with natural catalysts, we see that the highest oil yield was 27.55%. This means an increase of 27.3% when compared to the non-catalyst tests. The experiment with catalyst ratio of 5% gave an increase of only 8%, with the oil yield of 23.39%. A decrease in gaseous product yield was also observed with the natural catalyst, similar to that of the commercial catalysts, and for the value of 20% by weight that kept the oil yield at its optimum level, the gas yield was reduced to 26.97.

Putun et. al. (2001, Turkey)

He conducted fixed bed pyrolysis of Euphorbia rigida, sunflower presses bagasse and hazelnut shell, at a temperature of 823K and heating rate of 7K/min. Product yield was found to increase in all the three cases when the pyrolysis temperature was increased from 673K to 973K. Similar results (Table 4.5) were obtained on increasing the N_2 flow rate.

Ozbay et al. (2001, Turkey)

Slow pyrolysis of cottonseed cake

Slow pyrolysis of cottonseed cake at heating rates of 7°C/min in a tubular reactor was reported by Ozbay et al. (2001, Turkey). Pyrolysis experiments were conducted in two reactors, Heinz retort and a well-swept tubular reactor. From results (Table 4.6) it was seen that with the increase in the temperature the oil yield increased up to 600°C but decreased at around 750 °C. Char yield showed continuous decrease. Oil yield was maximum at N_2 flow rate of 100cm^3/min.

Onay and Kockar et al.

Onay and Kockar conducted slow pyrolysis experiments of rapeseed. Experiments were done in a Heinz retort and a tubular reactor with variable temperature, N_2 flow and particle sizes. Results (Table 4.7) showed that the increase in temperature increased the oil yield up to 550°C and later reduced beyond this temperature. There was continuous decrease in the char yield whereas gas increased throughout. For particle size 0.6<dp<0. 85 the oil yield was maximum. Char was found to least with the size of 0. 85<dp<1. 25.

Temp: (K)	Euphorbia rigida (% yield)		
	Char	**Oil**	**Water**
673	44	24	13
773	28	32	17
973	21	26	13
	Sunflower		
673	35	36	12
773	27	44	12
973	26	38	12
	Hazelnut shell		
673	47	20	14
773	41	23	14
973	36	21	14

Table 2.5: Yields of products (approx.) from various biomass at different temperatures

S. No.	Temp (°C)	Char	Oil	Water
		Yield %		
1	300	31.0	21.0	26.9
2	350	29.0	21.8	26.0
3	450	28.0	23.2	22.1
4	550	27.0	24.5	23.0
5	650	24.5	23.0	24.0

Table 2.6: Variation of product with temperature for cottonseed cake

Temp (°C)	Char	Oil	Gas
	(% yield)		
400	24	42	26
500	22	46	25
600	19	47	27
700	18	44	31
Particle size			
$d_p<0.425$	23	44	26
$0.425<d_p<0.6$	22	45	26
$0.6<d_p<0.85$	17	48	28
$0.85<d_p<1.25$	16	49	29
$1.25<d_p<1.8$	17	48	28

Table 2.7: Product yield varying with temperature and particle size

S. Yorgun et al.

Characterization of the pyrolysis oil produced in the slow pyrolysis of Sunflower-extracted bagasse.

In this study, pyrolysis experiments of sunflower extracted bagasse were carried out in a fixed-bed reactor under self-pyrolysis and nitrogen atmospheres. The maximum oil yield of 23% was obtained at a final pyrolysis temperature of 550^0C with a particle size of 0.425-0.850 mm, with a heating rate of 7^0Cmin^{-1}, and nitrogen flow rate of 100 $\text{cm}^3\ \text{min}^{-1}$. The oil product was characterized by elemental analysis and various chromatographic and spectroscopic techniques and also compared with currently utilized transport fuels by simulated distillation and presented as a biofuels candidate. For the evaluation of the employment of pyrolytic oil as a fuel, the following options are recommended:

- The liquid product may be used a source of low-grade fuel directly or may be upgraded to higher-quality liquid fuels.
- Oil seems to be more appropriate for the production of hydrocarbons and chemicals.
- There is a great potential for Turkey to exploit biomass reserves as possible synthetic petroleum sources.
- The findings of laboratory-scale studies are encouraging and warrant larger-scale applications of biomass pyrolysis for synthetic fuels.

Onay et al.

Fast pyrolysis of rape seed in a well-swept Fixed bed reactor

Onay (2003, 2004) conducted experiments on fast pyrolysis of rapeseed to investigate the affect of temperature, heating rate, particle size, and sweep gas flow on the product yield. From the data (Table4.8) it was concluded that char yield decreased from 27% to 14.5% with the increase in the temperature. Maximum oil yield of 73% was obtained at temperature of 550-600°C, particle size of +0.6-1.25mm, and sweep gas flow rate of $100\text{cm}^3/\text{min}$.

Parameter	**Oil**	**Char**	**Gas**
Particle size			
$d_p < 0.425$	42.5	22.5	26.2
$0.425 < d_p < 0.6$	45.0	20.0	26.4
$0.6 < d_p < 0.85$	47.5	17.5	27.2
$0.85 < d_p < 1.25$	50.0	16.0	29.2
$1.25 < d_p < 1.8$	47.5	17.5	27.2
$d_p > 1.8$	47.5	22.5	27.2
Temperature °C			
400	38	28	<5
500	60	20	<5
550	62	19	<5
600	60	18	<5
700	59	18	<5

Table 2.8: Yield % (approx) with variable particle size and temperature

Zhongyang Luo et al,[2003]

Research on biomass fast pyrolysis for liquid fuel

Biomass utilization is important for sustainable development of Zhejiang Province, for being able to solve the shortage of fossil fuel and exploit abundant biomass resource. Especially liquid produced from biomass fast pyrolysis could be substituted for traditional liquid fuel, such as diesel oil. And detailed experimental research was carried out on a small-scale pyrolysis fluidized bed reactor with a maximum feed rate of 3 kg h^{-1}.

Experimental result showed that the temperature of 773 K was more suitable for high-quality bio-oil production. Besides this, the composition of incondensable gas was also influenced by temperature. Higher heating-value gas could be obtained at a higher reaction temperature in pyrolysis. Results (Table-4.9) shows that P. indicus had the best characteristic for producing bio-oil, followed by C. lanceolata. and F. mandshurica, but Rice Straw was the worst. This was mainly because that higher ash content in biomass was disadvantageous to obtain high quality bio-oil production. However, upgrading of refining of bio-oil is necessary for its inferior property and complex composition.

Biomass	**Temp(K)**	**Particle Size (µm)**	**Yield (%)**	**Heating Value (Kj/Kg)**	**Water (%)**
F. mandshurica	823	74-154	40.2	22000	39.6
C.lanceolata	773	74-154	53.9	19000	31.4
P.indicus	773	250-355	55.7	19000	24.6
Rice Straw	773	154-250	33.7	19000	53.5

Table 2.9: Effect of biomass species on bio-oil production

According to the GC–MS analysis, bio-oil was mainly composed of levoglucosan, furfural, phenol and aldehyde. Table 4.10 shows the distribution of some detected compounds in the organic composition of bio-oil, which was produced from P. indicus.

Table 2.10- Relative content of main compounds in organic composition of bio-oil produced from P. indicus

Compound	Relative content (%)
Furfural	9.06
Acetoxyacetone, 1-hydroxyl	1.21
Furfural, 5-methyl	1.82
Phenol	2.55
2-Cyclopentane-1-one, 3-methyl	1.58
Benzaldehyde, 2-hydroxyl	2.70
Phenol, 2-methyl	5.04
Phenol, 4-methyl	0.51
Phenol, 2-methoxyl	0.27
Phenol, 2,4-dimethyl	9.62
Phenol, 4-ethyl	2.18
Phenol, 2-methoxy-5-methyl	4.15
Phenol, 2-methoxy-4-methyl	0.55
Benzene, 1,2,4-trimethoxyl	3.80
Phenol, 2,6-dimethyl-4-(1-propenyl)	4.25
1,2-Benzenedicarboxylic acid, diisooctyl ester	1.80
2-Furanone	5.70
Levoglucosan	6.75
Phenol, 2,6-dimethoxy-4-propenyl	3.14
Furanone, 5-methyl	0.49
Acetophenone, 1-(4-hydroxy-3-methoxy)	2.94
Vanillin	6.35
Benzaldehyde, 3,5-dimethyl-4-hydroxyl	4.54
Cinnamic aldehyde, 3,5-demethoxy-4-hydroxyl	2.19

Hasan Ferdi Gercel,[2002]

Production and characterization of pyrolysis liquids from sunflower-pressed bagasse

In this study, pyrolysis experiments on sunflower (H. annus L.)pressed bagasse were performed in a fixed bed tubular reactor under a nitrogen atmosphere. The highest bio-oil yield of 52.10 wt.% was obtained at a final pyrolysis temperature of 550° C with a particle size of 0.224–0.425 mm, with the heating rate of 5 $^{o}Cs^{-1}$, and nitrogen flow rate of 50 ml min^{-1}. The highest overall conversion of 79.01 wt.% was obtained at the final pyrolysis temperature of 700 °C with a nitrogen flow rate of 400 ml min^{-1}. The bio-oil was a mixture of aliphatic and aromatic hydrocarbons having an empirical formula of $CH_{1.68}O_{0.165}N_{0.059}$, H/C molar ratio 1.68 and O/C molar ratio 0.165 at optimum conditions. The heating value of the bio-oil was 35.013 $MJkg^{-1}$, which is very close to values of petroleum fractions.

C. Acıkgoz et al,[2003]

Fast pyrolysis of linseed: product yields and compositions

The formation of liquid product derived from linseed can be maximized using well-swept resistively heated fixed-bed reactor. Employing the higher heating rate of 300 $^{o}Cmin^{-1}$ breaks heat- and mass-transfer limitations, and the oil yield reached maximum 57.7 wt.% at a final pyrolysis temperature of 550 °C, particle size range of 0.6–1.8 mm, and sweep gas (N_2) flow rate of 100 cm^3 min^{-1}. Particle size is known to influence pyrolysis product. If the particle size is sufficiently small it can be heated uniformly, as is consistent with earlier studies. A working particle size range of 0.6–1.8mm for obtaining a high yield of liquid product in fast pyrolysis of linseed seems suitable. Working under a 50–400 cm^3 min^{-1} sweep gas flow rate showed that the minimum gas flow rate for well-sweeping in the reactor was more than 50 cm^3 min^{-1}.

S. Yorgun et al,[2000]

Flash pyrolysis of sunflower oil cake for production of liquid fuels

In this study, flash pyrolysis experiments of sunflower (*Helianthus annuus* L.) oil cake were performed in a tubular transport reactor under nitrogen atmosphere. The highest liquid yield of ca. 45% was obtained at a final pyrolysis temperature of 550°C with a particle size of 0.425–0.850 mm, and nitrogen flow rate of 300 cm3 min−1. The bio-oil is a mixture of aliphatic and aromatic hydrocarbons having an empirical formula of $CH_{1.512}O_{0.175}N_{0.070}$, H/C molar ratio 1.73 and O/C molar ratio 0.175 at optimum conditions. The liquid obtained shows a minimum oxygen content at the conditions of maximum liquid yield. The heating value of the bio-oil is 33.7 MJ kg^{-1} which is very close to those of petroleum fractions. Taking into account the oil yield of the Heinze retort, it can be clearly seen that the oil yield increased about 20% with flash pyrolysis. The pyrolytic oil was identified and presented as a biofuel candidate. The liquid product may be used as a source of low-grade fuel directly, or it may be upgraded to higher quality liquid fuels.

A.E. Putun et al,[1999]

Pyrolysis of hazelnut shells in a fixed-bed tubular reactor yields and structural analysis of bio-oil

The oil yield was 23.1 wt.% from the pyrolysis of hazelnut shells using a fixed-bed tubular reactor at a final pyrolysis temperature of 500°C with a heating rate of 7 K min^{-1} and a nitrogen flow rate of 100 cm^3 min^{-1}. The increment of 3 wt.% of the oil yield at the optimum temperature of 500°C with an increase of nitrogen flow rate from 50 to 100 cm^3 min^{-1} is relatively low as compared to oil shales and some other biomass samples such as sunflower pressed bagasse and *Euphorbia rigida* at the same conditions. As it is consistent with the literature, the maximum conversion is attained at 400°C is considered to be the consequence of the rapid devolatilization of cellulose and hemicellulose at this temperature.

The result of the yields leads to a conclusion that the mass transfer limitation of volatile evolution are much less pronounced for biomass than for coals and oil shales.

The oil and the subfractions analyzed by elemental analyzer, FTIR, GC/MS and H NMR. GC analyses have been shown that alkanes, alkenes and branched hydrocarbons are the main compounds of the pentane soluble fraction.

The results of the spectroscopic methods are in consistance with chromatography, confirming that the hydrocarbons of the pentane subfraction of the bio-oil is a mixtures of alkanes and alkenes.

Comparison of H/C ratios with conventional fuels shows that the H/C ratios of the oil obtained in this work is between those of light and heavy petroleum products.

Zanzi .R et al,[1997]

Rapid pyrolysis of straw at high temperature

A free fall reactor was implemented in the study of the rapid pyrolysis of biomass, which in this case were untreated straw and straw pellets. Subsequently, the results were compared with those previously obtained in wood pyrolysis. Before pyrolysis the straw is milled, sieved, and wind classified to obtain fractions of uniform particle size. The free-fall reactor has a heated length of 2.9 m and an inner diameter of 0.04 m. The char from the rapid pyrolysis is further pyrolysed in nitrogen atmosphere in a thermo balance with a slow heating rate (20°C/min) up to 850°C in order to obtain complete pyrolysis. This work focuses on the effect of the treatment conditions on the product distribution, gas composition and properties of the char obtained in pyrolysis. The product distribution in rapid pyrolysis of wood, untreated straw, and palletized straw was revealed to be similar. A little less char is produced by wood than straw. The higher treatment temperature has led to lower yields of tar and higher yields of gaseous products. At higher temperature, the heat flux and the heating rate are higher. The higher heating rate favours also the decrease of char yield.

3.1 APPARATUS USED

3.1.1 Fixed bed tubular reactor

The stainless steel tubular reactor was used which is 23.8 in. high x 1.6 in. i.d. and was heated externally by an electric furnace. A wire mesh was provided at about 3.5 in. from the bottom of the reactor to hold the biomass in the reactor. The N_2 was purged from the top of the reactor and gases leave from the bottom. The temperature of reactor inside and reactor skin was measured with the help of thermocouples. Two thermocouples were inserted from the bottom of the reactor to measure the temperature of the center and top of the reactor. The biomass bed height in the reactor was 15 in. from the wire mesh. The wall thickness of this reactor was less than the tubular reactor of smaller diameter. The reactor is shown in Fig. 5.1.

3.1.2 Electric Furnace

Two furnaces were used during the pyrolysis by two different reactors. In the first electric furnace (12.5" high x 2" i.d.) , only one heater was used.. In the second furnace (25" high x 2.5" i.d.), two heaters are used. The heating rate was high in the second reactor as compared to the first. Temperature variations along the reactor length were studied in both furnaces.

3.1.3 Rotameter

Rotameter was used to supply a controlled and measured sweep gas (Nitrogen) flow rate. Nitrogen is passed through the rotameter at different flow rates ranging from 50 to 200 cm^3/min. Rotameters were first calibrated using standard calibration instrument. The rotameters were also calibrated using Gas flow meter (Wet test meter). To calculate the flow rate, time was noted down for one complete cycle of Gas flow meter .The readings of calibration by gas flow meter are shown in Appendix-B.

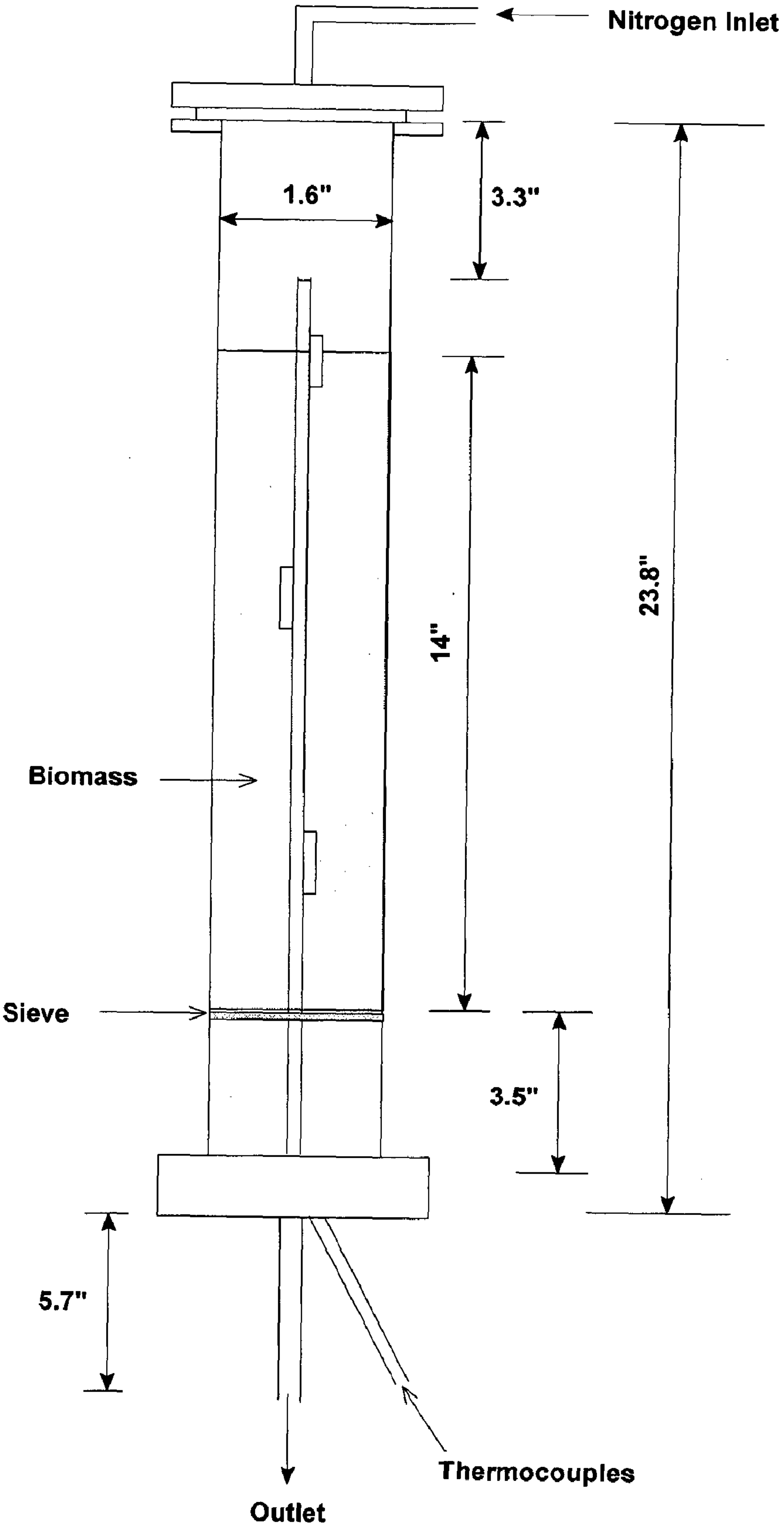


Fig. 3.1 Fixed bed tubular reactor

3.1.4 Preheater

The carrier gas entering the reactor was passed through the preheater to raise the temperature of the gas. The temperature of the preheater was maintained at 500 – 530 ^{0}C and was measured with the help of pyrometer. Preheater was made up of stainless steel and is 50 in. long and 0.4 in. internal diameter. The heat was provided with the help of heating coil, connected to the dimerstat.

3.1.5 Thermocouples

The thermocouples were used to measure temperature at the reactor skin and inside the reactor i.e. center and top of the reactor. Pyrometer was used to measure the temperature at the skin of the preheater. The thermocouples were calibrated with the help of thermometer.

3.1.6 Gas flow meter (Wet test meter)

Gas flow meter was used to measure the amount and rate of gas flowing out of the reactor. It was also used to measure the rate at which the gas was coming out of the reactor. The gases coming out of the reactor include nitrogen and gases produced during the reaction of pyrolysis.

3.1.7 Condenser

Condenser was used to condense the condensable gases produced during the pyrolysis. The temperature of the condenser varied from 0 to 55 ^{0}C.

3.1.8 Receiver

The liquid product formed during the reaction of pyrolysis was collected at the bottom of the receiver.

3.1.9 Cold Traps

Two ice traps were connected after the condenser, to condense the gases which escape through the condenser during the pyrolysis. The temperature of the traps was maintained at about 0 ^{0}C with the help of ice.

Experiment: Pyrolysis of biomass Jatropha curcas seed cake.

PROCEDURE: The following steps were done to obtain the products from the biomass:

4.1 Pretreatment of the biomass:

(i) Biomass sample was analyzed for moisture content, calorific value, metal contents, etc.

(ii) The bulk biomass was separated into three mesh sizes by sieving using meshes of different sizes. Three mesh sizes taken were -6 +8, -8 +12, and –12 +16.

(iii) Then a known amount of the biomass was taken and was dried in the air oven till it acquired a constant weight.

(iv) During this process of drying biomass was kept in the oven for one hour duration and cooled in the dessicator and then were weighed. This process was continued till it acquired the constant weight

(v) Once it had acquired the constant weight it was ready for to be fed into the reactor.

4.2 PROCEDURE

The fixed bed pyrolysis experiments were performed using a tubular reactor in an inert gas (Nitrogen) atmosphere. The reactor setup is shown in Fig 3.1. A 316 stainless steel tubular reactor (23” high x 1.6” i.d.) was used for pyrolysis experiments and is externally heated by an electric furnace (24” high x 2.5” i.d.) with the temperature being controlled by dimmerstat. The temperature was measured by four thermocouples. The thermocouples were placed at reactor center, reactor top (inside), reactor skin and preheater.

In the pyrolysis experiments, two different sizes of **JATROPHA CURCAS** (mesh no. -6+8,–8+12 and –12+16) were used. The Jatropha curcas was filled in the reactor up to a height of 17” from the mesh. Nitrogen flowrate was controlled and measured by the rotameter. The nitrogen flow rate of 50, 100, 150 cm^3/min. were employed. Nitrogen was preheated up to a temperature of 500 – 530 ^{0}C and fed to the top of the reactor. The reactor was heated at a constant heating rate of 10 ^{0}C/min. under a nitrogen atmosphere to a final temperature of 400, 500 and 600^{0}C.The experimental set is shown in fig-4.1.

The experiments were carried out in three series. The first was carried out to determine the effect of the pyrolysis temperature and the heating rate on pyrolysis yields with the particles size of -6+8 and-8+12 mesh number. The temperature was maintained at 400, 500 and 600 ^{0}C, while the heating rates were either 10 or 50 ^{0}C min^{-1}. Following pyrolysis, the condensable products (liquid) were collected in a series of traps maintained at about 0 ^{0}C. These liquid products contained an aqueous (pyrolignic acid or wood spirit) and an oil phase (tar or pyrolytic oil), which were separated and weighed. After pyrolysis, the solid char was removed and weighed. The soluble part of the oil phase which dissolved in a rotary evaporator and the quantity of bio-oil was established. Then, the gaseous phase was calculated from the material balance.

