Characterization of tar formation during high temperature gasification of different chemical compositions in biomass

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Abstract. The characteristics of tar generated from tropical-plant-based biomass with different chemical compositions during high temperature gasification are crucial to understand the tar formation. In this paper, lignin-rich palm kernel shell (PKS) and hemicellulose and cellulose-rich coconut shell (CS) were gasified in a downdraft fixed-bed reactor at 900 °C. Fourier transform infrared spectroscopy (FTIR) and gas chromatography coupled with mass spectrometry (GC-MS) were used to examine the functional groups and tar compounds. The results of FT-IR indicate that the PKS tar has a lower intensity peak in the fingerprint region than that of CS. The GC-MS results exhibit that the higher molecular weight of tar compounds, such as polycyclic aromatic hydrocarbons (PAHs) are higher in CS tar compared to that in PKS tar. PKS tar is susceptible to create a lighter molecular weight of tar compounds, such as phenolics. Both of the materials have a great potential to be used for renewable energy feedstock.

Keywords: Coconut shell; palm kernel shell; tar formation; downdraft gasification; characterisation.

1. Introduction
Biomass gasification is a promising technology because it converts solid materials, such as agricultural and residue wastes at high temperature (700–1200 °C) in the presence of air or steam mixture as a gasifying agent into the useful product syngas. Syngas, which is derived from gasification technology, can also be used for a wide range of applications, such as fuel cell and internal combustion engine for combined heat and power generation. The use of gasification has plenty of advantages but also has several drawbacks. Tar is one of the undesirable products of gasification, which is inevitable and has become a primary bottleneck to the commercialisation of biomass gasification. In solid-oxide fuel cell (SOFC) applications, fuel containing a high tar level may lessen the system efficiency because of the deposition of carbon, and thus, block the active side of SOFC anode especially on nickel-based catalysts...
Tar is an organic impurity, which was generated during the devolatilisation stage [2,3] and ranges from low molecular weight hydrocarbons to high molecular weight polyaromatic hydrocarbons (PAH) with high boiling points. Tar formation and content depend on many factors, including the nature and properties of the initial feedstock (e.g., biomass and coal), the reactor configurations, reaction conditions, the gasifying agent and the catalysts used [2,4].

Lignocellulose refers to dry plant, which is the so-called lignocellulosic biomass and is the widely available on Earth. Each of lignocellulose comprises the different values of carbohydrate polymers (cellulose and hemicellulose) and an aromatic polymer (lignin). The different values of chemical compositions in biomass influence the reactions of thermochemical and result in the generation of products. Yu et al. [5] examined the characteristics of tar generation from the gasification of pure lignin cellulose and hemicellulose in entrained-flow reactor and concluded that lignin-derived tar was susceptible to formed PAHs. Qin et al. [6] investigated the correlation between biomass composition and tar creation, lignin-rich sawdust and cellulose-rich cornstalks were gasified in a spout-fluidised bed reactor and they concluded that sawdust and cornstalk tar exhibited higher aromatic and aliphatic characters, respectively. In addition, cornstalk tar showed a higher aliphatic compound content than that of sawdust tar. However, no literature exists regarding the influence of different biomass compositions on tar formation during high temperature gasification in downdraft fixed-bed gasifier.

In this study, hemicellulose-rich CS and lignin-rich PKS were gasified in the downdraft fixed-bed gasifier under optimum and similar conditions. The off-line tar sampling method was used, and the collected tar was characterised using Fourier transform infrared (FTIR) spectroscopy and gas chromatography–mass spectrometry (GC-MS). The generation of tar and thermochemical conversion using different biomass components at high temperature were measured and compared.

2. Materials and methods
2.1. Raw materials and characterisation
PKS and CS were obtained from a local grocery store and palm oil factory, respectively, located in Teluk Intan, Perak, Malaysia. Both shells were crushed by using a grinding machine and were sieved in ranges of 9–11 mm, as presented in Figure 1. The feedstock was left in an oven for a day at temperature of 105 °C to ensure the removal of moisture (<15%).

