Thermal Cracking of Karanja de-oiled seed cake on Pyrolysis Reactor for producing Bio-oil with focus on its application in diesel Engine

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Abstract: A thermal cracking experiment was conducted on Karanja seed (de-oiled) cake at to determine its potential to be an automotive fuel. Experiment was conducted on a fluidised bed type Pyrolysis reactor. The production parameter such as particle size of de-oiled seed and temperature on the oil yield were studied. Fluidization was achieved with the help of Nitrogen gas that is why Nitrogen gas flow rate was also considered as production parameter. For the study purpose a particular particle size range were used. Similarly the Temperature and Flow rate of Nitrogen range were selected from the initial run data of experiment. After investigating the test data the optimized parameter were found for 65.56 wt % of bio oil. The temperature was 500°C and the particle size was in the range of 0.50-0.99 mm at sweep gas flow rate about 8 LPM for the optimized condition. The pyrolysis oil obtained after condensation can be used as fuel. And by some up-gradation technique like trans-esterification process, bio oil can be made suitable for the today’s engine technology. Non condensable gases were consisting of Hydrogen, Methane, Carbon Dioxide, Carbon Monoxide, Oxygen and Nitrogen as major fractions.

Keywords: Trans-esterification, Fluidization, Sweep gas, super critical

1. Introduction

India is among the fastest growing economics in the world. The development objectives focus on sustainable growth in development, equity and welfare. Energy is one of the major inputs for socio-economical development. In India, fossil fuels play a dominant role in energy scenario. In three decades, India’s energy consumption has increased many due to the rapid population growth and economic enrichment. India’s energy demandis growing rapidly and is largely dependent on the use of oil. India’s difficulty is that it does not have fossil fuel production large enough to fill even its current demands. India is heavily dependent on the imported crude oil. The primary energy consumption has grown in India by 7.9% in 2018 and continuously rises. Now India is the third biggest consumer after China and USA with 5.8% global share.[1] Biofuel may be the one of the solution of the current scenario[2]. In recent year, it has been observed that the utilization of seed cake such as karanja & Jatropha must be efficient. Most of the seeds edible and non-edible have the oil and cake ration about 25% and 70 % respectively considering 5% waste in the oil milling process by mechanical expellers.
Edible oil cakes are used for animal feeding. However, non-edible seed cakes are not used in allied agricultural activities due to the toxic nature of the cake. Karanja seed cake can be used in making of biogas but it will be associated with storage & handling problem. If bio oil is produced by pyrolysis from seed cake, it will reduce the storage and handling cost. Karanja seed cake will have the great significance through oil extraction from seed as well as seed cake. Thus, by use of the non-edible vegetable oils from Karanja (Pongamia pinnata) may be the one of the key that has potential to provide an environmental friendly fuel. And the production of these kinds of fuel results in fewer greenhouses responsible gas emission, which also leads reduction in current diesel emission. Thermo-chemical conversion (pyrolysis) of Karanja seed cakes to produce bio oil can contribute significantly towards the reduction of energy demand. Bio oil with upgraded fuel qualities can be used in diesel engine as a supplementary fuel[2][3]. It has very good potential to be used as transportation fuel in India.

2. Production of seed cake in India

As India is working on the massive plantation of the Karanja and Jatropha trees for the production of bio-diesel on wastelands under the biodiesel mission project. And aftermath of this massive yielding of seeds results in the extraction process. Which again leads to a large production of the de-oiled seed cake as approximately 25% oil is generally extracted by tree born oil.[4][5] So, another challenge is to utilize the generated de-oiled seed cake in and effective and environmentally manner. The table no. 1 is showing the potential annual production status of the different seed cakes in India.

