

RESIDUAL JATROPHA SEED CAKE VALORIZATION STUDIES

A MAJOR PROJECT REPORT

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By

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in this dissertation, Entitled "**Residual Jatropha Seed Cake Valorization Studies**", submitted in partial fulfillment of the requirement for award of the degree of **Master of Technology in Chemical Engineering** with the specialization in **Process Design Engineering (PDE)**, is an authentic record of my own work carried out under the supervision of **Dr. Sathish Kommoji/Dr. Murali Pujari** Assistant Professor (Selection Grade), Department of Chemical Engineering, University of Petroleum & Energy Studies, Dehradun and **Dr.D.T.Gokak**, Chief Manager, Corporate Research and Development Centre , BPCL, Greater Noida.

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ABSTRACT

Energy needs of the world are reaching greater heights with increasing population and technological advancements. Fossil fuel which forms the major fraction of the energy source is being consumed in an alarming rate and the Green House Emission of gases (GHG) is also increasing leading to pollution and global warming. Though renewable sources such as wind, hydro, solar etc. can be used, it falls short of the milestones as the processes are expensive and the produce energy which cannot be transported. Biomass which is derived from agricultural, forestry and natural sources are found to have the potentially aid the energy needs. One of the challenges needs to be addressed is the influence of biomass derived fuels over the nutritional needs of the country. Hence, non-edible biomass is preferred for the bio-fuels. *Jatropha Curcas* plant is considered as a wonder plant due to its short gestation period and yields up to 50 years. Among the conversion technologies, Thermo-chemical conversion of residual biomass such as *Jatropha* seed cake using Pyrolysis is used for “Trash to cash” process. Pyrolysis is a process which directly converts biomass into fuels such as bio-char (solid), bio-oil (liquid) and gases. Pyrolysis experiments on the *Jatropha* seed cake is carried out in a rotary tubular conveyor reactor at different residence times, temperatures and carrier gas. Results show better quality of fuel obtained when Steam is used instead of Nitrogen. In the GC-MS analysis, Compounds like Acetic acid and 2-Furanmethanol were the major compounds identified in bio-oil obtained by pyrolysis using Nitrogen. Similarly compounds like Dimethylamine, Ethyl Acetate and Ammonium Acetate are identified using GC-MS analysis in bio-oils obtained by pyrolysis using Steam. Maximum bio-oil yield 36.5% was obtained at 550°C using steam. Energy analysis of the pyrolysis process was also carried out. Energy yield as high as 79.90% has been determined in the steam assisted pyrolysis process. Energy Returns On Investment(EROI) was also determined and the value is found to be feasible.

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NOMENCLATURE

$\Delta G^{\circ}_{\text{Rref}}$	Gibbs free energy of the reaction at reference temperature (298K), in J/mol
$\Delta H^{\circ}_{\text{Rref}}$	Enthalpy of reaction at reference temperature (298K), (J/mol)
k_{ref}	Equilibrium constant at reference temperature(298K)
K	Equilibrium constant at specified temperature (298K)
R	Universal gas constant, 8.314 in J/mol .K
T	Specific Temperature, in K
T_{ref}	Reference Temperature (298K), in K.
EROI	Energy Return On Investment.

1. INTRODUCTION

The global energy demand and need for sustainable development renders research on renewable energy important. Of particular importance is, energy derived from biomass and related residual wastes which can be effectively transported, utilized with conventionally used fuels without any changes in the process or in the system. Utilization of biomass offers a reduction in emission of sulfur.

The maximum value addition by utilization of biomass can be realized in using feedstock which will use residual wastes. Thus, crops classified as non-edible are more important from the value addition point of view. The use of *Jatropha*, a non-edible crop is getting wide importance due to desirable properties such as low gestation period and production of seeds which have long terms of production (up to 50 years) [1,2].

Thermo – chemical route is the most suitable for energy extraction from *Jatropha* as it offers economical and simpler ways of valorization. The maximization of yield by the process is flexible and simpler by control of process parameters. Well known processes such as gasification, hydrothermal liquefaction, pyrolysis and combustion can be employed for energy extraction [3].

Conversion of biomass to gaseous products can be carried out by gasification at temperatures typically 700°C with limited supply of oxygen. Desirable product, gas yields up to 85% can be achieved by the technique, which also results in less quantity of liquid products such as bio-oil and bio-char. Combustion burns the feed completely with presence of oxygen to obtain heat, while liquefaction technology operating at low temperature and high temperature uses hydrogen, which makes the process economically not feasible. The difficulty in pumping of feedstock at higher pressures makes hydrothermal process not suitable to present application. [4, 5]

In view of developing a suitable value addition for residual waste (*Jatropha*), pyrolysis a thermo-chemical processes which convert biomass into solid, liquid, gaseous fuels by decomposing the different constituents of the biomass (Cellulose, Hemicelluloses and Lignin). The products obtained are char and ash(solids), Pyrolysis-oil also called as bio-oil(liquid), and volatile gases.

Reactor configurations play an important role in the techno-economic feasibility the process. A balance has to be made in terms of cost, yield and revenue so as to make the process commercially viable. Fluidized bed, Ablative, Rotating cone, Auger, Fixed bed and entrained flow are the various types of reactors used to carry out pyrolysis.[3]

Fluidized bed reactor, rotating cone and ablative reactors, has disadvantages like high energy requirement, high fluidizing gas requirement, complex design, feed size desirability, Heat carrier requirements and Catalyst de-activation [4]

Screw conveyor reactor (auger) gathers much interest of study. The feed is conveyed by the use of screw. The salient features as follows [5]

1. Compact design.
2. Control of residence by tuning the frequency of the screw rotation.
3. Smaller reactor size.
4. Moderate particle size.
5. Better separation of solids from vapors.

2. LITERATURE REVIEW

2.1 Biomass

The word “biomass” refers to any biological sources obtained from agriculture, forest and animals which are used to harness energy. This also includes wastes and residues such as municipal wastes, manure, straws, husks, seed cakes etc. [6] Biomass is considered as probably the oldest and the first form of energy from which energy is derived by burning wood.[7] Based on the type of growth, species and usability, biomass can be categorized as Woody and Non-woody, Edible and Non-edible biomass.[8].

2.2 Constituents of Biomass

Biomass comprises of the major constituents namely Cellulose, Hemi-cellulose and Lignin.

2.2.1 Cellulose

Cellulose is found to have the bulk fraction constituting 25-50 % of the biomass[9]. It is the polymeric unit formed by the d-glucose monomers. The molecule typically consists of 1000 units and can go up to 3000 units.[10]

2.2.2 Hemi-cellulose

Hemi-cellulose is a branched polymeric units consisting of pentoses such as Arabinose and hexoses such as Glucose. Hemi-cellulose are of shorter monomer chains as compared to the Cellulose, typically around 300 and constitutes for about 12-40% of the biomass.[6]

2.2.3 Lignin

Lignin is a complex structure containing predominantly the monomeric units of P-coumaryl alcohol, Sinapyl alcohol and coniferyl alcohol. [6] The monomer units vary according to the type of the biomass.

Table 2.1: Constituents of different biomass [11, 12, 13]

Feedstock	Cellulose (%)	Hemi-cellulose (%)	Lignin (%)
Wheat straw	33-40	20-25	15-20
Bagasse	19-24	32-48	23-32
Corn Stover	28	35	16-21
Softwood	52	9	32
Jatropha seed cake	53.5	16.6	24.9

Other than the above mentioned constituents, there are also fats, proteins etc which are converted in value added products.

2.3 Biomass to fuel conversion

Biomass to fuel conversion has attracted enormous interest in the recent past because of the increasing energy demands of the world and also it is the most under-utilized source in the world.[14].Biomass contributes to about only 14% of the world's energy consumption. Bio-fuels also are eco-friendly with very less sulfur content and carbon-dioxide neutral.[15] Apart from fuels, Biomass also can be used to obtain hydrocarbons & chemicals.

The technologies to convert biomass into fuels are as follows: [16]

- I. Biological conversion process**
- II. Chemical conversion process**
- III. Thermo-chemical conversion**

2.3.1 Biological conversion process

Biological conversion is carried out by action of microbial organisms. Anaerobic digestion and Fermentation are the different bio-conversion processes. Anaerobic digestion takes place in the absence of oxygen where the lignocellulosic biomass is disintegrated into energy rich bio-gas.[17] Enzymatic fermentation is primarily used for fermenting sugars into bio-ethanol which

can be used directly as fuel or as blending with petroleum. Biological conversion process, however has not been successfully commercialized as the process takes longer duration (several days) for the yield of products. [17, 18]

2.3.2 Chemical conversion Process

Chemical processes such as Trans-Esterification of oils which converts waste, edible or non-edible oils which has high triglyceride content into methyl esters which are also called as bio-diesel. The chemistry of the process is shown in fig2.1. Though the process yields fuels which can be used directly or as blends, it suffers major challenge of addressing glycerol which is the primary by-product of Trans-Esterification. [19]

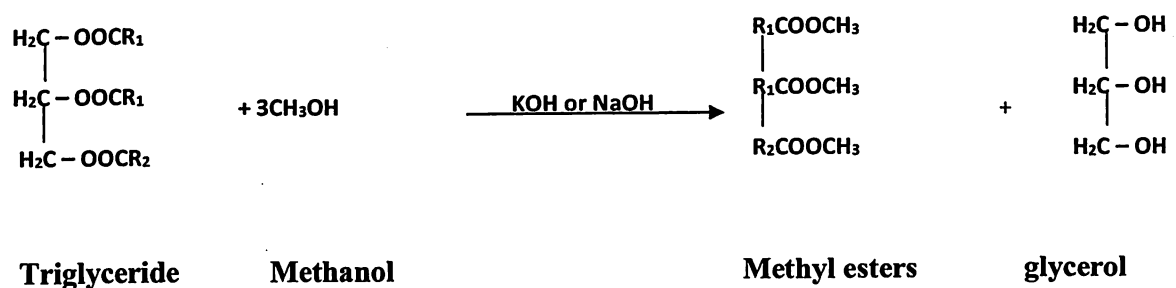


Fig 2.1 :General chemistry of trans-Esterification process [20]

2.3.3 Thermo-chemical conversion

Thermo-chemical conversion is the most suited as the feedstock is directly converted into second generation fuels and chemicals and its ease of operation. Pyrolysis, gasification and combustion are the major thermo-chemical processes that have attracted greater interest or research. Pyrolysis, in particular has attracted greater interest as the pyrolysis products yield liquid hydrocarbons which is also called as bio-oil that can be upgraded to fuels. [21]

Gasification and combustion are thermo-chemical processes which are carried out to high energy gases and heat. Gases obtained from the process can be used as heat directly or can be further converted to liquid fuels by Fisher-Tropsch synthesis. [22] Mohammed et al experimented gasification over a temperature range of 700-1000 °C. Results suggest that the maximum yield of gas was obtained at 1000°C with Hydrogen yield peaking at 850°C [23]

Pyrolysis is the thermo-chemical conversion process that takes place in the absence of oxygen. The biomass constituents decompose forming volatile, condensable, non-condensable gases and char. The bio-oil which is obtained by pyrolysis has heating values less than half of the petroleum fuels. Thus the pyrolysis bio-oil needs to be upgraded by different processes such as hydro-processing, catalytic cracking etc. [24]

2.4 Pyrolysis types

The types of Pyrolysis are based on varying the process parameters such as heating rates, vapor residence time and temperature. [25, 26]. The different pyrolysis types is shown in Table 2.2

Table 2.2: Different pyrolysis types and operation conditions

Pyrolysis type	Heating rate(K/s)	Residence time	Temperature (Kelvin)	Target product
Slow Pyrolysis	0.1-1	5- 30 minutes	550-950	Char
Intermediate Pyrolysis	1-20	10-300 seconds	450-600	Liquid bio-fuel (bio-oil)
Fast Pyrolysis	10-200	2-10 seconds	850-1250	Liquid bio-fuel (bio-oil)
Flash Pyrolysis	Greater than 1000	Less than 1 second	1050-1300	Liquid bio-fuel (bio-oil)

2.4.1 Slow Pyrolysis:

Slow pyrolysis, also called as the conventional pyrolysis is the most common form of pyrolysis with very long residence time lasting up to days and lower operating temperatures [27]. Slow pyrolysis yields more charcoal. Park et al [28], conducted slow pyrolysis of rice straw over a range of temperatures (300-700) and analyzed the product yields. Results show that bio-char is

the majority of the product yield and the yield decreased as the temperature increased. With the focus on maximum yield of liquid products, slow pyrolysis is not suited.