The method of Van Soest acid detergent fibre [2] was referred to analyse the biomass fibre component. In a typical procedure, extractions were executed by accounting the acid detergent fibre (ADF), neutral detergent fibre (NDF), and acid detergent lignin (ADL). NDF, ADL and ADF were obtained by using an ANKOM 220 Fibre Analyser. Hemicellulose was calculated as ADF content subtracted from NDF content, whereas cellulose was calculated as ADL content subtracted from ADF content [4].

![Fig. 1. Palm kernel shell (PKS) and coconut shell (CS)](image_url)

2.2. Experimental setup
A batch-type downdraft fixed-bed with an electrically heated reactor was made of 304 stainless steel tube with a radius of 34.25 mm and height of 600 mm. A ceramic electrical type was used to supply the desired heat for start-up and to maintain heat loss during operation. The operating temperature was measured by using a set of external PID controllers coupled with a K-type thermocouple mounted on the gasifier reactor. The system was heated to the desired operation temperature of 900 °C.

A certain amount of feedstock was fed through the open top of the gasifier upon reaching the desired temperature. The reproducibility of gasification results was evaluated by repeating a set of three
experiments under similar operational conditions. The raw gases were cooled down into a series of six impinger bottles containing isopropanol (99.9%) to separate the condensable components, thereby trapping liquid (tar and water). All the impinger bottles were placed in water and ice–salt mixture at 20 and −20 °C. Isopropanol and tar were mixed together in the impinger bottles upon completion of each experiment, and the tubing was washed with additional isopropanol. The tar was recovered by evaporating the isopropanol at 45 °C in a rotary evaporator under the vacuum condition of 100 mbar. Tar sampling was based on the tar protocol described in the CEN/TS 15439 biomass gasification-sampling and analysis [7].

2.3. Chemical characterization of tar

FT-IR spectroscopy. Functional groups of tar compounds were determined by utilizing a FT-IR 400 Perkin-Elmer. The 50 scans of FT-IR spectra resolution for the tar samples were recorded at 4 cm$^{-1}$ spectral in the range within 4000-400 cm$^{-1}$ wavenumber.

GC-MS. The detail chemical compositions of tar samples were analysed with a GC-MS-Agilent 7890A / 5957C embedded with a capillary column coated with DB-5MS UI (30 m × 250 μm i.d., 0.25 μm stationary phase film). The analytical grade isopropyl alcohol is used as a diluent and 1 μL of sample was introduced by splitless method into the capillary column. The initial GC oven temperature of 50 °C was held for 10 min, followed to 300 °C at a rate of 4 °C min$^{-1}$ with an isothermal time of 5 min. The identification of tar compound peaks was according to the matching of its mass spectrum embedded in NIST spectra library. A semiquantitative analysis of each single tar compounds was conducted by using the ratio of individual peak area with total ion chromatograms.

3. Results and discussion

3.1. Analysis of materials

The values of the main chemical composition of the feedstock, such as cellulose, hemicellulose and lignin can decide the product formation, i.e., biochar, liquid or gaseous yield [8], and these values have widely varying based on the plant species. The analysis results of PKS and CS are presented in Table 1, showing that their values are close to those in other referred literatures [9,10]. Results exhibited that lignin was the highest component in PKS, whereas cellulose and hemicellulose were the abundant composition in CS, as shown in Table 1.

| Sample                      | PKS  | CS  |
|-----------------------------|------|-----|
| Composition analysis        |      |     |
| (wt %)                      |      |     |
| Cellulose                   | 20.7 | 22.1|
| Hemicellulose               | 17.2 | 35.3|
| Lignin                      | 38.0 | 23.5|
| Neutral detergent fibre     | 72.9 | 80.9|
| Acid detergent fibre        | 58.7 | 45.6|

3.2. FTIR Analysis

FT-IR analysis was conducted for the tar samples to examine the functional groups present in the samples generated from different materials. Fig.1 illustrates the full infrared spectra of tar samples generated at 900 °C for PKS and CS. Results (Fig.2 PKS (top) and CS (bottom)) show a very similar spectra pattern obtained from both materials, indicating that the main chemical between 1500 and 4000 cm$^{-1}$ groups are similar. The broad bands disclosed between 3250 and 3500 cm$^{-1}$ correspond to the O-H stretching vibration, which indicates the exist of alcohol and phenol on both samples. The peaks between 2900 and 3100 cm$^{-1}$ correspond to C-H stretching vibration, whereas the bands between 1375 and 1475 cm$^{-1}$ indicate the C-H bending vibrations, which suggest the presence of alkanes [11].

