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BIO-OIL PRODUCTION FROM GROUNDNUT SHELL FAST PYROLYSIS IN SPOUTEDBED REACTOR

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ABSTRACT

The present study was carried out to utilize the groundnut shell biomass for bio-oil production which has significant use in commercial sectors for eco-friendly green fuel and chemical generation. Spouted bed reactor was designed and developed for the production of bio-oil under various temperatures. Properties of the bio-oil were found by standard procedures. Compositional analysis of bio-oil was done by GC-MS and FTIR methods. Optimized production (40.7 %) of bio-oil was obtained at 550°C temperature. Heating value of the bio-oil was found to be 21.5 MJ kg^{-1}. Chemical compounds such as phenols, amines, amides and acids were reported in the analysis. The obtainedbio-oil can be used as fuel in transportation sector after upgradation and the derived chemicals have potential applications in pharmaceutical and resin industries.

KEY WORDS : Bio-oil, spouted reactor, fast pyrolysis, calorific value

INTRODUCTION

Biomass, a renewable and energy intensive resource has attracted research interest as an alternative energy generation which leads to environmental and economical benefits. The total estimated potential of biomass power in India is about 18,000 MW (MNRE, 2019). Thermochemical process of biomass conversion includes combustion, pyrolysis, gasification and hydrothermal liquefaction. Pyrolysis is the thermal depolymerization of biomaterials in oxygen less environment, resulted in the production of solid product (biochar), liquid product (bio-oil) and gaseous products (non-condensable gases). Fast pyrolysis with higher heating rates of thousands of degrees per minute leads to the production of energy rich fuel known as bio-oil(Bridgwater and Peacocke, 2000; Bridgwater, 2011; Montoya *et al.*, 2015). Bio-oil is a dark brown, free-flowing organic liquid consists of highly oxygenated compounds. Hundreds of compounds are present in the bio-oil ranging from acids to aldehydes, ketones and alcohols (Kan *et al.*, 2016). An important application of bio-oil is the upgradation of this dark and viscous liquid product into refinery grade crude oil. Many industrially important chemicals can be extracted from bio-oil such as phenols, levoglucosan, hydroxyacetaldehyde etc., having significant economic potential in food, pharmaceutical and paint industries (Dhyani and Bhaskar, 2017).

Various types of reactors are used in fast pyrolysis process for bio-oil production such as fixed bed reactors (Asadullah *et al.*, 2007), fluidized bed reactors (Su *et al.*, 2010), rotating cone reactors (Venderbosch *et al.*, 2010), auger reactors (Luo *et al.*, 2017) and ablative reactors (Ingram *et al.*, 2008). Spouted reactor is one of the configurations of pyrolysis reactors with a simple technical concept compared to other fast pyrolysis reactors. It requires minimal amount of carrier gas (nitrogen) which increases the efficiency of bio-oil condensation due to higher partial pressure of pyrolysis vapours (Pattiya *et al.*, 2012).

In this study, fast pyrolysis of groundnut shell was experimented in pilot scale spouted reactor with varying temperatures and feed rates for bio-oil production. The properties of obtained bio-oil were also studied.

MATERIALS AND METHODS

Sample preparation

Groundnut shell biomass was selected for the study due to its large availability and the presence of higher cellulose and hemicellulose content which help in the production of higher volatile vapours. Ground nut shell sample was dried in hot air oven at 103±5°C to bring the moisture content to below $10(\%)_w$. After drying, the biomass was grounded and sieved to bring the particle size between 0.2 and 0.5 mm. Prepared biomass samples were used in the pyrolysis experiments.

Properties of Groundnut shell

The proximate analysis (volatile matter, ash content and fixed carbon), biochemical characteristics (cellulose, hemicellulose, lignin and extractives) and calorific value of groundnut shell were carried out according to the standard procedures and the results are presented in Table 1.

Table 1. Properties of groundnut shell

S.No.	Properties	Method	Values
1.	Volatile Matter (%)	ASTM, 2006	76.90
2.	Ash Content (%)	ASTM, 2006	6.20
3.	Fixed Carbon (%)	-	14.20
4.	Calorific value (MJ kg^{-1})	Jain *et al*, 2015	18.32
5.	Hemicellulose (%)	Sluiter *et al*., 2004	24.10
6.	Lignin (%)	Sluiter *et al*., 2004	30.70
7.	Cellulose (%)	-	45.20

Experimental Procedure

A pilot scale spouted reactor was designed and developed for carrying out fast pyrolysis studies of groundnut shell. To begin an experiment, the heater was turned on and allowed to heat the reactor space to the desired temperature. The temperatures between 450°C and 650°C were suggested as the optimum heating values for the common biomass (Gang *et al*., 2007). The sample was introduced into the reactor through an auger feeder after the desired temperature was reached. When the sample was processed at the specified temperature, the volatile vapours were produced. These volatiles were condensed in a heat exchanger and bio-oil (ml) was collected. Char was collected in char collection chamber fixed at the bottom. The flow rate of nitrogen was maintained at 10 l min^1.

Composition of obtained bio-oil was analysed using Gas Chromatograph (Model: 7890 B) and Mass Spectrometry (HP-5MS) - Agilent Technologies coupled with data processor to determine the organic compounds present in the obtained bio-oil.

RESULTS AND DISCUSSION

Characterisation of groundnut shell

The properties of the groundnut shell were found out by the standard procedures and the results are given in Table 1.