2.4.2 Fast Pyrolysis

Fast pyrolysis, characterized by high heating rates and less residence also facilitates rapid cooling and separation. Fast pyrolysis has gathered much attention as the product yields more of bio-oil. This is because the residence time is less thus reduces the secondary cracking of the molecules which forms char and gases. [29]. Xue et al [30], conducted fast pyrolysis on oak wood and HDPE at temperature range of 525 to 675°C. Maximum pyrolysis oil was obtained at 625°C with 57% oil yield.

2.4.3 Intermediate Pyrolysis

Intermediate pyrolysis is the type of pyrolysis which is usually carried out in the conveyor reactor such as Auger or screw conveyor reactor. As the name suggests, the operating parameters are in between fast and slow pyrolysis. The products are more evenly distributed. [31, 32]. Yang et al [16] performed intermediate pyrolysis on two different biomass. Oil yields of 34.1% and 12 % (wt basis) with 30% char content and 20% gas yield respectively. The content is found to be 24 MJ/kg with product energy yield of 75%.

2.4.4 Flash pyrolysis

Flash pyrolysis is similar to fast pyrolysis. The only difference is that it takes place at very short residence time, typically < 0.5 seconds with temperatures in the range of 800-1000 °C. The product distribution is similar to what is obtained in fluidized bed. The particle size requirement is that, the feed should be in the form of dust.[12]

2.5 Parameters for Pyrolysis yield

The yield of pyrolysis products are invariably depends upon the operating conditions and the feed specifications. The various parameters affecting the yield of pyrolysis products are Temperature, Residence time, heating rate, flow rate of sweep gas, steam/biomass ratio.[12]

2.5.1 Effect of Temperature

The distribution of products is highly dependent on the reactor temperature. At lower temperatures the decomposition and primary reactions are initiated thus resulting in high char content. At higher temperatures, secondary reactions and cracking takes place resulting in high yield of gaseous products which in turn reduces the bio-oil yield. Thus an intermediate temperature based on the reactor configurations will have an optimum primary and secondary reaction taking place yielding high liquid products. [25]

2.5.2 Effect of residence time

Similar to temperature, residence time is also highly influential in the product distribution. Low residence time favors bio-oil yield as the vapors are quickly removed avoiding the secondary reactions. In contrast, high residence time results in high yield of gases and char.[25]

2.5.3 Effect of sweeping gas

Sweeping gas is used in pyrolysis to provide inert atmosphere and to inhibit secondary reactions. However, use of sweeping gas is found to reduce the yield of bio-char thus improving the product distribution. [33]

2.5.4 Effect of steam to biomass ratio

Use of steam improves the product quality and also favors vapors yield. Kantarelis et al [34] experimented pyrolysis of biomass using steam at various Steam to biomass ratio and found that the increasing the ratio decreases the char yield and increases the gaseous products.

2.5.5 Effect of heating rate

Heating rate is one of the fundamental parameters that define the different types of pyrolysis such fast, intermediate etc.heating rates affects favors bio-oil yield but the extent of its influence is less.[33].

2.6 Pyrolysis reactor configurations

Several types of reactor configuration are experimented and each reactor has its own advantages and disadvantages to overcome. Control of parameters such as temperature, residence time & yield as in the case of pyrolysis plays a major role in determining the ideal reactor for the process. The following are the different reactor configuration used for the pyrolysis.

2.6.1 Fluidized bed reactor

In fluidized bed the feed inlet is at the centre of the reactor and fluidizing gas is sent from the bottom. The residence time is controlled by adjusting the velocity of the fluidizing gas, which holds up the weight of the feed in the reactor. For this purpose, the size of the feed particle must be smaller (less than 2-3mm). To process large quantity of the feed, large size of the reactor is required with high fluidizing gas requirement. There is another type of Fluidized bed called as Circulating Fluidized bed reactor. The major difference is that the heat carrier along with the char and catalyst is sent to a regenerator and burnt to remove coke deposition and efficient circulation of heat carrier. Catalyst is usually loaded in the reactor for upgrading the pyrolysis vapors. The up-gradation is hindered by the solid deposition on the catalyst surface resulting in catalyst deactivation. The mineral deposit de-activates the catalyst permanently.[35].

2.6.2 Rotating cone

In this configuration, the feed along with the heat carrier such as sand is injected into the rotating cone which is heated. The pyrolysis is carried by contact of the feed material with the heated walls of the rotated cone. The heat carrier along with char is burnt off in the combustor where the heat carrier is heated partially. The heat carrier is then mixed with the fresh feed and the process is carried out. Rotating cone is a complex design with a rotating cone pyrolyzer, combustor and riser reactors.[36].

2.6.3 Ablative reactor

Ablative reactors operate in a way that is entirely different from the other reactors. The reactor walls are heated to high temperatures and the heat melts the biomass when pressed. The feed melts forming vapors which are then condensed. This process has the advantage of handling feeds with high particle size which can effectively reduce the cost of size reduction. Also there is

no gas requirement. However large scale handling of feed and char removal is a major problem.[22].

2.6.4 Entrained reactor

In entrained flow reactor, the feed is entrained by carrier gas and are fed through externally heated tubes. Pyrolysis occurs due to the high thermal conductivity of the carrier gas and also due to the contact with the tube walls. Similar to fluidized beds, Entrained flow reactors also requires smaller particle size of the feed.[36]

2.6.5 Auger reactor

Auger reactors or screw reactors are the simplest design among the reactors discussed. The feed is conveyed by the by a screw within a tubular reactor which is heated externally. Heat transfer occurs through the walls and also through the screw. This configuration offer better separation of vapor and char which aids further up-gradation process. Also the gas requirement is very little compared to the other reactors. Because of the continuous movement of feed, a smaller reactor can operate large volumes of feed, thus[4] reducing the capital cost. Ricardo Maximino evaluated the potential of biomass residues in a screw reactor. He obtained a bio-oil yield of 51%at 580°C.[17]. The major parameters for the selection of the reactor is shown in Table2.3

Table 2.3: Summary of different reactor configurations and their potential [36]

Reactor	Bio-oil yield(wt%)	Complexity	Feed size criteria	Inert gas usage	Reactor size	Scale up
Fluidized Bed	75	High	High	High	Medium	Easy
Rotating cone	70	High	High	Low	Medium	Medium
Entrained flow	60	Medium	High	High	Medium	Easy
Auger or screw reactor	65	Medium	Medium	Low	Low	Medium
Ablative	75	High	Low	Low	Low	Difficult

2.7 Feedstock

Feedstock availability is an important concern for the sustainable yield of bio-fuels. The varied availability of the feedstock poses challenges on the operational of the bio-refineries. The physical properties and compositions of the biomass feedstock vary largely and a system that can adapt to process these different feed is difficult. The raw materials needed for the process can be classified as

- I. First generation feedstock**
- II. Second generation feedstock**
- III. Third generation feedstock**

The first generation feedstock consists of crops which are edible such as corn, soybean, wheat, rice etc. edible oil seed crops such as coconut, palmseed, rapeseed, sun flower are also considered as First generation feedstock for the production of bio-diesel.

The Second generation comprises of non-edible crops such as Jatropha, Karanja & Pongamia and also the residues of agriculture and forestry wastes. Grasses, oil crops, algae, woody crops are few major diversifications of second generation feedstock.

The third generation crops are bacteria and algae which can be used as feedstock due to high protein, carbohydrate and lipid contents.

Biomass feedstock can also be classified based on the origin of these crops [36]

Agricultural crops

These are crops originated by agricultural means such as rice, wheat etc and their corresponding residues.

Bio-renewable wastes

Organic wastes, municipal wastes, wood wastes etc.

Energy crops:

These are crops for generation of energy. Jatropha, karanja etc are some of the widely used.

Bio-organic sources

Biological sources such as algae, mosses, lichens etc.

Biomass from edible sources are often used as domestic fuel which are directly burned to produce fuel, used as cattle feed and also sometimes are discarded as waste. The non-edible sources are usually as manure for improving the soil fertility.

For the cultivation of crops for the purpose of energy generation, in order to provide continuous supply of raw material, the crop should have (1) low gestation, ability to grow in different climatic conditions and extreme environments with minimal consumption of resources such as water.

Table 2.4: A brief summary of Indian agriculture status of a few cultivations.[12]

Specifications	Indian scenario	World scenario	India's contribution(%)
Total arable land (Mha)	159	1411	11.3
Crop production (Million Tonnes)			
1.Wheat	86	701	12.3
2.Rice	157	722	21.7
3.Rapeseed	8.1	59	13.7
4.Sugarcane	342	1800	19.0

As mentioned earlier, physical properties and composition of the feedstock plays a vital role in the selection of process and yields. The various parameters that are looked upon the feedstock are proximate analysis of contents such as Volatile matter, ash content, moisture and fixed carbon. Table: 2.5 provide a detailed description on the contents of a few biomasses.

Table 2.5: A briefing of the above parameters in different biomass.[7]

Biomass	Volatile matter	Fixed carbon	Ash	Carbon	Hydrogen	Nitrogen	Oxygen
Oak wood	76.8	14.2	0.2	45.4	5.0	0.3	41.5
Wheat straw	74.2	13.0	6.9	52.9	6.3	0.4	40.4
Jatropha seed cake	43.6	4.4	-	49.3	6.1	3.4	41.2
Neem seed	71	8.1	4.9	38.4	8.3	7.5	45.1
Rice shell	63.4	15.9	16.7	39.7	4.0	0.5	34.1
Corn cob	80.7	7.6	2.1	42.9	6.4	0.6	45.5

2.7.1 Jatropha as feedstock

Jatropha has gathered much attention of the researches for the bio-fuel production. Jatropha is a non-edible plant, hence, prevents the necessity to compromise on the food crops. Jatropha has high free fatty acid contents which can be used to synthesize bio-diesel by Trans-Esterification with alcohol. Jatropha is considered magical as almost the whole plants valorized in different process to form different types of fuels for varied purpose. (Refer fig2.2)

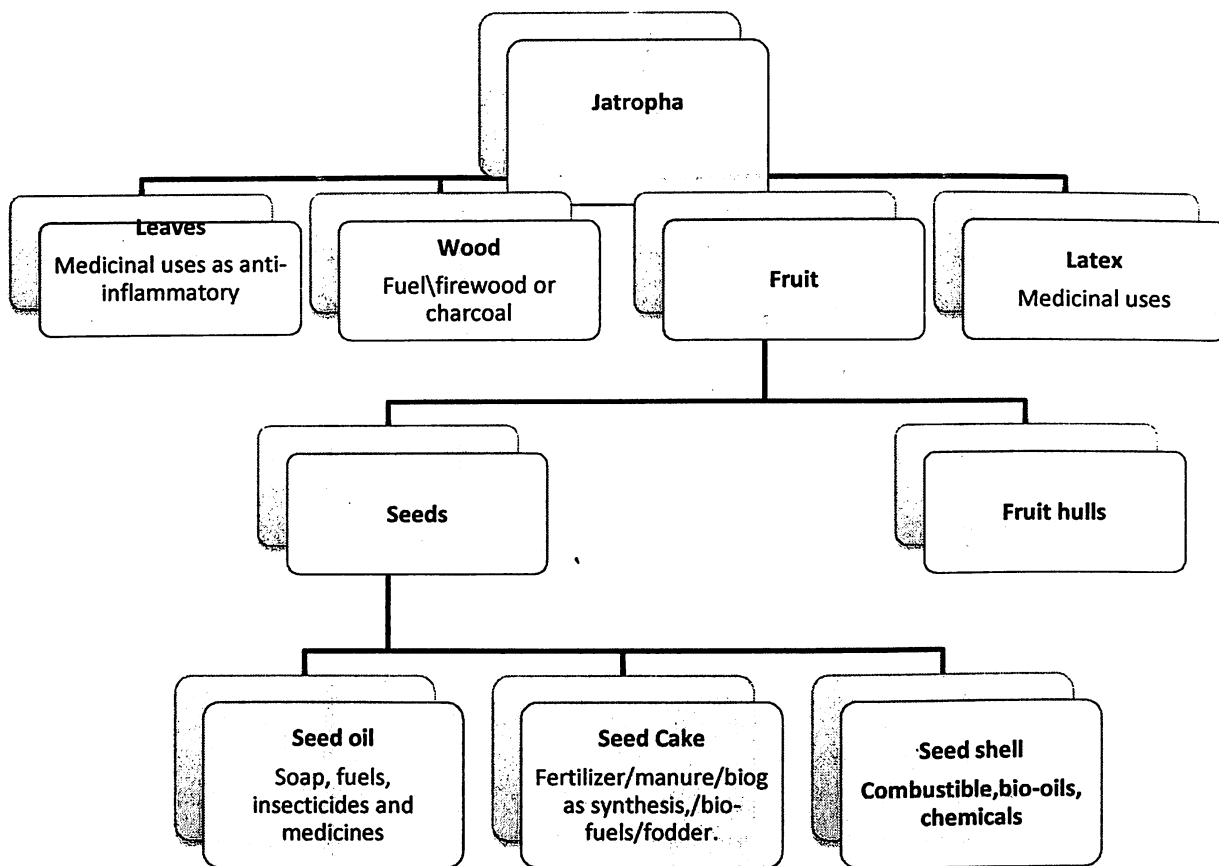


Fig 2.2: valorization of different parts of the Jatropha plant[37]