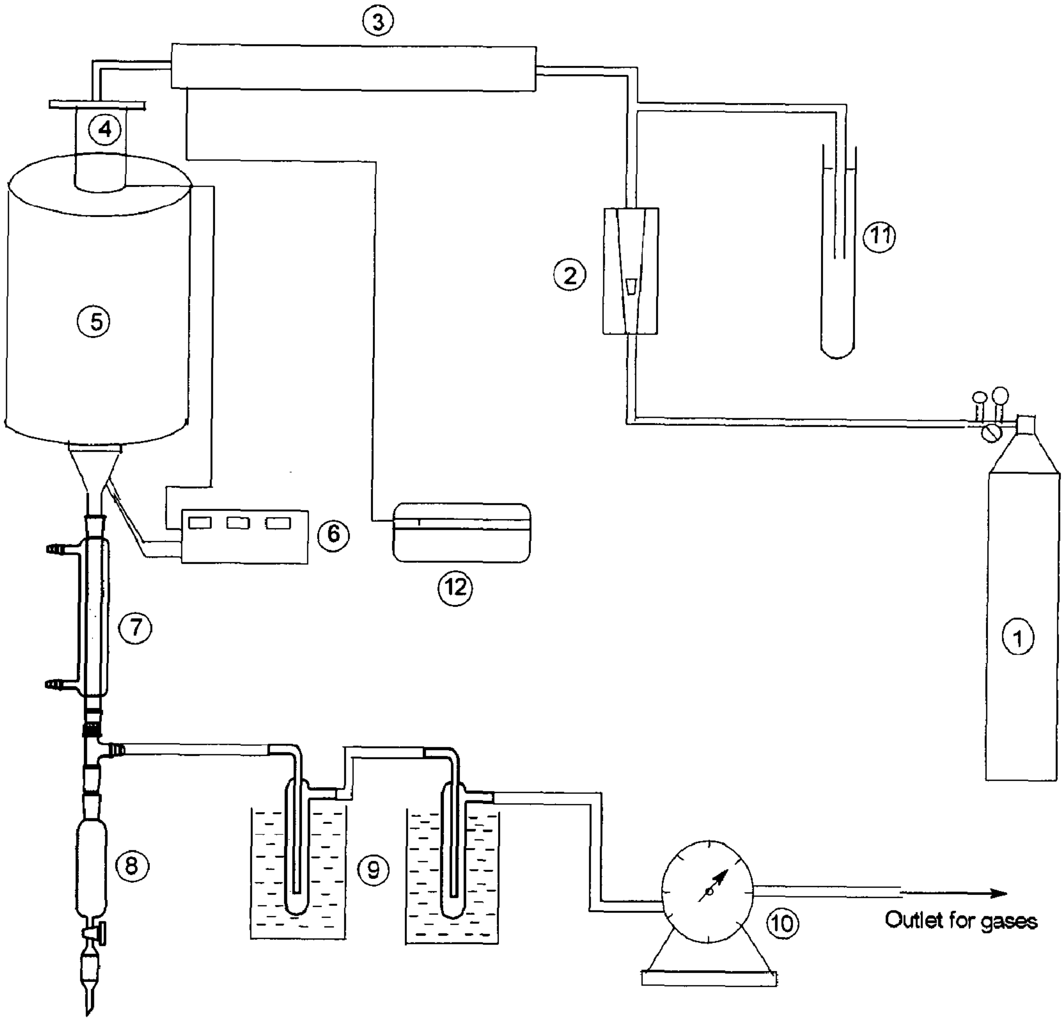
The second group of experiments was performed to establish the effect of particle size on the pyrolysis yields. The particle size of samples varied in a range of -6+8 and-8+12 mesh number. For all these experiments, the heating rate and final pyrolysis temperature were 10 ^{0}C min^{-1} and 500 ^{0}C, respectively, based on the results of the first group of experiments.

The last group of experiments was performed to establish the effect of sweep gas (nitrogen) velocity on the pyrolysis yields. The experiments were conducted at sweep gas flow rates of 50, 100, 150 and 200 cm^3 min^{-1}. For all these experiments, the heating rate, the final pyrolysis temperature and the particle size were 10 ^{0}C min^{-1}, 500 ^{0}C, and -6+8 and-8+12 mesh number, respectively, based on the results of the first two groups of experiments. All the yields were expressed on a dry ash free (daf) basis and the average yields from three experiments were presented within the experimental error of $<\pm 0.5$ wt%.

The vapours formed during the pyrolysis of biomass enter the condenser after coming out of the reactor. The condensable gases condense to the liquid and the collected in the receiver. The temperature of the condenser is maintained at 15 ^{0}C. The gases are further passed through a series of ice traps maintained at 0-5 ^{0}C to condense the gases which escape through the condenser. The amount of gas going out in the atmosphere was measured by gas flow meter. The final temperature was maintained for 20 minutes or until no further significant release of gas was observed.

First the water (aqueous phase) was collected from the receiver and weighed and then the colored liquid from the trap and receiver was collected and weighed. The amount of tar deposited on the receiver and condenser was also found out. The reactor was cooled by purging nitrogen to the room temperature. The reactor was opened and the solid product (char) was weighed. The volume of gas was calculated by subtracting the amount of N_2 supplied during the reaction from the total amount of gas passed through the gas flow meter.

Aqueous phase and non aqueous phase were separated using Dean stark apparatus and weighed separately using balance (Model: Saritorius) up to accuracy of two digits (+-0.01 gm). Known amount of toluene is added to the oil water mixture before charging it for water removed by Dean stark apparatus. The gas was collected in the toddler bags has been given for further characteristics. JULBO water was used to produce cooling effect in condensers made of 316 stainless steel (0.025" i.d and 1.0" o.d).



1. Nitrogen Cylinder 2. Rotameter 3. Preheater 4. Reactor 5. Heating Furnace
6. Temperature Indicator 7.Condenser 8. Reciever 9. Cold Traps 10. Gas Flow Meter
11. Safety Valve 12. Pyrometer

Fig4.1 Experimental set up of Pyrolysis of biomass using Modified fixed bed tubular reactor (larger diameter)

4.3 Characterization:

COMPONENT ANALYSIS OF BIOMASS-PROCEDURE

1. Analysis of moisture content

Some sample of biomass of (-60) mesh was weighed. It was dried in the oven at around 80^0C for 2 hrs. The sample was cooled in desiccator and then weighed. This procedure was continued till the constant weight was obtained. After getting the constant weight, then moisture was calculated as:

$$\text{Moisture content (Ad)} = \frac{\text{Initial weight of Biomass- Wt. of Biomass after drying}}{\text{Initial Wt. of Biomass}} \text{x100}$$

2. Analysis of extractive

Procedure

Some amount (G_0, gms) of dried biomass was taken in a thimbal. It was put in the Soxhlet apparatus. Benzene/ethanol mixture was taken in the volume ratio of 2:1. Biomass was leached at constant temperature for 3 hours. After this process kept the residue in Petridish at room temperature. Then residue was air dried in an oven at 105-110^0 C to a constant weight. The residue was cooled in a desiccator and weighed (G_1, gms).The extractive weight was calculated as:

$$W_1 \text{ (Wt \%)} = \frac{(G_0 - G_1)}{G_0} \text{x100}$$

3. Analysis of Hemicellulose:

Procedure

Known amount (G_1) of residue obtained from extractive analysis was taken in a flask. Prepared 150 ml NaOH solution (20gms/Lit) and added it to the flask. The mixture was boiled for 3.5 hrs with recycled distilled water. Filter and wash the residue till no more Na+, and it was dried to constant weight. The residue was then cooled to room temperature in a desiccator and weighted (G_2).The hemicellulose wt% was calculated as:

$$W_2\ (\text{Wt}\ \%) = \frac{(G_1\text{-}G_2)}{G_1} \times 100$$

4. Analysis of Lignin

Put about 1gm of residue after extractives analysis as above in a weighted flask and dry it to a constant weight. The sample was then cooled in a desiccators and weighted (G_3), gms). Slowly pour 30 ml of sulphuric acid (72%) in to sample and keep the mixture at 8-150 C for 24 hours. Dilute the mixture with 300 ml of distilled water. The sample was boiled for 1 hr with recycled distilled water. After cooling and filtration the residue was washed until there was no more sulphate ion in the filtrate. The residue was then dried to a constant weight. Cooled to room temperature in desiccators and weighted (G_4, gm).The lignin wt% was then calculated as:

$$W_3\ (\text{wt}\ \%) = [G_4\,(1\text{-}W_1/100)] \times 100$$

5. Analysis of cellulose

The cellulose was calculated as:

$W_4\ (\text{wt}\ \%) = 100\text{-}(Ad+W_1+W_2+W_3)$

Trace Metal analysis

Trace metal analysis of sieved Jatropha curcas were performed using atomic emission spectrometer (Model No: PS-3000 UV, IUPAES (Inductively Coupled Plasma Atomic Emission Spectroscopy))

BIOOIL CHARACTERISATION

Component analysis and elemental analysis were carried out on the **JATROPHA CURCAS** seed cake sample .The oil analyzed was obtained under experimental conditions giving the maximum oil yield (Pyrolysis temperature of 600^0C, particle size range of -6+8 to-8+12 mesh number., the heating rate of 10^0Cmin^{-1} and nitrogen flow rate of 100cm^3/min).The elemental composition and calorific values of the biooil and char were also determined.

Elemental Analysis

The carbon, hydrogen and nitrogen were determined by ASTM D-5291 method by using an instrument of Perkin Elmer, Series , CHN/O analyzer 2400.Gas was used in that instrument are He,N_2 and O_2.

Molecular weight

Molecular weight of biooil was determined by vapour pressure osmometer ,KNAUER instrument.

Density

The density of biooil was determined at 20°C and 40°C by oscillating U-tube or Digital density analyzer using ASTM D-5002 or IP-365 method.

Kinematic viscosity

Kinematic viscosity of biooil was determined by BS/IP/RF U tube reverse flow viscometer using IP-71 method.

Calorific value

Amount of heat liberated when a unit mass or volume of fuel is burnt in air saturated with water vapours under constant pressure and the products of combustion are cooled to a specified temperature.

Calorific value of biooil was determined according to IP-381 or ASTM D-4529 method.

$$\rho_p = 22{,}959\ 6 - 0{,}012\ 658\ 7\ A + 26\ 640{,}\ 9/D + 32622\ A/D - (6{,}690\ 3\ \mathrm{x}10^{-5})\ A^2 - (9{,}217\ 76\ \mathrm{x}10^{6})/D^2$$

Where

ρ_p = Net Specific energy at constant pressure on a sulfur free basis

A= is the aniline point, in degree Celsius

D=is the density at 15^0C, in Kg/m^3

Flash point

Flash point of biooil was determined by **Pensky-Martens closed cup** method in flash point bath using IP-34 method.

Pour point

Pour point is the lowest temperature at which a sample of petroleum product will continue to flow when it is cooled under specified standard conditions.

Pour point of biooil was determined by using IP-15 method in pour point bath.

Ash

Ash content in biooil was determined by using IP-4 method by Manual sampling.

CCR

The whole residue produced from the specific conditions of evaporation and pyrolysis described in this international standard.

The carbon residue value serves as an approximation of the tendency of petroleum products to form carbonaceous deposits under similar degradation conditions and can be useful in the assessment of relative carbon-forming tendencies of products with in the same class.

CCR of biooil was determined by Micro carbon residue Tester using IP-398 method.

H NMR

The H NMR spectra of the biooil were obtained at an H frequency of 500MHz using a **BRUKER AVANCE-500** instrument. The solvent used in this process is $CDCl_3$.

FTIR

1 gm of biooil was separated in to two fractions as n-pentane soluble (asphaltenes) and insoluble compounds (maltanes) by using 50 ml n-pentane.

Fourier transform infrared spectroscopic analysis of the biooil, n-pentane soluble fraction and n-pentane insoluble fraction was performed on a Perkin-Elmer model PE1760X FTIR spectrometer to determine its functional groups .Solvent used in this process is CCl_4 and KBr thin film.

GC/MS

GC/MS of n-pentane soluble fraction analysis was done using Perkin Elmer Clarus 500 model with HP1-5MS capillary column (32m x 0.32mm x 0.25μm) .The initial oven temp of GC was 60^0C for 2 min and then programmed to increase at a rate of $15^0C/min$ to 300^0C ,hold for 2 min. He gas was used as carrier gas with a flow rate of 1 ml/min.
The m/z (ratio of mass to charge) values, which represent the most probable fragments of the compounds explained, have been presented for each compound.

Experiment time =20 min
Detector = FID (Flame Ionization Detector)
Run time =20 min
Injection=Manual
Solvent=HPLC Grade Methanol

Gas analysis

Pyrolysis gas was subjected to GC using N_2 as mobile gas in a refinery gas analyzer by using chemitto, 8600 refinary gas analyzer.

Based on the procedure described in the previous chapter; an experimental setup was constituted. On carrying out the experiment, Pyrolysis of Jatropha curcas seed cake, the bio-oil , char and gas products are obtained.

The experimental observations maintained during the product formation (bio-oil) are shown in Appendix A. In this chapter explains the effect of parameters on product yields, a detailed analysis of biomass, bio-oil and gas product. And combined analysis of biomass, char and bio-oil, FTIR, H-NMR, GC/MS of bio-oil.

5.1 EFFECT OF PARAMETERS ON PRODUCT YIELDS

5.1.1 EFFECT OF TEMPERATURE

Table 5.1- Comparison of Oil, char & gas yield for different temperature at constant particle Size of 2.8445 mm and nitrogen flow rate of 100 ml/min.

Temperature	Yield Wt.%		
	Oil	Char	Gas
400	21.61	50	4.07
450	24.03	48	4.68
500	18.33	50	3.8
600	25.39	43.53	4.87

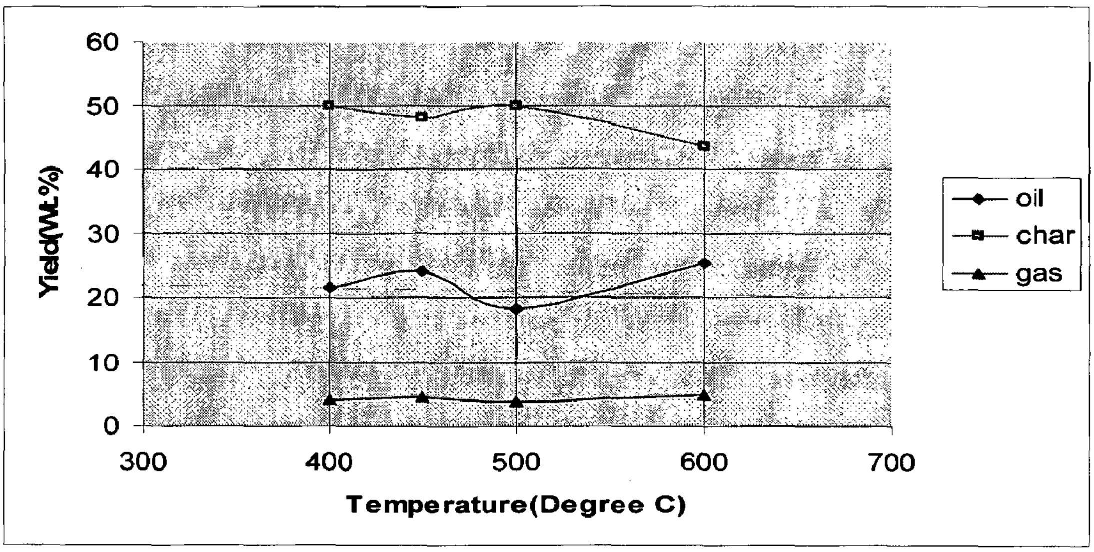


Figure 5.1 - Effect of pyrolysis temperature on yield of products from pyrolysis of biomass.

Figure-5.1 shows that product yields from pyrolysis of the Jatropha curcas seed cake with heating rate of 10^0C min^{-1} in relation to final pyrolysis temperature 400,450,500 and 600^0C, with nitrogen flowrate of 100ml/min. The bio-oil yield was 21.61 Wt. % at the temperature of 400^0C, it appeared to go through a maximum (25.39Wt. %) at the final temp temperature of 600^0C.

The gas product yield increased with pyrolysis temperature. The gas obtained was found to be of minimum 4.07% at 600^0C for heating rate of 10^0C/min. The increase in gaseous products is thought to occur predominantly due to secondary cracking of the pyrolysis vapours at high temperature.

The char yield was reduced as the pyrolysis temperature was increased. The decrease in char yield with an increase in temperature could be either due to greater primary decomposition of biomass at higher temperature or through secondary decomposition of the char residue. The secondary decomposition of the char at higher temperatures may also give non-condensable gaseous products which would also contribute to the increase in gas yield with increasing temperature of pyrolysis.

5.1.2 EFFECT OF N_2 FLOW RATE

Table 5.2- Comparison of Oil, char & gas yield for different N_2 flow rates at constant particle Size of 2.8445 mm, heating rate of 10^0Cmin^{-1} and temperature of 600^oC

N_2 Flow Rate	Yield Wt.%		
	Oil	**Char**	**Gas**
50	23.08	44.21	3.72
100	25.39	43.53	4.87
150	23.98	44.22	4.45

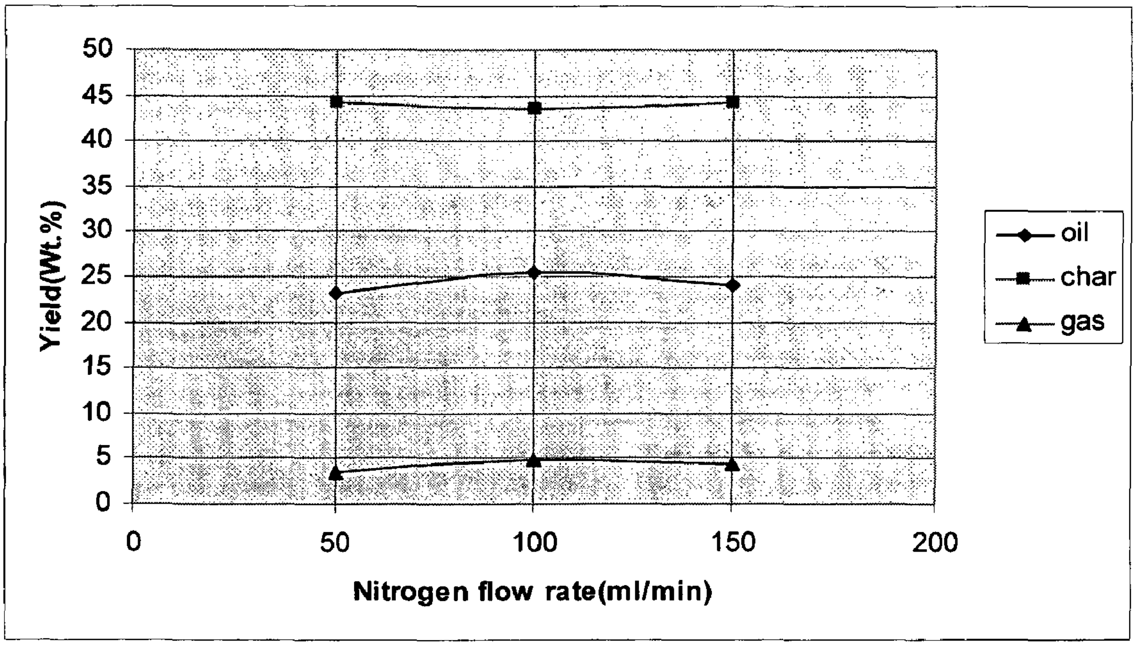


Figure 5.2 Effect of N_2 flow rate on yield of products from pyrolysis of biomass.

Table 5.3- Comparison of Oil, char & gas yield for different N_2 flow rates at constant particle Size of 1.8795, heating rate of 10^0Cmin^{-1} and temperature of 600°C

N_2 Flow Rate	**Yield Wt.%**		
	Oil	**Char**	**Gas**
50	22.25	47.86	2.99
100	18.08	45.09	4.5
150	24.34	46.42	3.98

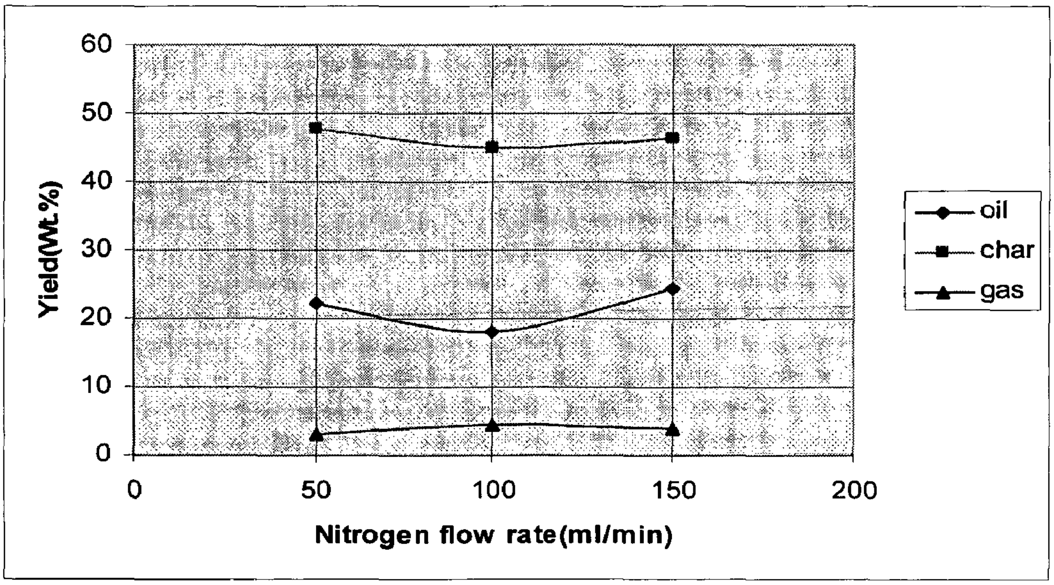


Figure 5.3 Effect of N_2 flow rate on yield of products from pyrolysis of biomass.

Table 5.4- Comparison of Oil, char & gas yield for different N_2 flow rates at constant particle Size of 2.8445 mm, heating rate of 10^0Cmin^{-1} and temperature of 500°C

N_2 Flow Rate	Yield Wt.%		
	Oil	**Char**	**Gas**
50	21.32	50.77	4.34
100	18.33	50	3.8
150	21.87	46.95	4.8

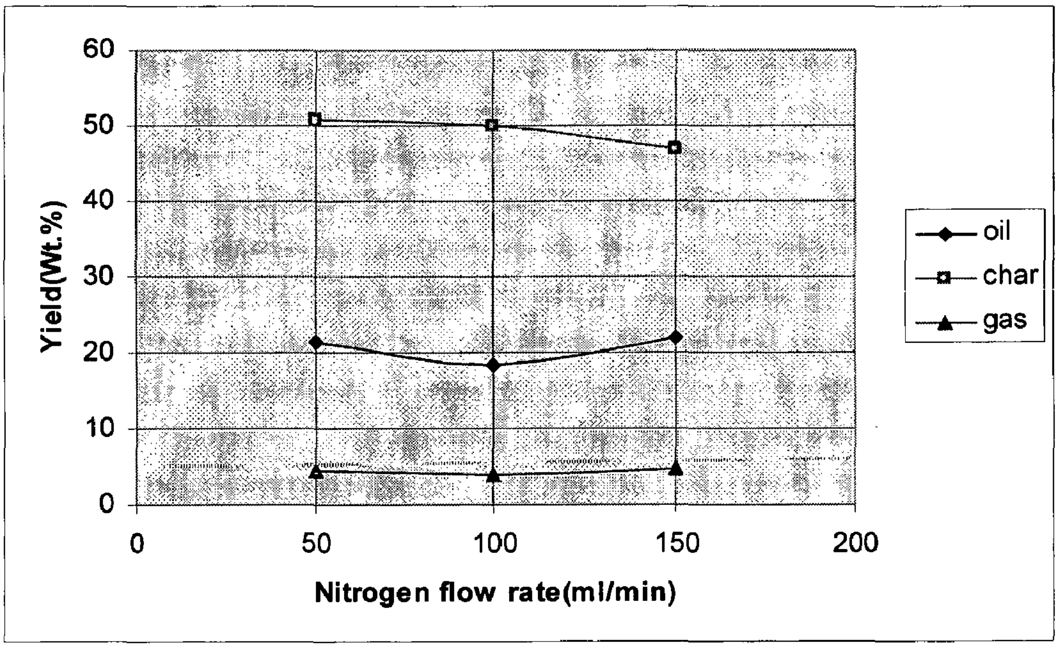


Figure 5.4 Effect of N_2 flow rate on yield of products from pyrolysis of biomass.

The third series of experiments was performed to establish the effect of N_2 flowrate on the pyrolysis product yields.

It is known that sweeping the reactor with N_2 could increase the oil yield because sweeping the environment shortens the residence time of volatiles and reduces their chances of being involved in char and radical forming secondary reactions.

