



Slow Pyrolysis of Jatropha Seed De-oiled Cake and Estimation of Kinetic Parameters

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ABSTRACT

Jatropha seed de-oiled cake is a potential source for the production of valuable hydrocarbons. The pyrolysis of the de-oiled cake yields bio-oils that could have several potential applications for use as fuel/chemicals. In this study the pyrolysis of jatropha seed de-oiled cake was carried out at different temperatures ranging from 300 to 500 °C. The maximum yield of bio-oil at 38.4 wt.% with a conversion of 63 % was obtained at 450 °C. After pyrolysis, these products were characterised using several physico-chemical characterisation techniques such as FT-IR, ¹H NMR, GC-MS, XRD and SEM. From these it was observed that the bio-oil obtained was primarily composed of phenolic compounds and the nature of bio-char indicated the conversion of the components of lignocellulosic biomass. The frequency factor and the activation energy calculated using the first order rate equation was 2.38 s⁻¹ and 5.31 kJ mol⁻¹ respectively. These values are much lower compared to those obtained from thermo-gravimetric analysis measurements indicating good heat and mass transfer in the experimental set up.

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1. Introduction

Researchers all over the world continue to search for sustainable energy sources which have become more critical owing to the geo-political and environmental problems associated with fossil fuels. Renewable energy is now receiving greater thrust for the production of energy due to the depletion of available fossil fuel resources. Recently, heat and electricity are being produced from renewable sources like the sun, wind, geothermal, ocean tidal energy etc. The electricity generated from these sources is used on a small scale possibly to power electric cars, however heavy duty vehicles and the aviation industry are still dependent on liquid fuels. Apart from transportation sector, the chemical and petrochemical industries are still solely dependent on biomass for renewable and sustainable sources of carbon (Meuwese et al., 2013). This gap in the energy demand and supply provides an opportunity for the use of another unconventional and clean energy source from biomass, which are now at the forefront in research for the production of alternative liquid fuels.

Biomass is defined as any organic matter that is derived by the process of photosynthesis. The second-generation of bio-fuels are obtained from feedstocks that are non-edible in nature, mainly from agriculture and forest residues in addition to energy crops specifically grown for bio-fuel manufacture.

Pyrolysis forms the basis of thermo-chemical conversion in most cases and is defined as the chemical changes occurring when heat is applied to any organic material in the absence of oxygen. Slow pyrolysis is characterised by slow heating rates ranging from 5 to 40 °C min⁻¹ with

residence time of 30-60 minutes under inert sweeping gas flow.

De-oiled cakes are secondary products that are obtained after the production of bio-diesel or jet fuel from non-edible oils. They are generally thrown away or burnt. Further as they do not compete for fodder this secondary processing of oil cakes provide a significant added advantage.

Several potential sources of de-oiled cake for use as feedstock have been studied previously and some of them are listed here. Chutia et al., have shown that *Mesua ferrea* L. de-oiled cake (Chutia et al., 2013) and *Pongamia glabra* de-oiled cake are potential feedstocks for thermo-chemical conversion to produce useful hydrocarbons. In the case of the *Pongamia glabra* de-oiled cake pyrolysis, maximum oil yield of 30.60 wt.% was obtained at 500 °C with a heating rate of 40 °C min⁻¹ (Chutia et al., 2014). Ground nut de-oiled cake has also been subjected to pyrolysis and 50 wt.% of bio-oil has been obtained (Agrawalla et al., 2011). Smets et al., have carried out the slow pyrolysis of rapeseed cake in the presence of catalysts such as Na₂CO₃, HZSM-5 and α-Al₂O₃. In the absence of catalysts at 550 °C, bio-oil yield of 47.1 wt.% and conversion of 72.1% were observed (Smets et al., 2013). For the raspberry seed cake, they observed that at 450 °C bio-oil yield of 44.4 wt.% was obtained by slow pyrolysis (Smets et al., 2014). De-oiled canola meal required an optimum temperature of 500 °C to get a maximum bio-oil yield of 10-24 wt.% (Azargohar et al., 2013). Soyabean oil cake is seen to require the lowest temperature so far reported at 400 °C to give bio-oil yield of 25.8 wt.% with a heating rate of 50 °C min⁻¹ (Sensoz & Kaynar, 2006).

