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Thermal Effect on Co-product Tar Produced with Syngas Through Co-gasification of Coconut Shell and Charcoal

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Abstract. Lignocellulosic biomass generated syngas is one of the most promising alternative bioenergy for the fulfillment of future energy demand. However, the presence of tar in syngas may hindrance the direct uses as transportation and electricity generation purposes. Moreover, tar elimination from syngas is one of the major challenges that can cause fouling in pipes and engines. Thus, this study investigates the decomposition of tar compounds by thermal treatment at the temperature of 700 °C, 800 °C, 900 °C and 1000 °C under a digital Muffle Furnace. The raw tar samples (before and after thermal treatment) were investigated by fourier-transform infrared spectroscopy analysis and morphological changes were observed using a scanning electron microscope analysis. From this study, it was found that tar reduction efficiency was significantly affected by thermal treatment and increased from 81.87% to 97.25% at the required temperature from 700 °C to 1000 °C, respectively. Moreover, the roughness of tar increased significantly with increasing the temperature. The phenolic compounds were eliminated from raw tar due to thermal treatment up to 1000 °C. Therefore, this tar-free syngas can be used as clean and sustainable bioenergy for the future energy crisis.

1. Introduction

Global energy consumption is increasing due to the rapid depletion of non-renewable energy sources [1, 2]. This critical situation forced us to search alternative energy sources which are clean and sustainable. As a result, energy production has got great attention considering energy security and environmental issue in recent time [2-4]. Biomass-based syngas is one of the promising alternatives for the fulfillment of future energy demand [5-7]. In this regard, mostly available lignocellulosic biomass is usually contributed to syngas production. Widjaya, Chen, Bowtell and Hills [8] reported that woody biomass has higher lignin content than non-woody biomass, and it contained the higher bioenergy. The uses of by-product charcoal with lignocellulosic biomass through co-gasification can reduce the tar content from syngas [5, 9, 10]. Moreover, syngas is produced from biomass through some thermochemical conversion process (pyrolysis, gasification, co-gasification, and torrefaction) using various type of gasifiers [11, 12]. This syngas is mainly comprised of hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), nitrogen (N₂) and some other compounds like C₂H₄, C₂H₆, NH₃, H₂S, and tar [11, 13-16]. However, tar containing syngas is affected its quality and damage the efficiency of engines. It also creates a problem like cracking in the gasification process



[17]. Tar is brownish in colour, sticky and highly viscous in nature. It is the mixtures of aromatic (single or multiple rings) compounds and other complex hydrocarbons that generated through the breakdown of complex polymers containing lignocellulosic biomass (cellulose, hemicellulose and lignin) during thermochemical conversion [14]. Because of its condensable nature and it exists at the downstream of the reactor, and as a result, it leads to clogging the gasification or co-gasification process equipment [18]. It also blockage the pipe, valve, nozzles, foaming coke and overall plugging the entire system [19].

The previous study has been performed for the production of syngas in a 50 kW downdraft reactor using coconut shell with charcoal [6]. The experimental parameters (temperature, pressure etc.) were optimized using a simulator (Aspen Plus®) for the minimization of experimental cost and time [9]. Moreover, tar was reduced through co-gasification process comparatively to single biomass gasification, but it was not completely eliminated from syngas. The previous study identified tar compounds (detected by GC-MS and NMR analysis) that were produced with syngas during co-gasification of coconut shell and charcoal in a pilot scale downdraft gasifier [6]. As a result, tar contents were exited in the syngas. The identified tar compounds were mainly phenols, naphthalene, and catechol [6]. The presence of these compounds is difficult to use directly for power generation or transport fuel purposes. In addition, the engines cannot work properly and damage their interior functions due to their existence. Valderrama Rios, González, Lora and Almazán del Olmo [19] also reported that tar in the syngas is one of the main barriers that occurred during biomass gasification. They also suggested that it can be reduced from syngas either gasification optimization or by thermal cracking treatment.