2.7.2 Jatropha seed cake

Jatropha seed cake also called as de-oiled cake is the residue obtained after the mechanical extraction of oil from the seeds. On extraction, about 70% of Jatropha seeds are obtained as seed cake. [15]. Just the way mentioned above the seed cake are rich in carbon and hydrogen, hence, can be valorized to useful hydrocarbon fuels and chemicals. Vipankumarsohpal and Rajesh kumar Sharma carried out slow pyrolysis of Jatropha seed cake resulting in 18.42 wt % bio-oil yield at a pyrolysis temperature of 500°C.[23]

2.8 Energy analysis of biomass

Analysis of energy is necessary in order to determine the efficiency and the economics of the process. This is determined by calculating Energy Returned On Investment (EROI) which is the ratio of output energy relative to the process energy. David Pimentel and Tad W.Patzek analyzed ethanol production from different biomass and found that Ethanol production required about 50% more fossil energy.[24]

2.9 Catalyst for up-gradation of pyrolysis oils

Catalytic biomass pyrolysis is a complex reaction process that includes numerous chemical reactions such decomposition, cracking etc. Research on catalysts for use in this process is often carried out specifically in relation to the pyrolyzer design or the biomass feed type. Pyrolyzers are classified depending on their design. Designing an optimum catalyst for upgradation of pyrolysis oil requires additional insights into pyrolysis kinetics and reaction mechanisms to predict the end reaction product composition distribution.

2.9.1 Types of catalysts currently used for the upgradation.

2.9.1.1 Zeolites

Zeolites are crystalline Alumino-silicates with a highly ordered crystalline structure. Cavities of a definite size are formed in the rigid, three-dimensional network composed of SiO₄ and AlO₄ tetrahedral. The lattice contains cavities of varying diameters, depending on the type of zeolite. Zeolite catalysts can be regenerated readily with air merely by burning off the coke, which is frequently responsible for their de-activation; after this treatment they generally regain their initial activity. Bo Zhang et al.(2015)[38], carried out Catalytic upgrading of vapors of fast pyrolysed corn Stover over fresh, spent, and regenerated ZSM-5 Zeolites (referred to as FZ, SZ and RZ, respectively) using quantitative pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) at 450°C and N₂ flow rate of 300ml/min. , FZ has the highest value, and SZ has the lowest value (FZ > RZ > SZ). The SZ and RZ lowered the total product yields compared to FZ (yield of FZ > RZ > SZ). The coke yields of these zeolites followed the order of FZ > RZ > SZ. Besides, RZ slightly promoted the production of phenols, whereas SZ reduced the relative content of phenols dramatically.

2.9.1.2 Raney Nickel

It is a fine-grained solid composed mostly of nickel derived from a nickel-aluminum alloy. Varieties of grades are known for this substance, but most are gray solids. Some are pyrophoric; most are used as air-stable slurries. Raney nickel is used as a reagent and as a catalyst in organic chemistry. Fré'dericVoge et al(2005)[39] studied the Production of synthetic natural gas (SNG) from wood by a catalytic hydrothermal process in a laboratory batch reactor suitable for high feed concentrations (10-30 wt %) at 300- 410 °C and 12-34 MPa with Raney nickel as the catalyst. A maximum methane yield of 0.33 (g of CH₄)/(g of wood) was obtained, corresponding to the thermodynamic equilibrium yield

2.9.1.3 Metal/ Metal Oxide based/Supported Catalyst

Varin Han-u-domlaryos et al [40] improved the quality of oil palm shell (OPS)-derived pyrolysis oil containing high amount of oxygenated compounds (molar oxygen/carbon (O/C) ratio = 1.09) and total acid number (TAN) (151 mg potassium hydroxide (KOH)/g) via catalytic de-oxygenation using nickel–molybdenum sulfide supported on gamma-alumina (NiMoS/c-Al₂O₃) in a fixed-bed reactor. the catalytic de-oxygenation using 0.50–1.00 (by wt) of catalyst fraction at 300–450 C under N₂ atmosphere yielded deoxygenated bio-oil with lower molar O/C ratio and TAN value of 0.11–0.29 and 43– 77 mg KOH/g, respectively. Gas chromatography–mass spectrometry (GC–MS) analysis revealed that the oxygenated compounds in the crude bio-oil were mainly converted as phenol and its derivatives. The results also showed that the major component in the deoxygenated bio-oil was in the range of naphtha fraction (ca. 40 wt%).

2.10 Motivation for the work:

The main motivation of the work is to valorize the residual Jatropha seed and also to study the performance of Rotary Tubular Conveyor reactor in processing the biomass feed, the effect of using different media for the process such as Nitrogen and steam and the process feasibility so as to improve the design and the process based on the study.

2.11 Objective

To valorize residual Jatropha seed cake by intermediate pyrolysis in a Rotary Tubular Conveyor reactor and observe the yields by varying operating parameters.

Analyse the products of the pyrolysis using FTIR, GC-MS, CHNO etc.

To carry out energy analysis by determining the energy involved in the process.

3. Experimental study of Intermediate Pyrolysis in Tubular Conveyor reactor

3.1 Analysis of Jatropha seed cake

Jatropha seed cake is obtained after the Jatropha oil is mechanically extracted from by the extractor. The seed cake is dried and crushed by vertical shaft impactor crusher. The size of the particles obtained is of 200 microns.

3.2 Thermo-gravimetric analysis of Jatropha seed cake

Thermo-gravimetric analysis of Jatropha seed cake is carried out to determine the decomposition characteristics of the feed characterized by the mass loss of the sample with respect to increase in temperature. The analysis is carried out in a Thermo-gravimetric analyzer in Nitrogen atmosphere with Nitrogen as sweep gas. Three different heating rates are analyzed (i.e. 5, 10 and 20°C/min). The plots are shown in Fig 3.1

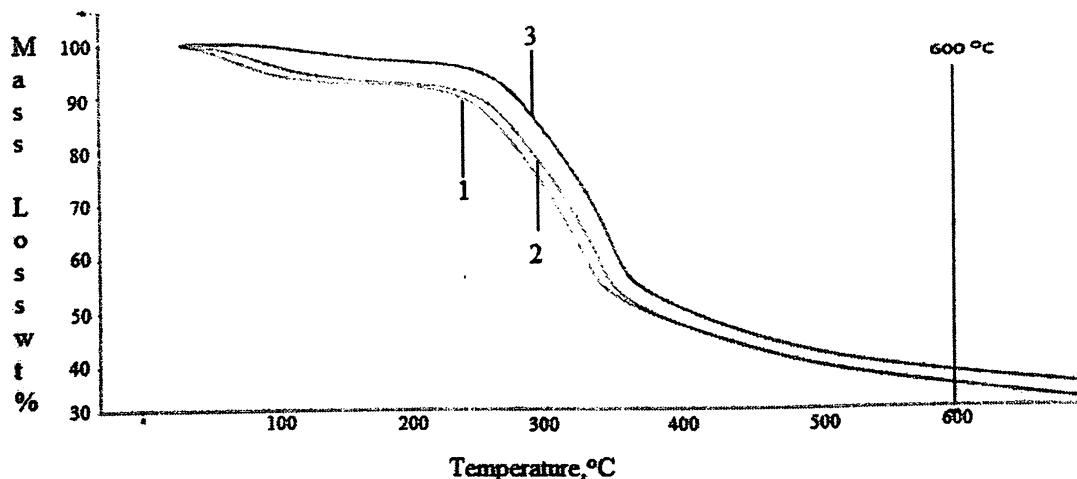


Fig 3.1: TGA curves of Jatropha seed cake at 5°C (1), 10°C (2) and 20°C (3).

From the Fig.3.1 it is seen that the drastic decomposition begins to occur between the temperature range around 200-400 which was reported as the range of decomposition of cellulose. As the temperature approaches beyond 600°C, the mass loss is fairly less inferring that the complete decomposition of the sample. It can also be inferred that the better decomposition

occurs at lower heating rates. However, heating rates must be high with short residence time for higher bio-oil yield.

3.3 Experimental Setup

The research scale rotary tubular helical coil pyrolyzer set-up was designed and fabricated (MOC: SS 316L) as per the temperature and pressure requirements (refer Fig 3.2). All necessary accessories including helical coil conveyor, vaporizer and feed pump for superheated steam generator, solid char collection bottle, gas liquid separator were also integrated with the experimental system for pyrolysis.

For experiments with Nitrogen as sweep gas, Nitrogen flow rate of 2000ml/min is provided to aid the transport of the biomass through the reactor. For experiments with steam, De-mineralized water is pumped at specific flow rate through a vaporizer to generate superheated steam at 250°C and 1 bar. The superheated steam is then fed to the rotary tubular conveyor reactor. Pulverized biomass is fed to the pyrolyzer from a hopper. The conveyor was fixed inside the pyrolyzer tube. Rotation of the pyrolyzer tube can be adjusted with the help of a motor. The residence time of the biomass can be varied with the help of motor rpm control. The temperature of the reactor tube is maintained by means of an external heater mounted over the tube in such a way that the tube can rotate freely inside the furnace. The furnace is equipped with three zone control and tilting device. There are three equidistant thermocouples attached to the furnace, which measure the skin temperatures of the tube. The downstream of the pyrolyzer tube is fitted with a char collection bottle immediately at the end of the reactor and a gas-liquid separator pot for separation of liquids from the gasified vapor. The separator pot is equipped with a fine filter in its dip leg, which can be easily dismantled for removal of solid deposition and clean-up. This helps in separation of fine particles from the product gas under hot condition. The condensable gases are condensed using condenser and chiller. The uncondensed product gas is driven out by a vacuum pump and the product gas from vacuum pump goes to the online gas analyzer which is used to measure the composition of gases (CO, CO₂ and H₂). Wet gas meter was used to measure the flow rate of gases.

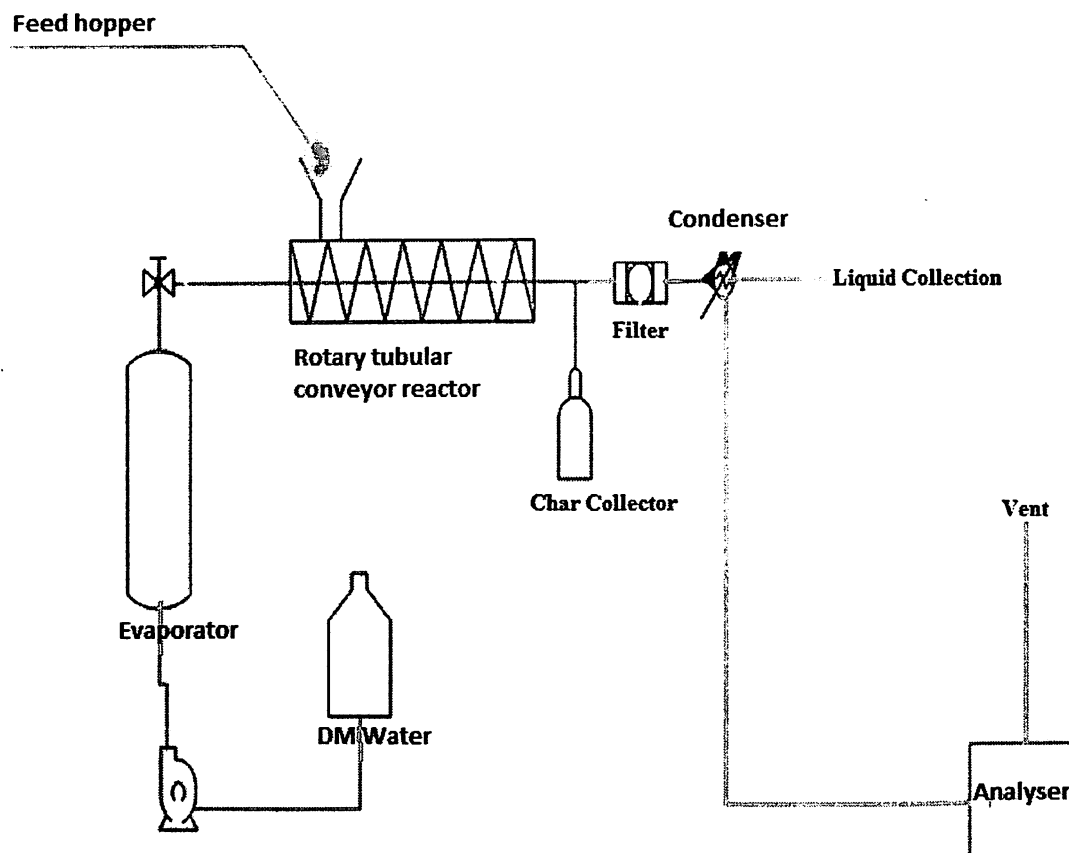


Fig 3.2: Process flow diagram of the pilot plant facility

3.4 Experimental procedure

Before the start of the experiment, temperature of the reactor was set at the desired set point by programming the system with desired heating time. Pyrolysis was carried out with a flow rate of 1kg/hr for 10 minutes. Nitrogen flow rate was maintained at 2 liter/min to propel the feed towards the conveyor. The feed was manually fed from the top. In order to prevent the supply of oxygen in the form of air from getting into contact, a double holed closure was placed on top of the hopper. Feed was sent through one of the hole and mild flow nitrogen gas is purged through the other hole. The rotation of the conveyor is controlled by tuner. The conveyor has 36 turnings. This means that if the rotation is set at 36 rpm(rotations per minute) then the residence time of biomass inside the reactor is 1 minute. The gas sample was collected from through a sample holder and the amount of gas collected is measured by bypassing to a wet gas meter. After the experiment is completed, the reactor is allowed to cool down. Liquid products are collected from

the condenser and char is collected from the char collector. The reactor is then cleaned for the next experiment.

