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Pyrolysis of Chickpeas Waste and Peanut Shells for the Production of Oil and its Analysis

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***Abstract*—** Pyrolysis is one of the widely used technique among the thermal conversion processes of biomass. Biomass in the form of agricultural residues is prevalent in new renewable energy sources, especially in view of its broad potential and rich use. In this paper, the pyrolysis of chickpeas and peanut shells in laboratory-scale tubular furnace reactors is studied, which is considered to be an effective method to utilize agricultural residues in China. The effects of raw material ratio and reaction temperature on the distribution of pyrolysis products are described quantitatively, as well as some characteristics of these products produced in the tubular furnace reactor system developed in this study. The main constituents of bio-oil are categorized into three kinds including aromatic compound, carbonyl compounds and carboxyl compounds that were analyzed with 1H NMR (nuclear magnetic resonance characterization). The maximum yield of bio-oil, about 44.80% from the peanut shell biomass, and 10.3% from the waste of chickpeas by weight was extracted, at a flow rate 10 L/min of N2 at a reaction temperature of 500°C was achieved.

***Keywords*—** Pyrolysis, Chickpeas, Peanut shells, Bio-oil analysis, tubular furnace reactor.

I. INTRODUCTION

In today's world, the extraction of second-generation fuels from biomass raw materials and waste feed is attracting large quantities of biofuels because of the negative impact of first-generation biofuels (fuels of sugar, starch, animal fats, and vegetable oils) on food resources. Fast pyrolysis is a thermochemical transformation process, described by fast heating of biomass raw materials to medium temperature levels without oxygen, and rapid extinguishing or quenching of volatile intermediary products in the absence of oxygen (O2), which is an attractive technology for the production of liquid biofuels [1-3]

Biomass is an economical substance and thought as a high energy renewable feed for the 2nd generation biofuel, which is reasonable to yield fuel oil and chemical substances of various platforms sustainably. Thus helps to overcome this very large dependency consumption of fossil fuels. Biomass fast pyrolysis yields a nominal quantity of bio oil, gaseous products, and solid bio char, so it's of particular interest [4-6]

Biomass residues produce a variety of energy through a variety of unique processes, such as mechanical, thermochemistry, and organic processes. Bio-treatment is highly selective, providing only a few unique products. Contrarily, in the majority of the thermochemical change process, pyrolysis is generally can create a wide scope of items in short response time, including bio-charcoal, bio-oil, and non-condensable gases [7, 8]

There have been considerable efforts on converting biomass to liquid bio-oil [12]. Fatimatul Zaharah Abbas [9] took a sample of oil palm fiber (OPF) and performed and performed pyrolysis, about 41.2 wt % of maximum yield of oil is obtained at the temperature of 500°C. Yunpu Wang [10] in his research work, co-pyrolysis of pretreated bamboo sawdust and soap stock was performed. After the pyrolysis experiment, the yield of (40.00 wt %) bio-oil was obtained at temperature of 200°C for 60.0 minutes with 0.50ml of hydrochloric acid.

Aziz et al. [11] in order to produce bio-oil using microwave power of 1kw over a temperature of 250-390°C in 2 to 10 minutes, microwave assisted pyrolysis on palm shells, sage and wood chips wastes was performed. Bio-oil yield of about 3.92 to 16.51 wt. % was reported according to the raw material and reaction conditions.

In China, Peanut shells and chickpeas waste are abundantly. They have good physical properties and a stable supply of peanut and chickpeas processing plants that is why considered as suitable raw material for bio oil production. For the pyrolysis of chickpeas and peanut shell a tubular furnace reactor was setup for bio-oil production in Southeast University. In this experimental work, fast pyrolysis of chickpeas and peanut shell was investigated with a maximal 10.32 and 52% yield of bio-oil in a tubular furnace reactor, and characterization of final product were also performed by spectroscopic technique which are 1H-NMR and elemental analysis.

II. EXPERIMENTAL

A. Materials

The peanut shells used as feedstock is obtained from a peanut-oil processing plant in Nanjing, Jiangsu Province and chickpeas from Youi foods in Suzhou. The chickpeas and peanut shells naturally dried in the sunlight for 5 days to remove surface water. And these raw materials were used without any pretreatment. Chickpeas was crushed and grounded to get a size fraction of 1–3 mm; peanut shells was grounded of size ~3 mm × 3 mm.