Moreover, biomass gasification is prone to change the high release of tar when it depicts the high amount of hydrogen, oxygen and volatile matters that indicating copious polar groups which increase the water-solubility of the product tar [14]. As a result, this tar is necessary to eliminate before releasing to the environment. Tar removal techniques can be categorized into three major methods reported by Ud Din and Zainal [17] are as (1) catalytic cracking (2) thermal cracking and (3) physical/mechanical removal of tar. The most common catalysts of Ni-based catalysts can reduce tar in situ gasifications whereas dolomites and calcites decompose of tar compounds up to 97% [17, 20] and required temperature for tar catalytic cracking is around ~900 °C. The thermal cracking of tar needs high temperatures of around ~1300 °C [17]. However, catalytic disintegration of tar has suffered by the demerits of deactivation because of poisoning, abrasion, thermal decomposition, corrosion and phase changes that resulted in a reduction of their activity [17]. For this reason, catalytic cracking is not suitable for tar reduction. On the other hand, physical tar cleaning processes involve cooling of producer gas that followed by their physical separation which is expensive. Moreover, systems are again plugged by the tar deposition and filters are not working properly. As a result, this tar reduction process is not a potential and suitable option. In the literature, a bottleneck work has been reported on the thermal cracking method on tar removal since a few decades. Thus, the aim of this study is to investigate the thermal treatment of co-product tar and identify its morphological changes.

2. Materials and Methods

2.1. Tar Sample Collection

The raw tar sample (figure 1) was collected from previous coconut shell (70%) and charcoal (30%) based co-gasification process. The thermochemical conversion process was performed in a downdraft gasifier and tar was produced along with the main product of syngas. The raw tar sample was taken from the reactor for further thermal treatment investigation.

2.2. Thermal Treatment of Tar

Prior to thermal treatment, the raw tar samples were weighted in order to evaluate the weight loss amount due to the thermal effect for specific temperatures. A digital Muffle Furnace (WiseTherm®)

was used in this experiment to investigate and maintained the temperatures at 700 °C, 800 °C, 900 °C, and 1000 °C. Each sample was thermally treated inside the furnace for 20 min. After the thermal treatment, tar samples were collected at the room temperature and again weighted. The thermal treated and raw tar samples were prepared for further SEM and FTIR analysis.

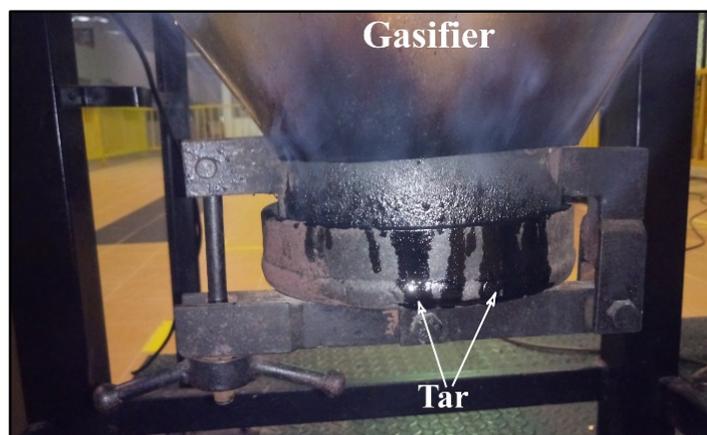


Figure 1. Raw tar sample generated during the co-gasification of coconut shell (70%) and charcoal (30%).

2.3. Analysis of Tars

The functional groups of pre-treated and thermally treated tar samples were analyzed by fourier-transform infrared spectroscopy (FTIR) analyzer (Perkin–Elmer, 670 FTIR). All FTIR spectra were identified with an FTIR spectrometer in a transmission mode and scanned over the ranges 400 to 4000 cm^{-1} wavenumber with a resolution of 4 cm^{-1} . During the sample preparation, potassium bromide (KBr) was mixed with pellets at the ratio of 10:1 and scanned at the rate of 0.5 cm/s . Each tar sample was analyzed by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM with EDX) analysis (FEI, Quanta 450) to characterize its elemental composition and morphological features. In this regards, Bahng, Mukarakate, Robichaud and Nimlos [21] reported that scanning electron microscopy (SEM) is one of the most important techniques for the analysis of micro-structural morphology and their transformations that occurred during thermal treatment of tar samples. In this analysis, the electron beam was scanned over the surface of the samples to create an image. It can also be used to achieve the information of tar regarding the surface topography.