3.5 Material balance for the process

For material balance of the process, flow rate of 1kg/hr is considered as basis. The reaction is carried out for 10 minutes and the sweep gas is calculated for 10 minutes. The Nitrogen is assumed to be inert and is subtracted from the outlet flow rate as well. Material balance for one of the experiment is shown below (Table 3.1).

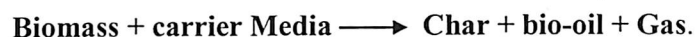


Table 3.1: Material balance of the process

INPUT			OUTPUT			
biomass(kg)	sweep gas(kg)	Total(kg)	solids	liquid	Gas	Total
0.16	0.0234	0.1834	0.075	0.0365	0.057	0.171

The total mass ratio of output by input gives efficiency as 91.96%. The loss occurred is due sampling taken for gas components and also incomplete removal of products from the reactor.

4.EXPERIMENTAL RESULTS AND ANALYSIS

4.1 Effect of residence time on the product yield

The first set of experiments was carried out at 600°C at different biomass residence times from 4 minutes to 0.8 minutes. The results are as follows.(refer Table 4.1)

Table 4.1: variation of product yields at different residence times.

Time(seconds)	Solid (wt%)	Liquid (wt%)	Gas (wt%)
0.8	22	34.6	43.4
1	26.8	27.8	45.4
2	34.2	19.8	46
4	39.3	13	47.7

As the residence time increases, the char and gas yields increases. The reason is that higher residence time aids the secondary reactions to take place which leads to the formation of gases and char.(refer Fig4.1) This is also supported by the decrease in bio-oil yield with increasing residence time. This phenomenon conforms well to literature as suggested by Tao Kan et al [9]. Thus in the current work the least residence time in the experiment is taken as the optimum residence time. Experiment with lesser residence time is limited by the maximum rotation speed of the reactor. Maximum yield of char is obtained at the maximum residence time and maximum bio-oil yield is obtained at the least residence time, which emphasize on the requirement of lesser residence time for the production of more liquid products.

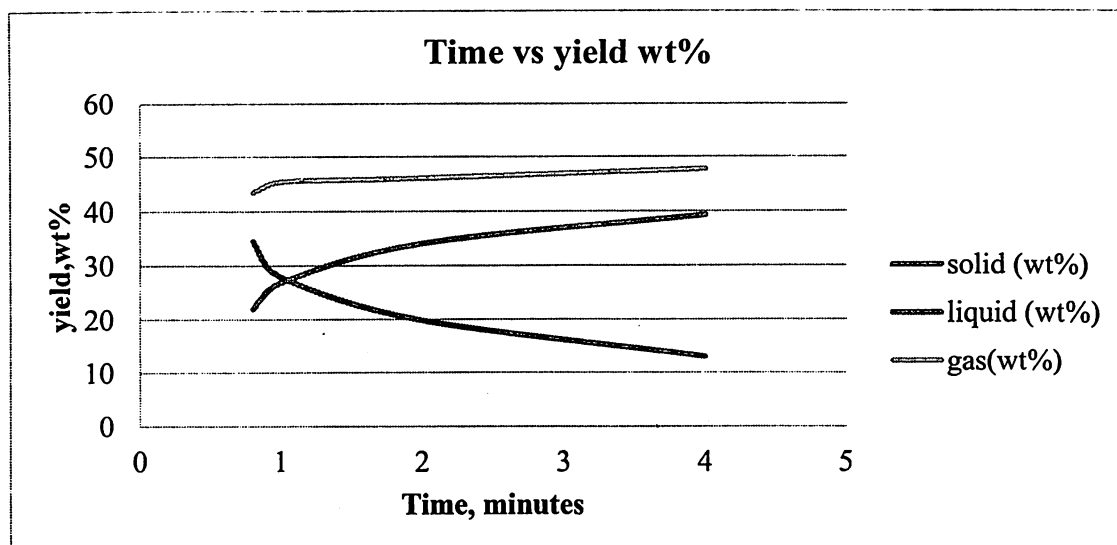


Fig 4.1: distribution of product yields at 600°C at different residence times

4.2 Effect of temperature on yield

Second set of experiments is carried out at three different temperatures (500,550 and 600°C) using Nitrogen as sweeping gas. The biomass residence time is kept constant based on the previous experiments for maximum yield of bio-oil (48 seconds). Similarly the experiment is repeated by using steam as carrier. The char obtained is then analyzed for C, H, N, O, S content. The bio-oil is analyzed with GC-MS and FT-IR to identify the compounds and C,H,N,O,S analysis for determining the calorific value. The Temperature is observed to have significant influence on the distribution of products. The peak bio-oil yield of 32% (approx) was obtained at 550°C and on further increase of temperature, the yield has decreased. Char in contrast decreases steadily with the increase in temperature. The gas flow increases steadily as the temperature is increased (refer Table 4.2 and Fig.4.2) This conforms to the trend found in the literature as wellputun et al [41].

Table 4.2: Product yields at different temperatures (using Nitrogen)

Temp	Solid (wt%)	Liquid (wt%)	Gas (wt%)
500	51.2	25.1	23.4
550	33.8	35.2	30.8
600	25.8	33.3	40.8

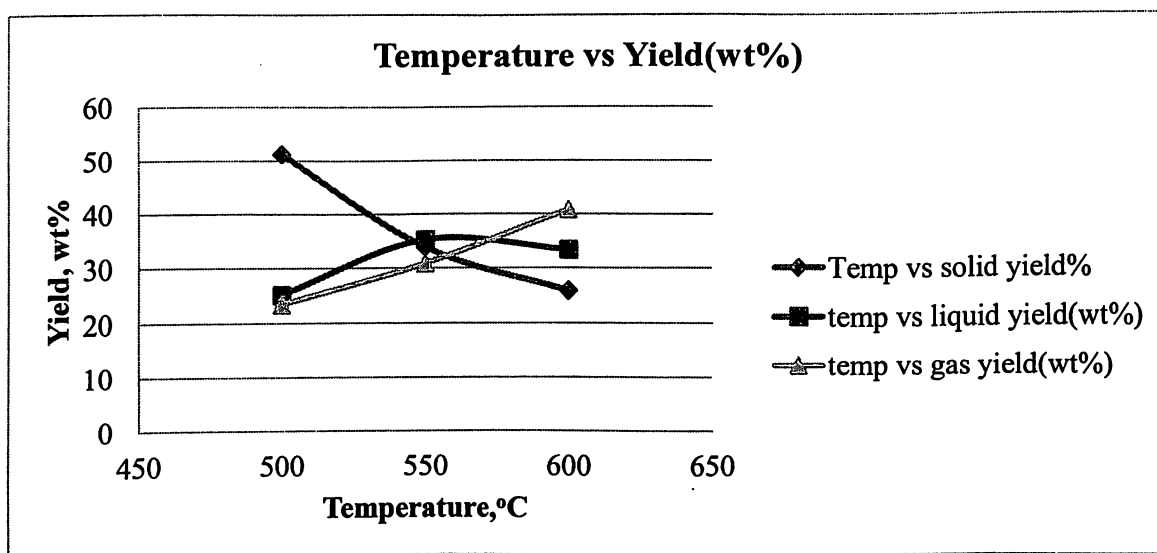


Figure 4.2: distribution of product yields at different temperatures using Nitrogen

Table 4.3 : yields at different temperatures (using Steam)

Temp	Solid (wt%)	Liquid wt(%)	Gas wt(%)
500	16.5	34.3	49.0
550	12.1	36.5	51.3
600	10.4	32.7	56.8

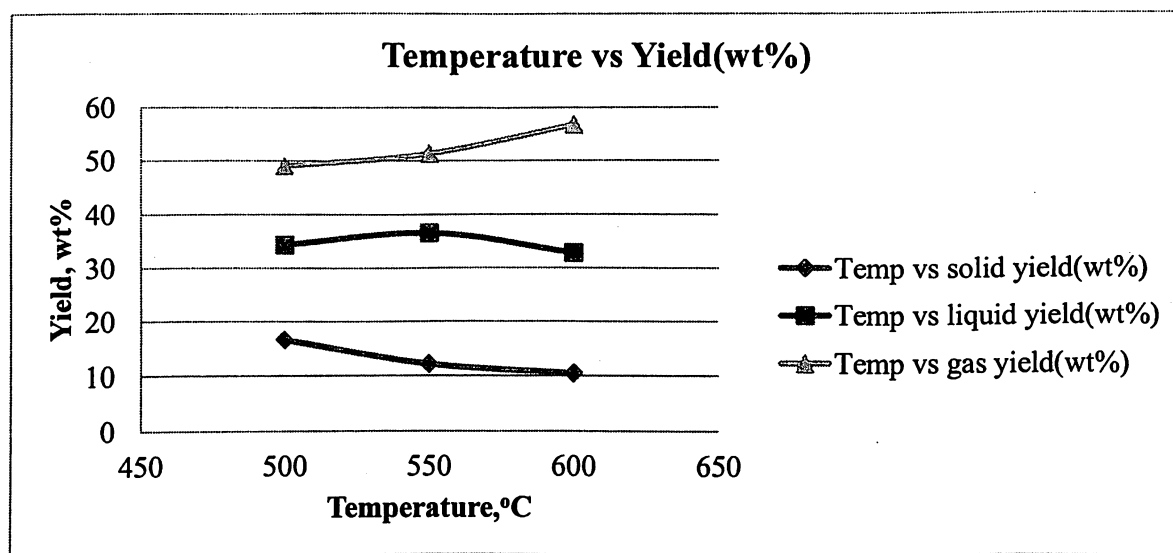


Fig 4.3: distribution of product yields at different temperature using steam

Similar to pyrolysis using Nitrogen, Steam also follows a similar trend of yield. However, the char yield is much lesser when compared to the pyrolysis using Nitrogen (Refer Table 4.3). Maximum bio-oil yield of 36.5% is obtained at 550°C.(refer fig 4.3) Considerable in gas yield was also observed.

4.3 Nitrogen versus Steam

A comparative study on the yields pyrolysis of Jatropha seed cake using steam and Nitrogen is carried out. Though both follow similar trends of product yields, there is difference in the yield of products.