Table-1 Potential production status of different seed cake in India[6]

| S.No. | General Name (Seed Cake) | (Seed Cake) Million Metric Tonnes/Year |
|-------|--------------------------|-------------------------------------|
| 1.    | Karanja                  | 0.145                               |
| 2.    | Jatropha                 | 0.035                               |
| 3.    | Kusum                    | 0.055                               |
| 4.    | Neem                     | 0.400                               |
| 5.    | Pilu                     | 0.033                               |
| 6.    | Tumba                    | 0.079                               |
| 7.    | Sal                      | 1.320                               |
| 8.    | Mahua                    | 0.320                               |

As per the table date we can assume that a large amount of the cakes are being produced and in near future more amount of the cakes will be generated. So, this issues needs to be addressed.
3. Problem associated with seed cake

In literature it is reported that during production of biodiesel through Jatropha and Karanja seeds a large amount of seed cake is generated as byproduct. Due to the toxicity of these seeds it cannot be used directly as live feedstock. A researcher claimed that the presence of Phorbol Esters in de-oiled seed cake makes it toxic[5]. So, it is very essential to utilize this seed cake. There are some problems, which are given below are of great concern. And if de-oiled seed cakes are left in open for the self-decomposition then they would generate CH₄, N₂O, H₂S, NH₃, CO₂ and Volatile organic compounds (VOCs). These gases again lead to environmental threats.

![Figure-1 Cake and oil content in different seed.[7]](image)

4. Utilization of seed cake

As mentioned above the casual disposal of de-oiled seed cake may raise other environmental threats. in other way if this de-oiled cakes are considered as Biomass resources rather than waste then this problem may results in some useful product by converting it into an energy resource. This may be achieved by thermal-chemical conversion (Pyrolysis) to produce bio-oil, which can contribute towards the reduction of energy demand. This Bio-oil with certain up-gradation could be utilized into the diesel engine as an alternate source of energy[8]. During the process of Pyrolysis along with the production of bio-oil some solid residue obtained as a char and hot gases are produced. These hot gases can be recirculated in the pyrolysis reactor to maintain the fluidization of bed and can also be used for removal of moisture content from the feedstock. Following figure shows the schematic diagram of utilization of seed cake[9][10]. The solid residue as a byproduct after the pyrolysis could be utilized as adsorbent for wastewater treatment, contaminated with dye, metal etc.

Importance of bio-oil increases due to:-

- Rising petroleum prices
- Limited fossil fuel reserve
- Environmental benefits of bio-oil
5. Physico-chemical properties of seed cake

The following table shows the ultimate and proximate analysis of Karanja seed cake[11].

Table -2 Proximate Analysis of seed cake [12]

| Properties               | Seed cake (Karanja) |
|--------------------------|---------------------|
| Moisture                 | 8.12%               |
| Ash                      | 4.41%               |
| V.M. (Volatile Matter)   | 70.08%              |
| F.C. (Fixed Carbon)      | 17.40%              |

Table –3 Karanja seed cake’s UA[12]

| Percentage Content (%) | Seed Cake (Karanja) |
|------------------------|---------------------|

Fig.2 Process flow diagram for the utilization of seed cakes
6. Production of bio-oil from non-edible oil seed cake (Karanja).

There are various thermo-chemical conversion processes such as direct combustion, liquefaction, pyrolysis, supercritical extraction, gasification etc., for the production of bio-oil through seed & seed cake. Pyrolysis is a process of thermal decomposition of materials in the absence of oxygen or air. The pyrolysis process is categorized normally in three types based on the operating conditions. Fluidized bed is one of them[13].

7. Experimental setup

For the experiment a fluidized bed pyrolysis unit was used pyrolysis-oil conversion. The schematic diagram of pyrolysis unit is in the below figure 3.

Main component of Pyroreactor:

1. Nitrogen cylinder
2. Worm geared motor
6. Condenser
7. Oil collector
3. Feeder 8. Ash pit
4. Electrically heated Pyroreactor 9. Cooling water in & out
5. Cyclone 10. Screw Feeder

8. Material and Up-gradation

- Materials
Karanja seed cake: Generated after expulsion of oil from the seeds through mechanical extraction.
Nitrogen Gas: Nitrogen gas of AR grade procured from the local suppliers was used for the Pyrolysis Experiments
Dehydrating Agents and Additives: Zeolite and sodium sulphate were used as Dehydrating Agents.