From this group of experiments the pyrolysis temperature, heating rate and particle size range were 600^0C, 10^0C min^{-1} and -6+8 mesh size respectively. The product yields of pyrolysis in relation to nitrogen flowrate are given in figure 5.2. It was observed that the liquid product yield increased by only 2.3Wt. % up on increasing the nitrogen flowrate from 50 to 100 ml/min. How ever, the increase in the N_2 gas flow rate from 50 to 150 ml/min is not consistent with the situation above, because of the insufficient cooling in the system at this flow rate. The increase in the N_2 flow rate from 100 to 150 ml/min reduced the bio-oil yield from 25.39 to 23.98 Wt. %.

Indeed, the highest yield of 25.39 Wt. % was obtained at a final temperature 600^0C,with a heating rate of 10^0Cmin^{-1} and N_2 gas flow rate of 100ml/min.The char yield decreases while the gas yield increases as N_2 gas flow rate increased from 50-100 ml/min. Gas increases from 3.72 to 4.45 Wt. %.

From figure 5.3, the highest bio-oil yield (24.34 Wt. %) was obtained at temp of 600^0C, particle size of -8+12 and N_2 flow rate of 150 ml/min. From figure 5.4 it was concluded that the maximum bio-oil yield (21.87 Wt. %) was obtained at temp of 500^0C, particle size 0f -6+8 and N_2 flowrate of 150 ml/min.

5.1.3 EFFECT OF THE PARTCLESIZE

Table 5.5- Comparison of Oil, char & gas yield for different particle size at constant N_2 flow rate of 100 ml/min, heating rate of 10^0Cmin^{-1} and temperature of 600^0C

	Yield (Wt.%)		
Particle size(mm)	**Oil**	**Char**	**Gas**
2.8445	**25.39**	**43.53**	**4.87**
1.8795	**18.08**	**45.09**	**4.5**

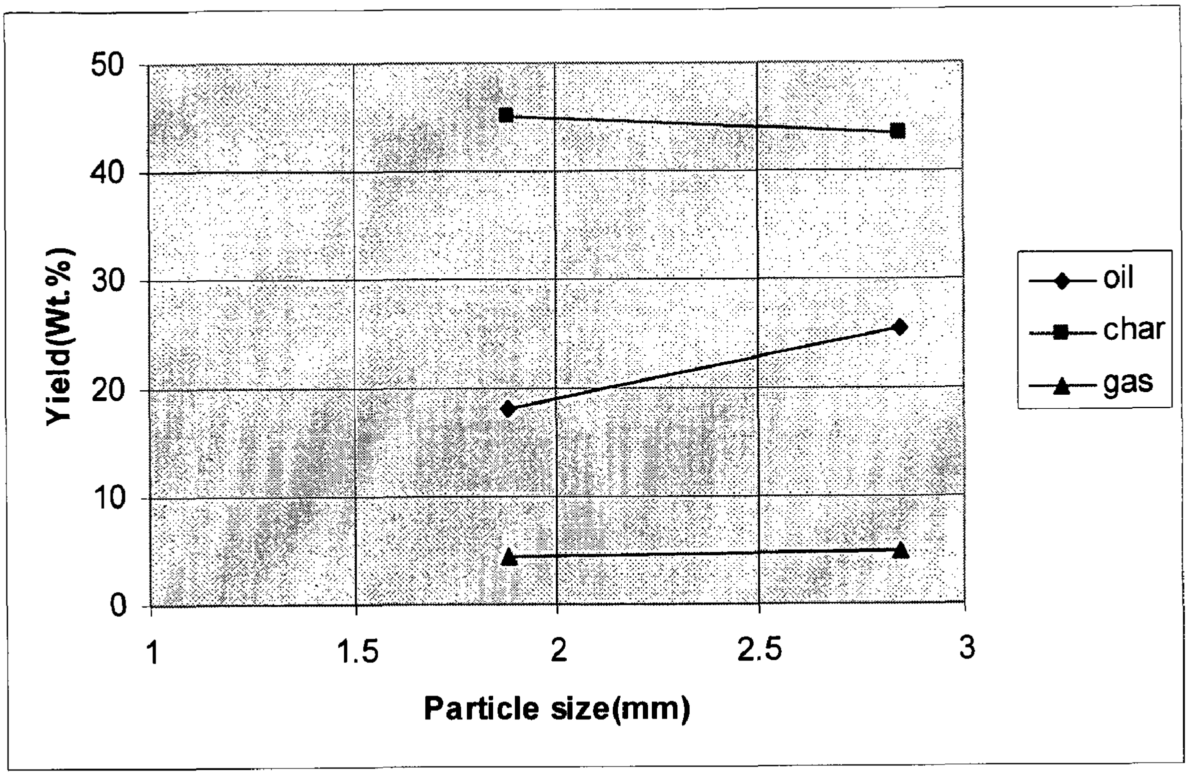


Figure 5.5 Effect of particle size on yield of products from pyrolysis of biomass.

The yield of pyrolysis oil is maximum for particle size of mesh number –6+8. The oil yield for the particle size of -6+8 mesh size (2.8445 mm) at 600 ^{0}C and 100 ml/min is 25.39 wt% and that for the particle size of -8+12 mesh size (1.8795 mm) at same temperature is 18.08 wt% .The char yield at same condition decreases from 43.53 wt% to 45.09 wt% and gas yield decreases from 4.87 to 4.5.

5.2 ANALYSIS OF BIOMASS

In this section, based on the procedure described in the previous chapter, a detailed trace metal analysis and component analysis are mentioned.

5.2.1. TRACE METAL ANALYSIS

Biomass: **Jatropha curcas seed cake**
Technique: **ICP-AES**
Model: **DRE, PS (3000) UV, LEEMAN LABS, INC USA**

Table 5.6 Trace metal analysis

Metal	Zn	Cr	Cd	Ni	Pb	Cu	Co
Amount (mg/L)	258.0	3.35	<1.00	6.90	4.80	38.35	1.30

5.2.2. COMPONENT ANALYSIS

Biomass: **Jatropha curcas seed cake**
Extractives : 1.11%
Hemicellulose : 40.0%
Cellulose : 28.89%
Lignin : 29.0%

5. 3 ANALYSIS OF BIO-OIL

In this section, based on the procedure described in the previous chapter, properties of bio-oil are mentioned.

Biomass: **Jatropha curcas seed cake**
Bio-oil: **Jatropha curcas seed cake pyrolysis oil**

Table 5.7 Experiment no1&2 **(PYR/JCS/1 & PYR/JCS/2)**

S.No	Property	Observed value	
		PYR/JCS/1	PYR/JCS/2
1	Density at(gm/cc)		
	15°C	1.0494	1.0626
	20°C	1.0463	1.0595
2	Kinematic viscosity at (cSt)		
	40°C	287.82	211.42
	100°C	13.54	10.50
3	Water Content	Insufficient sample	
4	CCR	8.06	8.79
5	Ash Content (wt %)	0.044	0.035

5.4 ANALYSIS OF GAS PRODUCT

In this section, based on the procedure described in the previous chapter, a detailed analysis of gas products are mentioned for each observation which are shown in Appendix-A

Table 5.8 Experiment No. 1&2 **(PYR/JCS/1 & PYR/JCS/2)**
Biomass: **Jatropha curcas seed cake**

Gas	Amount % wt	
	PYR/JCS/1	PYR/JCS/2
H_2	0.4	0.4
CO_2	56.5	60.9
Propane	0.3	0.3
Propylene	0.4	0.5
(Iso and n)Butane	0.3	0.3
Butenes	0.3	0.4
C_5	1.2	1.8
Ethane	0.7	0.7
N_2	11.2	12.1
CH_4	28.7	22.6

Table 5.9 Experiment No.3&4 **(PYR/JCS/3 & PYR/JCS/4)**
Biomass: **Jatropha curcas seed cake**

Gas	Amount % wt	
	PYR/JCS/3	PYR/JCS/4
H_2	0.9	2.2
CO_2	45.0	47.8
Propane	0.7	0.6
Propylene	0.6	0.8
(Iso and n)Butane	0.3	0.4
Butenes	0.6	0.7
C_5	0.1	0.1
Ethylene	0.1	0.1
Ethane	1.6	8.0
N_2	19.5	10.2
CH_4	23.3	25.5
Unidentified	7.3	3.6

Table 5.10 Experiment No. 5 **(PYR/JCS/5)**
Biomass: **Jatropha curcas seed cake**

Gas	Amount % wt
	PYR/JCS/5
H_2	2.3
CO_2	48.3
Propane	0.9
Propylene	0.9
(Iso and n)Butane	0.4
Butenes	1.0
C_5	0.1
Ethylene	0.1
Ethane	1.7
N_2	7.4
CH_4	21.2
Unidentified	15.7

Table 5.11Experiment No. 6&7 **(PYR/JCS/6 & PYR/JCS/7)**
Biomass: **Jatropha curcas seed cake**

Gas	Amount % wt	
	PYR/JCS/6	PYR/JCS/7
H_2	2.7	2.0
CO_2	56.4	55.9
Propane	0.7	0.9
Propylene	0.8	1.0
(Iso and n)Butane	0.2	0.4
Butenes	1.0	0.6
C_5	0.2	0.1
Ethane +Ethylene	1.8	0.5
N_2	11.3	11.5
CH_4	19.9	24.1
Unidentified	5.0	3.0

5.5 COMBINED ANALYSIS

In this section describes elemental analysis of biomass, bio-oil and char according to procedure described in the previous chapter.

Table 5.12 Elemental analysis of biomass, bio-oil and char

Elemental analysis	Biomass (Expelled)	Biomass (Extracted)	Bio-oil (-6+8 mesh)	Bio-oil (-8+12 mesh)	Char (expelled)	Char (Extracted)
C	48.6	44.3	67.3	65.4	63.1	69.5
H	6.7	6.3	7.8	8.1	3.6	2.6
N	2.7	-	-	-	-	-
O	42	49.4	24.9	26.5	33.3	27.9
H/C atomic ratio	1.654	1.706	1.39	1.49	0.683	0.449
Empirical formula	$CH_{1.654}N_{0.05}O_{0.65}$	$CH_{1.706}O_{0.836}$	$CH_{1.39}O_{0.28}$	$CH_{1.49}O_{0.304}$	$CH_{0.683}O_{0.394}$	$CH_{0.449}O_{0.301}$

Results of biomass-Jatropha curcas seed cake (extracted) pyrolysis.

Mesh size:-6+8 & Temp: 600°C			
N_2 flow rate ml/min	**Oil (g)**	**Char (g)**	**Gas (g)**
50	42.39	81.18	6.83
100	50.64	86.81	9.72
150	43.45	80.12	8.07
Mesh size:-6+8 & Temp:500°C			
50	39.84	94.88	8.11
100	34.56	94.40	7.30
150	40.57	87.09	8.90
Mesh size:-8+12 & Temp:600°C			
50	41.70	89.70	5.61
100	33.66	83.94	8.42
150	47.26	90.12	5.61

Table-5.13 Physico-chemical properties of Jatropha curcas seed cake pyrolysis bio-oil

S.No	Property	Observed value
		PYR/JCS/09
1	Density at 15°C (Kg/m^3)	1119.3
2	Kinematic viscosity at (cSt)	
	50°C	1074.26
	70°C	204.46
3	Pour point(°C)	+21
4	CCR (wt %)	12.12
5	Ash Content (wt %)	0.10
6	Flash point(°C)	48
7	Calorific value (MJ/Kg)	37.3
8	Molecular weight	447

The characteristics of the bio-oil sample were determined and results are given in table 5.12 and 5.13.The carbon, hydrogen, nitrogen and oxygen content were determined. Bio-oils does not contain sulfur content, therefore there SO_x emissions expected are very low from the bio- oil.

Bio-oils does not contain nitrogen content, therefore bio-oil fuels generate more than 50% lower NO_x emissions than the diesel oil in gas turbines.

As can be seen in Table 5.13, bio-oil was more viscous than No. 2 diesel fuels. Viscosity of the bio-oils was related to fatty acid chain length and number of unsaturated bonds. The bio-oil contained a heavy fraction as reflected by its high density.

The high flash point suggested that the bio-oil can be safely stored at room temperature.

The calorific value of bio-oil was 37.3 MJ/kg. Calorific value indicates that the energy content of the bio-oil was very close to those of petroleum fractions.

The average chemical composition of bio-oils analyzed was $CH_{1.39}O_{0.28}$ and $CH_{1.49}O_{0.304}$.

The bio-oil was characterized by lower oxygen content than that of the original feedstock. The decrease in the oxygen content of the bio-oil (42%) compared to the original feedstock (24.9%) is important because the high oxygen content is not attractive for the production of transport fuels. However, the high oxygen content of the bio-oil suggests that it may be an appropriate feedstock for catalytic steam reforming to H_2 and CO_2 using a conversion strategy similar to that of catalytic steam reforming of alcohols and oxygenated aromatics.

The presence of ash in the bio oil can cause erosion, corrosion problems. Ash content is problematic for gas turbine applications and the limit is 0.1 wt%. The ash content from the bio oil is 0.10 wt% which is very low and it meets the specifications of gas turbine fuels.

As can be seen from the table 5.12 biochar is a carbon-rich fuel and having $CH_{0.683}O_{0.394}$ empirical formula. H/C and O/C atomic ratios are 0.683and0.394 respectively. Biochar contains 15.30% ash. It has very small ratios of sulphur and nitrogen.

5.6 FTIR RESULTS

According to previous chapter procedure, Fourier transform infrared spectroscopic analysis of bio-oil, n-pentane soluble fraction and n-pentane insoluble fraction are mentioned.

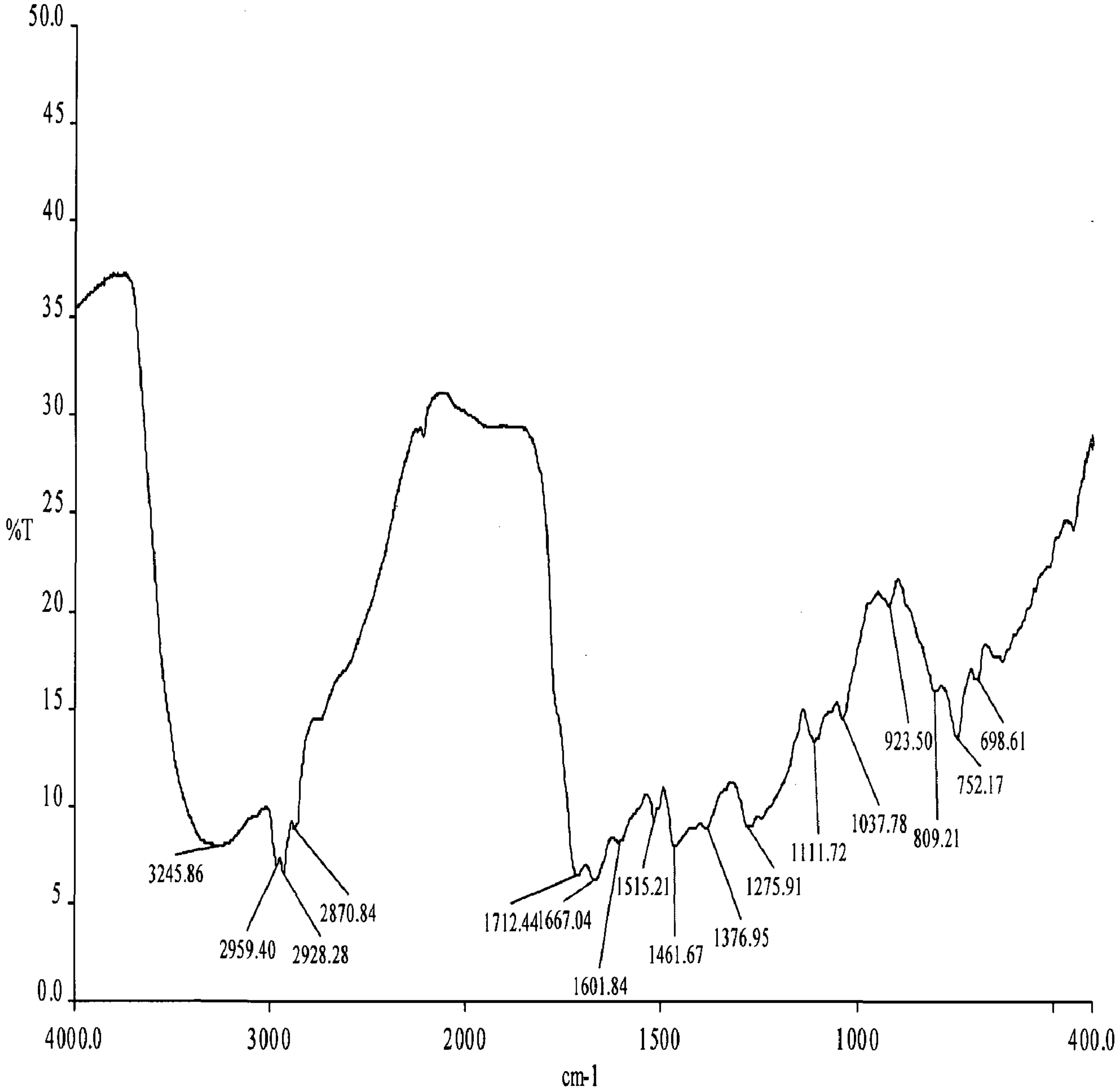


Figure 5.6 FT-IR spectra of bio-oil (Temp: 600^0C, N_2 flow rate: 100ml/min, particle Size: -8+12)

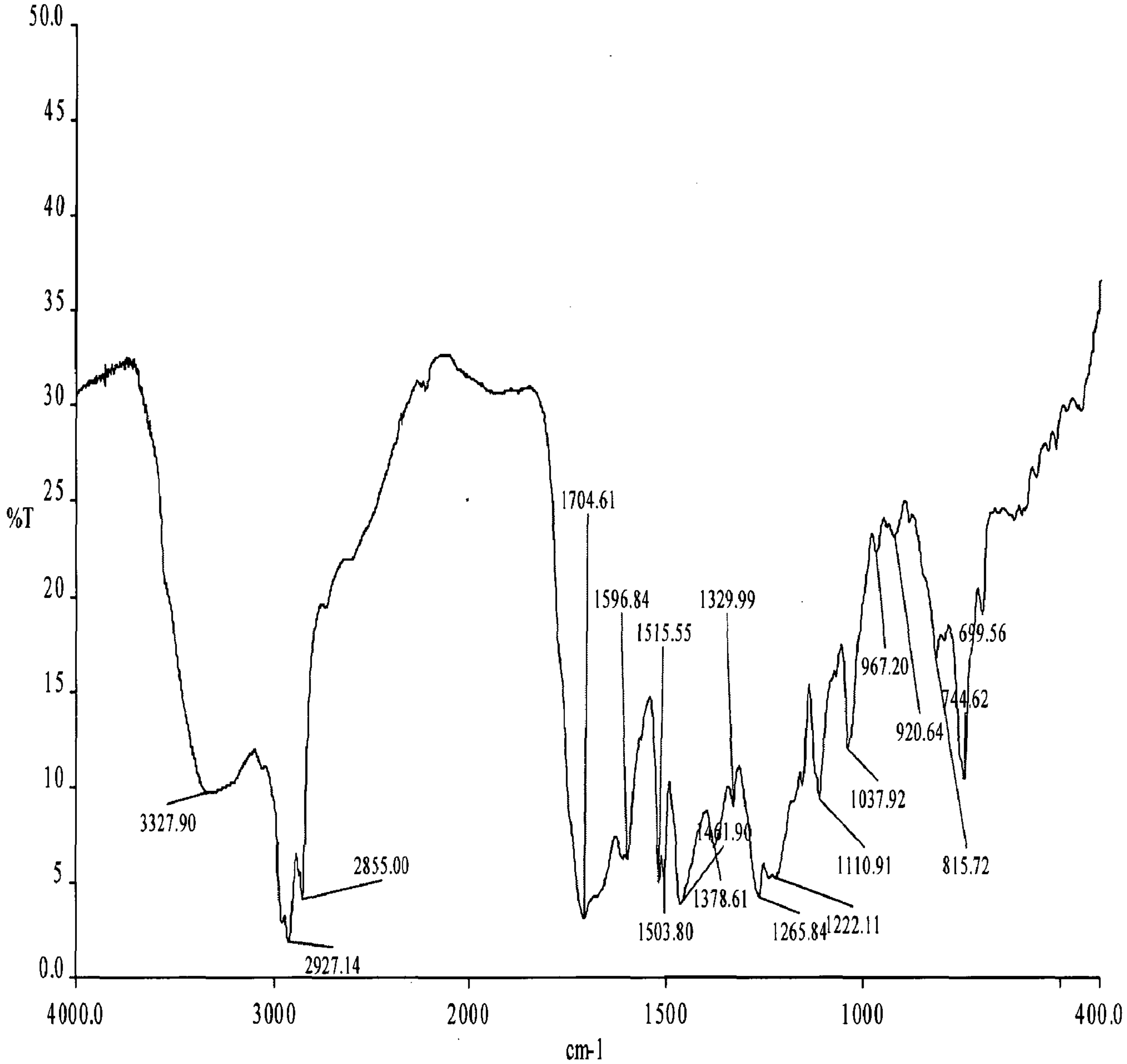


Figure 5.7 FT-IR spectra of n-pentane soluble fraction of bio-oil (Temp: 600^0C, N_2 flow rate: 100ml/min, particle size: -8+12)

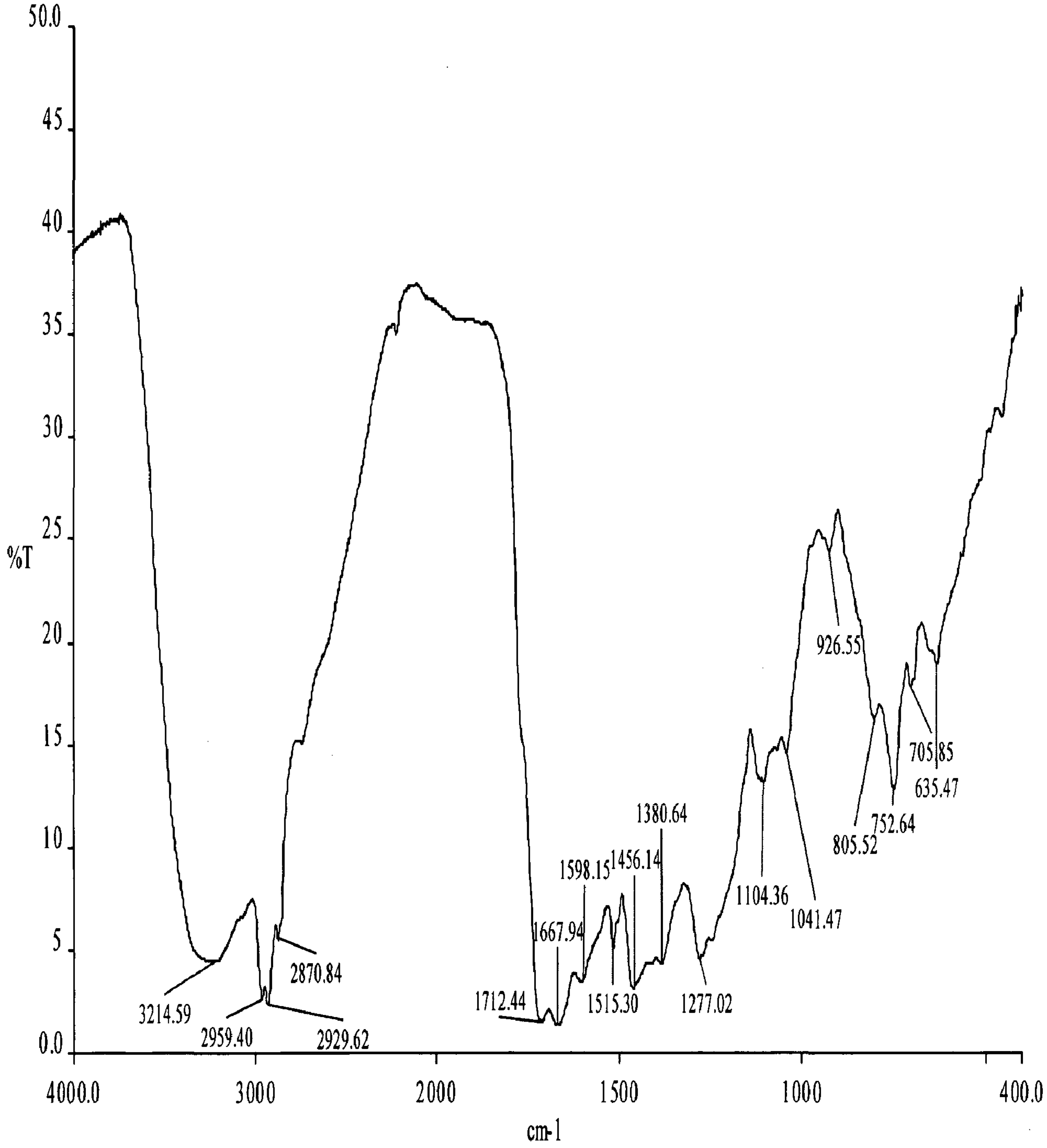


Figure 5.8 FT-IR spectra of n-pentane insoluble fraction of bio-oil (Temp: 600^{0}C, N_2 flow rate: 100ml/min, particle size: -8+12)