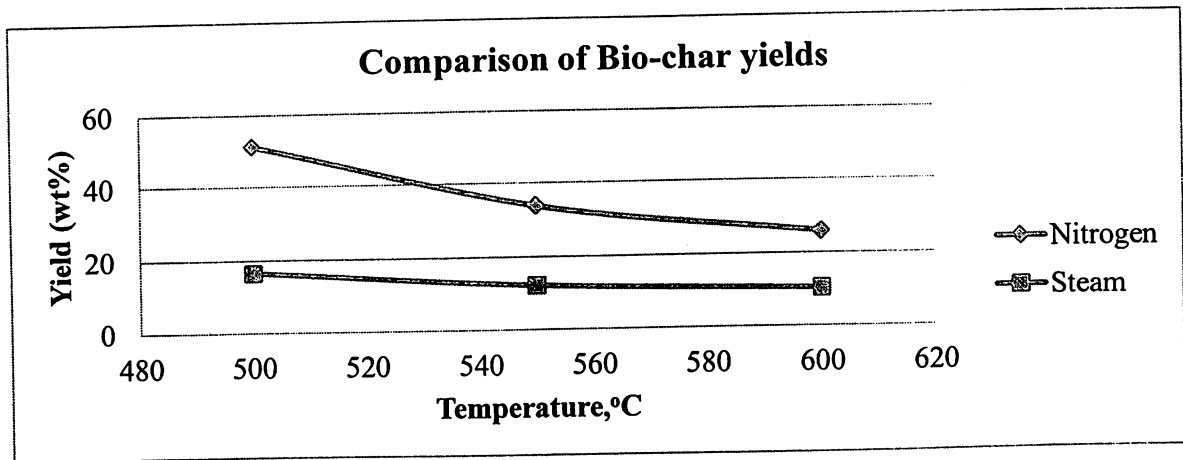


Fig 4.4: comparison of bio-char yield

As shown in fig 4.4, the use of steam inhibits char formation thus generates less bio-char.

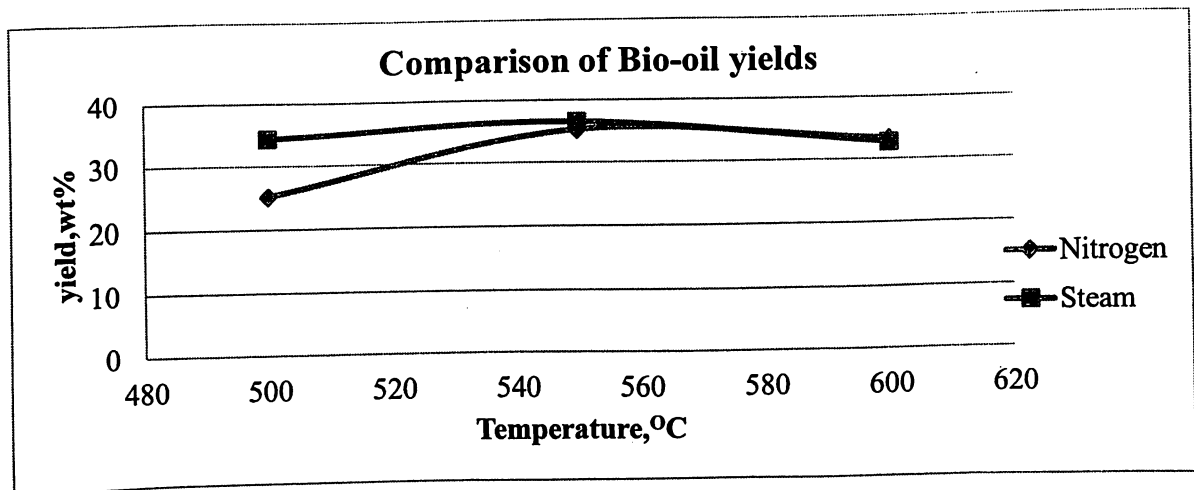


Fig 4.5: comparison of bio-oil yield

Bio-oil has a peak yield of 36.5% using steam as Carrying media. Though the peak yield of both is similar, difference occurs in the quality of the bio-oil (Refer Fig: 4.5)

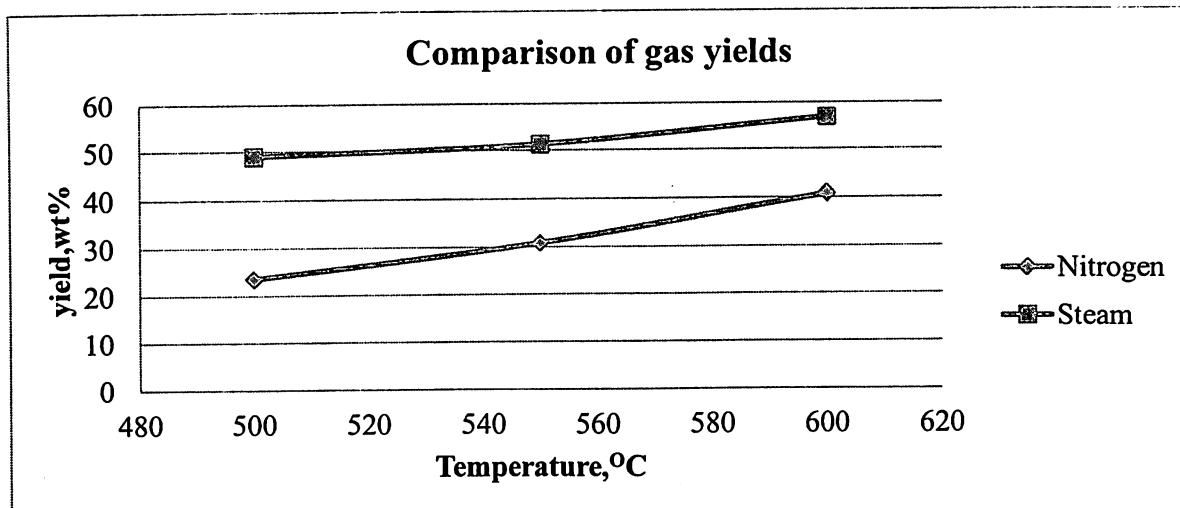


Fig 4.6: Comparison of gas yield

Steam also enhances the gas yields, which results in lower char yields as well (From Fig4.6). From the above figures it is pretty much evident that Steam enhanced Intermediate pyrolysis yields more valuable products.

4.4 Characteristics of products

4.4.1 Bio-char

Bio-char obtained is black, coarse material with smoky smell. The char is scraped off the reactor and analysis of elemental contents is done. The bio-char from obtained from Nitrogen assisted process is coarse and sometimes sticky while removal. Whereas, Bio-char obtained from steam assisted process was relatively fine and was easy to remove off the reactor.

4.4.2 Bio-oil

The liquid product obtained is dark brown in color and has an intolerable burnt odor. The liquid also contained minor quantities of char particles which are filtered using filter-paper. The liquid product was collected and distilled in rotary evaporator to remove the moisture. Two different temperature cuts were made at 110°C and 250°C respectively. The initial boiling point of the bio-oil was 100°C. The 110-250°C cut was considered for further analysis. There was presence of black sticky residue leftover which contains carbon and heavy tar which was discarded.(refer Fig:4.7)

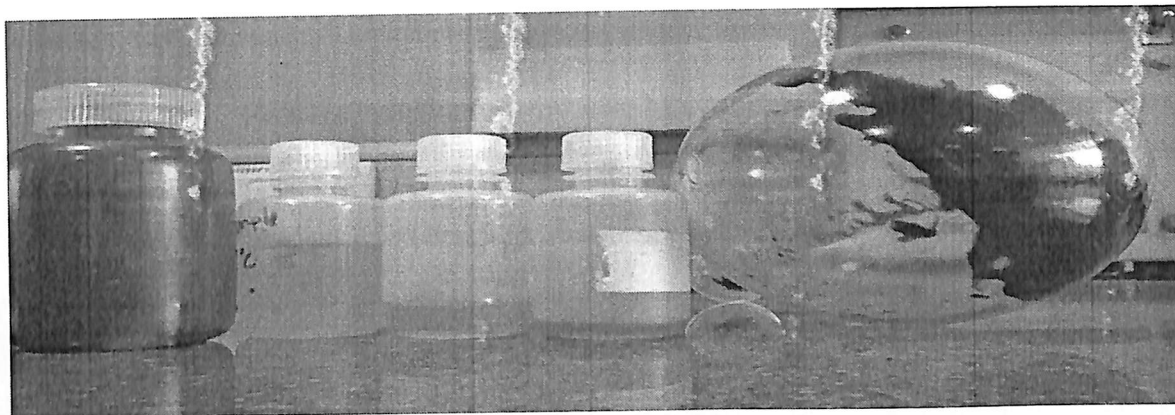


Fig 4.7: Bio-oil sample obtained on pyrolysis and the cut fractions.

4.4.2.1 FTIR analysis

Fourier Transform Infrared spectroscopy is an effective analysis to predict and determine the functional group associated with the sample. Since pyrolysis is a black box process, where the material is thermally decomposed to breakdown the different constituents of biomass, the product contents are not well known. FTIR provided a broad idea of the various functional groups of compounds present in the bio-oil distillate. For the analysis Perkin-Elmer –Frontier was used.

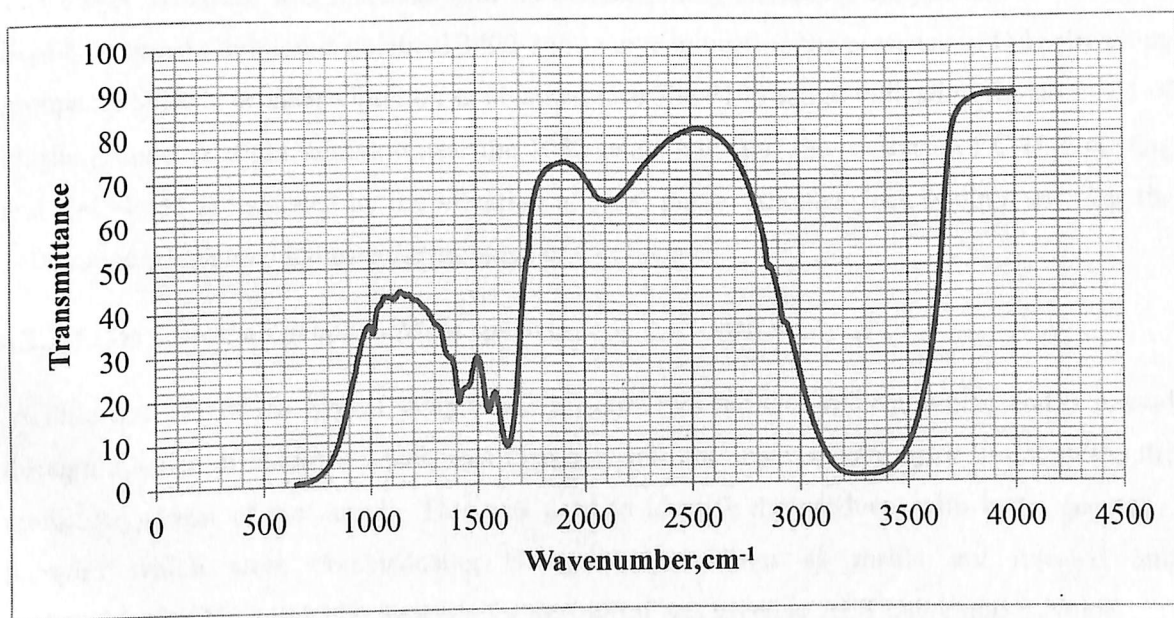


Fig 4.8: FT-IR analysis of bio-oil

FT-IR aids in identifying the possible compounds by identifying the functional groups using the characteristic wave number.

Table 4.4: Important IR absorbance frequencies [42]

Wave number (cm^{-1})	Vibrations
2960-2850	Sp^3 C-H
3100-3020	Sp^2 C-H
1850-1630	C=O
3650-3400	O-H
2000-1600	Aromatics
3400-3250	N-H

The FT-IR spectrum was matched with its corresponding stretching frequencies as shown in Fig 4.8. A broad vibration is obtained 3400-3650 range indicating the presence of O-H stretching groups. A slightly broader vibration is obtained near the 2100 range indicating the presence of Nitrile groups. A slight vibration near the 1050 range indicates the presence of C-O stretching and C=O bond is indicated by the vibration at 1600 range. Another peak is observed near the 1600 range which may indicate the presence of C=C bonds.

4.2.2.2 Gas Chromatography –Mass spectroscopy (GC-MS) analysis

A little quantity of the bio-oil sample was injected into the GC-MS equipment and is passed through a series of columns which was then sent into the mass spectrometer to determine the molecular weight of the sample. This was used to identify the products with better accuracy. Samples which were obtained using Nitrogen and Steam as media are injected and analyzed. (refer Fig 4.9-4.12). Analysis for the bio-oil was given to AES Laboratories, Noida.