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We have already reported the hydrolysis of jatropha seed de-oiled cake (Balagurumurthy et al., 2013b) along with its kinetic parameters (Balagurumurthy et al., 2013a). In this manuscript we report for the first time the results of the slow pyrolysis of jatropha seed de-oiled cake along with the kinetic parameters assuming a first order reaction.

2. Materials and methods

2.1. Materials

The feedstock jatropha seed de-oiled cake (JSDC) was obtained from a local bio-diesel production unit. The gross calorific value was found using the Parr 6300 Bomb Calorimeter. The trace metal analysis was carried out using the DRE, PS-3000 UV, Leeman Labs Inc., Inductively Coupled Plasma-Atomic Emission Spectroscopy instrument. The moisture content was obtained from the HR- 83 Mettler Toledo Halogen Moisture Analyzer.

The elemental analysis was carried out in an Elementar Micro Vario Cube unit. The ^1H NMR spectra was recorded in the Bruker Ultrashield 500 Plus instrument using CDCl_3 as a solvent.

Powder X-ray diffraction patterns were collected on Bruker D8 advance X-ray diffractometer fitted with a Lynx eye high-speed strip detector and a Cu K α radiation source. Diffraction patterns in the 2° - 80° region were

recorded with a 0.04 step size (step time= 4s).

The FT-IR spectra were recorded on a Nicolet 8700 FT-IR spectrometer with the sample powder diluted in KBr. SEM images were collected on the FEI Quanta 200 F, using a tungsten filament doped with lanthanum hexaboride (LaB_6) as an X-ray source, fitted with an ETD (Everhart Thornley Detector), which preferentially work as a secondary electron detector. The sample for the SEM was subjected to dispersal on a carbon paper coated adhesive followed by a gold coating step.

2.2. Experimental procedure

Thermal pyrolysis of jatropha seed de-oiled cake was carried out at various temperatures of 300, 350, 400, 450 and 500 $^\circ\text{C}$ under atmospheric pressure of nitrogen. The batch fixed bed reactor is made up of glass (length: 280 mm; i.d. 34 mm) and K-type thermocouples have been used as shown in figure 1. The feed samples used in this study were milled in a laboratory ultra-centrifugal mill and the sample then obtained was sieved in standard mesh to obtain particle size of 0.5-2 mm. At first, 10g of the feed was loaded into the reactor and the reactor was purged with nitrogen to remove the inside air. The nitrogen flow rate during pyrolysis was 50 ml min^{-1} . The starting temperature was the ambient room temperature at 25 $^\circ\text{C}$ and the heating rate to reach the pyrolysis temperature was set around 25 $^\circ\text{C min}^{-1}$. Once final pyrolysis temperature was attained, the

