1. Introduction

The scarcity of fossil fuels, increasing their costs and increasing the environmental pollution from fossil fuel combustion will make renewable energy sources as more attractive one. Agricultural residue is one form of biomass, which is readily available but is largely not utilized in energy recovery schemes. Pyrolysis is one of thermal chemical process which converts the solid biomass in to liquid (bio-oil), gas and solid. The liquid product, pyrolytic oil, approximates to biomass in elemental composition, and is composed of a very complex mixture of oxygenated hydrocarbons. It is useful as a fuel, may be added to petroleum refinery feed stocks or upgraded by catalysts to produce premium grade refined fuels, or may have a potential to be used as a chemical feed stock. Bio-oils are generally preferred products because of their high calorific value, the gross calorific value of the bio oil obtained from pyrolysis of rapeseed oil cake (Suat Ucar and Ahmet, 2008), empty fruit bunches (Abdullah and Gerhauser, 2008) and Cashew nut shell (Das et al., 2004) were 33, 36 and 40 MJ/kg respectively, their ease of transportation and storage, their low nitrogen and sulphur content and their opportunity to be converted into chemicals.

Coconut shell as an agricultural residue is available abundant in India with an annual production of more than 0.94 million tones in the year of 1994 and projected with the production of more than 1.50 million tones for the year of 2010. Coconut shell is more suitable for pyrolysis process, since they contain less amount of ash, more amount of

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volatile matter and available with lower cost in rural areas during all the sessions of the year. Its higher fixed carbon content leads to the usage of solid obtained from the pyrolysis process as an activated carbon material for water treatment purpose. Therefore, a practical method should be applied to pyrolyse coconut shell for providing the valuable product.

Ozlem Onay et al. (2006) pyrolyzed rapeseed in a free fall reactor under nitrogen flow to determine the role of pyrolysis temperature and sweeping gas flow rate on the bio-oil yield at atmospheric pressure. Esin Apaydin-Varol et al. [(2007)] investigated the effects of temperature on the product yields and its composition of pistachio shell in a slow pyrolysis with fixed bed reactor. Ozlem Onay (2007) performed fast pyrolysis of safflower seed to identify optimum process conditions for maximizing the bio-oil yield in a fixed bed reactor, the optimum process conditions were: final pyrolysis temperature 600°C, sweeping gas flow rate 100 cm³/min and heating rate 300 °C/min. Fixed-bed slow and fast pyrolysis experiments have been conducted on a sample of rapeseed to investigate the effects of heating rate, pyrolysis temperature, particle size and sweep gas velocity on the pyrolysis product yields and its chemical compositions by Ozlem Onay et al. (2004). Sevgi Sensoz et al. (2008) pyrolyzed safflower seed press cake in a fixed-bed reactor to determine the effects of pyrolysis temperature, heating rate and sweep gas flow rates on the yields of the products using pyrolysis temperatures between 400 and 600 °C with a heating rates of 10, 30 and 50 °C/min. Ayse E. Putun et al. (2002) conducted the slow pyrolysis of soybean cake in a fixed-bed reactor under three different atmospheres: static, for determining the effects of pyrolysis temperature and particle size, nitrogen and steam for determining the product yields. Pyrolysis of corn stalks with batch wise in a laboratory captive sample reactor wire mesh at atmospheric pressure was carried out by Zabaniotou et al. (2007) by varying the temperature (470-710 °C) with an average heating rate of 60 °C/s and a reaction time of 0.2 s. The effect of the process conditions such as heating rate, temperature and particle size on the product distribution, gas composition and char reactivity of olive waste and straw at high temperatures (800 -1000°C) in a free-fall reactor at pilot scale was carried over by Rolando Zanzi et al. (2002). Olive bagasse was pyrolyzed in a fixed bed reactor (Senoz et al. 2006). Alberto J. Tsamba et al (2006) studied the pyrolysis characteristics and global kinetics of coconut and cashew nut shells. For the coconut shell, the greater mass loss was reported at the temperature interval of 280-415 °C at the heating rate of 10°C/min.

The literature study shows, the yield and composition of pyrolysis products greatly depends on the reaction parameters: temperature, particle size of the fuel, heating rate and residence time. Presently, there are limited researches that reported specifically about the effect of temperature, heating rate, particle size and residence time on the product yields of coconut shell pyrolysis. The optimum process conditions to produce highest liquid yield from coconut shell are also not available in the literature.