3. Results and Discussion

3.1. Thermal Effect on Tar Morphology

The surface morphology and elemental composition of pretreated and treated tar samples are shown in figure 2. In this SEM image analysis, significant morphological changes were observed on the tar surfaces due to thermal variations. In these images represent a smooth surface with minor pitting. This was occurred on the tar surface due to the release of volatile gases under pressure during the co-gasification of coconut shell and charcoal.

The major elements on raw tar were identified by EDX analysis were carbon (81.76%) and oxygen (17.89%). The other elements were aluminum (0.17%), potassium (0.10%) and trace amounts of sodium, sulfur, and calcium (figure 2a). The empty amount of sulfur (0.00%) found that it was the least potential for environmental pollution considering SO_x formation during the co-gasification of coconut shell and charcoal using the downdraft gasifier. In the SEM image of tar, it shows that the roughness of tar surface increased significantly with increasing the temperature. In addition, more than 80% of carbon was present in the tar sample that was confirmed from EDX analysis. The pores were

detected in the treated tar surface by SEM analysis that was formed due to thermal activity (figure 2b-d).

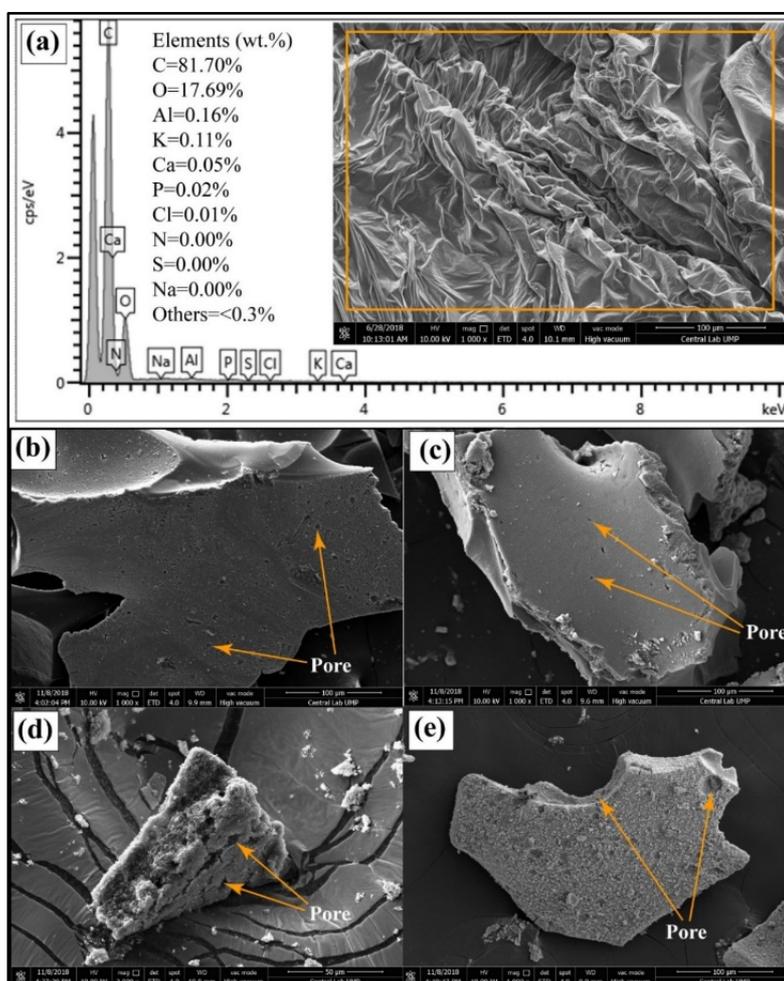


Figure 2. SEM images of raw and thermal treated tars: (a) SEM image with EDX of raw tar produced from the co-gasification of coconut shell and charcoal in a downdraft gasifier (b) SEM image due to thermal treatment at 700 °C (c) SEM image due to thermal treatment at 800 °C (d) SEM image due to thermal treatment at 900 °C and (e) SEM image due to thermal treatment at 1000 °C.