B. Pyrolysis procedure

A tubular furnace reactor is used to perform the pyrolysis of biomass mass samples (chickpeas and peanut shells) fig 1. It is made of stainless steel tubes with an inner diameter of 55mm and a length of 540 mm. Concisely, the reactor consisted of a cylindrical quartz glass tube heated by a stainless steel block furnace. To measure the temperature, inside the furnace an alumel/ chromel thermocouple was placed, fixed in the tube. A sample carrier boat made of porcelain in which samples was placed in the middle of the tube, and nitrogen as the carrier gas was supplied having a flow rate of 10L/min. At the beginning, the furnace is heated in an empty part of the tube, and the desired temperature is balanced between 300 and 600°C. When the desired temperature is reached, the biomass is moved into the furnace for pyrolysis. These operations are carried out at temperatures of 300 to 600°C under atmospheric pressure and under approximate isothermal conditions. The gases released during the pyrolysis leaved the furnace and passed through the condenser arrangement. The bio-oil portion was collected in a beaker placed in cold water. To achieve a fast condensation, gases were extracted by the vacuum pump and also cooled. The bio-oil was separated and weighed. The following conditions used during pyrolysis:

Heating rate: 15°C /min

Temperature: 350, 400, 450, 500, 550 and 600 °C

Cooling temperature set at = -10°C

TABLE I. DATA OF PROXIMATE AND ULTIMATE ANALYSES PERFORMED ON PEANUT SHELLS

Chemical properties	**As received Value**
Proximate analysis, (wt %)	
Ash	12.44
Volatile matter	72.47
Fixed carbon	15.75
Moisture	9.39
Elemental composition, wt%	
Oxygen [a]	36.12
Hydrogen	6.75
Nitrogen	0.8
Carbon	45.46

[a]by difference

TABLE II. DATA OF PROXIMATE AND ULTIMATE ANALYSES PERFORMED ON CHICKPEAS WASTE

Chemical properties	As received Value
Proximate analysis, wt%	
Fixed carbon	17.85
Volatile matter	79.27
Ash	11.24
Moisture	10.49
Elemental composition, wt%	
Oxygen [a]	32.87
Hydrogen	5.45
Nitrogen	0.4
Carbon	47.22

[a]by difference

Figure 1. tubular furnace reactor used in experiment

C. Analysis method

The ultimate analysis was conducted using elemental analyzers (Elementar Vario EL) for bio-oils extracted from the waste of chickpeas and peanut shells. . It was determined the hydrogen, nitrogen and carbon content of the bio-oil with chickpeas and peanut husk wastes. Oxygen content in this studies was calculated by difference. The oil analyzed in this section is obtained under experimental conditions, which give maximum oil yields.

The 1H NMR spectra of Bio-oil were obtained at 400M HZ frequency using the Bruker ARX 400 device. As an internal standard, anhydrous samples are dissolved in chloroform D containing the tetra methyl silane (TMS).

III. RESULTS AND DISCUSSION

A. Product yields

In the nitrogen atmosphere, the pyrolysis of chickpeas and peanut shell waste was carried out in 350, 400, 450 and 500°C , and the distribution of products was shown in table 3 and table 4. As can be seen from table 3, in the case of peanut shells, the yield of bio-oil increases with the increase of temperature, reaching a 500°C after that it goes reduces. Due to the increase of secondary cracking reactions at high temperatures, the yield of gas increases with the increase of temperature from 350 to 500°C. The output of bio-Char is the opposite of gas production, that is, the yield decreases with the increase of temperature.

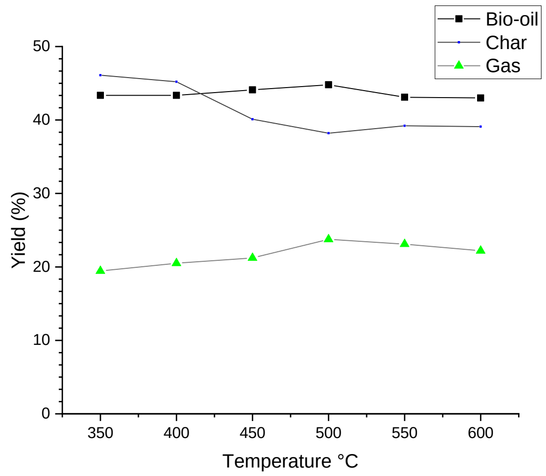

Figure 2. The graph shows the effect of temperature on yield when peanut shells used as biomass with heating rate 15◦C min-1

TABLE III. THE FINAL PRODUCT OF PYROLYSIS OF PEANUT SHELLS AT DESIRED TEMPERATURES.