Yun Ju Hwang et al. (2008) extracted high capacity disordered carbons from coconut shells as anode materials for lithium batteries. Afrane et al. (2008) and Gratuito et al. (2008) produced activated carbons from the coconut shells under the physical methods. Dinesh Mohan et al. (2008) studied the wastewater treatment by the low cost activated carbons derived from coconut shells and coconut shell fibers. Amadua et al. (2007) produced a highly effective adsorbent material from the coconut shell combined with aquatic waste for the removal of heavy metal from industrial wastewater. Wei Su et al. (2006) prepared micro porous activated carbon from raw coconut shell. Furthermore, the former pyrolysis systems, the pyrolysis process were carried out under the flow of inert gas medium and the residence time was varied by means of inert gas flow rate. Hence, some experiments of pyrolysis of coconut shell with the effect of different process parameters on the yield of liquid, gas and solid yield are described in this paper. The experiments were conducted with the aim of determining the optimum process conditions to maximize the liquid yield from the slow pyrolysis of coconut shell in a fixed bed reactor.

2. Materials and Methods

2.1. Raw Material-Coconut Shell

Samples of coconut shell in the present study were originated from Pollachi, Coimbatore district, located in the Tamilnadu, India. Immediately after getting, the coconut shells were sun dried for few days to remove the moisture content, after which they were ground in a high speed rotary cutting mill and screened by standard sieve (IS designation 460-1962) separator to give fractions of less than 0.15 mm, 0.15-0.30 mm, 0.30-0.60 mm, 0.60-1.18 mm and 1.18-1.80 mm. The fixed carbon, volatiles and ash present in the sample were determined by ASTM standards. The elements carbon, hydrogen, nitrogen, oxygen and sulphur content on the sample were also identified by the ASTM standards. The calorific value and moisture content of the sample were measured with ASTM D 5865:2007 and ASTM D 3173:2003 standards respectively. The properties of sample, components and elements are given in Table 1.

<table>
<thead>
<tr>
<th>Components</th>
<th>Volatiles</th>
<th>72.93%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fixed carbon</td>
<td>19.48%</td>
</tr>
<tr>
<td></td>
<td>Ash</td>
<td>0.61%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Elemental analysis (b) (%)</th>
<th>Carbon</th>
<th>53.73%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hydrogen</td>
<td>6.15%</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>38.45%</td>
</tr>
<tr>
<td></td>
<td>Nitrogen</td>
<td>0.86%</td>
</tr>
<tr>
<td></td>
<td>Sulphur</td>
<td>0.02%</td>
</tr>
<tr>
<td></td>
<td>Calorific value (MJ/kg)</td>
<td>20.88</td>
</tr>
<tr>
<td></td>
<td>Moisture content (%)</td>
<td>6.98%</td>
</tr>
</tbody>
</table>

(a) Weight percentage on dry basis
(b) By difference

Table 1. Components and elemental analysis of Coconut shell
2.2. Experimental Apparatus and Procedure

As shown in Fig. 1, the 316 stainless steel tubular reactors with a length of 200 mm and 300 mm, and an internal and external diameter of 27 mm and 33 mm were used to conduct the experiments, respectively. In each run, a 15 g of the sample biomass was placed inside the reactor then the reactor was placed inside the electric furnace with the capacity of 2 kWh, which was specifically designed and manufactured for this study. The reactor was heated externally by an electric furnace. The temperature inside the reactor was measured by a Cr - Al: K type thermocouple. The temperature and heating rate was controlled by an external PID (Proportional-Integral-Derivative) controller. A 6.5 mm ID and 9 mm OD stainless steel pipe was used to connect the reactor and glass condenser. The connecting pipe between the reactor and the condenser system was maintained at 200°C to avoid condensation. The condensable liquid products (bio-oil + water) were collected in a 300 mm length coil type glass condenser. The temperature of the condenser was maintained at 25°C by circulating the water in the condenser. After each experiment, the condensed liquid was collected into the sample bottle and the liquid weight was calculated by the weight difference of sample bottle before and after the liquid was collected. After pyrolysis, the solid residue was removed and weighed. Then the gaseous phase was calculated from the material balance. The biomass sample input, liquid and solid char were measured by the electro balance weighing machine with an accuracy of ± 0.01 g. All the yields were at an average yield of at least three with an experimental measurement error of less than ± 1.5%.

The experiments performed in the fixed-bed reactor were carried out in four groups. In the first, to determine the effect of the pyrolysis temperature on the coconut shell pyrolysis yields, a 15 g of the sample with the particle size of 1.18-1.80 mm was placed in the 200 mm length reactor then the reactor was placed inside the furnace and the temperature was raised at 60 °C/min to a final temperature of 400, 450, 500, 550, or 600 °C and held for until no further significant release of gas was observed. The second group of experiments was performed in order to determine the effect of particle size on the pyrolysis yields. The experiments were conducted at particle sizes less than 0.15 mm, 0.15-0.30 mm, 0.30-0.60 mm, 0.60-1.18 mm or 1.18-1.80 mm. For all these experiments, the heating rate, the final pyrolysis temperature (based on the results of first group of experiments) and the reactor lengths were 60°C /min, 550 °C and 200 mm respectively.