3.2. Thermal Effect on the Reduction of Functional Groups

Figure 3 represents the FTIR spectra of pretreated and treated raw tar samples obtained from the co-gasification process (coconut shell and charcoal). The FTIR spectra of raw tar were compared with the thermal-cracked tar samples considering the temperatures of 700 °C, 800 °C, 900 °C and 1000 °C. From the FTIR analysis (figure 1), it is observed that numerous high molecular weighted tar compounds were decomposed at the temperature ranges from 700 °C to 900 °C. The main spectral differences were observed that involves the attribute spectral brands of O-H at 3600 to 3200 cm^{-1} , C=C ring stretching at 1513.92, 1452.09 cm^{-1} and δ O-H band at 1363.61 cm^{-1} due to the phenolic compounds existed in raw tar sample.

The spectral band for raw tar sample (before thermal treatment) at 3337.60 cm^{-1} signifies OH stretching (figure 3a). The spectral band positioned at 2925.22 cm^{-1} which are conforming to the distribution of aliphatic (CH_2) functional group. A minor band at 1452.09 cm^{-1} was observed corresponding to the symmetric bending of CH_2 . Another spectral band at 1363.61 cm^{-1} attributed to

the distribution of aliphatic (CH_3) group. Moreover, $\text{C}=\text{C}$ ring stretching bands at 1600.86 cm^{-1} and 1513.92 cm^{-1} is also represent in raw tar sample. Therefore, in the presence of phenol, it is known that this band is strongly exalted. Similar corresponding bands are consistent with the literature [22].

