

Analysis of Physiochemical Properties of De-Oiled Mahua Seed Cake for their Suitability in Producing Bio-Oil

H. V. Mulimani¹, M. C. Navindgi²Research Scholar, Department of Mechanical Engineering, PDA Engineering College, Kalburgi, Karnataka, India¹Professor, Department of Mechanical Engineering, PDA Engineering College, Kalburgi, Karnataka, India²

ABSTRACT: In developing countries like India, efforts were being made for using non-edible seeds for production of biodiesel. The biodiesel program would be sustainable only when the generated waste cake is converted into valuable energy products. Considering the future scenario of non edible seed's utilization, there is an urgent need for development of a suitable technology for conversion of the seed cake into the more useful products. Otherwise, the seed cake will lead to many problems such as waste disposal management, space occupation. The main focus of this paper is to analyze the physiochemical properties of Mahua de-oiled seed cake for their suitability in producing bio-oil. The de-oiled seed cake is analyzed by proximate analysis, ultimate analysis, calorific value, thermo gravimetric analysis (TGA), fourier transform infrared spectroscopy (FTIR). The proximate and ultimate analysis of Mahua de-oiled seed cake reveals that, it contains 74.9% of volatile matter, 0.32% of sulphur, 6.2% of ash. The high volatile matter, less sulphur and less ash content makes the Mahua de-oiled seed cake suitable for producing liquid fuel. The calorific values of Mahua de-oiled seed cake is found to be less (19.97 MJ/kg) due to presence of oxygen. TGA analysis reveals that the operating pyrolysis temperature of Mahua de-oiled seed cake are 420-500 °C. The FTIR analysis of de-oiled seed cake reveals that it mainly consists of aliphatic and aromatic compounds, which could be a viable option of biomass energy source.

KEYWORDS: De-oiled seed cake, Pyrolysis, Proximate, Ultimate, TGA, FTIR.

I. INTRODUCTION

The world's economic development is directly linked with energy consumption. The higher energy consumption implies higher gross domestic product (GDP). The highest primary energy consumption in the world is crude oil as compared to other resources such as hydro, nuclear, coal and natural gas. The problems such as depletion of crude oil resources, energy security and environmental concerns put forward all the world to search renewable fuel resources. In order to overcome the issues, renewable energy such as bio-fuel appears to be an option [1].

Biomass fuels and residues can be converted to more valuable energy forms via a number of processes including thermal, biological, and mechanical or physical processes. While biological processing is usually very selective and produces a small number of discrete products in high yield using biological catalysts. Thermal conversion often gives multiple and often complex products in very short reaction times with inorganic catalysts often used to improve the product quality. Among the biomass to energy conversion processes, thermal process-pyrolysis has attracted more interest in producing liquid fuel product because of its high-value bio-oil, advantages in storage, transport and versatility in application such as combustion engines, boilers, turbines etc. Hence, pyrolysis has been receiving more attention as an efficient method in converting de-oiled seed cake into bio fuel during recent decades [2,3]. The production of bio liquids and other products (char and gas) by pyrolysis of different biomass species has been extensively investigated in the past. Some of these biomass species include wood, bagasse, straws, de-oiled seed cakes and municipal solid waste[4].

Pyrolysis can act as the residue management option because bio-oils derived from biomass pyrolysis could act as feedstocks for producing hydrocarbons that may be readily integrated into the existing petroleum refineries or future

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 4, April 2016

bio-refineries [5]. Pyrolysis is the thermal degradation of biomass by heat in the absence of oxygen, and results in the production of charcoal (solid), bio-oil (liquid), and fuel gaseous products. Pyrolysis processes are of three types namely slow or conventional pyrolysis, fast pyrolysis and flash pyrolysis. In slow pyrolysis operating temperature is around 500 °C with lower heating rate and vapour residence time is in the range of 0.5-5 min. The yield of solid liquid and gas products are almost same. The fast pyrolysis process is a high temperature about 650 °C produces 60-75 wt.% of liquid bio-oil, 15-25 wt.% of solid char and 10-20 wt.% of gases depending upon feedstock used. Flash pyrolysis is the promising route for production of bio-oil from seed cake. The type of pyrolysis process has to be chosen for specific application.