- Up-gradation
For improving the quality of bio oil produced by pyrolysis process, fractional distillation and sodium sulphate were used to remove the water content[14][15].

9. Results and discussion

9.1 Density of Bio-oil
The density of the crude bio-oil and the upgraded bio-oil was measured by using 25 cc density bottles. The weight of the empty bottle with stopper and bottle fully filled with bio-oil were determined. By doing so the weight of bio-oil was determined. Mass divided by volume was considered as the density of the oil in Kg/m3. For Karanja crude oil density was 1050kg/m3.

9.2 Proximate analysis
It can be observed from the table 4 as temperature increases the VM (volatile matter) is also increasing. It is because of the secondary cracking phase. The result indicates that the seed cake of 75% volatile matter is having potential for the production of the pyrolysis oil. So, if pyrolysis is done above the temperature 600°C, leads more yield of gaseous product rather than bio-oil. So, it could be concluded that high yielding of bio-oil could be achieved at the temperature below 500°C. Ash content was found to be around 4% at 900°C. The basis for the analysis was air dried and temperature range from 500 °C to 700°C.

Table 4 (Proximate Analysis of Karanja seed cake)
Temperature effect on Product yielding:

The pyrolysis oil yield can be observed in relation with particle size and reactor temperature in fig. 4. The temperature range was 450°C to 550°C at the difference of 50°C. The particle size range was 0.5 to 0.99 mm with fluidized gas velocity of 8 LPM. At 500°C, oil yield was maximum around 65.56 wt% as observed in figure no.9. From the figure, it can be verified that the pyrolysis temperature affect the process yield in very significant manner. Figure shows the increase in the yielding with increase in temperature and obtains a maximum level then it decreases with increase of temperature. Carbon conversion to the gas is increasing with the reactor temperature increment as observed in primary stage and it can be said that in pre stage of increasing temperature, reactions of the volatile fraction and decomposition of char portion took place with increasing reactor temperature. The same behavior is also reported by many literatures with different biomass categories. The experiment also showed the reduced yielding of char and liquid while the increase in gas yield at 500°C. In the pre-stage of the pyrolysis in the current experiment, the decomposition was slow as compare to later stage of the reaction. 31.2 wt % and 8.35 wt % were the wt% of the gas and char yield respectively at pre-stage of the temperature range 400-450°C. When the temperature was increases at later stages, yielding of crude oil was decreased to 63 wt% and the char yield was also decreased. If all the results are analysed then it can be clearly seen that the optimized temperature for the present set of the condition was 500°C. At the temperature above 500°C, decomposition of secondary volatile matter and organic components decrease that is why oil yield decreases while the gasification increases at pyrolysis temperature from 550°C to 700°C.

| Sample          | Temp (°C) | Volatile matter (%) | References |
|-----------------|-----------|---------------------|------------|
| Karanja Seed Cake | 500       | 74.25               | Present study |
|                  | 600       | 82.22               | Present study |
|                  | 700       | 83.17               | Present study |
9.4 Effect of Sweep Gas Flow Rate

The Nitrogen gas was used as sweep gas in this experiment. Sweep gas is responsible for the residence time in the reactor so if the velocity of the gas increases then the residence time will be short. As it can be observed from the fig. the increase of the Nitrogen flow rate from 6 to 8 LPM results in increasing the oil yield by 2.5 %. It is because of the short residence time which leads less secondary reactions. From the fig it can also observed that the maximum oil yield was 48 wt % with particle size of 0.5-0.99 mm at sweep gas flow rate of 8 LPM and the temperature was about 500°C. The char yield lower down with increase of flow rate of the Nitrogen gas. From the figure-5, when flow rate changes from 6 to 8 LPM then in results char yield decrease by 7.6 wt%.