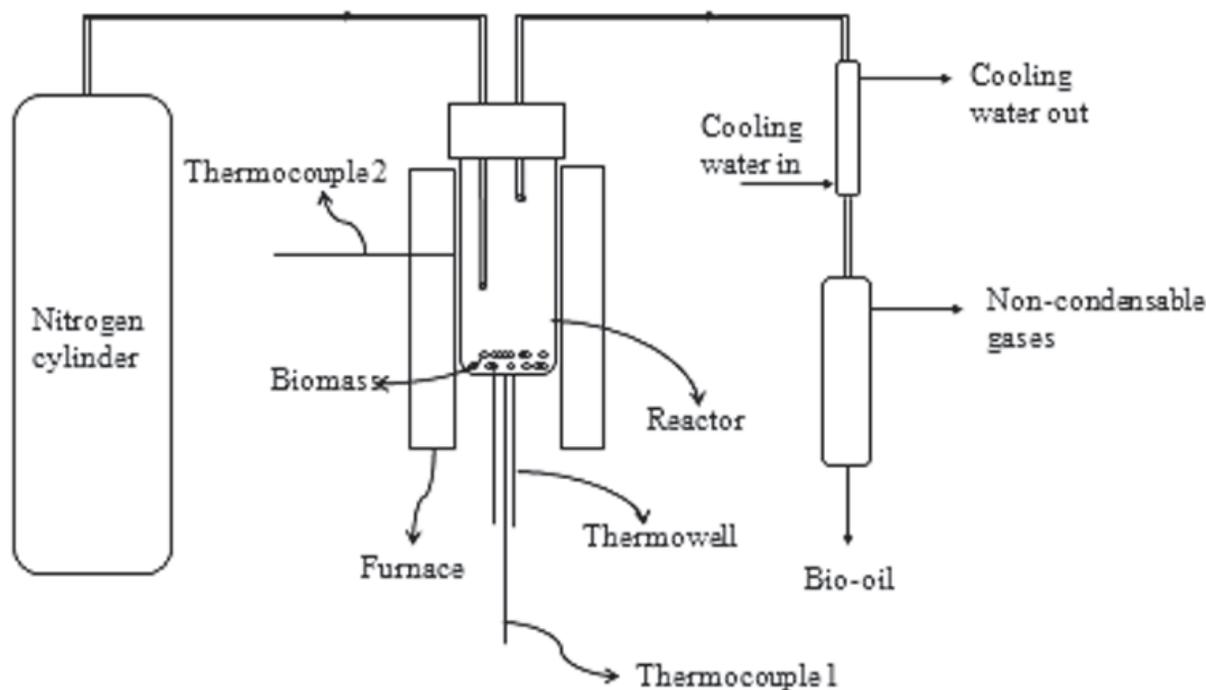


Fig. 1 Line diagram of experimental unit

reactor was maintained at the required temperature for a period of 1 h to ensure that all condensable vapours were collected. Biomass bed temperature has been taken as the pyrolysis temperature and another thermocouple indicated the skin temperature of the reactor. The vapours formed after the reaction was condensed using cooling water maintained at 2 $^\circ\text{C}$. Water in bio-oil was removed by the addition of anhydrous sodium sulphate and acetone was used to recover the organic fraction. Conversion as defined in this process is the amount of solid that has been converted into liquid or gaseous products. The remaining solid after the reaction left in the reactor is termed as bio-char. The experiments have been carried out in duplicates and the average values have been reported which are within a standard deviation of ± 1.0 wt%.

Bio-char yield, wt.% = $\frac{[(\text{Weight of reactor after reaction}) - (\text{Weight of empty reactor})]}{(\text{Weight of feed taken})} \times 100$

Gas yield, wt.% = $100 - (\text{Bio-oil yield, wt.%} + \text{Bio-char yield, wt.%})$

Conversion, % = $100 - (\text{Bio-char yield, wt.%})$

3. Results and discussions

The organic fraction of the bio-oil was characterised using FT-IR, ^1H NMR and GC-MS. The solid bio-char has been characterised using FT-IR, XRD and SEM. The elemental analysis of JSDC was found to contain: carbon (43.63 wt.%), hydrogen (5.35 wt.%), nitrogen (3.91 wt.%) and sulphur (0.43 wt.%). The gross calorific value of the feedstock was found to be 20.05 MJ/kg and moisture content was 7.2 wt.%. Na, Mg, P and Ca are the major trace metals present in the feedstock and these are known to naturally occur in their structure. The compositional analysis of jatropha curcas seed de-oiled cake are as follows: 10.3 wt.% ash, 43.5 wt.% holocellulose, 13.9 wt.% lignin and 5.5 wt.% pentosan content.

The yields of bio-oil, gas and bio-char from slow pyrolysis of jatropha seed de-oiled cake at various pyrolysis temperatures of 300, 350, 400, 450 and 500 $^\circ\text{C}$ have been shown in table 1. With increase in temperature from 300 to 450 $^\circ\text{C}$, the yield of bio-oil is seen to increase. At 300 $^\circ\text{C}$, the bio-oil yield was 34.5 wt.% and increased slightly to 34.7 wt.% at 350 $^\circ\text{C}$. Further as the temperature was increased to 400 $^\circ\text{C}$, the yield of bio-oil

Table 1: Product yields by slow pyrolysis of jatropha seed de-oiled cake at different temperatures

Temperature, °C	Bio-oil, wt. %	Gas, wt. %	Bio-char, wt. %	Conversion, %
300	34.5	19.5	46	54
350	34.7	22.3	43	57
400	36.5	24.5	39	61
450	38.4	24.6	37	63
500	37.8	26.2	36	64

increased to 36.5 wt.% and reached a maximum of 38.4 wt.% at 450 °C. The yield of bio-oil reduced to 37.8 wt.% at 500 °C. The conversion followed a similar increasing trend from 54 to 63 % as the temperature was raised from 300 to 450 °C. At 500 °C, there was a slight increase in the conversion to 64 % but as mentioned before the bio-oil yield was reduced.