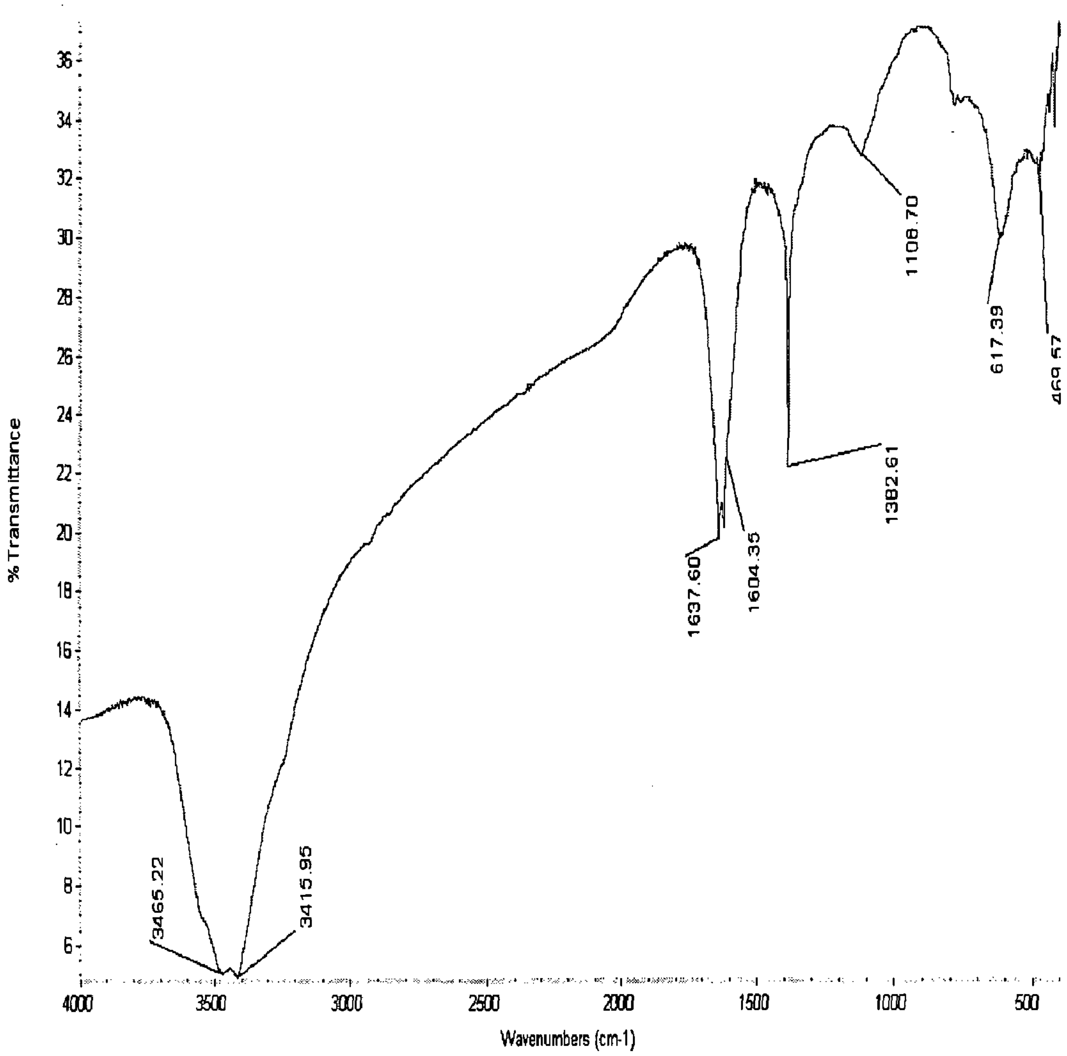

% Transmittance
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
3465.22
3415.95
1637.60
1604.35
1382.61
1108.70
617.39
469.57
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

Table: 5.14 Functional groups of Bio-oil

Functional group	**Frequency Range, (cm^{-1})**		
	Oil-1	**Oil-2**	**Oil-3**
O-H stretching	3550-3200 (3245.86)	3327.9	3214.59
C-H stretching	2960-2850 (2966.78,2928.28)	2959.40, 2927.14 2855.00	2960.39, 2929.62 2872.54
C=O stretching	1710-1700 (1708.75)	1704.61	1712.44
C=C stretching	1670-1640 (1667.04)	absent	1667.94
Aromatic-C=C stretching	1600,1580,1500, 1450 (1601.84,1515.21,1461.67)	1596.84, 1515.55 1503.80, 1461.90	1605.52, 1515.3 1456.14
C-H deformation or bending	1485-1340 (1376.95)	1378.61, 1329.99	1376.95
C-C stretching	1300-800 (1275.91)	1265.84, 1222.11	1277.02
Aromatic C-H deformation	900-700 (923.50, 805.52, 752.17, 698.61)	967.20,920.64,815.72 815.72,744.62,699.56	926.55, 805.69 752.64, 705.85, 635.47
Alcoholic C-O stretching	1250-1000 (1111.72,1038.78)	1110.91, 1037.92	1104.36, 1042.15

Oil-1 =Bio-oil **Oil-2=N-pentane soluble fraction of bio-oil**

Oil-3=N-pentane insoluble fraction of bio-oil

Table: 5.15 Functional groups of Bio-oil (PYR/JCS/05)

Functional group	**Frequency range(cm^{-1})**
O-H stretching	3550-3200 (3465.22,3415.95)
C=O stretching	1650-1580 (1637.60,1604.35)
C-H deformation	1485-1340 (1382.61)
Alcoholic C-O stretching	1200-1000 (1108.70)

FTIR

FTIR spectra of the oils are given figure 5.6 to 5.9

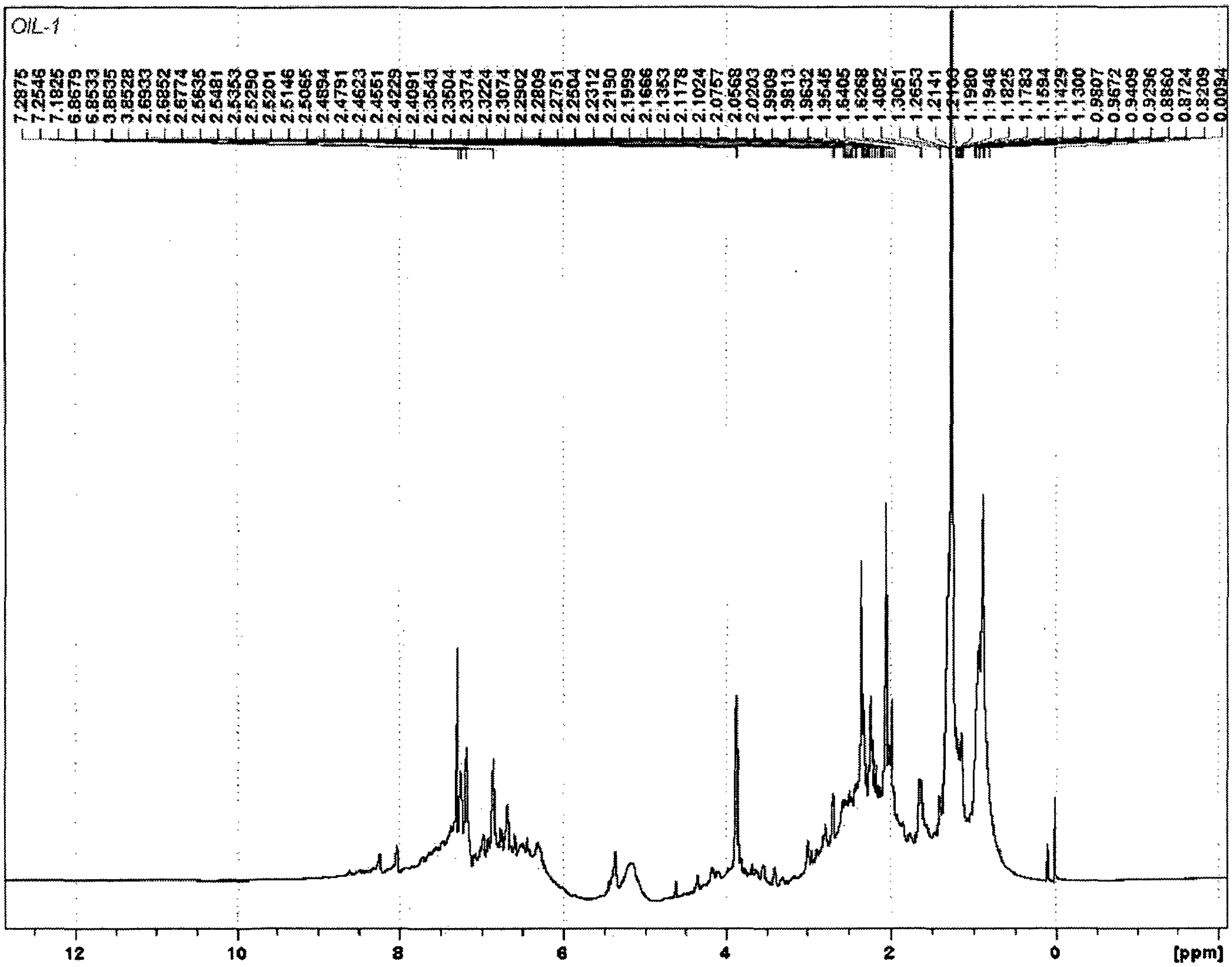
- The O-H stretching vibrations between 3550 and 3200 cm^{-1} indicate the presence of phenols and alcohols.
- The C-H stretching vibrations between 2960 and 2850 cm^{-1} and C-H deformation vibrations between 1485 and 1340 cm^{-1} indicate the presence of alkanes.
- The C=O stretching vibration with absorbance between 1710 and 1700 cm^{-1} indicate the presence of ketones, aldehydes and quinone.
- The absorbance peaks between 1670 and 1640 cm^{-1} represent C=C stretching vibrations indicative of alkenes.
- The absorbance peaks at 1600, 1580, 1500 and 1450 cm^{-1} represent C-C stretching vibrations indicative of aromatics.
- The C-C stretching vibrations between 1300 and 800 cm^{-1} indicate the alkanes.
- The C-H deformation vibrations between 900 and 700 cm^{-1} indicate the aromatics.
- The C-O stretching vibrations between 1250 and 1000 cm^{-1} indicate the alcohol and ester.

Mainly the values 1111.72, 1037.78, 1110.91 and 1042.15 cm^{-1} indicate the alcohol groups.

- From table-5.14, the absorbance peak of 1667.04 and 1667.94 cm^{-1} for bio-oil and n-pentane insoluble fractions represent the C=C stretching vibrations indicative of alkenes. These vibrations are present in bio-oil and n-pentane insoluble fractions, but not in n-pentane soluble fractions.

5.7 H-NMR Results

In this section; based on previous chapter procedure H-NMR (Proton Nuclear magnetic resonance) of bio-oil was done. The H-NMR results are explained in this section.



Chemical shift

Figure 5.9 H-NMR spectra of bio-oil (Temp: 600^0C, N_2 flow rate: 50ml/min, particle size:- 6+8)

Table: 5.16 H-NMR results of bio-oil from pyrolysis of biomass at temp 600^{0}C

Type of hydrogen	Chemical Shift (ppm)
Aromatic	7.0-8.5
Phenolic(OH) or olefinic proton	4.5-6.9
Ring join methylene (Ar-CH_2-Ar)	3.0-4.0
CH_3,CH_2 and CH_α to an aromatic ring	2.0-2.5
CH_2 and CH_β to an aromatic ring (naphathenic)	1.5-2.0
β-CH_3,CH_2 and CH_γ or further from an aromatic ring	1.0-1.4
$CH_{3\gamma}$ or further from an aromatic ring and paraffinic CH_3	0.5-0.98

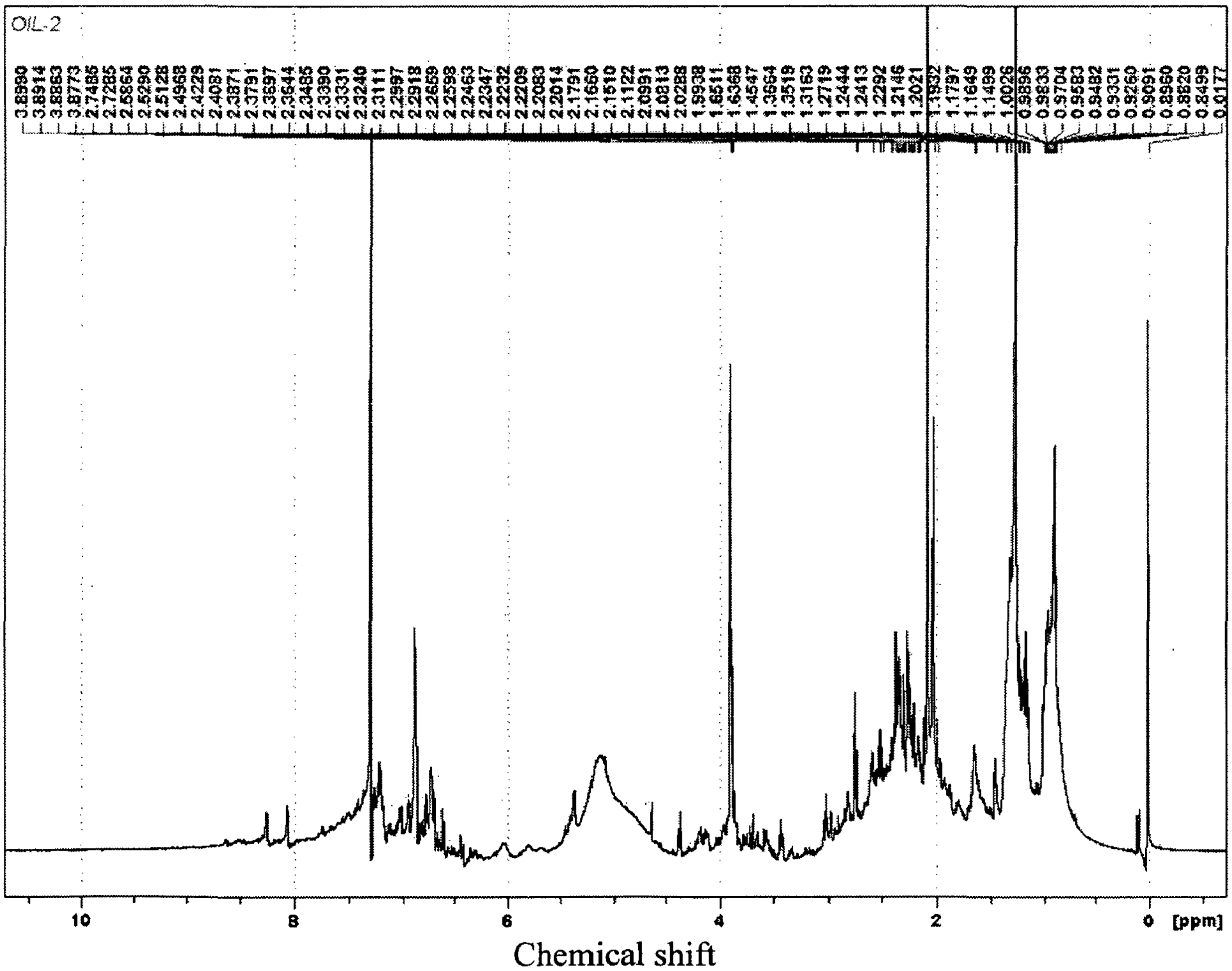


Figure 5.10 H-NMR spectra of bio oil (Temp: 600^{0}C, N_2 flow rate: 100ml/min, particle Size:-8+12)

Table: 5.17 H-NMR results of bio-oil from pyrolysis of biomass at temp 600^0C

Type of Hydrogen	Chemical Shift (ppm)
Aromatic	7.0-8.5
Phenolic(OH) or olefinic proton	4.5-6.9
Ring join methylene(Ar-CH_2-Ar)	3.5-4.0
CH_3,CH_2 and CH_α to an aromatic ring	2.2-2.7
CH_2 and CH_β to an aromatic ring (naphathenic)	1.5-2.2
β-CH_3,CH_2 and CH_γ or further from an aromatic ring	1.0-1.4
$CH_{3\gamma}$ or further from an aromatic ring and paraffinic CH_3	0.5-1.0

H-NMR

Above Figure represents the H-NMR spectrum of Jatropha curcas seed cake pyrolysis bio-oil product .The hydrogen distribution of H-NMR is listed in table 5.16 and 5.17

Resonances between 7 and 8.5 ppm were assigned to aromatic structures. Resonances between 4.5 and 6.9 ppm (i.e., exactly 6.853) have been attributed to conjugated olefins, Aromatic ring joining methylene protons ,so called H_F , were observed in bio-oil and their characteristic peaks are in the range of 3.0-4.0 ppm. The protons in the α position to an aromatic ring were indicated as the majority in the Bio-oil of Jatropha curcas seed cake. The naphthenic protons (β to CH and CH_2), and β-CH_3, CH_2, CH_γ (1.25ppm) protons were indicated as the majority in the bio-oil but in different amounts. $CH_{3\gamma}$, i.e., CH_3 at γ position (or) further from an aromatic ring and paraffinic CH_3 protons are observed in the Bio-oil.

5. 8 GC-MS Results

Gas chromatography/Mass spectroscopy of N-pentane soluble fraction was done according to previous chapter procedure. This section explains the GC/MS of N-pentane soluble fraction. Mass spectroscopy of each peak is shown in Appendix-C.

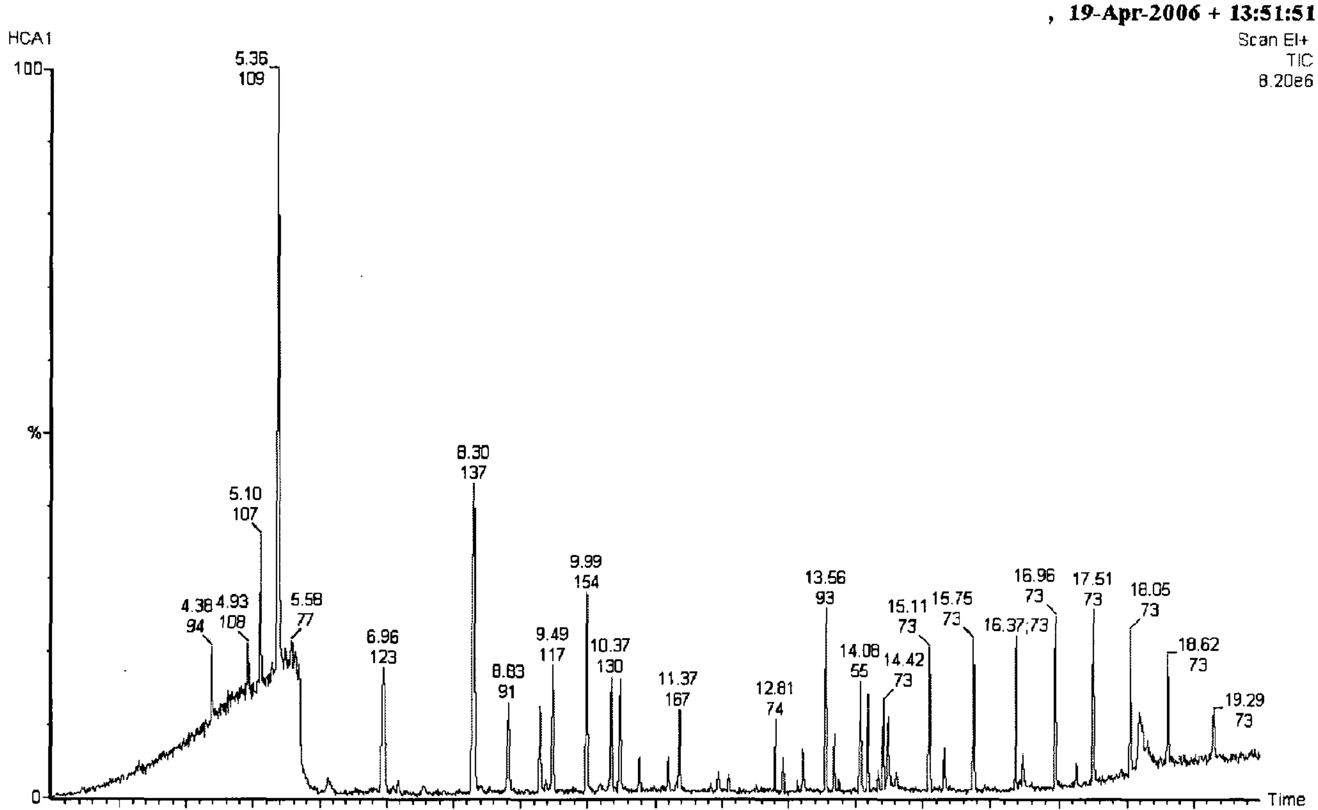


Figure 5.11 GC/MS of N-pentane soluble fraction of bio-oil (Temp: 600^0C, N_2 flow rate: 100ml/min, particle size: -8+12)

From above graph and MS graphs of each peak gives the its retention time and mass to charge ratio. The m/z (ratio of mass to charge) values, which represent the most probable fragments of the compounds explained, have been presented for each compound. From that we found some compounds present in n-pentane soluble fractions. Compounds which are present in bio-oil, its molecular weight and formula are given in table 5.18

Table: 5.18 Relative content of main compounds in organic composition of bio-oil produced from pyrolysis of biomass

Compound name	Molecular Weight	Formula
Phenol	94	C_6H_6O
Benzene, Ethoxy	122	$C_8H_{10}O$
Phenol, 2-methyl-	108	C_7H_8O
Phenol, 4-methyl	108	C_7H_8O
2 acetyl-5-methyl Furan	124	$C_7H_8O_2$
Phenol, 2-methoxy-4methyl	138	$C_8H_{10}O_2$
2 methoxy-5-methyl phenol	138	$C_8H_{10}O_2$
Phenol, 4-ethyl-2 methoxy-	152	$C_9H_{12}O_2$
Benzaldeyde, 4-(Phenyl methoxy)	212	$C_{14}H_{12}O_2$
Phenol, 2,6-Dimethoxy	154	$C_8H_{10}O_3$
Benzene,1,2,3-trimethoxy-5-methyl	182	$C_{10}H_{14}O_3$
Cyclohexanethanol	128	$C_8H_{16}O$
Phenol,2-methoxy-4-propyl	166	$C_{10}H_{14}O_2$
Phenol,2-methoxy-4(1-propyl)	164	$C_{10}H_{12}O_2$

CONCLUSIONS

- In this study, pyrolysis of ***JATROPHA CURCAS SEED CAKE*** was performed on a fixed bed tubular reactor in an inert atmosphere of nitrogen. The maximum bio-oil yield obtained is 25.39 wt%, at the final temperature of 600 ^{0}C, N_2 flow rate of 100 cm^3/min and particle size of mesh number-6+8 (2.8445 mm). It was observed that the liquid product yield increased by only 2.3Wt. % up on increasing the nitrogen flowrate from 50 to 100 ml/min.
- The bio-oil obtained is highly viscous at room temperature and its density is also higher than other bio-oils and other fuels like gasoline, diesel etc.
- The bio-oil obtained was a mixture aliphatic and aromatic hydrocarbons having an empirical formula of $CH_{1.39}O_{0.28}$, H/C atomic ratio 1.39and O/C atomic ratio 0.28 at optimum conditions.
- Comparison of the H/C ratios with those of conventional fuels indicates that the bio-oils obtained in this work lay between light and heavy petroleum products.
- The energy content of pyrolysis oil is 37. 3 MJ/kg which is slightly lower than that of gasoline (47 MJ/kg), diesel (43 MJ/kg) or petroleum (42 MJ/kg) but approximately equal to coal (32-37 MJ/kg).
- The low sulfur content of bio-oil is quite promising for its evaluation as fuel from the viewpoint of environmental pollution. The ash content of the bio-oil is also very low.
- Chemical fractionation showed that the bio-oil is composed almost entirely of oxygenated components with only low quantities of hydrocarbons present.
- Also, FTIR analysis showed that the bio-oil composition was dominated by oxygenated species.
- The high oxygen content is reflected by the presence of mostly oxygenated fractions such as carboxyl and carbonyl groups produced by pyrolysis of the cellulose and phenolic and methoxy groups produced by pyrolysis of the lignin.
- The pyrolytic oil may be used as a raw material in fractionating processes for obtaining fuels. By its distillation, gasoline, diesel oil or alternative fractional

products to fuel oils are obtained. These fractions may be either used directly or by mixing with other conventional fuels.