Non edible *Jatropha curcas* de-oiled seed cake (the residue left after extraction of oil from seed) was converted into bio-oil through pyrolysis process in fluidized bed with maximum feed rate of 12 g/min. Author carried out pyrolysis experiments using *Jatropha curcas* de-oiled seed cake as a feedstock with different sizes of 0.175 mm–0.5 mm, 0.5 mm–0.99 mm and 0.99 mm–1.66 mm. The nitrogen gas was used as a sweep gas for the fluidization of the feed in the reactor at different flow rates of 6, 8, 10 and 12 LPM. The experiments were carried out at different temperatures of 425, 450, 475 and 500 °C with a heating rate of 30 °C/min. It was reported that the optimum temp, particle size and sweep gas flow rate as 450 °C, 0.5 mm - 0.99 mm and 8L/min respectively for obtaining 48% bio-oil and 38.1% bio-char[1]. Slow pyrolysis experiments have been conducted on a sample of polanga seed cake in a semi batch stainless steel reactor to determine the influence of temperature between 450–600 °C at a heating rate of 20 °C/min and produced the maximum yield of bio-oil about 46 % at a temperature of 550 °C. The results show the potential of polanga seed cake as an important source of alternative fuel [6].

Madhuca indica, commonly known as Mahua, is mainly cultivated in central and southern parts of India. The annual production of seed in the country is around 0.50 million tons. After the extraction of oil, much of the material goes as a waste. Presently Mahua seed cake finds application in dye removal, low quality cattle feed and fertilizer, as a biopesticide, insecticide and a piscicide. The later properties are conferred by the presence of bitter saponins in seed cake. However, their presence in the cake limits its extensive usage. Mahua de-oiled seed cake is rich in volatile matter[7]. Hence that is the motivation to choose one of the de-oiled seed cake-Mahua as a feedstock for producing bio-oil by pyrolysis.

II. MATERIALS AND PROCEDURES

The Mahua de-oiled cake was bought from "Biodiesel Production Centre" Kalburgi- Karnataka, which was left out after extraction of crude oil for producing the biodiesel. The cake was in the form of flakes and was powdered using a household grinder, for checking its suitability for producing it bio-oil from pyrolysis process. Its suitability is determined carrying out analysis of physiochemical properties of Mahua de-oiled seed cake using proximate analysis, ultimate analysis, bomb calorimeter, thermo gravimetric analysis (TGA) and fourier transform infrared spectroscopy (FTIR).

The proximate analysis was done by ASTM D3173-75 and carried out in Bangalore Test House Bangalore. Ultimate analysis was carried out at Indian Institute of Science (IISc) - Bangalore with a Instrument Model Thermo Scientific Flash 2000 Organic Elemental Analyzer using Eager Experience software under CHNS/O analysis mode with reference and carrier gas as Helium. Calorific value was determined using a Bomb Calorimeter of MAC make in Bangalore Test House Bangalore. TGA was carried out in Sipla Labs Limited Hyderabad using thermal gravimetric analysis Q500 V20.13 Build 39 (Universal V4.5A TA Instruments) for the Mahua de-oiled seed cake sample weighing 23.998 mg with nitrogen as carrier gas at the heating rate of 20 °C/min. Functional groups present were identified by using Perkin Elmer Model M15 fourier transform infrared spectroscopy in Bangalore Test House Bangalore.

III. RESULTS AND DISCUSSIONS

1) Proximate analysis

Proximate analysis is the quickest and simplest way of investigating the fuel quality of solid materials. The proximate analysis of Mahua de-oiled seed cake indicates that the volatile matter contents are almost nearer to the values of other biomass materials as shown in table 1. Mahua de-oiled seed cake has high volatile matter content of around more than

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 4, April 2016

70%. The carbon content is around 22% in Mahua de-oiled seed cake, which can be converted into de-volatilized residue (bio-char).

It has been reported that feedstock containing high percentage of volatile matter and less percentage of ash content strongly influences its combustion behaviour and thermal decomposition. These characteristics also suggest good potentiality of the feedstock for energy production by pyrolysis and gasification. Moisture content of the feedstock has a marked effect on the conversion efficiency of pyrolysis processes, its energy content and the product yield. It has been reported that to ensure rapid heat transfer rates in a pyrolysis reactor, the moisture content should be less than 10 wt%. In this regard Mahua de oiled seed cake seems to be suitable for thermal conversion [8].