The gas yield increased steadily from 300 to 400 °C. Initially the yield was 19.5 wt.% at 300 °C and increased to 22.3 wt.% at 350 °C and then was observed to be 24.5 wt.% at 400 °C. There was not much difference in the gas yield at 400 and 450 °C but at 500 °C, the gas yield increased to 26.2 wt.%. This increase in non-condensable gases yield at higher temperatures of 500 °C might be due to the increased primary cracking of the biomass. It might also be due to the secondary cracking of the bio-char formed which could also be the reason for reduced bio-char formation or in turn increased conversion. Thus, the optimum pyrolysis temperature for jatropha seed de-oiled cake is concluded to be 450 °C at the given experimental conditions.

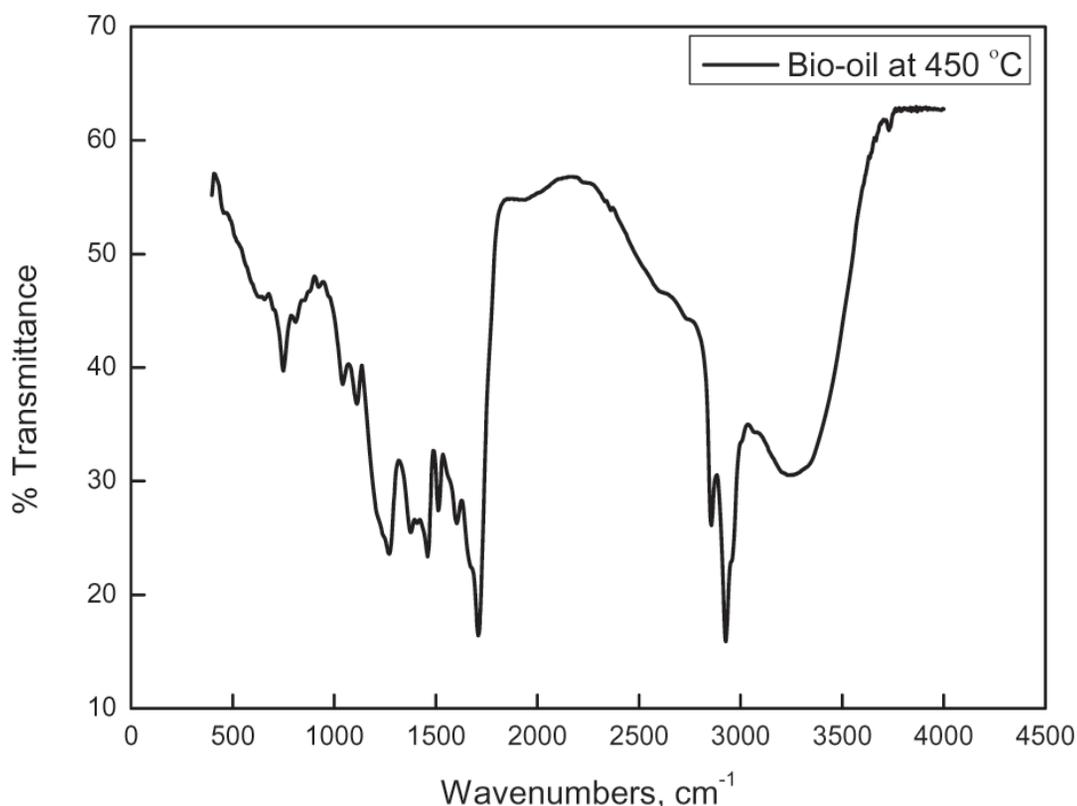
The optimum conditions observed in this study are in line with those observed for raspberry seed cake (Smets et al., 2014) and ground nut de-oiled cake (Agrawalla et al., 2011) at 450 °C though the bio-yields observed in both the cases was around 50 wt.%. De-oiled canola meal required optimum temperature of 500 °C to produce liquid bio-oil yield of 10-24 wt.% which was less than jatropha seed de-oiled cake (Azargohar et al., 2013). In case of rapeseed cake with lower holocellulose and lignin content than the feed used in this study, higher optimum temperatures of 550 °C were observed but the yield of bio-oil (47 wt.%) was higher than

de-oiled canola meal and jatropha seed de-oiled cake as in this study (Smets et al., 2013).