- The liquid product may be used as a source of chemical feedstock or it may be upgraded to higher quality liquid fuels.
- Biochar is a carbon-rich fuel and having $CH_{0.683}O_{0.394}$ empirical formula. H/C and O/C atomic ratios are 0.683and0.394 respectively. Biochar contains 15.30% ash. It has very small ratios of sulphur and nitrogen.
- The gases and tar product from pyrolysis may be used as fuel for heating the pyrolysis reactor and thus leading to environmental pollution free process.

RECOMMENDATIONS FOR FUTURE WORK

For the evaluation of the employment of pyrolytic oil as a fuel, the following options are recommended:

- The liquid product may be used a source of low-grade fuel directly or may be upgraded to higher-quality liquid fuels.
- Oil seems to be more appropriate for the production of hydrocarbons and chemicals.
- The findings of laboratory-scale studies are encouraging and warrant larger-scale applications of biomass pyrolysis for synthetic fuels.

APPENDIX A

OBSERVATIONS

Pretreatment of biomass:

Constant weight determination of Jatropha Curcas seed cake

Serial No.	Time of heating (Hr)	Biomass size			
		-6+8	-8+12	-12+16	-16
1	3	459.71	680.42	405.56	663.03
2	2	449.68	675.16	398.15	649.95
3	2	447.14	673.63	394.74	645.78
4	2	444.14	673.61	392.8	643.83
5	2	444.05	673.62	390.28	642.15
6	2	443.72	673.63	389.76	641.85
7	2	443.64	673.62	388.99	641.34
8	2	435.54		388.83	641.25
9	2	434.80		387.62	639.73
10	2	434.68		387.16	639.34
11	2	434.66		387.07	639.21
12	2	434.67		387.05	639.20
13	2			387.06	639.20

Results:
Constant weight for the mesh size –6+8 was at 434.67gm.
Constant weight for the mesh size –8+12 was at 673.62gm.
Constant weight for the mesh size –12+16 was at 387.06gm.
Constant weight for the mesh size –16 was at 639.20gm

Moisture content of Jatropha curcas seed cake

Mesh size	Particle size (mm)	% moisture
-6+8	2.8445	5.5%
-8+12	1.8795	.99%
-12+16	1.194	4.5%
-16	0.991	3.6%

Experimental run no: **PYR/JCS/1**
Weight of biomass: **260.31gm** Temp: **400°C (max 415°C)**
Mesh size: **-6 +8** N_2 flow rate: **100 ml/min**

Time (min)	D1	T1 °C	D2	T2 °C	D3	T3 °C	T4 °C	T5 °C	Gas flow	Rota meter	Remarks	Bath °C
1:50	-		-		-	-	-	-	-	-	Pre heater started	15
2:15	-		-		-	-	-	-	-	-		15
2:30	0	28	0	30	210	262	28	25	-	10	D1 D2 started	15
2:45	120	28	120	32	140	292	28	25	3400.6	10		15
3:00	140	234	140	278	140	279	-	43	4000.2	10		15
3:10	200	395	200	440	160	255	-	93	4000.2	10		15
3:15	200	421	200	465	160	265	-	141	4000.3	10-15	Light color liquid +gas started, gas collection started	15
3:17		-		-	160		-		4000.8	10-15	Colored liquid started coming	15
3:20	200	442	200	483	160	298	-	237	4001.8	10-15		15
3:25	220	458	220	501	160	301	-	321	4002.5	10-12		15
3:30	140	456	140	493	160	305	-	411	4003.2	10	Gas collection stopped	15
3:45	0	395	0	438	0	272		415	4003.3	9-10	Reaction stopped	15

Amount of biomass fed: 260.31g
Amount of oil collected: 47.87g
Amount of gas collected: 9.03g

Amount of liquid collected: 101.7g
Amount of water collected: 52.10g
Amount of char collected: 110.73g

Experimental run no: **PYR/JCS/2**
Weight of biomass: **260.31g**
Mesh size: **-6 +8**

Temp: **450°C**
N_2 flow rate: **100 ml/min**

Time (min)	D1	T1 °C	D2	T2 °C	D3	T3 °C	T4 °C	T5 °C	Gas flow	Rota meter	Remarks	Bath °C
2:00					180	23	20	22	3000.5	9		5.2
2:10	0	21	0	25	160	209	20	22	3001.2	9-10		5.2
2:15	0	25	0	27	160	236	20	22	3001.9	9.5		5.2
2:17	140	27	140	27	160	258	20	23	3002.2	9.5		5.2
2:20	140	45	140	132	160	281	20	23	3002.6	----		5.2
2:25	140	73	140	183	160	292	20	25	3003.0	----		5.2
2:26	240	125	160	257	160	299	22	32	3003.4	----		5.2
2:30	240	231	160	340	100	295	40	68	3004.3	----		5.2
2:35	240	354	160	412	100	288	120	139	3009.0	----		5.2
2:40	240	427	160	439	100	291	180	233	3018.0	10-12		5.2
2:45	0	457	0	439	140	309	360	437	3030.8	10-12		5.2
2:50	0	426	0	384	140	311	410	445	3033.5			5.2

Amount of biomass fed: 260.31g
Amount of oil collected: 53.04g
Amount of gas collected: 10.33g

Amount of liquid collected: 104.43g
Amount of water collected: 49.22g
Amount of char collected: 105.97g

Experimental run no: **PYR/JCS/3**
Weight of biomass: **220.24g**
Mesh size: **-6 +8**

Temp: **600°C**
N_2 flow rate: **100 ml/min**

Time (min)	D1	T1 °C	D2	T2 °C	D3	T3 °C	T4 °C	T5 °C	Gas flow	Rota meter	Remarks	Bath °C
11:40	200	50	200	62	220	538	55	62	0000	10	Preheater on at 11:25	0.9
11:50	200	421	200	484	220	550	110	141	3.7	10	Light liquid started	0.9
11:55	220	459	220	525	220	548	180	286	11.4	10	Colored liquid started	0.9
12:00	260	494	240	549	220	552	360	478	21.8	10		0.9
12:05	260	526	260	573	220	550	460	534	26.7	9-10		0.9
12:10	260	527	260	573	220	548	480	545	28.5	-----	Pyrolysis stopped	0.9
12:15	260	528	260	573	220	550	480	545	30.2	-----	D1,D2&D3 off	0.9

Amount of biomass fed: 220.24g
Amount of oil collected: 50.64g
Amount of gas collected: 9.72g

Amount of liquid collected: 102.89g
Amount of water collected: 52.03g
Amount of char collected: 86.81g

Experimental run no: **PYR/JCS/4**

Weight of biomass: **220.24g** Temp: **600°C**

Mesh size: **-6 +8** N_2 flow rate: **150 ml/min**

Time (min)	D1	T1 °C	D2	T2 °C	D3	T3 °C	T4 °C	T5 °C	Gas flow	Rota meter	Remarks	Bath °C
14:10	0	12	0	15	200	20	22	14	00	12	Preheater started	14.8
14:15	0	13	0	15	200	456	22	15	00	13		14.5
14:20	0	14	0	17	200	525	22	16	00	13		12.3
14:25	0	15	0	18	160	530	22	17	0.9	12		12.3
14:30	0	17	0	20	160	543	22	18	1.75	----		9.4
14:35	0	17	0	22	160	549	22	19	2.5	----		7.1
14:40	0	19	0	23	160	552	22	20	3.3	----		4.6
14:45	200	22	200	38	160	548	22	21	4.2	----	D1,D2 Started	2.2
14:50	260	129	260	348	160	545	22	30	5.05	----		0.6
14:55	260	412	260	526	160	546	22	164	9.4	----	Gas started at T5=100°C	-0.8
15:00	260	545	260	556	160	552	220	464	26.0	----	Water started T5=120	-1.3
15:05	0	612	0	587	160	555	470	581	35.0	----		-1.5
15:10	260	622	260	555	160	551	560	551	39.2	12-13		-1.9
15:15	0	648	0	553	0	456	590	600	41.3	12-13	Pyrolysis stopped	-2.0
15:20	0	615	0	505	0	365	580	560	42.2	12-13		-2.2

Amount of biomass fed: 220.24g **Amount of liquid collected: 92.97g**

Amount of oil collected: 43.45g **Amount of water collected: 49.52g**

Amount of gas collected: 8.07g **Amount of char collected: 80.12g**

Experimental run no: **PYR/JCS/5**
Weight of biomass: **220.24g**
Mesh size: **-6 +8**

Temp: **600°C**
N_2 flow rate: **50 ml/min**

Time (min)	D1	T1 °C	D2	T2 °C	D3	T3 °C	T4 °C	T5 °C	Gas flow	Rota meter	Remarks	Bath °C
10:25	0	20	0	21	80	20	20	20		6-7	Preheater started	-0.8
10:30	0	21	0	23	80	122	20	21				-1.3
10:35	0	22	0	24	80	196	20	21	0.06			-1.7
10:40	0	24	0	25	80	258	20	22	0.340			-1.9
10:45	0	25	0	7	140	363	20	22	0.530			-1.9
10:50	200	28	200	42	200	572	22	22	0.920		Heating started	-1.9
10:55	200	200	200	335	200	567	30	32	1.340			-1.9
11:00	260	420	260	526	200	547	80	137	2.5		Liquid started	-2.0
11:05	260	552	260	576	200	540	200	458	16.6			-2.0
11:10	260	593	260	578	200	553	480	583	27.3			-1.7
11:15	100	622	100	599	200	548	540	608	30.45		T5 max:612	-1.5
11:20	0	607	0	567	200	551	560	602	31.25			-1.5
11:25	100	584	100	555	200	595	540	577	32.31			-1.6
11:30	100	592	100	570	200	598	540	587	32.78			-1.6
11:35	100	607	100	587	200	548	540	603	33.15		Stopped after this	-1.6

Amount of biomass fed: 220.24g
Amount of oil collected: 42.39g
Amount of gas collected: 6.83g

Amount of liquid collected: 95.61g
Amount of water collected: 52.18g
Amount of char collected: 81.18g

Experimental run no: **PYR/JCS/6**
Weight of biomass: **220.24g** Temp: **600°C**
Mesh size: **-8 +12** N_2 flow rate: **150 ml/min**

Table: Observations

Time (min)	D1	T1 °C	D2	T2 °C	D3	T3 °C	T4 °C	T5 °C	Gas flow	Rota meter	Remarks	Bath °C
10:25	0	16	0	15	140	23	15	23		13	Preheater started	-0.4
10:30	0	21	0	27	140	382	25	23		13		-1.9
10:35	0	22	0	29	140	447	25	23		13		-1.9
10:40	180	25	180	30	200	527	25	24	2000	13	Heating started	-1.8
10:45	240	85	240	138	200	546	30	31	2000	13		-1.7
10:50	260	255	260	285	160	117	40	160	2001	13	Liquid started	-1.7
10:55	260	548	260	559	200	551	200	587	2010	13		-1.4
11:00	120	556	140	571	200	552	260	616	2024	----		-1.2
11:05	100	519	100	527	200	347	499	588	2028	----		-1.1
11:10	220	529	220	555	200	545	499	596	2029	----		-1.0
11:15	100	548	100	576	200	551	499	620	2030	----		-1.0
11:20	240	502	240	528	200	546	499	582	2031	13		-1.0
11:25	240	550	240	588	200	546	499	620	2032	13	Reaction stopped	-1.0

Amount of biomass fed: 220.24g
Amount of oil collected: 47.26g
Amount of gas collected: 7.73g

Amount of liquid collected: 96.29g
Amount of water collected: 49.03
Amount of char collected: 90.12g

Experimental run no: **PYR/JCS/7**
Weight of biomass: **220.24g** Temp: **600°C**
Mesh size: **-8 +12** N_2 flow rate: **100 ml/min**

Time (min)	D1	T1 °C	D2	T2 °C	D3	T3 °C	T4 °C	T5 °C	Gas flow	Rota meter	Remarks	Bath °C
14:10	0	29	0	30	160	29	30	28	1000	9	Preheater started	-0.2
14:15	0	29	0	31	160	373	30	28	1000	9		-0.8
14:20	0	28	0	33	160	480	30	30	1000	9-10		-1.0
14:25	0	29	0	34	160	502	30	31	1000	9-10		-1.1
14:30	0	29	0	35	160	501	30	31	1000	9-10		-1.2
14:35	0	29	0	35	220	512	30	31	1000	9-10	D1, D2started	-1.2
14:40	180	30	180	35	220	552	30	31	1003	----		-1.2
14:45	200	201	240	94	220	556	35	36	1003	----		-1.1
14:50	260	429	260	325	220	546	40	150	1004	----	Gas started	-1.0
14:55	260	544	260	563	220	547	140	490	1015	----	Liquid started	-0.7
15:00	260	598	260	585	220	547	325	574	1028	----		-0.6
15:05	260	523	260	602	220	548	480	600	1035	----		-0.6
15:10	260	527	260	601	220	553	520	601	1038	9-10		-0.6
15:15	260	531	260	600	220	552	535	601	1040	9-10		-0.6
15:20	260	539	260	600	220	547	540	602	1042	9-10	Reaction stopped	-0.6

Amount of biomass fed: 220.24g **Amount of liquid collected: 93.77g**
Amount of oil collected: 33.66g **Amount of water collected: 53.19g**
Amount of gas collected: 8.42g **Amount of char collected: 83.94g**

Experimental run no: **PYR/JCS/8**
Weight of biomass: **220.24g**
Mesh size: **-8+12**

Temp: **600°C**
N_2 flow rate: **50 ml/min**

Time (min)	D1	T1 °C	D2	T2 °C	D3	T3 °C	T4 °C	T5 °C	Gas flow	Rota meter	Remarks	Bath °C
10:25	0	28	0	30	180	146	28	30	08100	5-6	Preheater started	2.8
10:30	0	28	0	31	180	435	30	30	08100	5-6		1.4
10:35	0	29	0	32	180	494	32	31		5-6		0.3
10:40	0	30	0	33	200	517	32	31		5-6		-0.2
10:45	0	31	0	34	200	544	32	31		5-6		-0.9
10:50	0	32	0	35	200	548	32	31		5-6		-1.5
10:55	200	45	200	54	200	547	32	29		5-5	D1 & D2 started	-1.8
11:00	200	345	200	362	200	553	40	49		5-6		-2.0
11:05	240	516	240	526	200	551	40	200		5-10	Gas and liquid started	-2.0
11:10	270	548	260	553	200	548	40	347		5-10		-2.0
11:15	270	568	260	567	200	549	370	523		5-15		-1.9
11:20	270	590	260	584	200	547	450	560		----		-2.0
11:25	270	607	260	597	200	547	490	583		----		-2.0
11:30	270	615	260	602	200	545	510	602		----		-2.0
11:35	270	611	240	600	120	520	515	605		5-6	Heating stopped	-2.0

Amount of biomass fed: 220.24g
Amount of oil collected: 41.70 g
Amount of gas collected: 5.61g

Amount of liquid collected: 92.40 g
Amount of water collected: 50.70g
Amount of char collected: 89.70g

Experimental run no: **PYR/JCS/9**
Weight of biomass: **220.24g**
Mesh size: **-6+8**

Temp: **500°C**
N_2 flow rate: **150ml/min**

Time (min)	D1	T1 °C	D2	T2 °C	D3	T3 °C	T4 °C	T5 °C	Gas flow	Rota meter	Remarks	Bath °C
10:45	0	39	0	43	200	309	40	37	81000	11-12	Preheater started	0.1
10:50	0	39	0	43	120	428	40	38	81000	10-11		-0.0
10:55	0	39	0	44	100	438	40	38	81000	10-11		-0.1
11:00	0	40	0	44	100	439	40	38	81000	10-11		-0.1
11:05	200	40	200	44	90	433	40	38	81000	10-11	D1 & D2 started	-0.1
11:10	240	79	240	79	90	428	40	38	81000	11-12		-0.2
11:15	260	105	260	103	100	422	40	43	81000	12-13	Gas and liquid started	-0.1
11:20	240	210	240	151	140	358	75	77	81015	12-13		0.2
11:40	240	550	240	447	100	430	140	190	81026	12-13		0.4
11:45	140	574	140	486	100	431	160	397	81036	12-13		0.6
11:50	0	542	0	475	0	406	160	478	81039	12-13		0.6
11:55	220	509	220	432	120	332	160	455	81041	12-13		0.6
12:00	220	579	20	499	120	407	160	500	81042	12-13	Heating stopped	0.6

Amount of biomass fed: 220.24g
Amount of oil collected: 40.57g
Amount of gas collected: 8.9

Amount of liquid collected: 89.52
Amount of water collected: 45.46
Amount of char collected: 87.09

Experimental run no: **PYR/JCS/10**
Weight of biomass: **220.24g**
Mesh size: **-6+8**

Temp: **500°C**
N_2 flow rate: **100 ml/min**

Time (min)	D1	T1 °C	D2	T2 °C	D3	T3 °C	T4 °C	T5 °C	Gas flow	Rota meter	Remarks	Bath °C
3:20	0	31	0	34	180	32	40	34	1007	9-10	Preheater started	1.5
3:25	0	32	0	36	60	403	40	35	1008	9-10		1.4
3:30	0	33	0	37	80	395	40	36	1009	8-9		1.4
3:35	220	155	220	156	80	406	40	37	1009	9-10	D1 & D2 started	1.4
3:40	260	455	260	437	80	410	42	49	1010	9-10		1.5
3:45	260	523	260	517	80	418	42	148	1019	10-11	Water started at 3.42	1.6
3:50	260	547	260	542	100	436	45	457	1033	15	Brown liquid started at 3.48	1.5
3:55	0	486	0	484	100	451	42	521	1039	15	D1 & D2 stopped	1.5
4:00	260	468	260	473	100	454	42	478	1040	9-10		1.5
4:05	260	528	260	526	100	454	42	507	1041	15		1.5
4:10	0	480	0	482	100	456	42	517	1042	15	Heating stopped	1.5

Amount of biomass fed: 220.24g
Amount of oil collected: 34.56g
Amount of gas collected: 7.30g

Amount of liquid collected: 86.81g
Amount of water collected: 44.12g
Amount of char collected: 94.40g

Experimental run no: **PYR/JCS/11**
Weight of biomass: **220.24g**
Temp: **500°C**

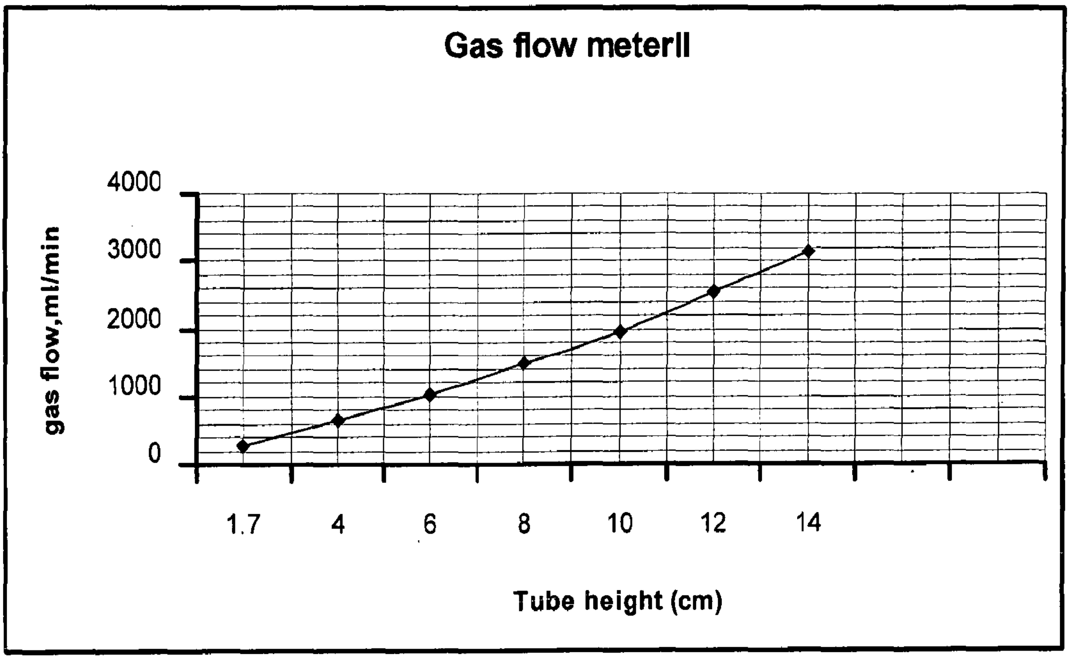
Mesh size: **-8 +12**
N_2 flow rate: **100 ml/min**

Time (min)	D1	T1 °C	D2	T2 °C	D3	T3 °C	T4 °C	T5 °C	Gas flow	Rota meter	Remarks	Bath °C
12:00	0	34	0	37	140	124	40	36	1054	4-5	Preheater started	1.3
12:05	0	36	0	39	140	360	40	36	1054.5	4-5		1.2
12:10	220	189	220	196	100	418	42	36	1054.9	5	D1 & D2 started	1.1
12:15	260	466	260	468	100	432	42	68	1056	4-5		1
12:20	260	514	260	518	100	436	42	171	1065	5-6	Water started at 12.17 Brown liquid started at 12.20	1.1
12:25	260	540	260	542	100	437	40	495	1080	15		1.1
12:30	0	498	0	562	100	438	40	533	1083	7-8	D1 & D2 stopped	2.1
12:35	0	435	0	447	100	439	40	492	1083.5	5-6		2
12:40	220	500	220	508	100	438	40	485	1084	5-6		1.8
12:45	0	517	0	512	100	523	40	523	1085	5-6	Heating stopped	1.8

Amount of biomass fed: 220.24g
Amount of oil collected: 39.84g
Amount of gas collected: 8.11g