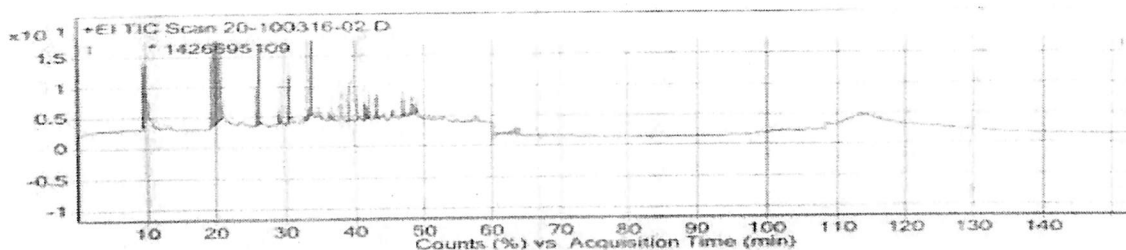


Fig 4.9: GC of Jatropha seed cake (using Nitrogen at 550°C)

Table 4.5: Compounds identified in bio-oil using Nitrogen at 550°C

Compounds	Weight %	Compounds	Weight %
9-Hexadecenoic acid	0.62	Benzeneethanamine,2,5-difluoro-.beta.,3,4-trihydroxy-N-methyl-	0.99
Acetic acid	73.43	Methyl N-[N-benzyloxycarbonyl-beta-l-aspartyl]-beta-d-glucosaminide	1.09
Propanoic acid	6.03	4-Amino-1-.beta.-d-robofuranosylpyrazolo[3,4-d]pyrimidine 5'-phosphate	0.27
L-Gala-1-ido-Octose	1.42	Acetic acid,2-[2-methyl-4-(1-piperidylmethyl)-1,3-dioxolan-2-yl]-ethyl ester	2.25
Pentanoic acid	1.82	4-Pyridinamine,2,6-dimethyl-	0.60
Pentanoic acid,3-methyl-	2.82	4-Aminobutyramide,N-methyl-N-[4-(1-pyrrolidinyl)-2-butynyl]-N'-aminoacetyl	1.28
2-Furanmethanol	4.75	5-[2-(4,5,5-Trimethyl-cyclopent-1-enyl)ethylidene]pyrimidine-2,4,6(1H,3H,5H)-trioone,	0.494
11-Hexadecyn-1-ol	0.52	Spirol[4.5]dec-6-en-8-one,1,7-dimethyl-4-(1-methylethyl)-	0.376
Phenol	1.18		

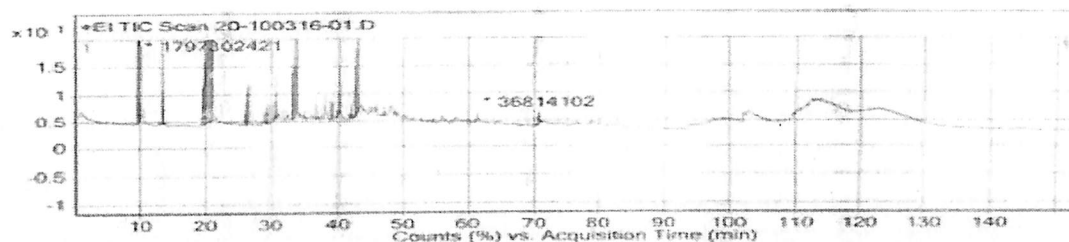


Fig 4.10: GC of Jatropha seed cake (using Nitrogen at 600°C)

Table 4.6: Compounds identified in bio-oil using Nitrogen at 600°C

Compounds	Weight %	Compounds	Weight %
(2-Aziridinylethyl)Amine	22.3	2-Furanmethanol	2.46
2-Heptanol	3.6	Tetraacetyl-d-xylonic nitrile	0.119
Acetic acid	51.01	2-Isobutyl-3-methylpyrazine	0.404
Cyclopropanetetradecanoicacid,2-octyl-,methyl ester	3.92	17-octadecynoic acid	0.456
9,12,15-octadecatrienoicacid,2,3-dihydroxypropyl ester	0.188	Phenyl-beta-D-glucoside	0.918
[1,1-Bicyclopropyl]-2-octanoic acid,20hexyl.methyl ester	0.873	Deoxyspergualin	0.371
D-mannose	1.976	Androsta-1,4-dien-3-one,17-hydroxy-17-methyl-	0.289
8,11,14-Eicosatrinoic acid,methyl ester	0.145	D-glycero-d-ido-heptose	7.62
Pentanoic acid,3 Methyl-	1.79	N,N-Bis(carbobenzyloxy)-lysine methyl (ester)	0.422

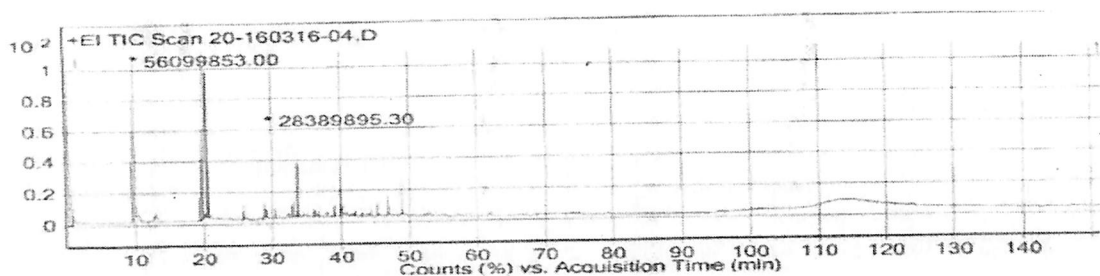


Fig 4.11: GC of Jatropha seed cake (using steam at 550°C)

Table 4.7: Compounds identified in bio-oil using Steam at 550°C

Compounds	Weight %	Compounds	Weight %
Dimethylamine	13.4	d-Glycero-d-ido-heptose	0.89
Ammonium acetate	34.5	17-Octadecynoic acid	0.70
Ethyl acetate	18.7	5,7-Octadien-3-ol,2,4,4,7-tetramethyl-,(E)-	0.47
Phenol	9.48	Ethanol,2-nitro-,propionate	2.80
6-nonynoic acid	1.50	2-Isobutyl-3-methylpyrazine	1.35
Butanoic acid,3-methyl-	01.33	N-.alpha.,N-.omega,-Di-cbz-L-arginine	0.58
Hexanoic acid,2-methyl-	0.58	Phenol,3-methyl-	0.40
2-Furanmethanol	5.63	P-cresol	0.75
Mequinol	4.51	11-(2-Cyclopenten-1-yl)undecanoicacid,(+)-	0.77
2,2-Dimethyl-3-vinyl-bicyclo[2,2,1]Heptane	1.45		

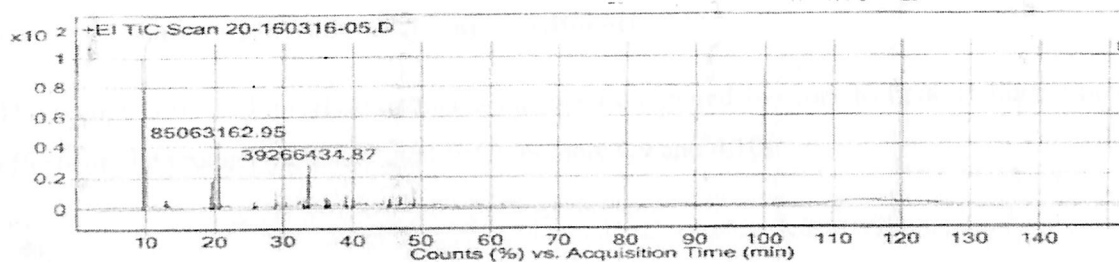


Fig 4.12: GC of Jatropha seed cake(using steam at 600°C)

Table 4.8: Compounds identified in bio-oil using Steam at 600°C

Compounds	Weight %	Compounds	Weight %
Dimethylamine	27.04	Furan,2-ethyl-yl-5-meth	2.15
Ammonium acetate	1.66	2-Isobutyl-3-methylpyrazine	1.62
Ethyl acetate	14.44	6-Methyl-bicyclo-4.2.0]octan-7-one	1.64
Ethanol,2-nitro-,propionate(ester)	15.85	Phenol	2.97
2-Cyclopentene-1-Methanol	2.15	2-pyridinemethanamine,N-methyl-	6.44
Butanoic acid,3-methyl-	3.066	2-Cyclopenten-1-one,2,3-dimethyl-	1.67
Hexanoic acid,2-methyl-	1.59	Phenol,2-methyl-	2.21
3-Furanmethanol	0.89	P-cresol	2.71
2,4-Dimethyl furan	7.31	Mequinol	4.51

4.4.2.2.1 Comparative study of bio-oil constituents.

The composition of bio-oil components has been compared in order to understand the process effects on the product yield and quality.(refer table 4.9 and 4.10)

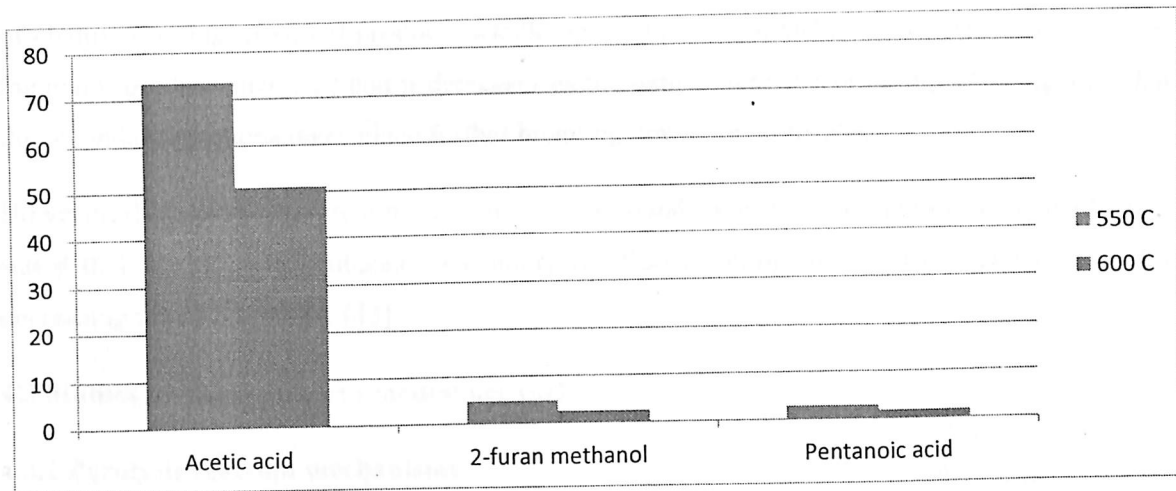


Fig 4.13: Comparison of yields of major compounds of bio-oil using Nitrogen 550 and 600°C

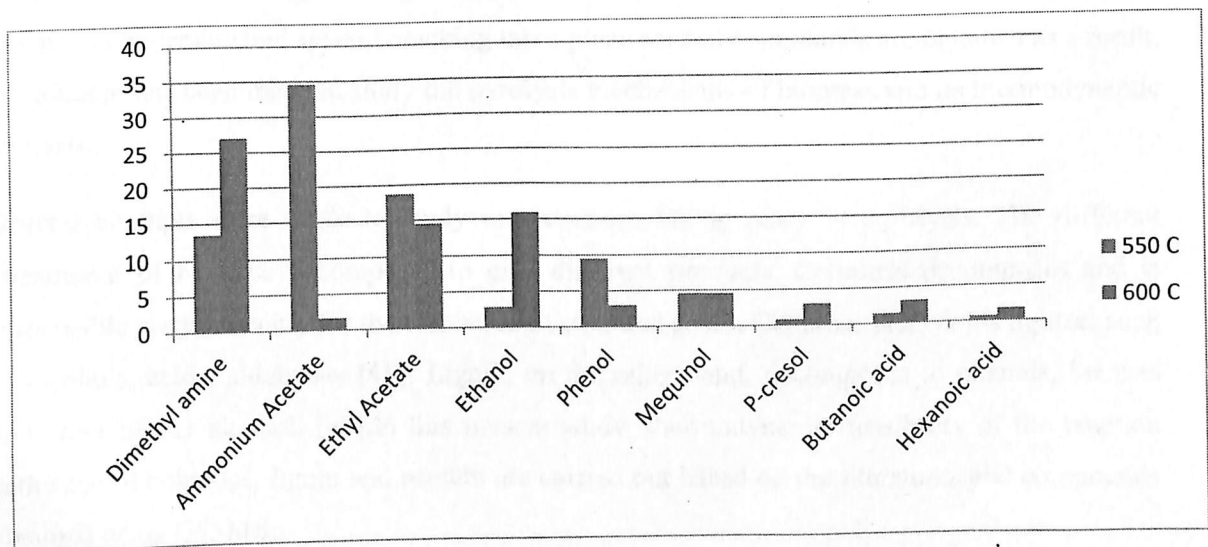


Fig 4.14: Comparison of yields of major compounds of bio-oil using Nitrogen 550 and 600°C

4.4.2.2.2 Inferences from GC-MS

The GC-MS of bio-oil using Nitrogen follows a less structured pathway with irregular breakage of chains resulting in varied products which cannot be compared (Fig 4.13). Also acetic acid is the major product identified and it decreases as the temperature is increasing. This suggests that the secondary reactions takes place further breaking down the molecules.