3.1. Bio-oil characterisation

The organic fraction of the bio-oil was characterized using FT-IR, ¹H NMR and GC-MS. The bio-oil obtained at 450 °C was seen to be rich in functionalities due the presence of several peaks in the FT-IR spectra (figure 2). The broad peaks at 3253 cm⁻¹ indicates the presence of the stretching O-H band due to the presence of phenols or alcohols. The presence of alkanes can be identified by the peaks at 2925 and 2856 cm⁻¹ attributed to the C-H stretching. The C=O stretching vibrations at around 1710 cm⁻¹ might be due to the presence of carbonyl compounds such as aldehydes, ketones, carboxylic acids or esters. The presence of nitrogenous compounds or aromatic rings leads to some of the peaks in the range of 1500-1610 cm⁻¹ (Agrawalla et al., 2011). The other peaks in the spectra are attributed to the out of plane bending vibrations of the C-H groups, and the stretching of the C-O-C bonds in polar aromatic compounds etc (Putun et al., 2007).

The ¹H NMR technique illustrated that the downfield region from 0.5-1.5 ppm corresponds to the protons present in the short chain aliphatics attached to carbon atoms which are atleast 2 bonds away from C=C or heteroatom. The next region from 1.5 to 3.0 ppm corresponds to protons on the aliphatic carbon atoms which are bonded to C=C either on the aromatic or olefinic or are two bonds away from a heteroatom. The organic fraction of the bio-oil obtained is seen to be rich in aliphatic protons (77%) as observed in other de-oiled cake pyrolysis liquids as

**Fig. 2** FT-IR of bio-oil obtained at 450 °C

well (Azargohar et al., 2013). The next region 3.0-4.4 ppm corresponds to protons that are attached to the carbon atoms next to an aliphatic alcohol or ether or a methylene group which bonds two aromatic rings. The amount of protons resonating in this region is 6%. The region from 4.4-6.0 ppm represents hydrogen atoms of carbohydrate-like molecules. The amount of protons in this region is negligible which clearly indicates the conversion. The range 6.0-8.5 ppm represents the aromatic region of the spectrum. It encompasses the protons in benzenoid molecules and heteroaromatics which amounts to 16% (Mullen et al., 2009).

The compounds identified by GC-MS are grouped into phenolic compounds and aromatic ethers, acids/ esters, hydrocarbons, carbonyl compounds, nitrogen compounds and non-classified compounds and their area percentage are shown in table 2.

The organic fraction of the bio-oil is rich in phenolic compounds and aromatic ethers which are mainly derived from the lignin fraction of the biomass. As it is a de-oiled cake, some long chain acids and esters have also been identified. Nitrogen containing compounds have also been identified which corroborates the findings through FT-IR. Hydrocarbons and carbonyl compounds are also found in small quantities in the bio-oil. Similar compounds have been identified in case of de-oiled groundnut cake (Agrawalla et al., 2011).

Table 2: Compounds identified by GC-MS

Compound	Area %
Phenolic compounds and aromatic ethers	
Phenol	2.67
Phenol, 2-methyl-	4.95
Phenol, 2-methoxy-	18.00
Phenol, 2,4-dimethyl-	2.36
Phenol, 3-ethyl-	3.08
Creosol	5.33
Catechol	4.07
1,2-Benzenediol, 3-methoxy-	1.97
Phenol, 4-ethyl-2-methoxy-	7.98
2-Methoxy-4-vinylphenol	3.25
Phenol, 2-methoxy-3-(2-propenyl)-	1.21
Phenol, 2-methoxy-4-propyl-	1.88
trans-Isoeugenol	5.06
Homovanillic acid	6.28
4-Methyl-2,5-dimethoxybenzaldehyde	1.37
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	2.89
Acids/ esters	
Propanoic acid	1.29
9-Octadecenoic acid, methyl ester, (E)-	2.73
Methyl stearate	0.63
Pentadecanoic acid, 14-methyl-, methyl ester	1.25
Methyl 10-trans,12-cis-octadecadienoate	0.93
Hydrocarbons	
2-Pentene, 3,4-dimethyl-, (E)-	3.10
4-Propyl-1,1'-diphenyl	1.63
Carbonyl compounds	
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	0.81
2-Acetylcyclopentanone	1.24
2-Cyclopenten-1-one, 3-methyl-	1.36
Nitrogen compounds	
5-Hepten-2-amine, N,6-dimethyl-	2.32
2-Propanone, (1-methylethylidene)hydrazone	0.84
Cyclopentanemethanol, 1-amino-	1.91
4-Piperidinone, 2,2,6,6-tetramethyl-	2.44
9-Octadecenamide, (Z)-	0.63
Non-classified compounds	
2H-Pyran-2-one, 4-hydroxy-3,6-dimethyl-	0.66
2H-Pyran-2-one, 3-acetyl-4-hydroxy-6-methyl-	2.18