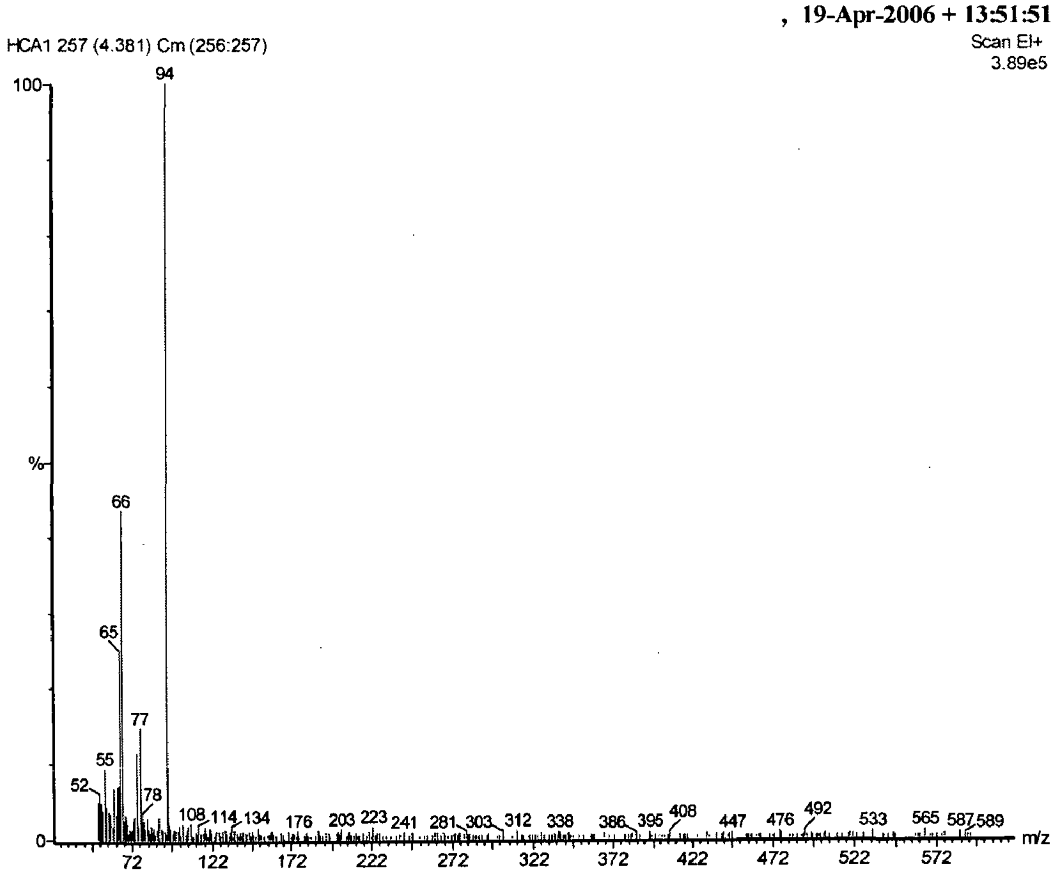
Amount of liquid collected: 83.89g
Amount of water collected: 41.35g
Amount of char collected: 94.88g