The experimental results in the present experiment shows that the significant effect of fluidized media on yielding of oil and other by product such non condensable gases and char. As Nitrogen gas makes the fluidized media for the suspension of the cake’s particles and it decides how long the Karanja seed cake’s particle would be in the thermal cracking zone. Its flow also effects the water yielding. In this case the Sweep gas (Nitrogen Gas) keep the matter in the pyrolysis zone and when the flow increases
from 8 LPM and above then for the primary and secondary reactions time remains minimum that is why the yielding decreases. So for the maximum yielding matter has to be in the pyrolysis zone at a optimum flow rate which was found 8LPM , for the maximum oil.

9.5 Effect of particle size

In the next phase of the experiment, the effect of particle size upon the oil yield was studied. Figure no-6show the yield of oil, gas, and char at 500°C and nitrogen flow rate of 8 LPM.It can be observed by the fig that the particle size varies from 0.175 mm to 0.991 mm at the Nitrogen flow rate of 8 LPM, theoil yielding increases from 59.4 wt% to 65.46 wt %. It indicate that the particle size of 0.5 -0.99 mm is the optimum size for the product yield as when the particle size is less then that the particle burn easily and the gas yielding is high. And when the particle size is more than the 0.99 mm then again gas yield increases and char yield also increase as higher size particle were not able to suspend in to the heating Zone.

![Figure -6 (Effect of particle size on oil yield at 8 LPM Gas Flow Rate)](image)

9.6 Composition of Non-Condensable Gases.

At the last stage of the experiment the composition of the non-condensable gas, which was coming out from the reactor’s condenser, was determined. For the determining the composition gas analyzer were used. The concentrations of the gases coming out from the condenser are given below in a pie- chart. The optimum condition was selected when the compositions were determined.

Table-5Composition of Non-Condensable Gases at temperature 500°C

| S.N. | Temperature | % Fraction |
|------|-------------|------------|
| 1    | CO          | 2.026      |
| 7    | CO2         | 7.276      |
| 3    | O2          | 1.727      |
| 4 | HC | 0.364 |
|---|----|-------|
| 5 | N2 | 88.607 |

CONCLUSION

In this pyrolysis experiment the Karanjade-oiled cake was heated in an electrically controlled heating fluidized bed reactor under the nitrogen atmosphere. After investigating the test data the optimized parameter were found for 65.56 wt % of bio oil. The temperature was 500°C and the particle size was in the range of 0.50-0.99 mm at sweep gas flow rate about 8 LPM for the optimized condition. The yielding of char was lowered by 5.85 wt % when the temperature increases from 450°C to 550°C. The oil yield was maximum 48 wt% when the Nitrogen flow rate increases from 6 LPM to 8 LPM. In the present investigation it was found that the sweep gas (Nitrogen) had the significant effect on the oil yield as it provides the suspension non-reactive media in the reactor. The exhaust gases from the reactor can also be used as reheating system for reactor to save energy. In the product yielding particle size was also plying great role as when the 0.5 to 0.99 mm particle size was used then the yielding was increased by 6 wt %. This indicates that heat transfer and particle weight had imminence effect on the oil yielding. Larger size and too small size were having negative effect on the yielding. When the particle size is smaller than 0.55 mm then the gas yield was maximum around 38.2 wt % because large heat transfers at very less retention time. The pyrolysis oil obtained after condensation can be used as fuel. And by some up-gradation technique like trans-esterification process, bio oil can be made suitable for the today’s engine technology. For the running into the modern technology engines the main problem is viscosity. And the viscosity can be reduced by thermal cracking in presence of the catalytic and Transesterification processes in a better way. Carbon residual in the oil may affect the engine life so this value should be minimum. Non condensable gases were consisting of Hydrogen, Methane, Carbon Dioxide, Carbon Monoxide, Oxygen and Nitrogen as major fractions.

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