The peak between 1680 and 1710 cm$^{-1}$ assigned to the C=O stretching vibrations probably indicates the existence of oxygen containing compounds, such as ketones, carboxylic acid, aldehyde groups and
some of phenol. The peak between 1570 and 1620 cm\(^{-1}\) is represented by the C=C stretching vibrations from the alkene functional group. The C-O stretching was detected between 1300 and 1020 cm\(^{-1}\) probably indicates the existing of different ethers, alcohols and esters. The peaks detected between 680 and 960 cm\(^{-1}\) probably can be represented by the mono- and polycyclic aromatic compounds with C=C bending and C-H bending [12]. The indistinguishable functional group of PKS and CS tar generated at a temperature lower than 600 °C is also found in various literatures [8,13–15].

According to the results, both tars exhibited various band of oxygenated and aromatic containing compounds especially in the main and fingerprint regions. However, the results in CS tar showed a slightly higher aromatics peaks intensity than that of PKS tar. The functional groups identified in the FTIR spectra were corresponded and distinguished with the results of GC–MS.

**Fig. 2.** FT-IR spectra of PKS (top) and CS (bottom) tars produced at 900 °C

### 3.3. GC-MS Analysis

The tar collected from the experiments were analysed by using GC-MS and only the higher probable (>80%) compounds those matching with NIST chromatogram library are selected. The various organic product compositions were found in the PKS and CS tar samples, as shown in Figure 3. Phenol was the major detected compound in the samples and followed by polycyclic aromatic hydrocarbons (PAHs) as the second largest organic compounds in the samples. Furthermore, the phenol contents of PKS exhibited a significantly higher than that of CS which were 61.4% and 57.1%, respectively. In addition, the ketones content of PKS also led by 0.72% than that of CS by 0.26%. And only the nitrogen containing aromatics was detected by GC-MS in PKS tar with 0.65%. The higher phenols and ketones content in the PKS were probably acquired from the abundance of p-coumaryl alcohol decomposition inherent in lignin [16]. The higher content of phenols is very useful to produce phenolic resin that can be used in automotive and electronic industries.

By contrast, the PAHs and aromatic compounds content of PKS showed slightly lower than that of CS which were 29.2% and 33.7% and 4.14% and 5.19%, respectively. Moreover, the acid and its derivatives and furans of PKS also showed a similar trend with 0.29% and 0.27% different compared to CS. This pattern was probably due to the low amount of hemicellulose and cellulose in PKS.
higher content of acids and furans in CS is mainly obtained from the reactions of 4-O-methyl-D-glucuronic acid which totally acquired from the hemicellulose reaction [17].

![Organic composition of PKS and CS](image)

**Fig. 3.** Organic composition of PKS (left) and CS (right) produced at 900 °C

4. Conclusion

Tar generated from the gasification of PKS and CS at high temperature of 900 °C was conducted to investigate the relationship between the different cellulose, hemicellulose and lignin compositions of PKS and CS towards the functional groups and compounds of tar generated. The FTIR characterization indicated that the CS tar exhibited slightly higher intensity of aromatics peaks than that of PKS tar in the region between 600 and 1500 cm\(^{-1}\). The GC-MS data showed that the PKS tar had higher phenol content than that of CS tar while CS tar showed higher aromatic compound content than that of PKS tar. These results indicated that PKS having lighter molecular weight compounds is a better source for the production of high quality bio-oil while CS having higher molecular weight compounds is a suitable source for high quality gasification. This information can be used as a reference for the chemical and energy producing industries.

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