The third group of experiments was performed in a 200 mm length reactor to determine the effect of heating rate on the pyrolysis yield. At first, 15 g of sample was placed in the reactor then the reactor was placed inside the furnace and the temperature was raised at either 20 °C/min, 40°C/min or 60 °C/min by PID controller. For all these experiments, the final pyrolysis temperature and particle size were 550 °C and 1.18-1.80 mm respectively, based on the results of the first and second group of experiments. Finally, the effect of residence time on the pyrolysis yield was determined by varying the reactor lengths. The experiments was performed with the reactor lengths of 200 mm and 300 mm. Based on the first three groups of experiments the final pyrolysis temperature, particle size and heating rate were maintained at 550 °C, 1.18-1.80 mm and 60 °C/min respectively.

The pyrolysis oil obtained at optimum condition was tested for its properties and functional groups. Fourier transform infrared spectroscopy (FT-IR) analysis was performed on a Perkin Elmer Spectrum device with a Resolution of 1.0 cm-1 for finding the functional groups present in the bio oil.

3. Results and Discussion

3.1 Effect of Temperature on the Pyrolysis Yield

Figure 2 presents the product distribution from slow pyrolysis of coconut shell at a pyrolysis temperature of 400 - 600 °C. The liquid and gas yield were increased from 38 to 43 wt% and 30 to 33 wt% respectively, when the pyrolysis temperature was increased from 400 to
600°C, whereas the solid yield significantly decreased from 32 to 22 wt%. The decrease of liquid yield and increase of gas yield were observed at higher temperature. The decrease in liquid and gas yield at lower temperature is due to incomplete decomposition of the shell (pyrolysis is not complete). Decrease in liquid and char yield and increase in gas yield at higher temperature is due to not only the secondary cracking of pyrolysis vapor but also solid char. Similar results were observed in the fixed - bed slow pyrolysis of rapeseed at 30°C/min in which the liquid yield increased from 41 to 47 wt% when the pyrolysis temperature increased from 400°C to 550 °C (Ozlem and Kocker, 2004), but the liquid yield of safflower seed press cake and soybean cake were found to be 30 to 33 wt% and 26 to 30 wt% respectively at the same temperature range (Sensoz and Angin, 2008; Putin et al. 2002). This similarity and variation of the liquid yield could be due to the variation of the components present with individual biomass.

3.2. Effect of Particle size on Pyrolysis Yield

From Fig. 3, the solid and liquid yields are significantly increased as the particle size is increased from less than 0.15 mm to 1.80 mm and gas yield is found to decrease. The study found that solid and liquid yield increases from 23 to 26 wt% and 37 to 43 wt% respectively and gas yield decreases from 39 to 30 wt% when the particle size is increased from less than 0.15 to 1.18-1.80 mm. The increases in the solid yield with the increasing particle size for the sample biomass could be due to greater temperature gradient inside the particles. So that at a given time the core temperature is lower than that of the surface, which possibly gives rise to an increase in the solid yield (Zanzi et al. 2002). Decrease in particle size leads to decreases of liquid yield because the residence time of the volatiles in the reactor is longer, favor the cracking of hydrocarbons, when smaller particles are used (Sensoz et al. 2000). More residence time of volatiles inside the reactor leads to cracking of heavier molecules (tar) in to lower molecules at lower particle size ranges and it results in increase of gaseous product. There is a significant effect of particle size on the char, oil and gas yield in the pyrolysis of olive bagasse and pine sawdust (Sensoz et al. 2006; Wei et al. 2006).

3.3. Effect of Heating Rate on Pyrolysis Yields

Figure 4 shows the pyrolysis product yields of coconut shell at different heating rates of 20, 40 and 60 °C/min with a constant pyrolysis temperature of 550 °C and particle size of 1.18-1.80 mm in a 200 mm length reactor. The liquid yield was low at lower heating rate and increased with increase of heating rate; the liquid yield was 40 wt% at the heating rate of 20 °C/min and increased to 43 wt% when the heating rate increased to 60°C/min. The gas yield also increased with increase of heating rate, but the char yield decreased with the increase of heating rate. The char yield was decreased from 29% to 25 wt% when the heating rate increased from 20 °C/min to 60 °C/min (Fig. 4). The increase of the oil yield with the increase of heating rate may be due to higher heating rates that break the heat and mass transfer barriers in the particles (Haykiri et al. 2006). The cracking of the pyrolysis vapors at higher heating rates leads to increase of gas yield. The same trend was predicted by other researchers (Sensoz 2003; Sensoz and Angin, 2007; Onay 2007 and Karaosmanoglu et al. 1999) on pine bark, Safflower seed press cake, pistacia khinjuk seed and straw and stalk of the rapeseed plant.