Temperature, °C	Bio-oil, wt.%	Bio-char, wt.%	Gas, wt.%
350	43.35	46.10	19.41
400	43.35	45.20	20.50
450	44.10	40.10	21.21
500	44.80	38.20	23.70
550	43.10	39.22	23.12
600	43	39.11	22.20

It can be concluded from table 4 that biofuel yield of chickpeas as a biomass sample increases with the increase of temperature up to 500°C, after that it goes reduces. In case of chickpeas waste we get higher amount of the gas yield. So, in comparison with peanut shells sample we get less amount of bio-oil from chickpeas waste.

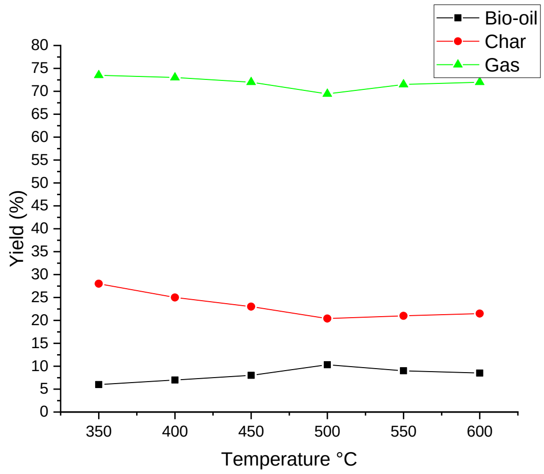

Figure 3. the graph shows the effect of temperature on yield when chickpeas waste used as biomass with heating rate 15◦C min-1

TABLE IV. THE FINAL PRODUCT OF PYROLYSIS OF CHICKPEAS AT DESIRED TEMPERATURES.

Temperature, °C	Bio-oil, wt.%	Bio-char,wt.%	Gas, wt.%
350	6	28	73.5
400	7	25	73
450	8	23	72
500	10.3	20.4	69.4
550	9	21	71.5
600	8.5	21.5	72

B. Bio oil chemical analysis

The 1H NMR spectra comprise of primarily two regions, namely aliphatic and aromatic and hydrogen resonances (Table 5). The aliphatic hydrogen resonances occurs in the 0.5–6.5 ppm range. In the range of 6.5-9.0 ppm the aromatic hydrogen resonances occurs. [12]

The molar percentages of the hydrogen types that were calculated on the basis of the chemical deviation values obtained from the 1H NMR spectra of oils extracted from both peanut shell and chickpeas samples are in Table 5 and 6. The 1HNMR spectra of bio-oil obtained from peanut shells shows that majority of the bio oil belongs to the aromatic region (CH_3, CH2, and CHα) having 39.45 mol percent. In case of chickpeas waste, 29.74 mol percent of bio-oil recorded in aromatic region (CH_3, CH2, and CHα).Hence, it is concluded that oil obtained from peanut shells having more aromatic compounds as compared to the bio-oil obtained from chickpeas waste.

TABLE V. EXTRACTED BIO-OIL FROM PEANUT SHELLS AND THEIR 1H NMR ANALYSIS RESULTS

Type of Hydrogen	Chemical Shift (ppm)	Bio-oil
$CH_{3}\gamma$	0.5–1.0	11.2

β-CH_3, CH2, and CHγ	1.0–1.6	6.54
CH_2 and CHβ	1.6–2.0	14.74
CH_3,CH_2, and CHα	2.0–3.3	39.45
Ring-join methylene(Ar-CH2-Ar)	3.3–5.0	19.43
Phenolic (OH) or olefinic proton	5.0–7.0	1.51
Aromatic	7.0–9.0	2.38

Table VI. Extracted bio-oil from chickpeas waste and their 1H NMR analysis results

Type of Hydrogen	Chemical Shift (ppm)	Bio-oil
CH3γ	0.5–1.0	13.87
β-CH3, CH2, and CHγ	1.0–1.6	9.78
CH2 and CHβ	1.6–2.0	13.54
CH3,CH2, and CHα	2.0–3.3	29.74
Ring-join methylene(Ar-CH2-Ar)	3.3–5.0	17.88
Phenolic (OH) or olefinic proton	5.0–7.0	3.55
Aromatic	7.0–9.0	4.88

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CONCUSLION

Pyrolysis temperature have great effect on pyrolysis yield. The maximum yield of oil obtained in case of peanut shells as biomass sample was 44.80% at temperature of 500°C and in case of chickpeas waste it was only 10.30% and during the experiment the heating rate fixed around 15°C min-1. It was concluded that peanut shells waste gave more value aided bio-oil as compared to chickpeas waste biomass. The spectroscopic analysis results show that the bio-oil obtained from peanut shells waste have more aromatic compounds that is 39.45 mol percent as compared to the bio-oil 29.74 mol percent obtained from chickpeas.

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