However, the bio-oil using steam forms many compounds which are comparable (Fig: 4.14). It is stated that use of steam enhances secondary reaction resulting in high CO and CO₂, thereby decreasing the char content. [43]

4.3 Studies on the pyrolysis reaction network.

4.3.1 Pyrolysis reaction mechanisms

The mechanism of pyrolysis is a black box [44]. Many reactions takes place simultaneously or in series. To say a few, the reactions include Dehydration Dehydroxylation, dehydrogenation, cracking, steam reforming, water gas shift reaction, Boudard reactions etc. Since it is a thermo-chemical conversion and several cracking takes place several compounds are obtained as a result. An attempt has been made to study the pyrolysis mechanisms of biomass and its thermodynamic analysis.

Several attempts were made to study the reactions taking place in pyrolysis. The different constituent of biomass decomposes to give different products. Cellulose decomposes and is responsible predominantly for the formation of char and gases. Cellulose also yields lighters such as alcohols, acids, aldehydes [45]. Lignin, on the other hand, decomposes to phenols, ketones and other higher alcohols.[46].In this present study, thermodynamic feasibility of the reaction pathways of cellulose, lignin and protein are carried out based on the literatures and compounds obtained using GC-MS

The following set of reactions is considered for the reaction pathway feasibility. Cellulose is considered to be polymeric unit of glucose and Hemi-cellulose is considered as five carbon sugars. The cellulose and hemi-cellulose are considered as same as the decomposition as

cellulose decomposition also will result in five carbon structures which will further decompose giving lighter products.

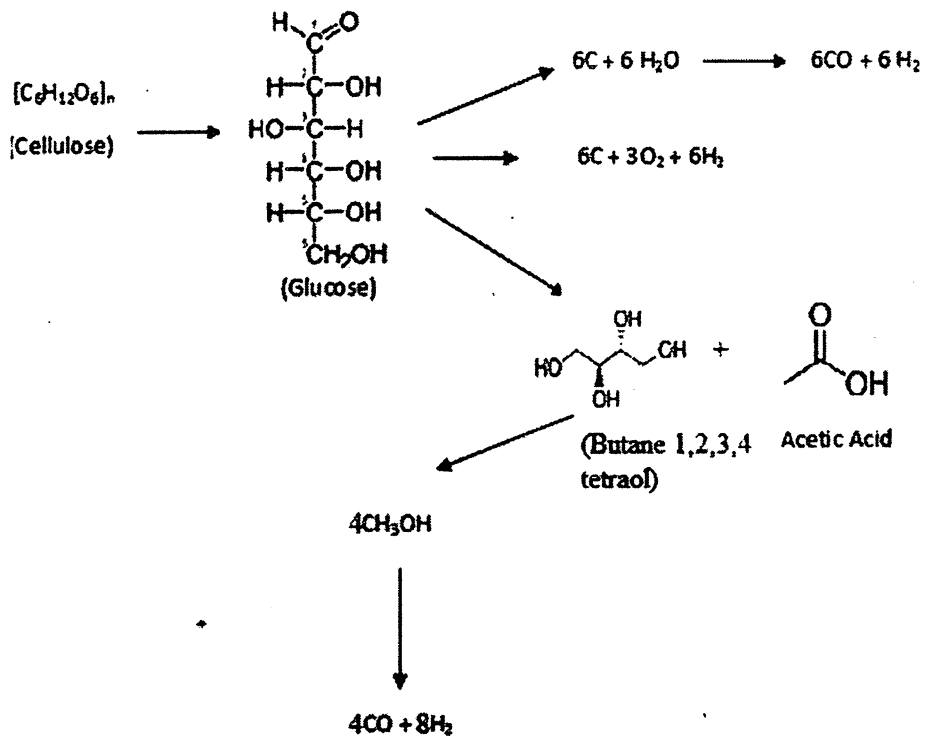


Fig4.15: Proposed reaction Network of Cellulose[47]

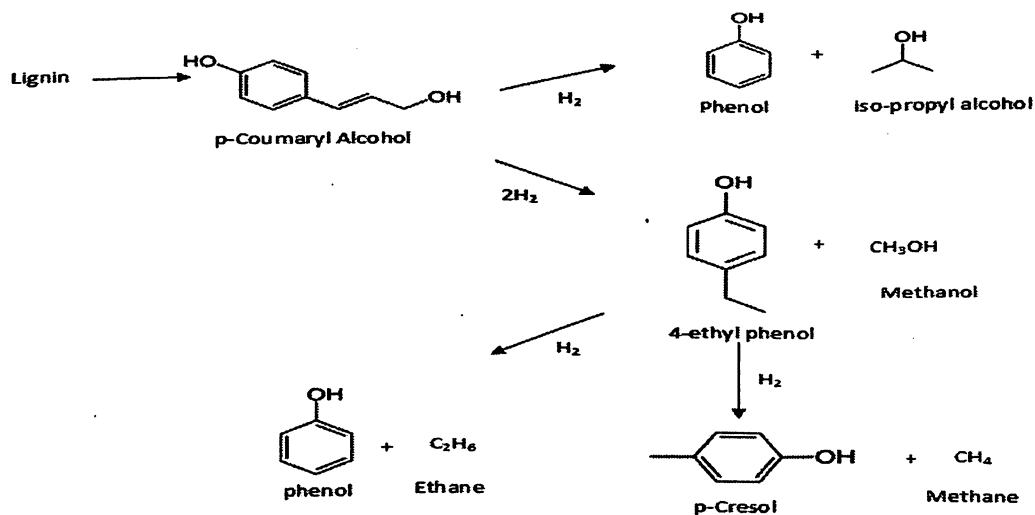


Fig4.16 :Proposed reaction Network of Lignin[47]

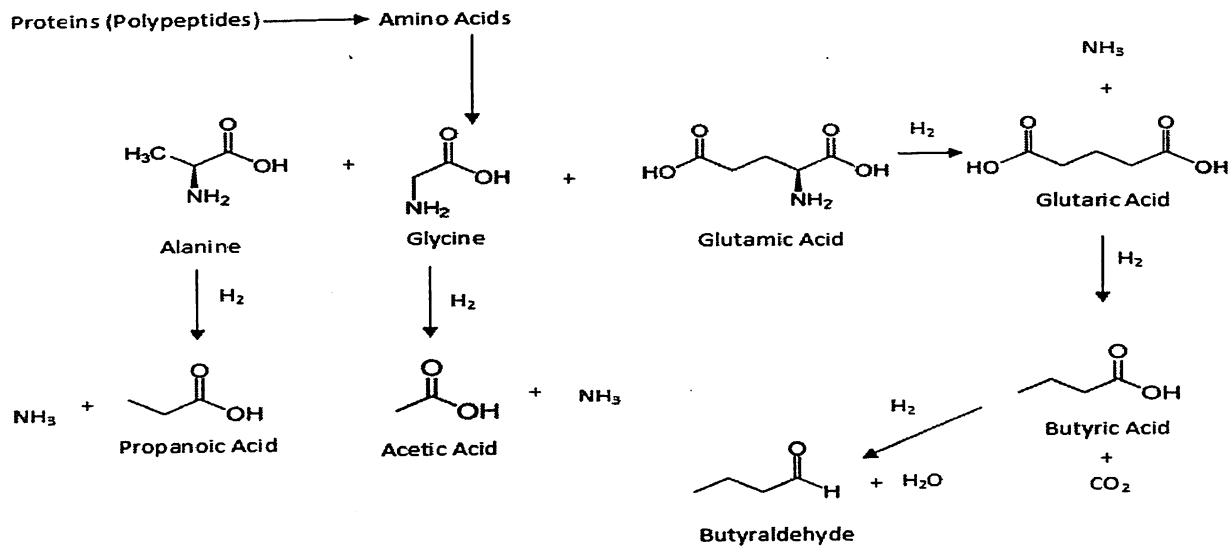


Fig 4.17: Proposed reaction Network of protein[47]

Gibbs free energy is determined using the above data which an indication on the possible reactions happening which can be related to the products of the pyrolysis. A plot of Gibbs free energy versus temperature is plotted from 298 K to 873K.

4.3.2 Methodology for reaction network studies

The feasibility study was carried out by considering the Gibbs free energy of formation and Enthalpy of formation at 298 K. the Gibbs free energy at the desired temperature was determined using the thermodynamic equation $\Delta G^0_{Rref} = -RT \ln(k_{ref})$. and vant-hoff equation.

$$\ln\left(\frac{k}{k_{ref}}\right) = \left(\frac{\Delta H_{ref}}{R}\right)\left(\frac{1}{T} - \frac{1}{T_{ref}}\right).$$

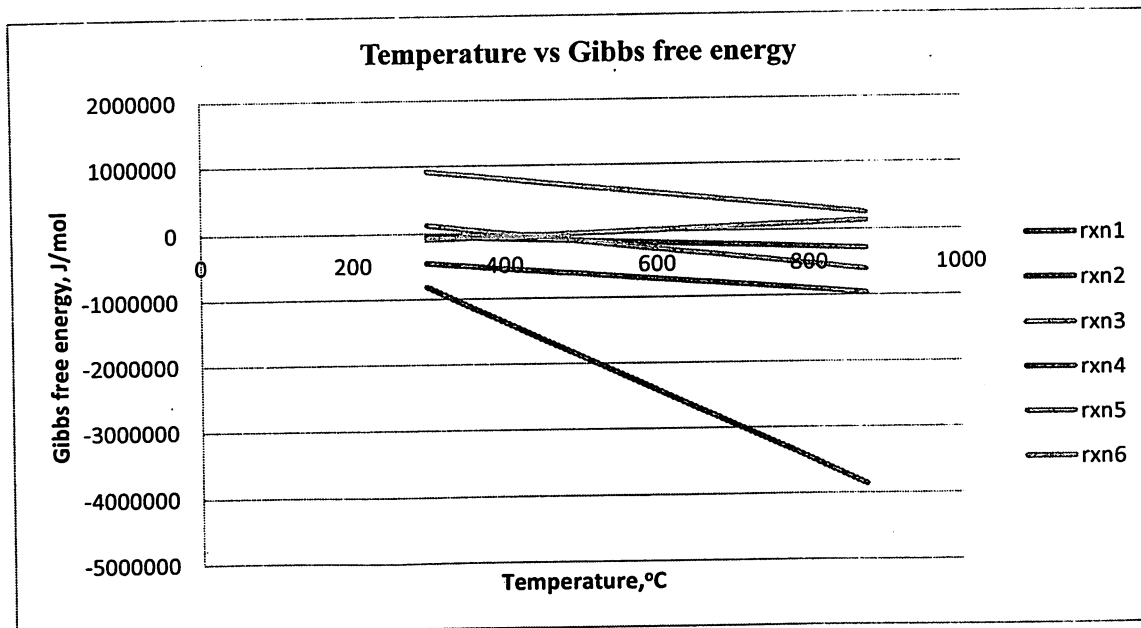


Fig 4.18: Gibbs free energy vs Temperature for cellulose pathway

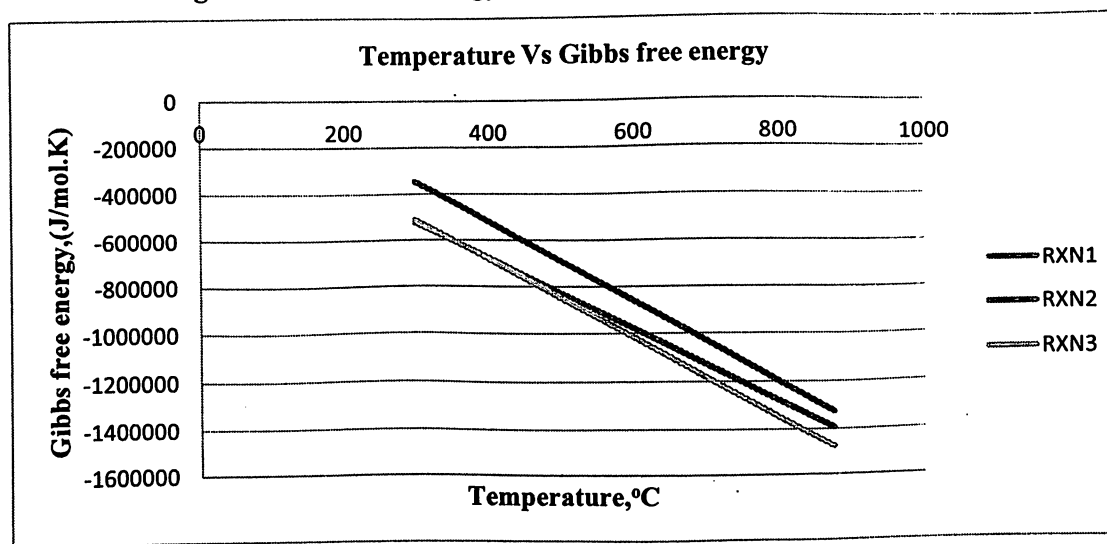


Fig 4.19: Gibbs free energy vs Temperature for lignin pathway

From the plot, it can be that the formation of acetic acid, have negative Gibbs free energy indicating that the feasibility of the reaction. However elemental decomposition of glucose into gases O_2 , C and H_2 has a positive Gibbs free energy which is also partially proven by the gas analyzer which indicated negligible presence of hydrogen possibly due to other reactions. There

is no formation of methanol as well in the GC analysis. Formations of lighter molecule like methane, CO, ethane, ethylene, propylene etc. by way of secondary reactions could be observed are secondary reactions. The presence of compounds like acetic acid in GC proves that the secondary reactions are occurring at these temperatures.