2) Ultimate analysis

Ultimate analysis is performed to determine the elemental composition of the material. The ultimate analysis of Mahua de-oiled seed cake indicates that the carbon (C), hydrogen (H), nitrogen (N), sulphur (S) and oxygen (O) contents are almost nearer to the values of the other biomass materials as shown in table 2. Mahua de-oiled seed cake has lower sulphur content and the end product derived from the lower sulphur feedstock would be a good quality fuel, which can be used as a fuel for combustion engines. The higher oxygen content effects the calorific value.

The lower the ratios of hydrogen/oxygen H/O and carbon/oxygen C/O the higher the energetic content. This can be explained by Dulong's Equation defined as $HHV (MJ/kg) = (33.5 * \%C + 142.3 * \%H - 15.4 * \%O)/100$. The materials with a relatively low O/C ratio have more energy density and higher HHV because there is more chemical energy in C-C binds and in C-O bonds[9].

Based on the ultimate analysis empirical formula was established as $CH_{1.65}N_{0.04}S_{0.002}O_{0.68}$ for Mahua de-oiled seed cake.

Table 1. Proximate analysis of different seed cakes

Sample	Moisture wt.(%)	Volatile matter wt.(%)	Ash wt.(%)	Fixed carbon wt.(%)	References
Mahua de-oiled seed cake	6.5	74.9*	6.2*	18.9*	Present Study
Pongamia de-oiled cake	12	71.21	5.08	11.71	[10]
Sunflower oil cake	5.6	73.8	5.9	14.7	[11]
Groundnut de-oiled cake	5.6	83	4.8	6.6	[12]
Jatropha seedshell cake	2.65	79.80	3.42	14.13	[5]
Maize stalk	7.67	71.95	8.33	12.05	[13]
Linseed	6.9	84.9	4.1	4.1	[14]
Rice husk	6.37	81.93	11.7	-	[15]

*Results on dry basis.

Table 2. Ultimate analysis of different biomass materials

Sample	C wt.(%)	H wt.(%)	N wt.(%)	S wt.(%)	O (wt.%)	References
Mahua de-oiled seed cake	47.28	6.52	2.55	0.32	43.33*	Present Study
Polanga seed cake	42.22	6.7	3.35	0.815	46.915	[6]
Jatropha de-oiled seed cake	42.3	4.8	5.8	0.36	46.74	[1]
Castor de-oiled seed cake	46.75	7.24	8.55	-	37.46	[16]
Coal	78.2	5.2	1.3	1.7	13.6	[18]
Wood	52.3	5.2	0.5	-	42.0	[10]
Bagasse	50.2	5.6	1.1	0.1	40*	[17]

* By difference

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 4, April 2016

3) Calorific value

The calorific value of Mahua de-oiled seed cakes is nearly in the same range of the values of other biomass as shown in table 3. This indicates that de-oiled seed cake has a great potential to be a feed stock for production of alternative fuel. The biodiesel produced by esterification reported that calorific value of Rubber seed oil, Rape seed oil, Cotton seed oil and Soybean oil were in the range of 35.0 to 40.0 MJ/kg [19]. The calorific value of de-oiled seed cake is lesser than diesel and biodiesel due to the higher oxygen content.

Table 3. Gross calorific value of different biomass materials

Sample	Calorific value (MJ/kg)	References
Mahua de-oiled cake	19.97	Present study
Pongamia de-oiled cake	17.65	[10]
Jatropha de-oiled cake	16.86	[1]
Cotton seed oil	39.6	[19]
Mahua biodiesel	38	[20]
Castor biodiesel	36	[20]
Wood	18.5	[10]

4) Thermo Gravimetric Analysis (TGA)

TGA is the most common technique for investigating the de-volatilization behaviour of biomass at higher temperature. Temperature for effective pyrolysis of the non edible de-oiled seed cake is determined using TGA. It is used to determine a materials thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a de-oiled seed cake is heated. The nature of a TGA curve gives a clear indication of number of stages of the thermal degradation.