3.2. Bio-char characterization

The bio-char obtained at temperatures from 300 to 500 °C was also characterized using FT-IR. Characterization of bio-char obtained at 450 °C and feed JSDC have been carried out using XRD and SEM.

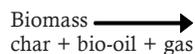
The bio-chars are seen to have a reduced functionality since they are converted into bio-oil or non-condensable gases (figure 3). The intensity of the O-H stretching vibrations at around 3400 cm⁻¹ is seen to reduce with increase in the pyrolytic temperature due to the decomposition reactions leading to the formation of phenolic compounds as observed in the bio-oil. The intensity of the symmetric and asymmetric C-H group peaks also reduce with the increase in temperature as the bio-char becomes more aromatic in nature. This is corroborated by the presence of peaks due to the C=C vibrations of aromatics at around 1600 cm⁻¹. The peak due to the -CH₂- scissoring of alkanes at around 1400 cm⁻¹ is also seen to reduce with increase in temperature. The peak due to O-H deformation is also observed in the bio-char spectra. Bio-char was of similar nature in case of de-oiled canola cake as well (Azargohar et al., 2013).

The XRD patterns of the feed along with bio-char obtained at 450°C is shown in figure 4. The peak at 2θ approximately around 15 ° and 21 ° in the feed corresponds to several crystallographic planes of cellulose. These peaks are not observed in the bio-char indicating the conversion of cellulose in the feed. The bio-char is amorphous in nature and also seems to be rich in carbon content further corroborating the conversion (Wu et al., 2012).

The SEM images of jatropha seed de-oiled cake feed and bio-char at optimum conditions (450 °C) are shown in figure 5. All the images are provided at the same resolution and the scale is 10µm. The feed has a non-porous and rough surface but the bio-char has tiny eruptions on its surface. This might be due to the loss of moieties from the macromolecular backbone of the biomass.

3.3. Kinetic parameter estimation

In this study, we have assumed a Global model where the lignocellulosic biomass is taken as such and is not divided into its individual components. The reaction is assumed to be a first order reaction and it is also assumed that the feedstock is decomposed in a single step directly to liquid bio-oil, gas and bio-char.



$$-\ln(1-X) = Kt$$

Where X= conversion (100-char %)

t= 1 hour (residence time in the reactor once the pyrolysis temperature is reached)

The model can be expressed with Eq. (1) below, where n is the reaction order and k (T) is the reaction rate constant defined by the Arrhenius equation Eq. (2).

The Arrhenius rate equation was employed to calculate the frequency factor, A and activation energy, E.

$$dX/dT = k(T) * (1-X)^n \dots\dots\dots (1)$$

$$K = Ae^{-E/RT}$$

$$\ln K = \ln A - E/RT \dots\dots\dots (2)$$

The slope of graph of ln K vs. (1/T) (table 3 and figure 6) gives the value of E and the intercept gives the value of A. The value of A and E are found to be 2.38 s⁻¹ and 5.31 kJ/mol respectively which are less than those observed by TGA (Chutia et al., 2013). The low value of activation energy and frequency factor indicates that there is good mass and heat transfer in the reactor used here.