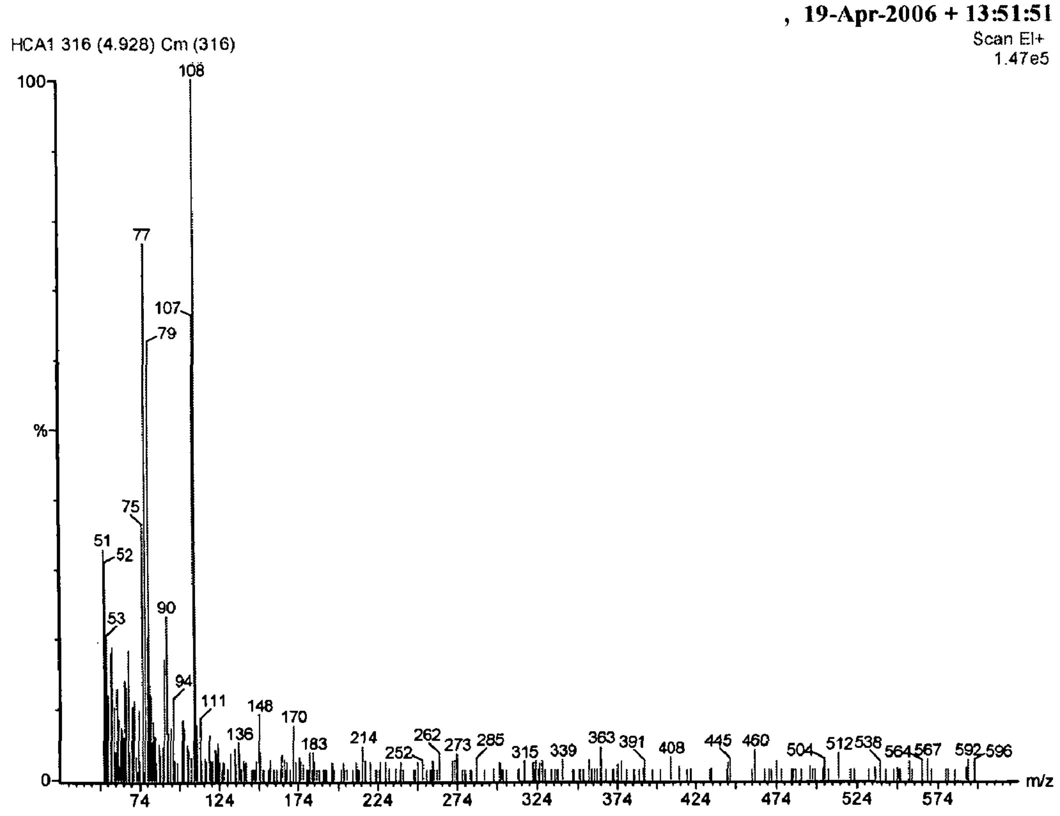
Calibration curve of wet gas flow meter

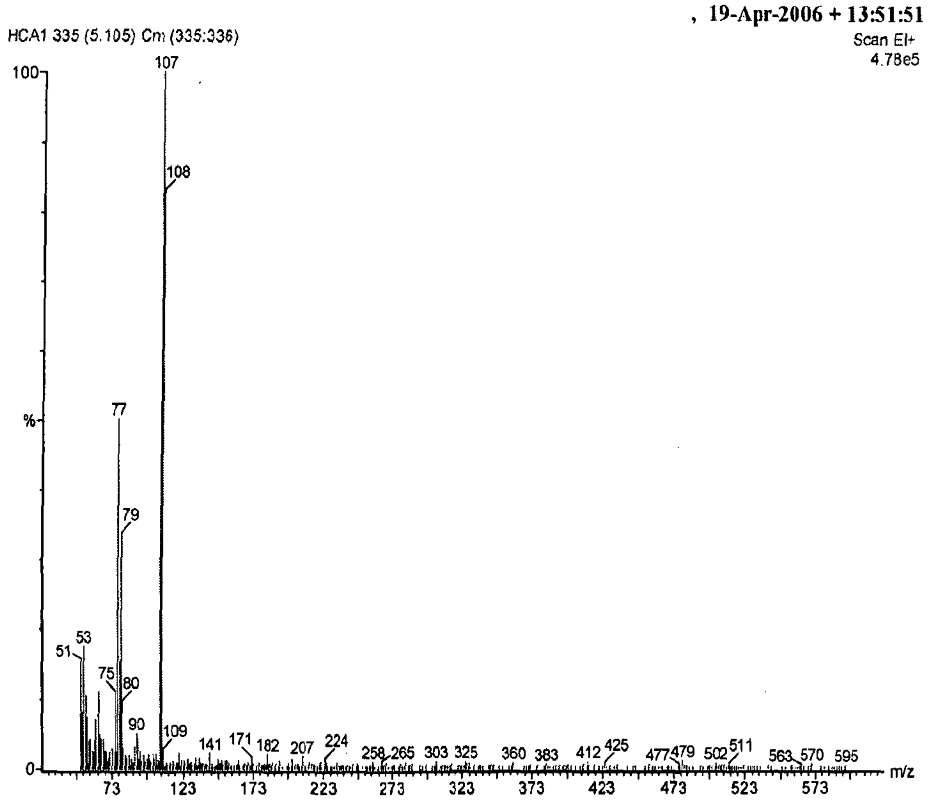


APPENDIX C

Mass spectroscopy of each peak from GC/MS graph



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77
79
51
53
75
80
90
109
141
171
182
207
224
258
265
303
325
360
383
412
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323
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423
473
523
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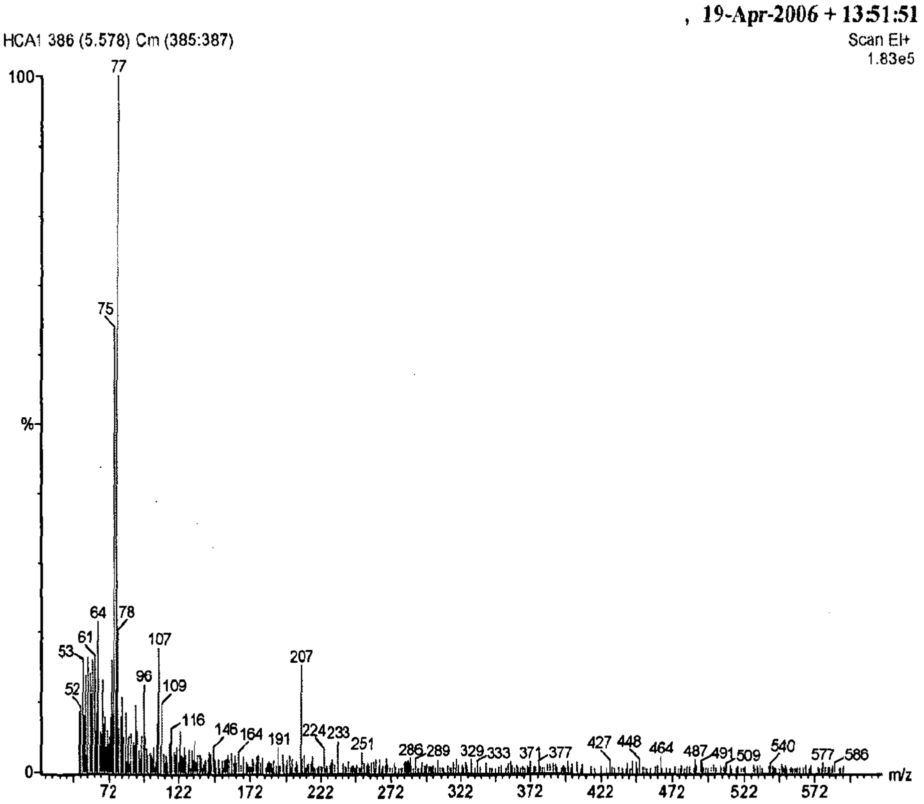
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61
53
107
52
96
109
207
116
146
164
191
224
233
251
286
289
329
333
371
377
427
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m/z
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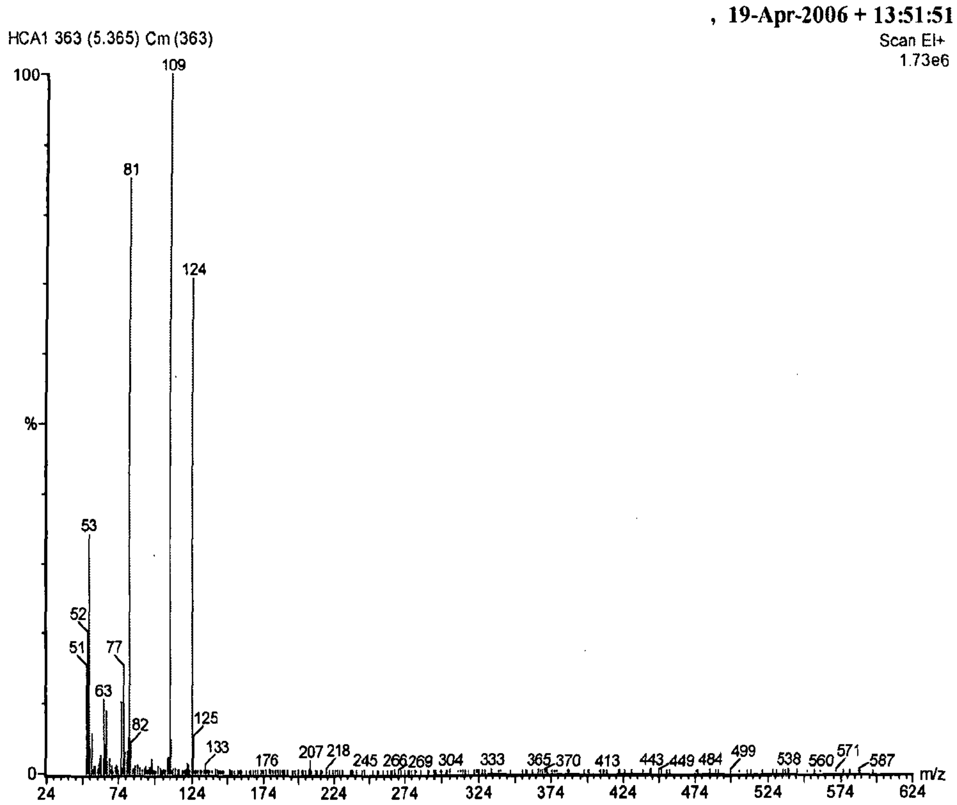
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53
52
51
77
63
82
125
133
176
207
218
245
266
269
304
333
365
370
413
443
449
484
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524
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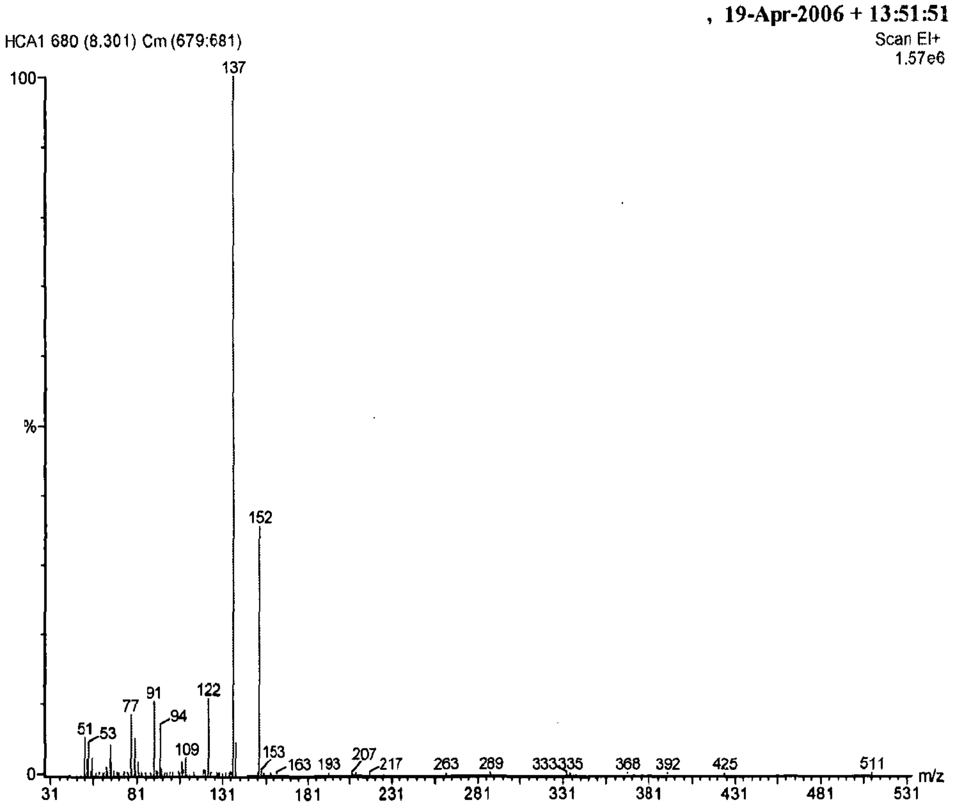
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%
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91
94
122
109
153
163
193
207
217
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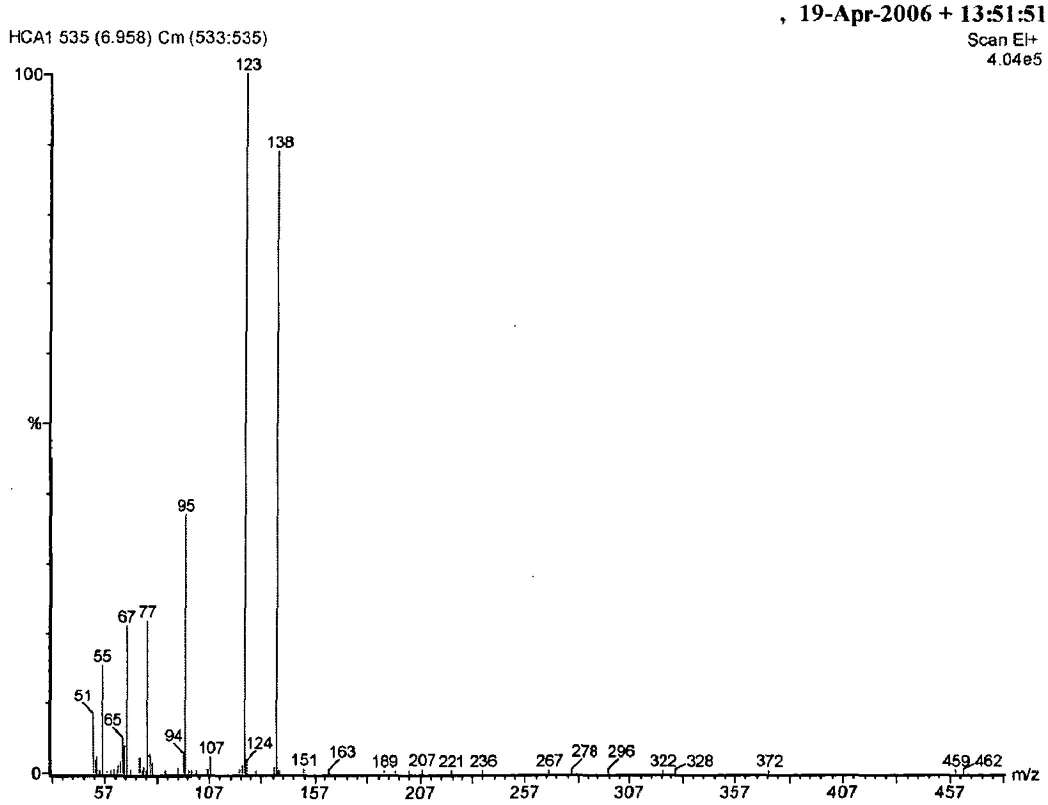
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55
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189
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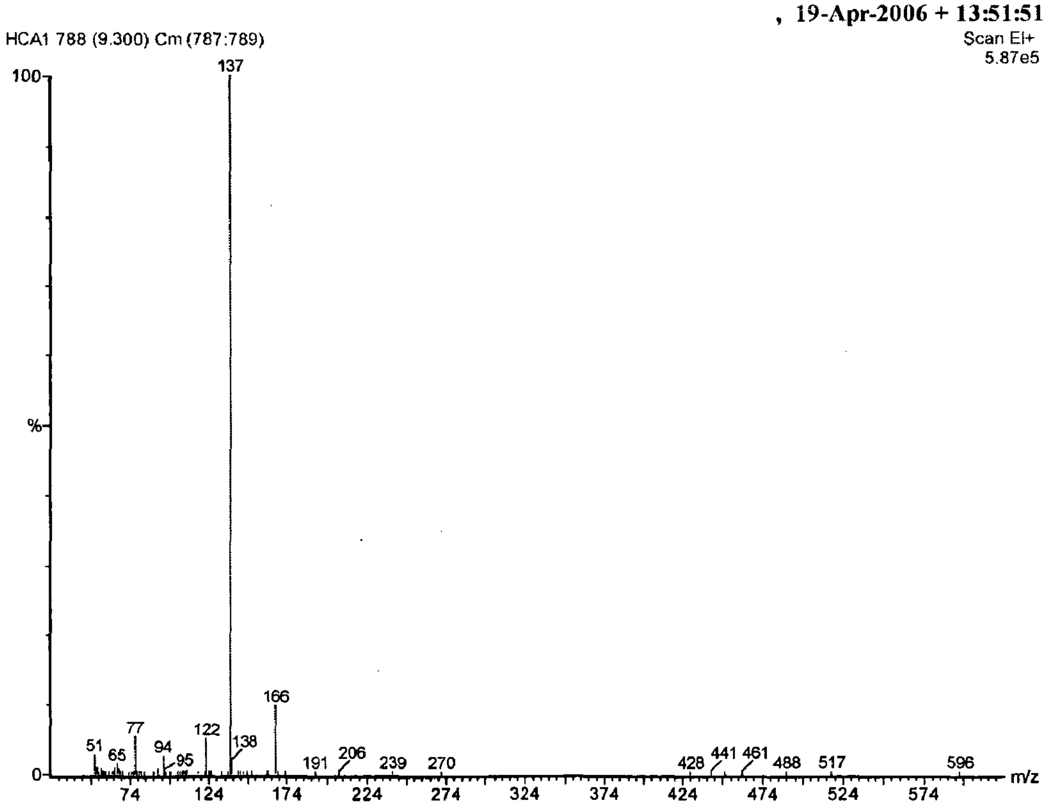
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122
51
65
94
95
138
191
206
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517
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m/z
74
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174
224
274
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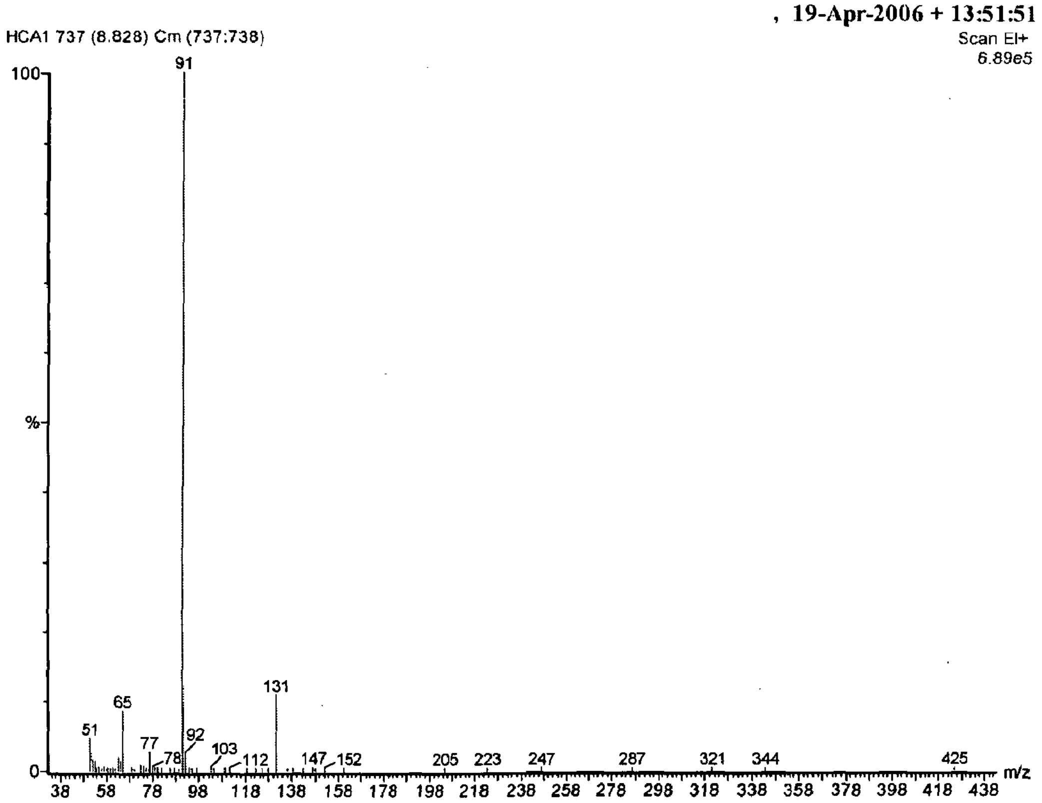
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78
92
103
112
147
152
205
223
247
287
321
344
425
m/z
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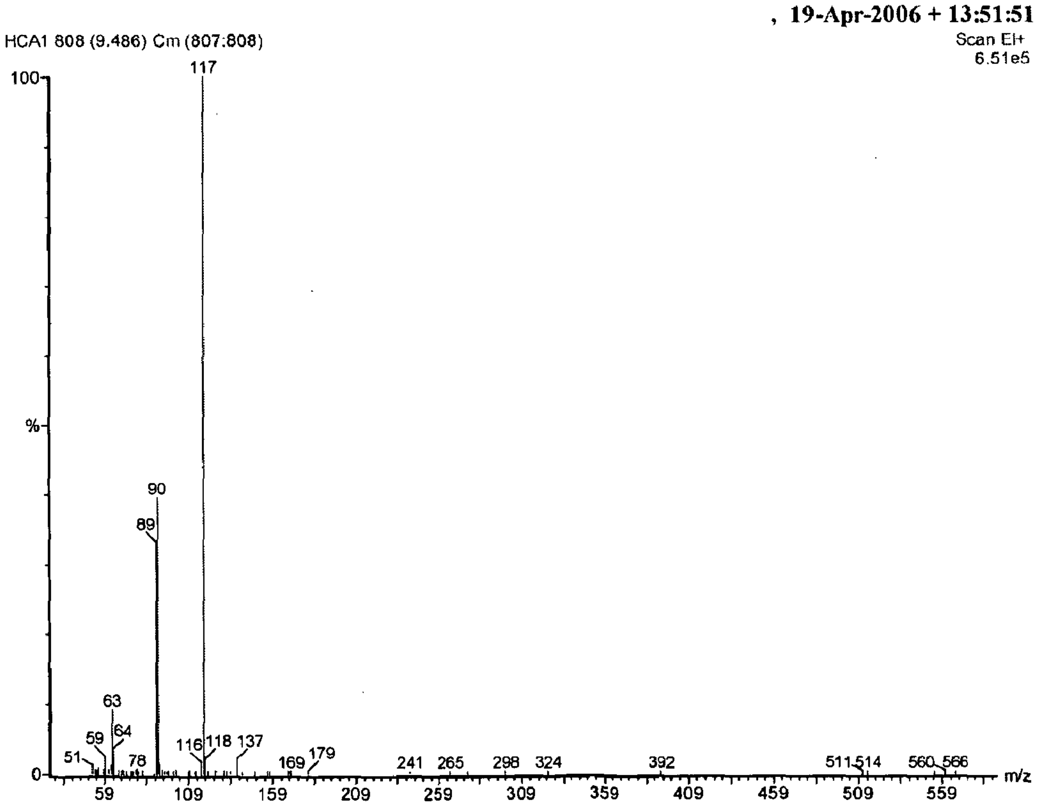
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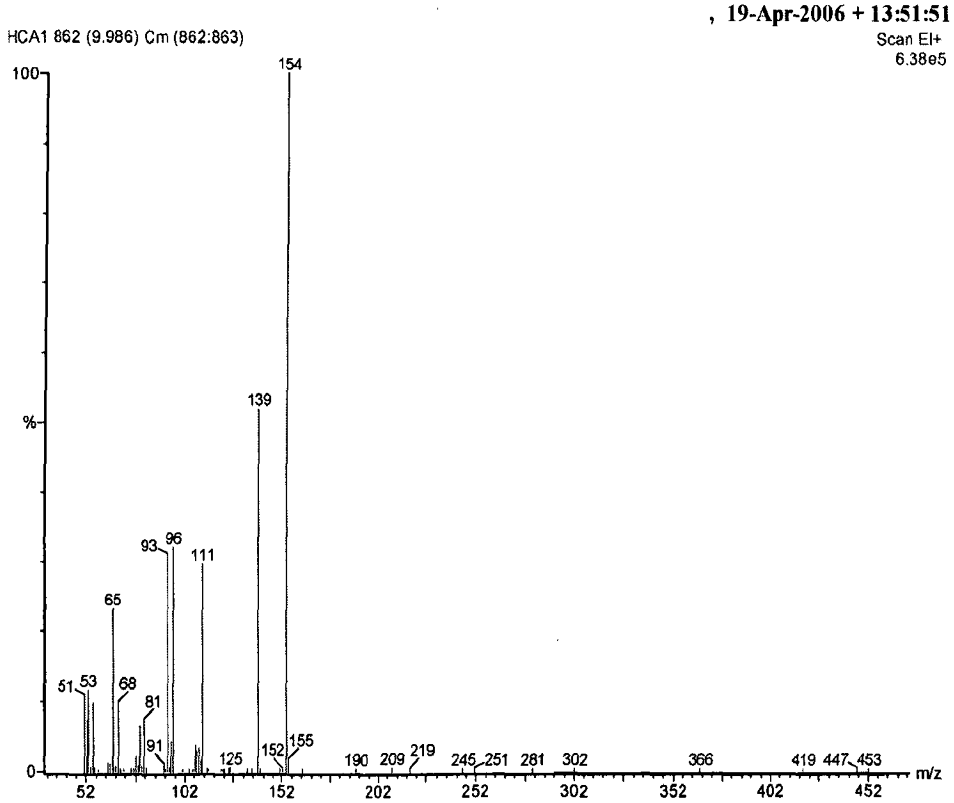
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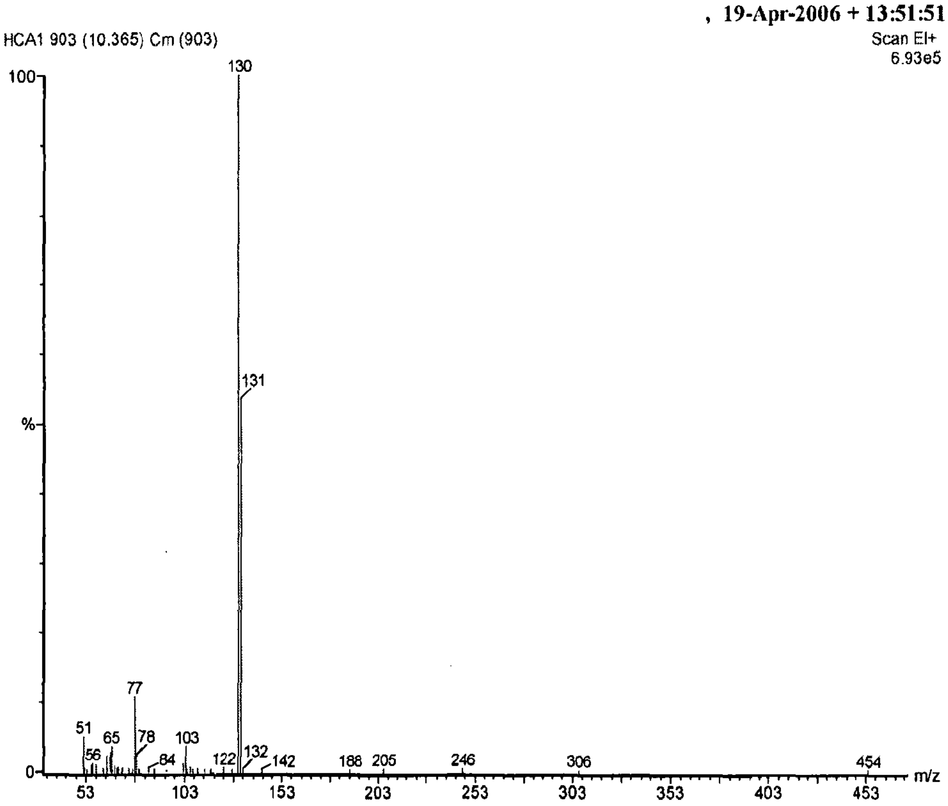
402
452
m/z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403
453
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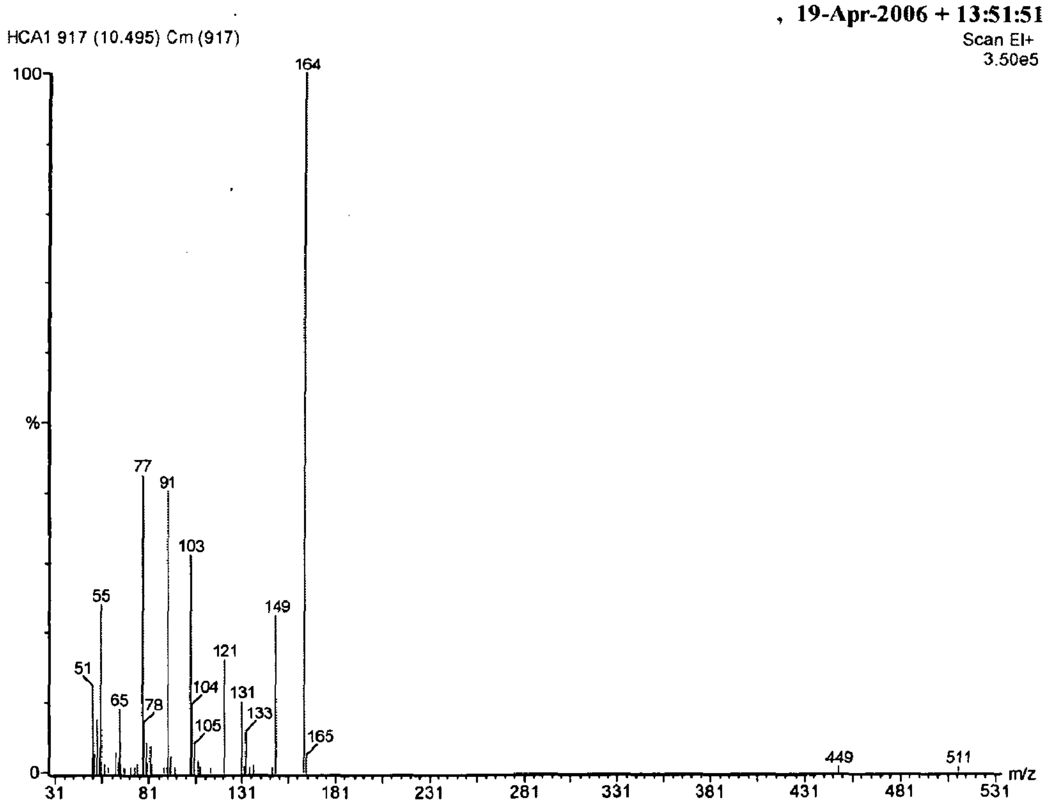
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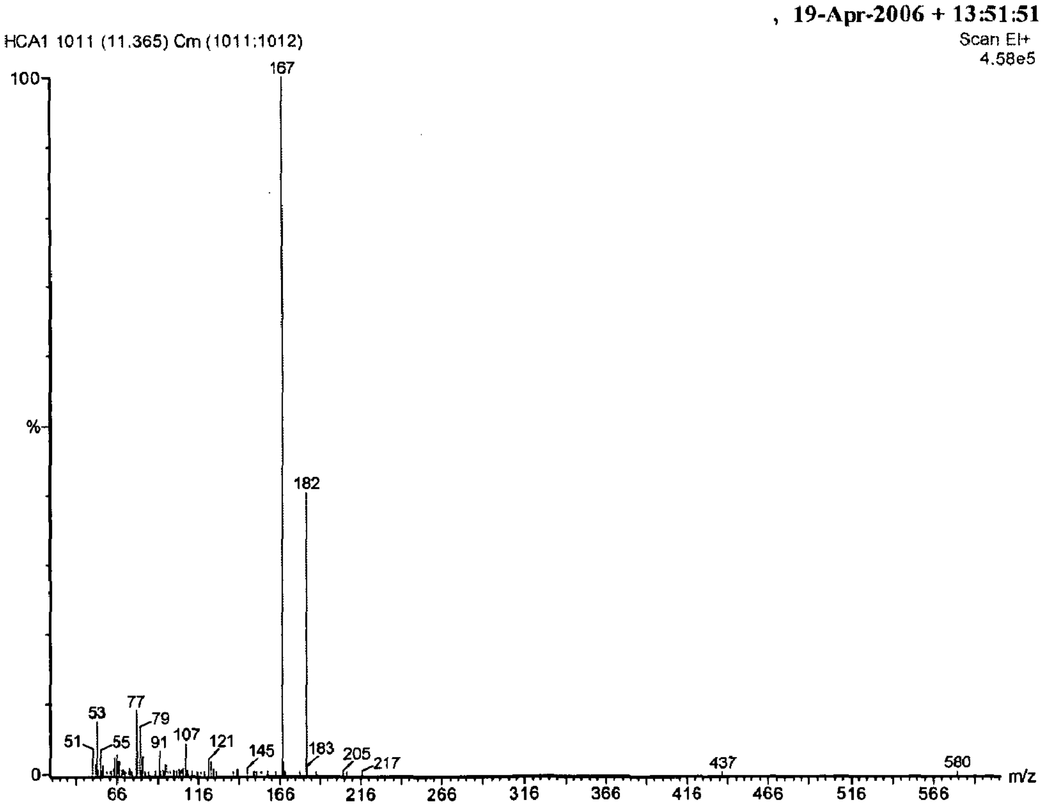
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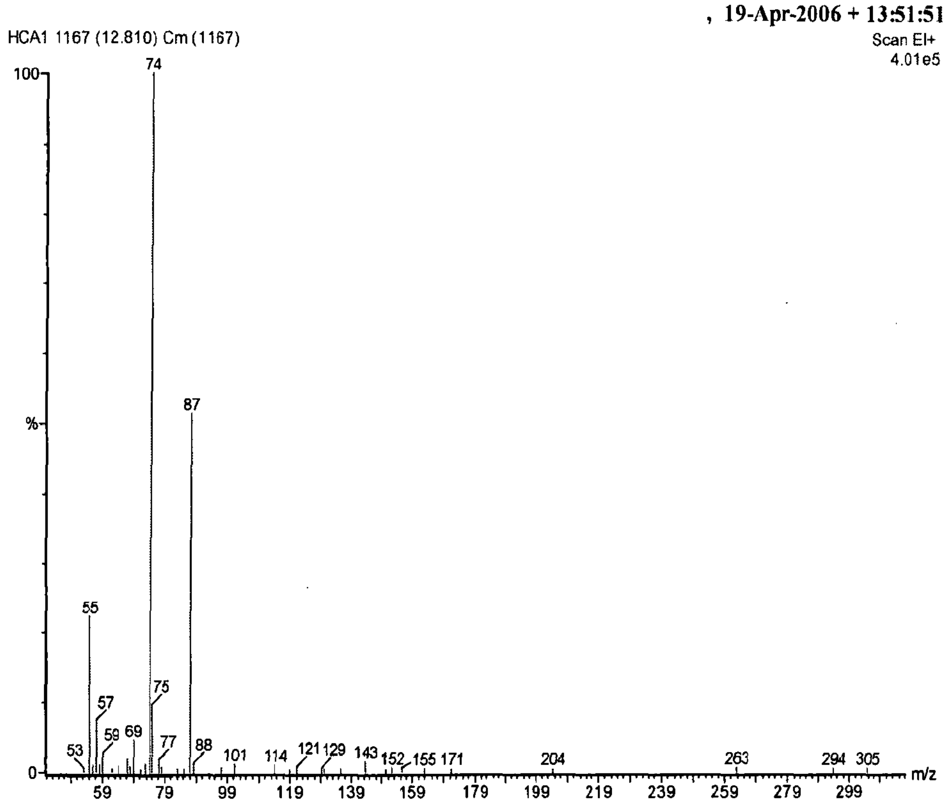
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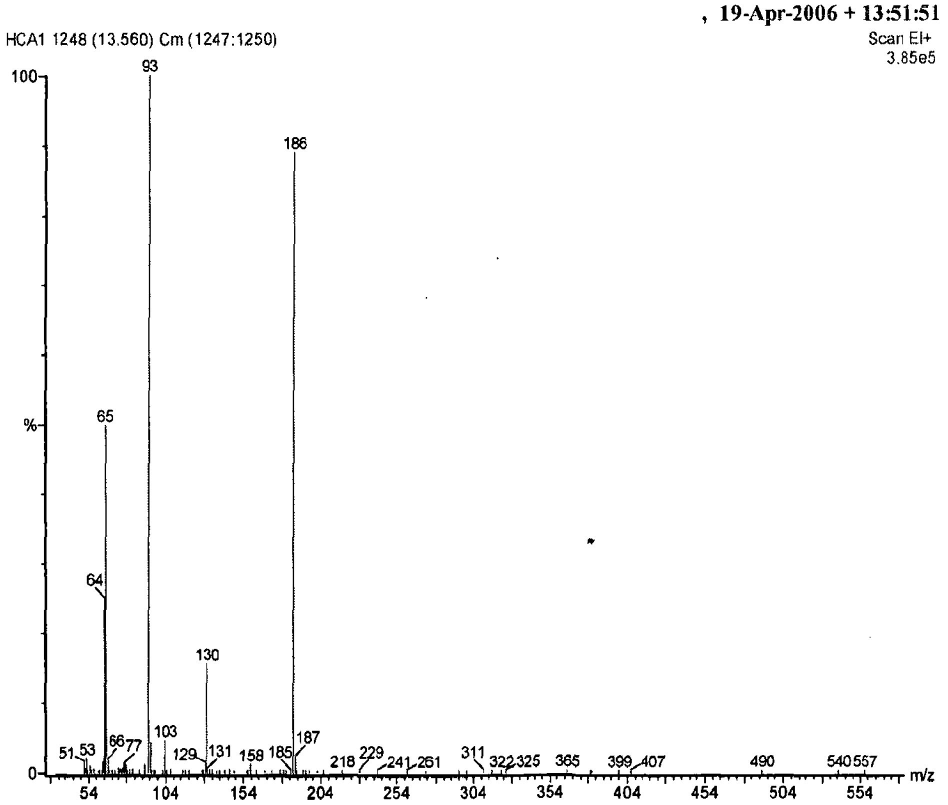
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187
51 53
66 77
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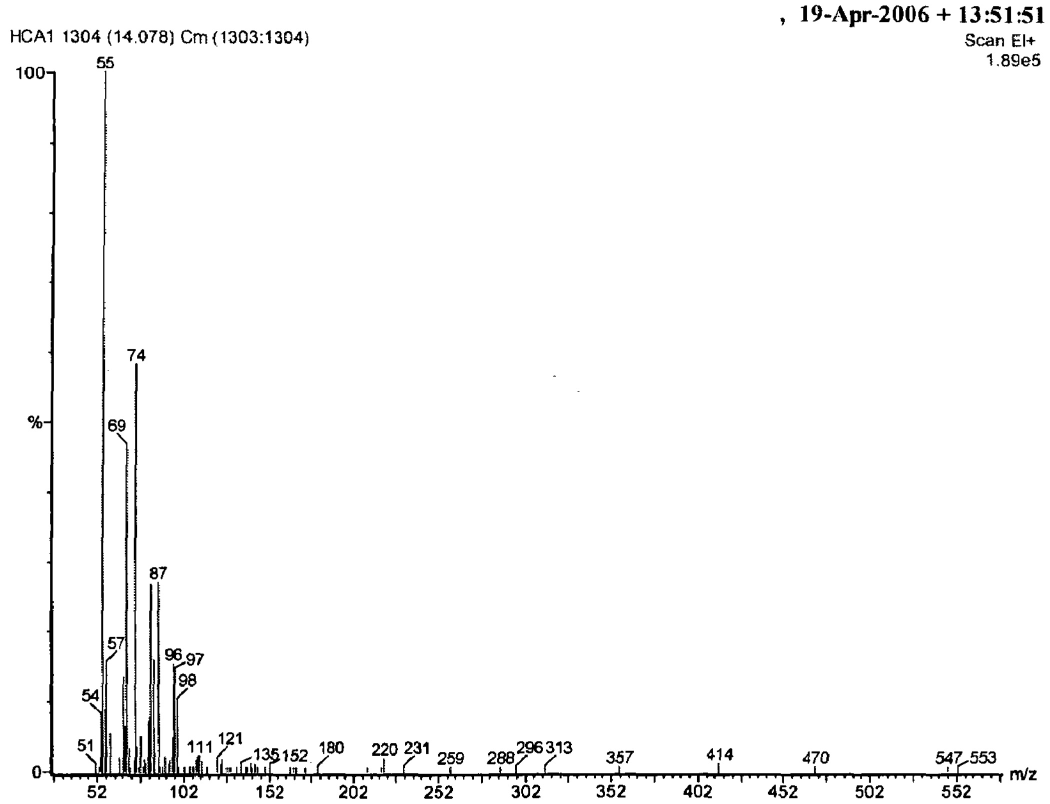
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98
54
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135
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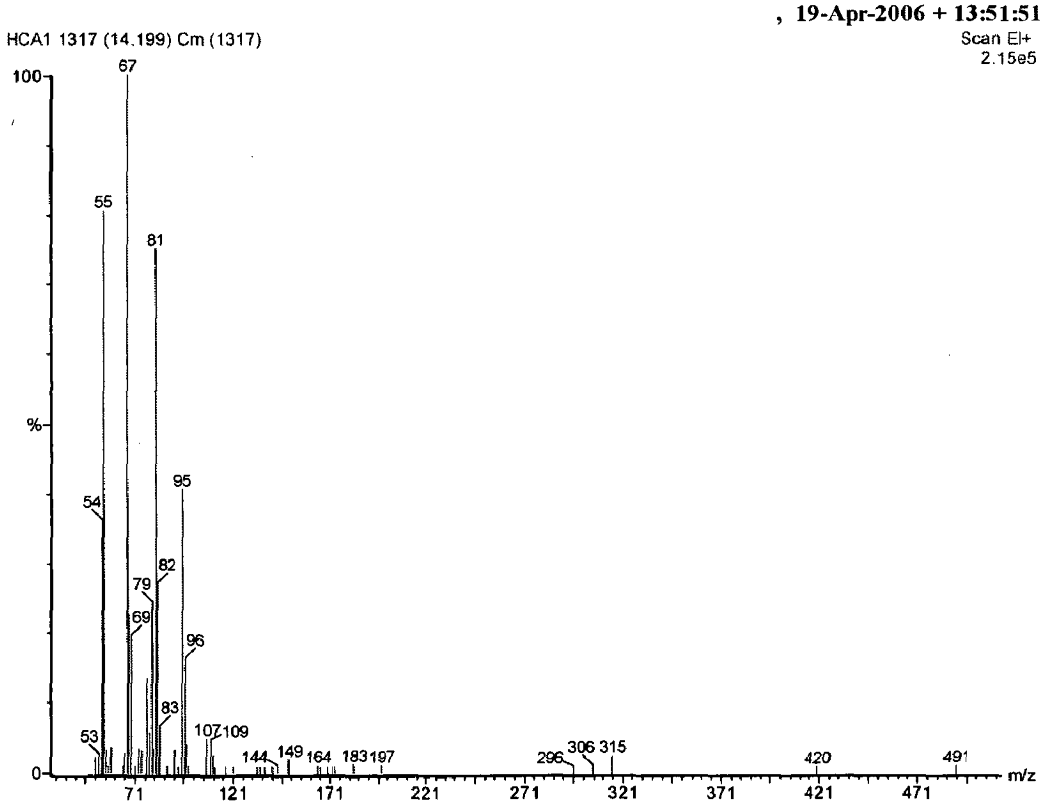
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%
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83
53
107
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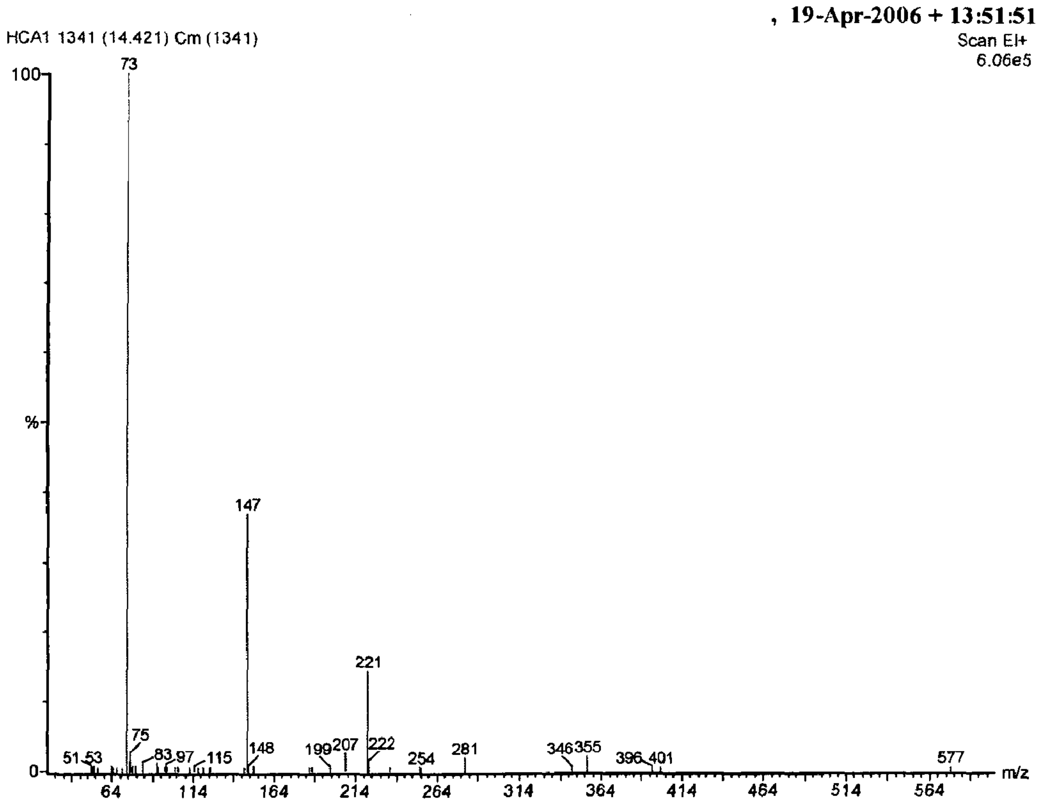
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%
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83
97
115
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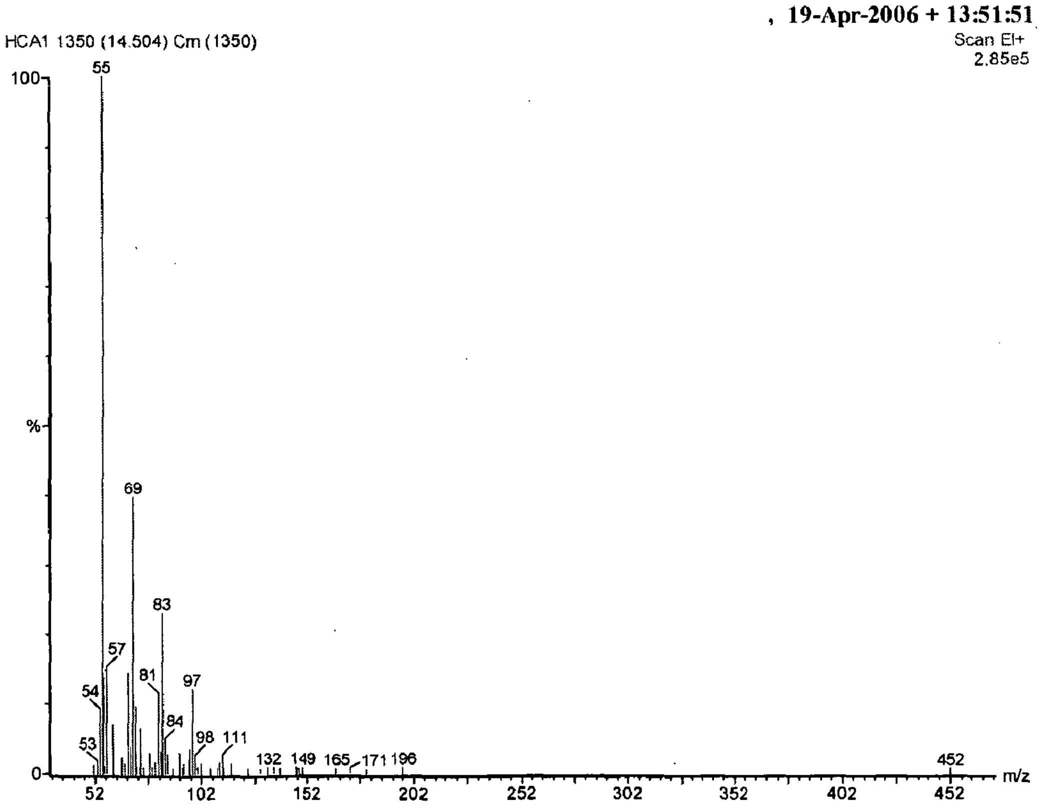
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%
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97
84
53
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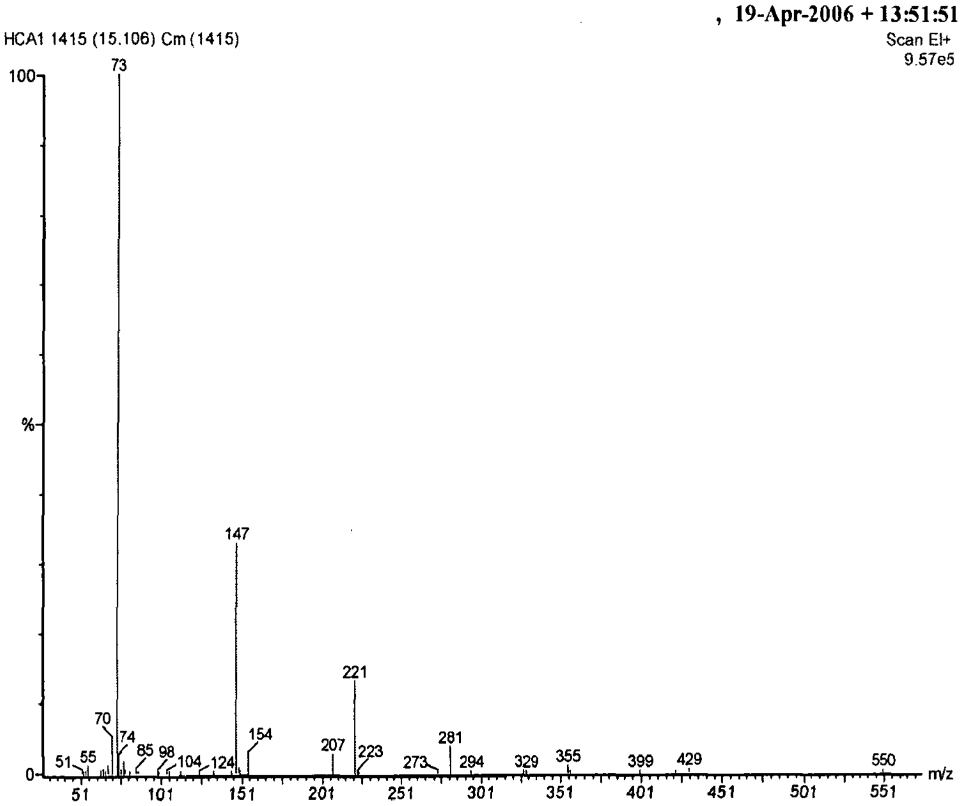
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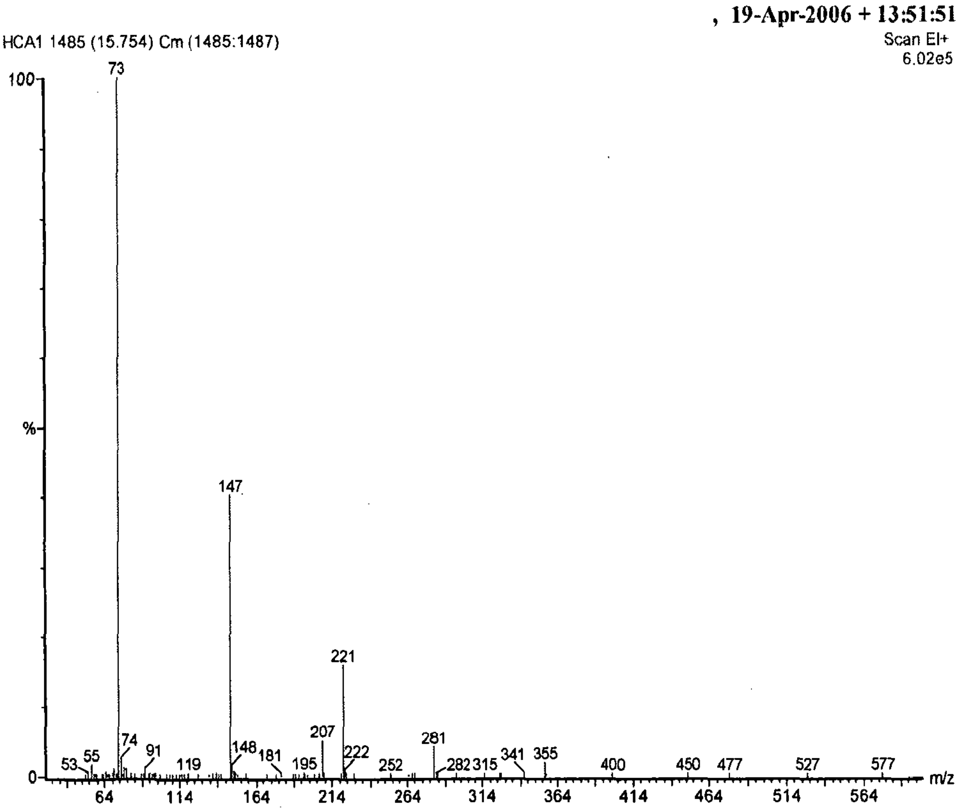
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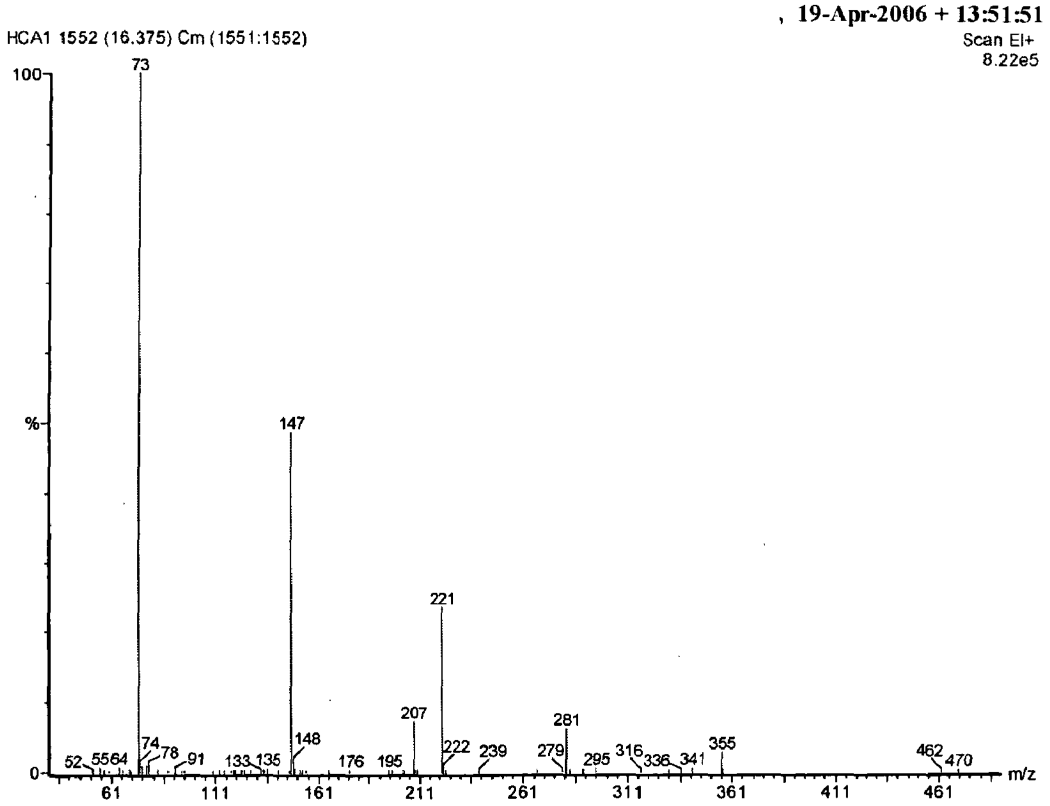
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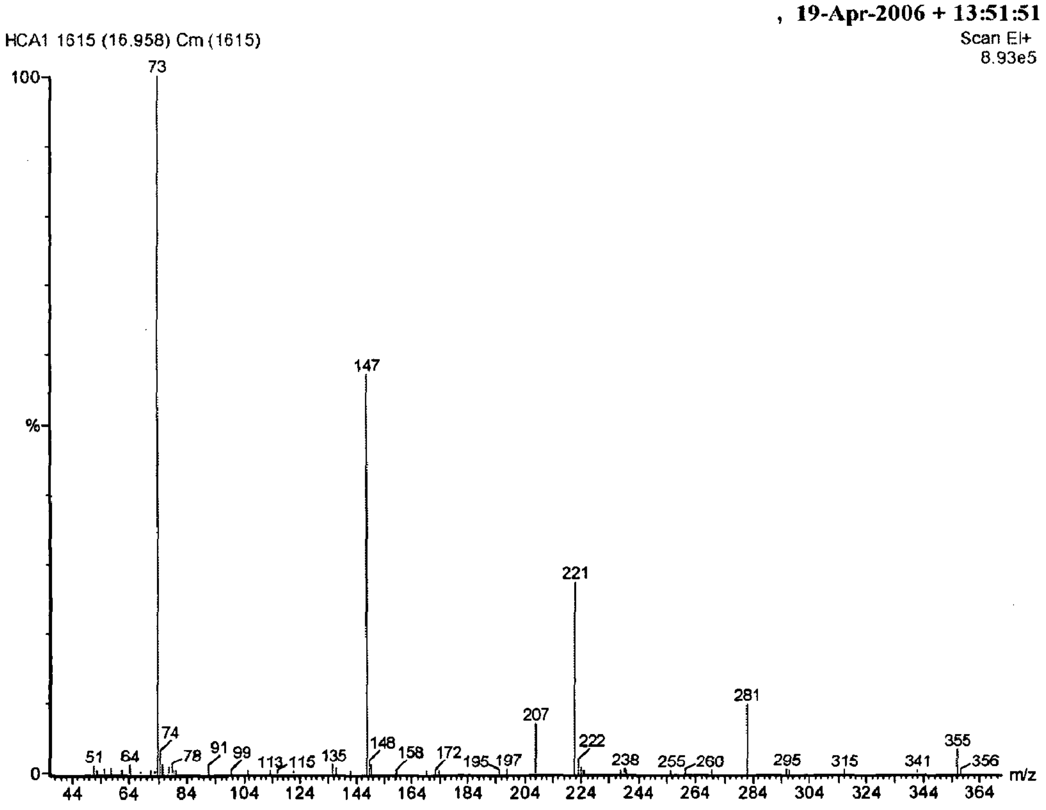
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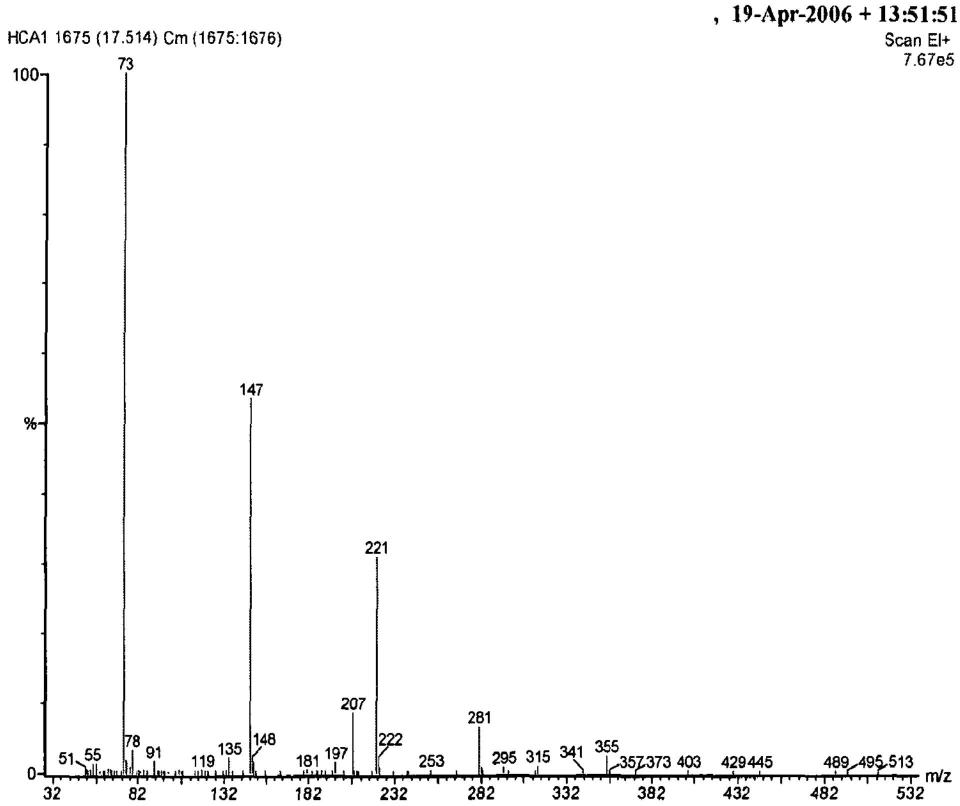
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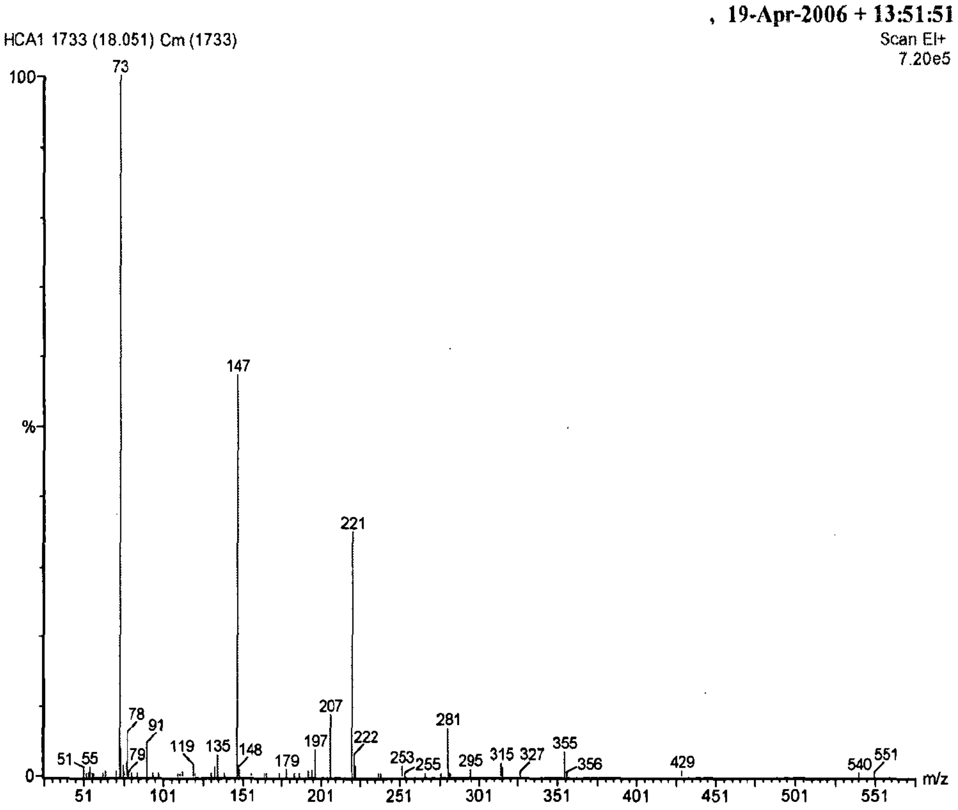
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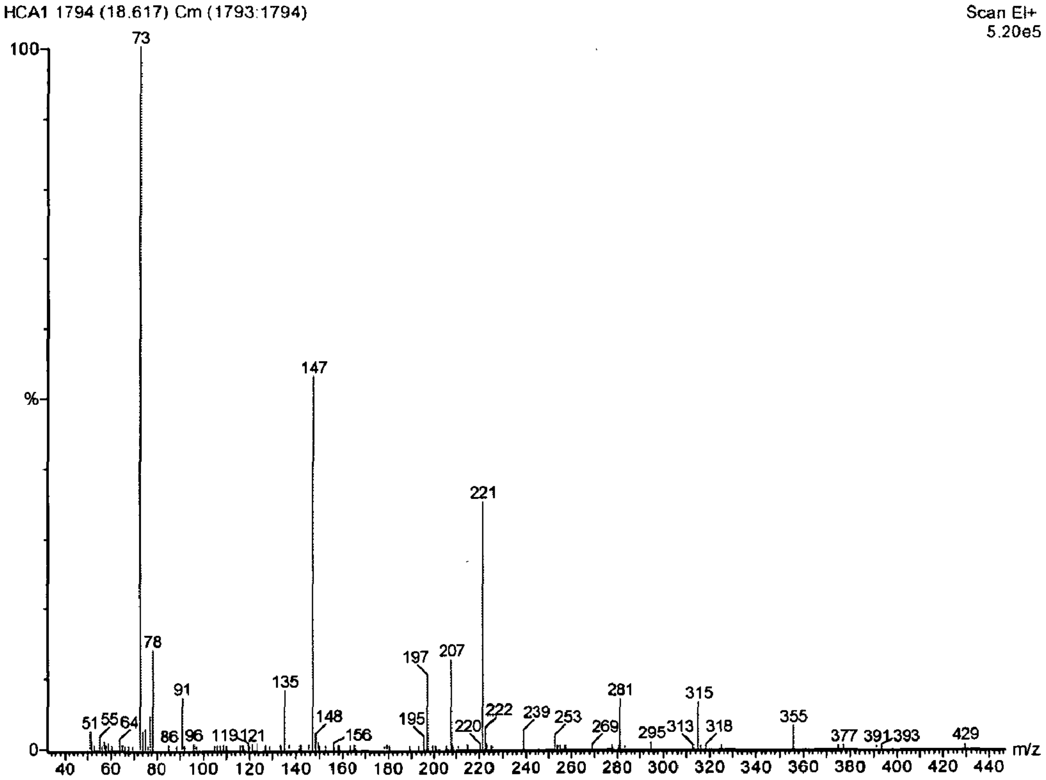