Experiments with TGA comprise of three stage weight loss. The first stage the initial decomposition represents the evaporation of moisture contents. The second stage is treated as active zone due to high decomposition rate per unit time where the decomposition indicates the formation of volatiles mainly CO and CO₂. During the active pyrolysis zone, the intermolecular associations and weaker chemical bonds are destroyed. The side aliphatic chains may be broken and some small gaseous molecules are produced. During the third stage, the pyrolysis residue is slowly decomposed, the chemical bonds are broken, and the parent molecular skeletons are destroyed [14,21].

TGA of Mahua de-oiled seed cake is shown in figure 1. The first initial mass loss which is due to moisture occurs from room temperature to 200 °C, the second mass loss occurs between 200 and 480 °C, whereas third mass loss extended up to 600 °C. TGA analysis reveals that the operating pyrolysis temperature of Mahua de-oiled seed cake is 420 - 500 °C and the variation of temperature ranges mainly depends on the moisture content.

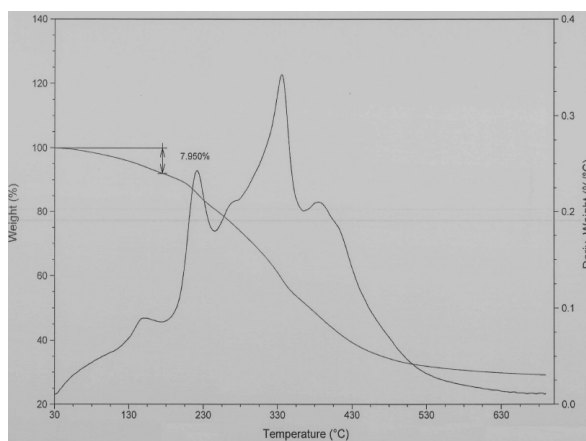


Fig.1. TGA analysis of Mahua de-oiled seed cake

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 4, April 2016

A similar trend of mass loss was seen for Pongamia de-oiled seed cake, the first mass loss had occurred approximately between 30 to 166 °C, second mass loss occurred between 166 to 480 °C and third mass loss occurred up to 700 °C and also revealed that heating rate of 20 °C/min is better as compared to the higher heating rate of 30 °C/min [10]. Same tend of mass loss was reported, when TGA is carried on Mahua de-oiled seed oil cakes at the heating rate of 25 °C/min [22].

5) Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a fast, cheap, reliable, accurate, and non destructive method, which provides information regarding functional groups present in the sample [21]. FTIR can provide the information about, it can identify unknown materials, it can determine the quality of a sample and it can determine the amount of components in a mixture. On interaction of an infrared light, chemical bond will stretch, contract and absorb infrared radiation in a specific wave length range regardless structure of the rest of the molecules [22].

The FTIR spectra were recorded in the transmission mode between 4000 cm⁻¹ and 500 cm⁻¹ for Mahua de-oiled seed cake is shown in figure 2. The functional groups identified from the FTIR are shown in above table 4, which mainly consists of aliphatic and aromatic compounds. Aliphatics include alkanes, alkenes and alkynes.

The C–H stretching at 2924, 2853 and C-H bending at 1379 indicate the presence of alkanes. The C=C Stretching at 1637 indicate the presence of alkenes. The C=C stretching at 1547, 1458 and C-H bending at 772 and 669 indicates aromatic compounds in Mahua de-oiled seed cake.

The pronounced oxygenated functional groups O-H, C=O, C-O and aromatic compounds showed that the de-oiled seed cake was highly hydro oxygenated and therefore, it is acidic in nature. The oxygenated compounds reduce the calorific value of the de-oiled seed cake. However, presence of hydrocarbon groups C-H, C=C, and alcohols indicate that de-oiled seed cake has a potential feedstock for bio-oil.