4.3.2 Energy analysis of the process

The energy analysis of the pyrolysis process is done by determining the energy content of the reactant, product as well as the process energy required to convert the reactant into products. The energy content of the reactants and products are determined using C, H, N, O, S values. The highest heating values (HHV) of C, H, N, O, and S of biomass and bio-char are obtained using analysis. For, bio-oil, this is calculated from by determining the empirical formula based on the compounds obtained by the GC-MS of the bio-oil samples. The empirical formula[48] for the bio-oil obtained from Nitrogen and Steam is determined as $\text{CH}_{2.12}\text{N}_{0.14}\text{O}_{0.57}$ and $\text{CH}_{2.29}\text{N}_{0.16}\text{O}_{0.21}$ respectively. For ease of convenience representative samples are used for the calculations. The process energy is carried out by calculating the energy required to maintain the reactor at the operating temperature. For reaction involving steam, the energy content of the steam is also taken into account. The Highest heating value of Jatropha seed cake and char is found to be 26.98 and 18.24 MJ/kg respectively. Highest heating value for the bio-oil obtained using Nitrogen is determined to be 22.57 MJ/kg and using steam 32.08 MJ/kg. There is energy required to increase the temperature of the reactor to the operating temperature which is considered as startup energy and is not included in the calculation.

General Energy balance of the process considered

Input energy (Biomass+media)+ Process Energy \longrightarrow Output Energy (Product Energy) + losses

Table 4.9: Energy data of the process using Nitrogen

Using Nitrogen /Temperature(°C)	Reactant energy(MJ)	Process energy(MJ)	Product energy	Energy yield%	EROI
500	4.3178	0.525	3.05	70.6	5.8
550	4.3178	0.63	2.77	64.2	4.4
600	4.3178	0.7	2.42	56.1	3.4

Table 4.10: Energy content of the process using Steam.

Using Steam	Reactant energy(MJ)	Process energy(MJ)	Product energy	Energy yield%	EROI
500	4.8398272	0.525	3.82	79.90	7.2
550	4.8398272	0.63	3.37	70.5	5.3
600	4.8398272	0.7	2.94	61.4	4.1

It was found that the pyrolysis using steam provides better energy yields and better quality of the fuel in terms of higher HHV. The Energy Returns Of Investment (EROI) which is the ratio of product energy and the processing energy was found to be within the literature ranges. The energy yield value shows the conversion efficiency of the process and the EROI indicates scalability of the process for large scale continuous mode process [48,49].

CHAPTER 5

Conclusion and Future scope

5.1 Conclusion

The pyrolysis of Jatropha seed cake in the Rotary tubular conveyor reactor was studied. The effect of various parameters such as residence time and temperature on the pyrolysis process showed that there is a great scope of optimization and energy generation in the process. The comparative study on the pyrolysis using Nitrogen and steam provided an insight on the improvement of the process by the use of steam over Nitrogen. The better energy yields indicate that the process is a viable option for the generation of fuels. Further study on the reaction Network would be helpful to understand the actual chemistry of the process which can be used to select and promote the desired reactions in the process.

5.2 Future Scope

The process itself has some challenges which need to be addressed. Firstly, the use of Nitrogen makes the char become sticky and will require frequent cleaning. Secondly, the pyrolysis operates like a black box with no specific control on the reaction kinetics or product selectivity. Catalyst used for these processes improve the reactions by producing better quality such as less oxygenated compounds so that the bio-oil has better heating value. However, developing catalyst with high selectivity and to operate efficiently at such elevated temperatures is a challenging task. The reaction pathways of these pyrolysis pathways are also not clearly understood adding more challenge to face. Though numerous works on the pyrolysis pathways are carried out, not much success has been achieved owing to a vast range of products obtained which are difficult to predict and model.

However, on the brighter side, bio-oil can be upgraded and technology to improve on the bio-oil quality has been widely researched and there is much scope on this front. Simulation on the pyrolysis process could be a useful prospect considering the technological advancement in the field of software and simulations. However, again the concept of black box reaction mechanisms throws less light on the scope of improvement of the process.

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Appendix -A

Sample calculation for the determination of reaction.

		Reaction 1							
		C6H12O6--> 6C+6H2O							
		assumption	1000 units						
		Species	ΔG_f	ΔH_f	Stoichiometry				
			kJ/mol	kJ/mol			Reference temperature,k	298.15	
		Glucose	-915900	-1262190	1		Gas constant	8.314	
		H2O	-228400	-241800	6		Formula	(C6H12O6)	
		C	0	0	0		Mol.wt. glucose	180.15	
							Vanthoff Predictions		
Temp, K	ΔG_R^0	ΔH_R^0	Kref	k/kref	k	ln(k)	1/T	ΔG_R	
298	-454500	-188610	4.26E+79	1.039043	4.43E+79	183.3917	0.003356	-454366	
300	-454500	-188610	4.26E+79	0.625494	2.66E+79	182.8842	0.003333	-456150	
325	-454500	-188610	4.26E+79	0.001862	7.93E+76	177.0673	0.003077	-478445	
350	-454500	-188610	4.26E+79	1.27E-05	5.42E+74	172.0814	0.002857	-500740	
375	-454500	-188610	4.26E+79	1.69E-07	7.2E+72	167.7603	0.002667	-523035	
400	-454500	-188610	4.26E+79	3.85E-09	1.64E+71	163.9794	0.0025	-545330	
425	-454500	-188610	4.26E+79	1.37E-10	5.84E+69	160.6432	0.002353	-567625	
450	-454500	-188610	4.26E+79	7.07E-12	3.01E+68	157.6777	0.002222	-589920	
475	-454500	-188610	4.26E+79	4.98E-13	2.12E+67	155.0244	0.002105	-612215	
500	-454500	-188610	4.26E+79	4.57E-14	1.95E+66	152.6364	0.002	-634510	
525	-454500	-188610	4.26E+79	5.27E-15	2.24E+65	150.4759	0.001905	-656805	
550	-454500	-188610	4.26E+79	7.39E-16	3.15E+64	148.5118	0.001818	-679100	
575	-454500	-188610	4.26E+79	1.23E-16	5.24E+63	146.7184	0.001739	-701395	
600	-454500	-188610	4.26E+79	2.38E-17	1.01E+63	145.0745	0.001667	-723690	
625	-454500	-188610	4.26E+79	5.23E-18	2.23E+62	143.5621	0.0016	-745985	
650	-454500	-188610	4.26E+79	1.3E-18	5.52E+61	142.1661	0.001538	-768280	
675	-454500	-188610	4.26E+79	3.56E-19	1.52E+61	140.8734	0.001481	-790575	
700	-454500	-188610	4.26E+79	1.07E-19	4.56E+60	139.6731	0.001429	-812870	
725	-454500	-188610	4.26E+79	3.5E-20	1.49E+60	138.5556	0.001379	-835165	
750	-454500	-188610	4.26E+79	1.23E-20	5.26E+59	137.5126	0.001333	-857460	

775	-454500	-188610	4.26E+79	4.65E-21	1.98E+59	136.5368	0.00129	-879755
800	-454500	-188610	4.26E+79	1.86E-21	7.94E+58	135.6221	0.00125	-902050
825	-454500	-188610	4.26E+79	7.89E-22	3.36E+58	134.7628	0.001212	-924345
850	-454500	-188610	4.26E+79	3.52E-22	1.5E+58	133.954	0.001176	-946640
873	-454500	-188610	4.26E+79	1.74E-22	7.41E+57	133.2508	0.001145	-967151
875	-454500	-188610	4.26E+79	1.64E-22	6.99E+57	133.1915	0.001143	-968935

Appendix -B

Thermal data for the calculations

Species	ΔG_f° (J/mol.K)	ΔH_f° (J/mol.K)
C ₆ H ₁₂ O ₆ (Glucose)	-915900	-1262190
H ₂ O(water)	-228400	-241800
C(Carbon)	0	0
C ₄ H ₉ O ₄ (Butane 1,2,3,4-Tetraol)	-569000	-745370
CH ₃ OH(Methanol)	-166200	-258600
CO	-137200	-116500
H ₂	0	0
CH ₄	50600	-74900
C ₃ H ₇ OH(Iso-propyl alcohol)	173600	-261100
O ₂	0	0
C ₉ H ₁₀ O ₂ (P-Coumaryl alcohol)	316859.4	-284500
C ₆ H ₅ OH(Phenol)	-32900	-96400
C ₇ H ₇ OH(P-cresol)	-30900	-125400
C ₂ H ₆ (Ethane)	-33000	-84500

Appendix -C

Method for GC

GC		
Oven	On	
Temperature		
Setpoint		
(Initial)		35 °C
Hold Time		17 min
Post Run		280 °C
Program		
#1 Rate		8 °C/min
#1 Value		125 °C
#1 Hold Time		65 min
#2 Rate		8 °C/min
#2 Value		200 °C
#2 Hold Time		50 min
Equilibration Time		0.5 min
Max Temperature		325 °C
Maximum		
Temperature Override		Disabled
Slow		
Fan		Disabled
Cryo		Off
QQQ Collision Cell EPC		2.5
He Quench Gas	On	mL/min
		1.5
N2 Collision Gas	On	mL/min
ALS		
Front Injector		
Syringe Size		10 µL
Injection Volume		1 µL
Solvent A Washes (PreInj)		2
Solvent A Washes (PostInj)		2
Solvent A Volume		8 µL
Solvent B Washes (PreInj)		2
Solvent B Washes (PostInj)		2
Solvent B Volume		8 µL
Sample Washes		1
Sample Wash Volume		8 µL
Sample Pumps		3
Dwell Time (PreInj)		0 min
Dwell Time (PostInj)		0 min
Solvent Wash Draw Speed		300 µL/min
Solvent Wash Dispense Speed		3000 µL/min

Sample Wash Draw Speed
Sample Wash Dispense Speed
Injection Dispense Speed

300 $\mu\text{L}/\text{min}$
3000 $\mu\text{L}/\text{min}$
6000 $\mu\text{L}/\text{min}$

Appendix -D

Calculations regarding energy analysis

Temp	Using Nitrogen		Process energy		Product energy				EROI	Energy yield %	
	Reactant energy(MJ)		Energy to maintain in temperature in the reactor(MJ)	Energy required to increase the temperature to the operating temperature	Char (MJ)	oil(MJ)	gas(MJ)	Total (MJ)			
	Jatropha seed cake										
500	4.31		0.525	12.6	2.02	0.81	0.11	2.94	5.61	68.30	
550	4.31		0.63	15.75	1.29	1.12	0.20	2.62	4.17	60.87	
600	4.31		0.7	18.9	0.94	1.01	0.29	2.25	3.22	52.33	
	using Steam		Total (MJ)								
		steam									
500	4.31	0.46	4.78	0.525	12.6	2.02	1.66	0.09	3.78	7.19	79.04
550	4.31	0.464	4.78	0.63	15.75	1.29	1.76	0.22	3.28	5.20	68.60
600	4.31	0.464	4.78	0.7	18.9	0.94	1.56	0.31	2.82	4.03	59.06