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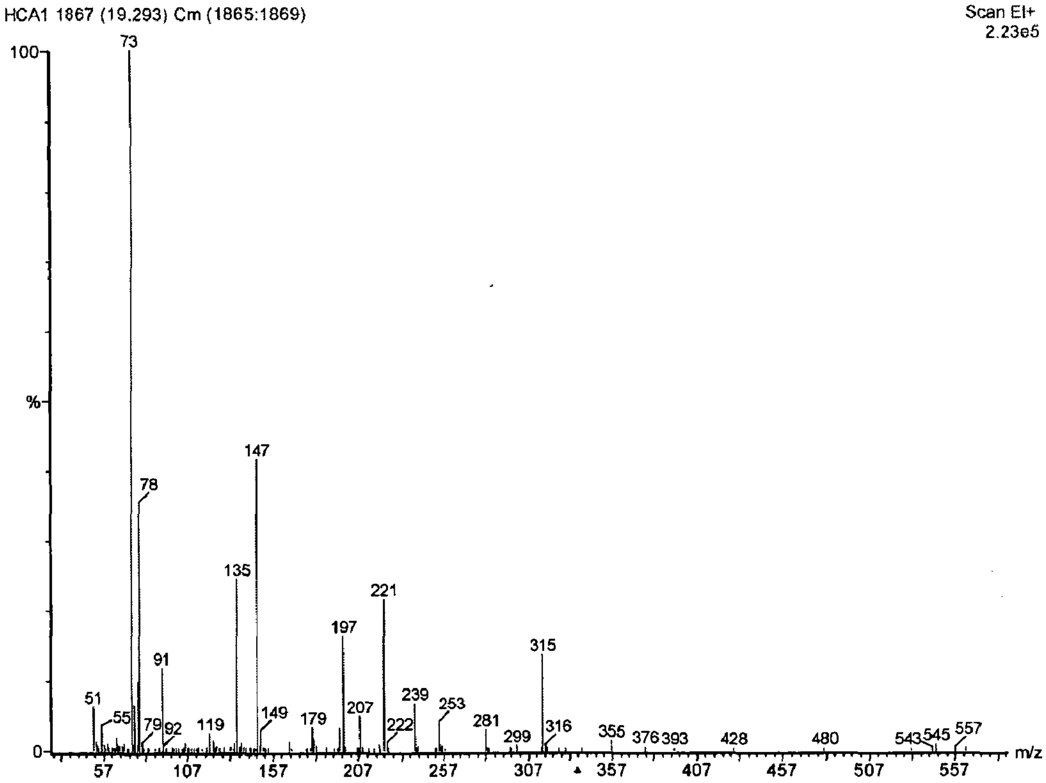

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