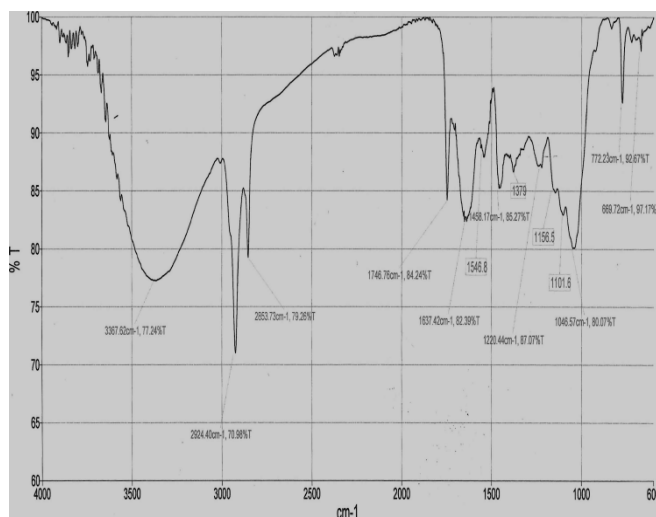


Fig.2. FTIR analysis of Mahua de-oiled seed cake

The combustion of any alkane produces energy, which makes alkanes useful as fuels. As the length of the carbon chain increases, the amount of energy released during combustion increases. A longer carbon chain contains more C-C bonds and more C-H bonds. The overall process of breaking C-C and C-H bonds and making C=O and O-H bonds releases energy. The more C-C and C-H bonds broken, and the more C=O and O-H bonds formed, the greater the amount of energy released. The reactive site in alkene molecules is the carbon-carbon double bond (C=C). In chemical reactions this double bond either opens out to leave a carbon-carbon single bond (C-C) or it breaks completely to separate the molecule into two smaller fragments. Complete combustion of alkenes produces carbon dioxide and water. Alcohols

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 4, April 2016

burns with clean flame producing carbon dioxide and water vapour. FTIR results showed that this waste de-oiled seed cake could be a viable option of biomass energy source.

Table 4. FTIR functional groups and indicated compounds in Mahua de-oiled seed cake

Sl No	Wave number (cm ⁻¹)	Groups	Class of compounds
1	3367	O-H Stretching	Alcohols , Phenols
2	2924	C-H Stretching	Aliphatics (Alkanes)
3	2853	C-H Stretching	Aliphatics (Alkanes)
4	1746	C=O Stretching	Aldehydes & Ketones
5	1637	C=C Stretching	Aliphatics (Alkenes)
6	1547	C=C Stretching	Aromatic
7	1458	C=C Stretching	Aromatic
8	1379	C-H Bending	Aliphatics (Alkane)
9	1220	C-O Stretching	Phenol
10	1157	C-O Stretching	Ternary alcohol
11	1102	C-O Stretching	Secondary alcohol
12	1046	C-O Stretching	Primary alcohol
13	772 & 669	O-H Bending	Aromatic compound

IV. CONCLUSION

This study is an attempt to show that the de-oiled seed cake left after biodiesel production contains high volatile matter which indicates high source of energy. Pyrolysis could be one of the option for producing bio-oil which can be used for many applications including in diesel engines. Mahua de-oiled seed cake has high volatile matter (74.9%), less moisture (6.5%), ash (6.2%) and sulphur (0.32%) content and the end product derived from this feedstock will be a good quality fuel. TGA results showed the operating pyrolysis temperature of Mahua de-oiled seed cake is 420-500 °C. FTIR results showed that the waste de-oiled seed cake consisting of mainly aliphatic and aromatic could be a viable option of biomass energy source.