4. Conclusions

Slow pyrolysis of jatropha seed de-oiled cake was carried out and the optimum temperature was found to be 450 °C for maximum bio-oil yield. Phenolic compounds and aromatic ethers were the major fraction of compounds that were present in the organic fraction of the bio-oil. The physico-chemical characterization of bio-char indicated the opening of the macromolecular structure of biomass and led to the conversion of the feedstock into bio-oil or non-condensable gases. The first order rate equation was used to calculate the frequency factor and activation energy of the process. They were found to be 2.38 s⁻¹ and 5.31 kJ mol⁻¹ respectively. It was noted that these are lower compared to those obtained from the thermo-gravimetric analysis indicating efficient heat and mass transfer in the reactor system.

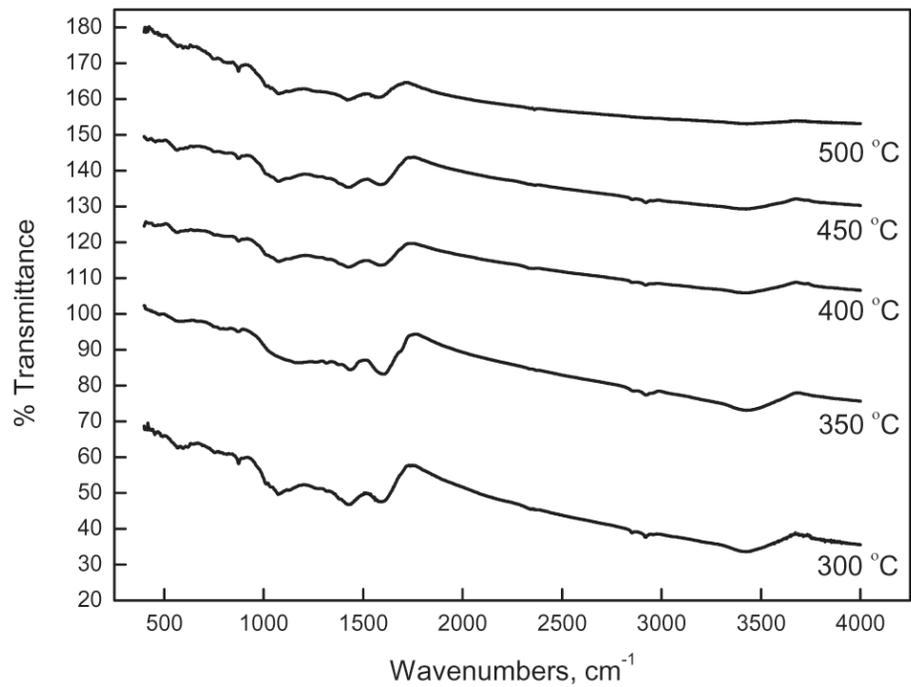


Fig. 3 FT-IR of bio-char obtained at 300, 350, 400, 450 and 500 °C

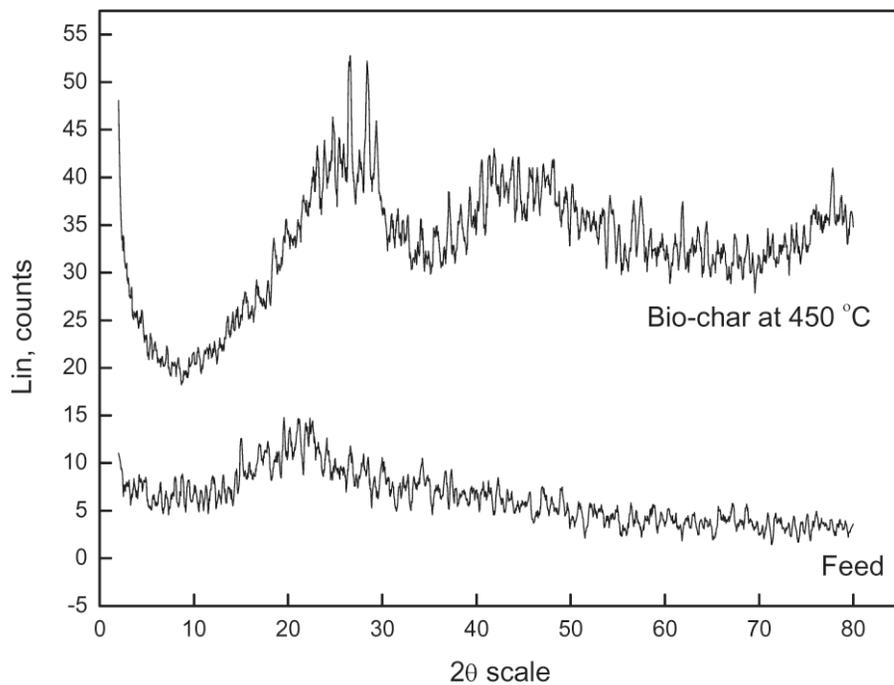


Fig. 4 XRD patterns of feed and bio-char obtained at 450 °C

Table 3: Kinetic parameter estimation

T (°C)	T (K)	Conversion	K	ln K	1/T, (K ⁻¹)
300	573	0.54	0.776529	-0.25292	0.001745
350	623	0.57	0.84397	-0.16964	0.001605
400	673	0.61	0.941609	-0.06017	0.001486
450	723	0.63	0.994252	-0.00576	0.001383
500	773	0.64	1.021651	0.02142	0.001294

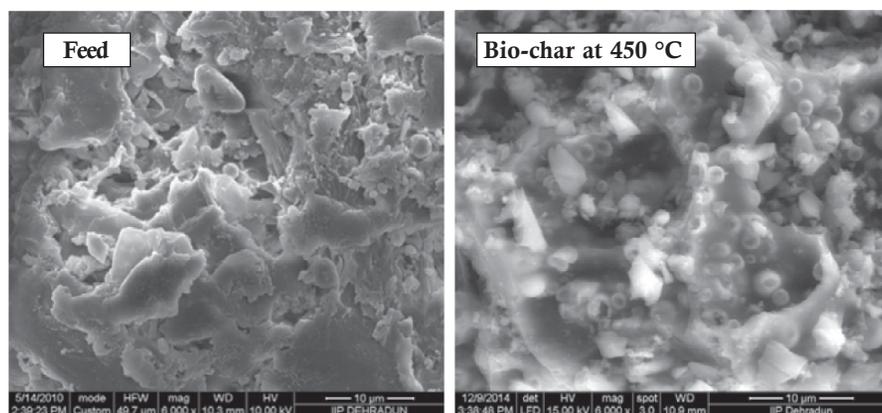


Figure 5: SEM of feed and bio-char obtained at 450 °C

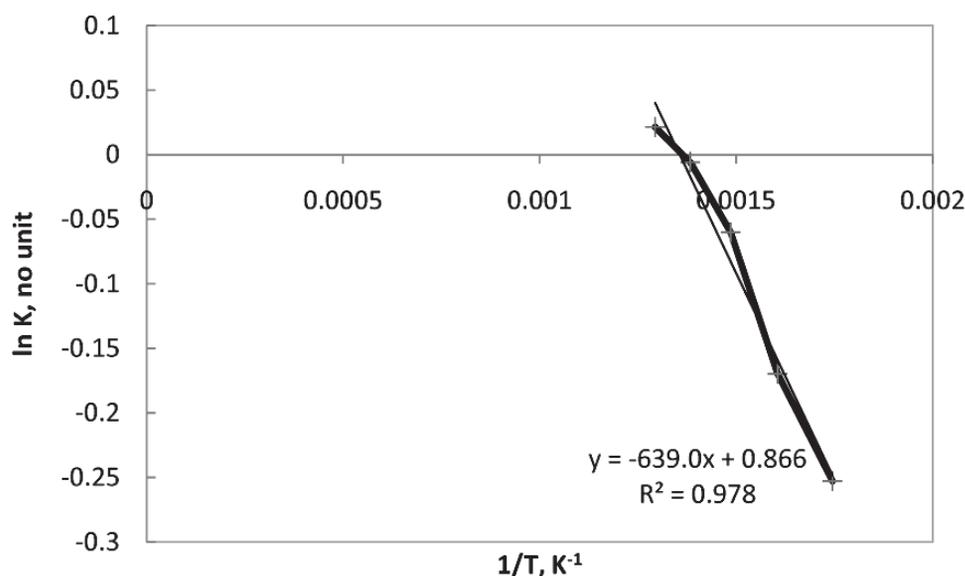


Figure 6: ln K vs. 1/T graph for kinetic parameter estimation

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