3.4. Effect of Residence Time on Pyrolysis Yield

The effect of residence time on the pyrolysis yield was investigated by varying the reactor length. Figure 5 shows the influence of residence time on the pyrolysis yield. The gas yield from 300 mm reactor was higher than that from the 200 mm length reactor. The liquid yield from 200 mm reactor was higher than that from the 300 mm reactor. This
shows the opposite trends in the liquid yield. This could be due to the secondary cracking of the liquid yield in the 300 mm length reactor due to prolonged residence time of the vapours inside the reactor. The solid residue yield in 300 mm reactor was higher than that in the 200 mm reactor.

4. Properties of Pyrolysis Oil

Physical properties were determined for the bio-oil using the American Standards for Testing and Materials (ASTM). The physical, chemical properties and calorific value of the bio-oil obtained under optimum conditions are given in Table 2.

Table 2. Properties of bio-oil under optimum conditions

<table>
<thead>
<tr>
<th>Properties</th>
<th>Bio-oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental (wt %)</td>
<td>75.4</td>
</tr>
<tr>
<td>Carbon</td>
<td>11.7</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.4</td>
</tr>
<tr>
<td>Oxygen</td>
<td>10.5</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>1090</td>
</tr>
<tr>
<td>Viscosity, 50°C (cSt)</td>
<td>36</td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td>80</td>
</tr>
<tr>
<td>Higher heating value (MJ/kg)</td>
<td>38.6</td>
</tr>
</tbody>
</table>

The IR spectrum of the bio-oil at optimum condition is given in Fig. 6. The O-H stretching vibrations between 3200 and 3400 cm⁻¹ indicate the presence of phenols and alcohols. The C-H stretching vibrations between 3200 and 3400 cm⁻¹ and C-H deformation vibrations between 1350 and 1475 cm⁻¹ indicate the presence of alkanes. The C=O stretching vibrations with absorbance between 1650 and 1750 cm⁻¹ indicate the presence of ketones or aldehydes. The absorbance peaks between 1575 and 1675 cm⁻¹ represent C=C stretching vibrations indicative of alkenes and aromatics. The C-H stretching and bending vibrations between 1380 and 1465 cm⁻¹ indicates the presence of alkane groups in pyrolysis oils derived from biomass. Absorptions between 1300 and 900 cm⁻¹ indicates the carbonyl components (i.e. alcohols, esters, carboxylic acids or ethers). The absorbance peaks between 900 and 690 cm⁻¹ represent O-H stretching vibrations indicative of aromatic groups.

Figure 5. Effect of residence time on pyrolysis yield

Figure 6. FT - IR spectra of pyrolysis oil
5. Conclusions

In this study, pyrolysis experiments of the coconut shell are carried out in a fixed bed reactor with different pyrolysis temperature, particle size, heating rates and reactor length. The bio oil obtained at the optimum parameters are tested for finding its properties. The following are the findings from pyrolysis experiments of coconut shell in the fixed bed reactor:

- The optimum process conditions for maximizing the liquid yield of slow pyrolysis of coconut shell in a fixed bed are: pyrolysis temperature 550 °C, particle size 1.18-1.80 mm, heating rate 60 °C/min and the reactor length 200 mm. The maximum liquid yield of 45 wt% was obtained at the optimum condition.
- Employing higher particle size results in more amounts of liquid and solid yield and less amount of gas yield compared to lower particle size. The gas yield decreases from 40 to 30 wt % when particle size is increased from less than 0.15 to 1.8 mm.
- The liquid yield increased from 40 to 43 wt% when the heating rate was increased from 20 °C/min to 60°C/min. The effect of heating rate on the pyrolysis yield is not significant compared to other parameters in this study.
- The rapid devolatilization of cellulose and hemicellulose increased the pyrolysis conversion from 69 to 88 wt% when the temperature was increased from 400 to 550°C.
- The maximum liquid yield of 43 wt% and 35 wt% were obtained at reactor length of 200 mm and 300 mm respectively.
- The elemental composition of bio-oil is found to be better than that of feedstock. The heating value of the bio-oil is found to be similar to that of diesel fuel. FTIR analysis showed that the bio-oil composition was dominated by oxygenated species. The high oxygen content is reflected by the presence of mostly oxygenated fractions such as carboxyl and carbonyl groups produced by pyrolysis of the cellulose and phenolic and methoxy groups produced by pyrolysis of the lignin.

References