REFERENCES

- [1] C.H. Biradar, K.A. Subramanian, M.G. Dastidar "Production and fuel quality upgradation of pyrolytic bio-oil from Jatropha Curcas de-oiled seed cake", Fuel, 119, pp.81–89, 2014.
- [2] A.V. Bridgwater "Review of fast pyrolysis of biomass and product upgrading" Biomass and Bioenergy 38 pp.68-94, 2012.
- [3] S. Czernik and A. V. Bridgwater "Overview of Applications of Biomass Fast Pyrolysis Oil" Energy & Fuels 18, pp.590-598, 2004.
- [4] Mohammad I. Jahirul, Mohammad G. Rasul, Ashfaqe Ahmed Chowdhury and Nanjappa Ashwath "Biofuels Production through Biomass Pyrolysis —A Technological Review" Energies 5, pp. 4952-5001, 2012.
- [5] Sung Won Kim, Bon Seok Koo, Jae Wook Ryu et al. "Bio-oil from the pyrolysis of palm and Jatropha wastes in a fluidized bed" Fuel Processing Technology 108, pp. 1-124, 2013.
- [6] Krushna Prasad Shadangi a, Raghubansh K. Singh "Thermolysis of polanga seed cake to bio-oil using semi batch reactor" Fuel 97, pp.450–456, 2012.
- [7] Aditi Gupta, Ashwani Kumar, Satyawati Sharma, V.K. Vijay "Comparative evaluation of raw and detoxified mahua seed cake for biogas production", 102, pp. 1514-152, 2013.
- [8] Neonjyoti Bordolai, Rumi Narxari, Rahul Singh Chutia, Thallada Bhaskar, Rupam Kataki "Pyrolysis of mesua ferrea and Pongamia glabra seed cover: characterisation of bio-oil and its sub-fractions" Bioresource Technology (2014).

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 4, April 2016

- [9] Carlos Eduardo M Braz, Paula M. Crnkovic " Physical – Chemical Characterization of Biomass Samples for Application in Pyrolysis Process" Chemical Engineering Transactions 37, pp. 523-528, 2014.
- [10] Lalta Prasad, P.M.V. Subbarao, J.P. Subrahmanyam "Pyrolysis and gasification characteristics of Pongamia residue (de-oiled cake) using thermogravimetry and downdraft gasifier" Applied Thermal Engineering 63, pp379-386, 2014.
- [11] S. Yorgun, S. Sensoz, O.M. Kockar "Flash pyrolysis of sunflower oil cake for production of liquid fuels" Journal of Analytical and Applied Pyrolysis 60, pp.1-12, 2001.
- [12] Ankit Agrawalla, Sachin Kumar, R.K. Singh "Pyrolysis of groundnut de-oiled cake and characterization of the liquid product" Bioresource Technology 102, pp.10711-10716, 2011.
- [13] Zheng Ji-Lu "Pyrolysis oil from fast pyrolysis of maize stalk" J. Anal. Appl. Pyrolysis 83 (2008) 205-212.
- [14] Rahul Sinha, Sachin Kumar and R. K. Singh "Production of biofuel and biochar by thermal pyrolysis of linseed seed" Biomass Conv. Bio ref. 15, 2013.
- [15] W.T. Tsai, M.K. Lee b, Y.M. Chang "Fast pyrolysis of rice husk: Product yields and compositions" Bioresource Technology 98, pp.22-28, 2007.
- [16] I. A. Aldobouni, A. B. Fadhil & I. K. Saied " Conversion of De-oiled Castor Seed Cake into Bio-oil and Carbon Adsorbents" Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 37:24, pp.2617-2624, 2015.
- [17] Marion Carrier, Thomas Hugo, Johann Gorgens, Hansie Knoetze "Comparison of slow and vacuum pyrolysis of sugar cane bagasse" Journal of Analytical and Applied Pyrolysis 90 , 18-26, 2011.
- [18] Stanislav V. Vassilev, Christina G. Vassileva, Vassil S. Vassilev, "Advantages and disadvantages of composition and properties of biomass in comparison with coal: An overview" Fuel 2015.
- [19] A.S. Ramadhas, S. Jayaraj, C. Muraleedharan "Biodiesel production from high FFA rubber seed oil" Fuel 84, pp. 335-340, 2005.
- [20] M C Navindgi, Maheswar Dutta and B. Sudheer Prem Kumar "Performance Evaluation, Emission Characteristics And Economic Analysis Of Four Non-Edible Straight Vegetable Oils On A Single Cylinder Ci Engine" ARPN Journal of Engineering and Applied Sciences VOL. 7, NO. 2, 2012.
- [21] R.K. Singh, K.P. Shadangi "Liquid fuel from castor seeds by pyrolysis" Fuel 90, pp. 2538-2544, 2011.
- [22] Vikranth Volli, R.K. Singh "Production of bio-oil from de-oiled cakes by thermal pyrolysis" Fuel 96, pp.579-585, 2012.