From Table 1, it is inferred that the volatile and ash content were 76.90 and 6.20 per cent. Higher amount of volatile vapours and lower ash content resulted into better bio-oil production. Fixed carbon was found to be 14.20 per cent. Cellulose, hemicellulose and lignin content were observed to be 45.20, 24.10 and 30.70 per cent, respectively. During thermal degradation, maximum amount of volatiles were produced from cellulose and hemicellulose (Yang *et al*., 2007). Calorific value of the groundnut shell was found to be 18.32 MJ kg^{-1}. Production of bio-oil with higher calorific value was obtained when the calorific value of the biomass is high.

Bio-oil production from groundnut shell

Fast pyrolysis of groundnut shell was carried out in the developed spouted reactor and it is observed that the maximum bio-oil production (40.7%) from groundnut shell was obtained at temperature of 550°C. Higher volatile and cellulose content favoured the maximum production of bio-oil. The bio-oil production was maximum at 550°C and decreased when the temperature was further raised. This may be due to the secondary reactions of heavier molecular weight compounds in volatile vapours which became active at temperatures above 550°C (Evans and Milne, 1987). Similar pattern of biocrude production was reported at 450°C for ground nut shell biomass (Alagu and Sundaram, 2015). At lower temperature of 400°C, the char production was maximum (30.3%). The decrease in char yield could be either due to higher primary decomposition of lignin in groundnut shell or secondary decomposition of the char residues at higher temperatures. This may be due to the improper devolatilization of biomass because of higher feeding rate.

Gas Chromatography-Mass Spectrometry

GC-MS analysis of groundnut shell was conducted and the components identified were reported in Table 2. From the GC-MS analysis, it is observed that in the bio-oil sample, the concentration of acetic acid was maximum. It may be due to the presence of carbon dioxide and methane in volatile output which resulted to the formation of acetic acid. The second abundant concentration was found to be phenols in the bio-oil generated from groundnut shell. The concentration of phenol and its derivatives was increased with increase in pyrolysis temperature (Thangalazhy-gopakumar *et al.*, 2010). The other major compounds identified in the bio-oil include amines, cylobutanol, amides and phenol substitutes. In addition to these oxygenated compounds, bio-oil contains 15 to 30 $(\%)_w$ of water which decreases the heating value. This has to be reduced for further use in transportation sector through various upgradation methods such as hydrodeoxygenation, catalytic cracking methods, distillation techniques etc.

Chemicals present in bio-oil have significant potential in pharmaceutical and resins industry. Phenolic resins were utilized for the production of particleboard and plywood because of their higher mechanical strength (Zheng *et al*, 2018). This reduces the dependency on petro-based phenols for resin manufacturing (Dhyani and Bhaskar, 2017). These compounds also have lower toxicity and cost compared to petro based phenols (Czernik and Bridgwater, 2004). Other applications of bio-oil derived chemicals include the production of adhesives, insulating material and polyurethane foams (Adsul *et al.*, 2011). Hexene is used in the production of polyethylene and hydroxylamine compounds and are used as reducing agents. Cyclopropyl carbinol is used as intermediate for

Table 2. Components in groundnut shell bio-oil

S. No.	Compound	Retention time (min)	Area (%)
1.	Hydroxylamine	1.698	4.40
2.	Acetic acid	2.135	0.91
3.	Dihydroxymaleic acid	2.534	0.77
4.	Cystine	2.678	2.30
5.	Acetic acid	2.942	17.95
6.	2 – Propanone, 1 – hydroxy -	3.176	8.12
7.	Oxaloacetic acid	3.385	0.72
8.	Cyclobutanol	3.713	0.45
9.	Octodrine	3.854	0.87
10.	Ethanol, 2- (1- methylethoxy) -	3.962	2.20
11.	Cyclopropyl carbinol	4.189	0.60
12.	Pyridine, 2 – methyl -	4.664	0.43
13.	2 – Pentanamine, 4 – methyl -	5.000	0.18
14.	Cyclobutanol	5.367	0.17
15.	3 – Hexene	6.117	2.01
16.	3,6 – Dimethylpiperazine – 2,5 – dione	6.241	0.17
17.	Phenol	7.137	10.22
18.	1,2 – Cyclopentanedione, 3 –methyl -	8.335	0.43
19.	Phenol, 2 – methyl	8.675	1.25
20.	Phenol, 3 – methyl -	9.131	3.02
21.	Phenol, 2 – methoxy -	9.449	1.37
22.	Propanamide	9.703	0.33
23.	Phenylephrine	10.235	0.11
24.	p – hydroxyamphetamine	10.463	0.90
25.	Pentanal	11.338	1.61
26.	Metaraminol	11.645	0.54
27.	Propanamide	11.739	0.69
28.	Piperazine	12.070	1.12
29.	2,4 – dimethoxyamphetamine	12.680	2.32
30.	Phenylephrine	16.314	1.11

pharmaceuticals, agrochemical and organic synthesis reactions such as polymer additives, adhesives and surfactants.

CONCLUSION

Bio-oil production from groundnut shell through pyrolysis was assessed in spouted reactor. The study showed that the bio-oil obtained through fast pyrolysis is a promising method for the production fuels and chemicals. The maximum bio-oil obtained was 40.7 per cent at process temperature of 550°C. Properties of the bio-oil were found out by various standard methods. The calorific value of the bio-oil was found to be 21.5 MJ kg^{-1}. Flash and fire point of groundnut shell bio-oil were 102 and 108°C, respectively. After down streaming, bio-oil obtained can be used as a substitute for transportation fuels and feed chemicals in different industrial applications.

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