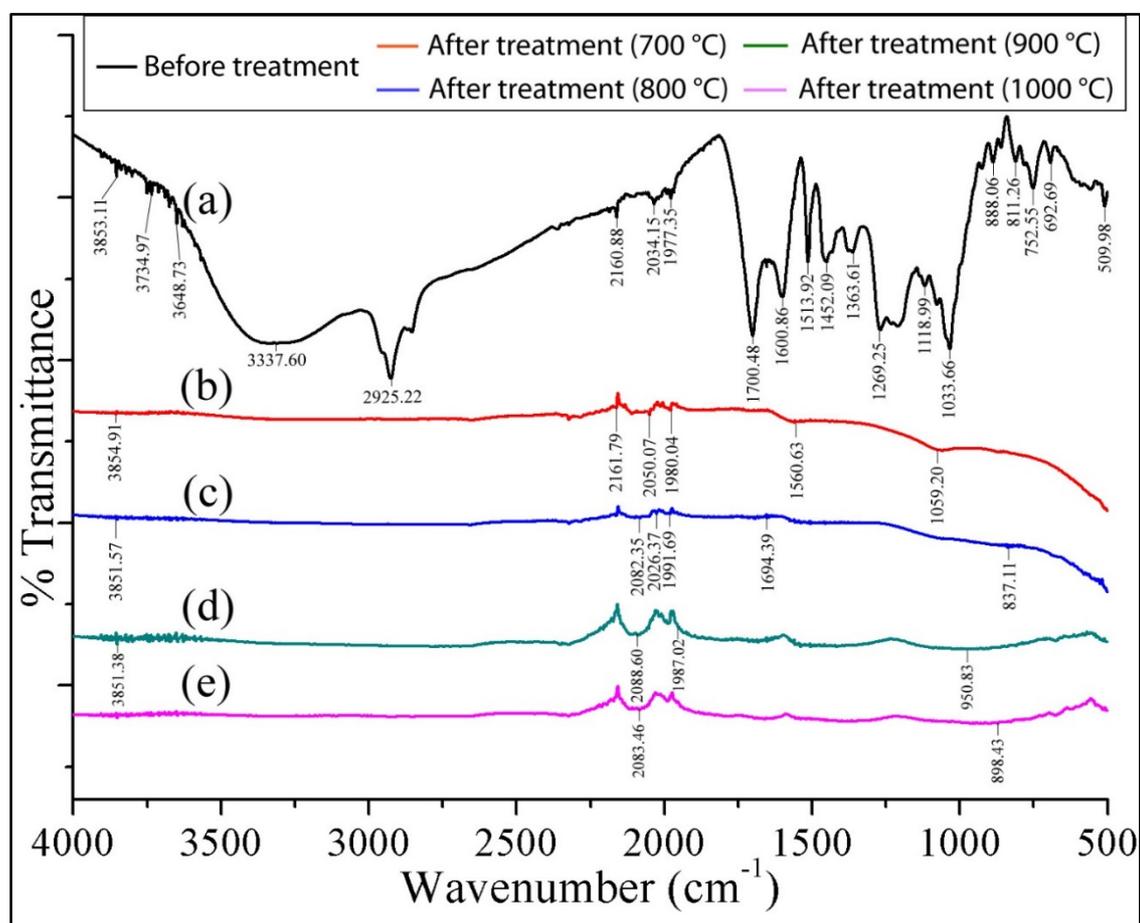


Figure 3. FTIR spectra of tar sample obtained from the co-gasification process: (a) before thermal treatment (b) thermal treatment at $700\text{ }^{\circ}\text{C}$ (c) thermal treatment at $800\text{ }^{\circ}\text{C}$ (d) thermal treatment at $900\text{ }^{\circ}\text{C}$ and (e) thermal treatment at $1000\text{ }^{\circ}\text{C}$.

The presence of spectral band at 692.69 , 752.55 and 811.26 cm^{-1} represents the aromatic mono-substitution attributed to phenol in raw tar sample (figure 3a). On the other hand, there were no significant FTIR spectra was observed in these ranges in the thermal-treated samples (figure 3b-e). This was happened due to the thermal effect on phenolic compounds that were eliminated. It can also be seen that the strong $\text{V}_{\text{C}=\text{O}}$ stretching absorption band ($1600.86\text{-}1700.48\text{ cm}^{-1}$) appeared in raw tar sample, whereas at $800\text{ }^{\circ}\text{C}$ very insignificant FTIR spectra was appeared, and the rest of the temperature based tar samples, it was not visible significantly that attributed to the functional groups of ketones, aldehydes, carboxylic acids, esters etc. This results also consistent related to the tar analysis reported in the literature [22].

From this analysis, it is clearly shown that due to the thermal effect ($700\text{ }^{\circ}\text{C}$ to $1000\text{ }^{\circ}\text{C}$) high molecular compounds (functional groups) were reduced. In conclusion, it is suggested that syngas could be tar free by applying the thermal cracking technique. These results were also consistent with the SEM images analysis.

3.3. Thermal Effect on Tar Reduction Efficiency

The significant effect was observed on tar samples after thermal treatment. The weight loss percentage of tars (thermal treated) was 81.87%, 90.01%, 95.15% and 97.25% at the corresponding temperatures of 700 °C, 800 °C, 900 °C, and 1000 °C, respectively (figure 4). As a result, it was observed that tar compounds were reduced due to the thermal effect. Therefore, tar containing syngas was cleaned by thermal treatment at around 1000 °C, and it can be used directly for electricity and power generation purposes.

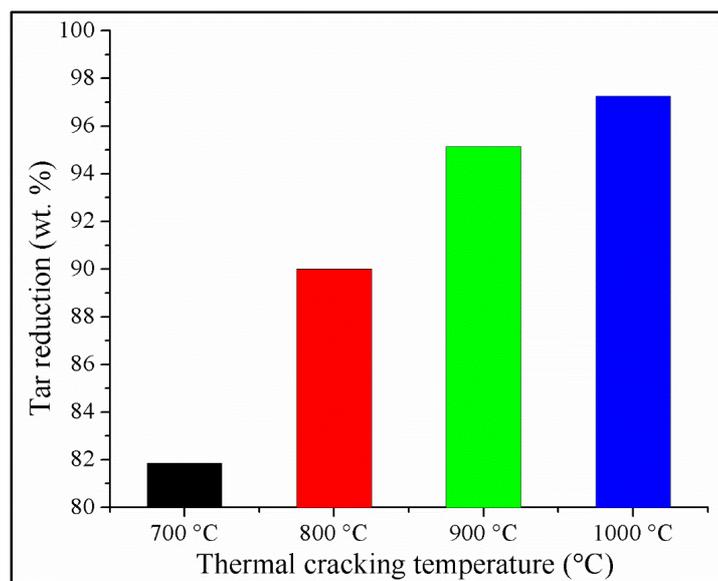


Figure 4. Tar reduction efficiency (wt.%) at a temperature of 700 °C, 800 °C, 900 °C, and 1000 °C.

4. Conclusion

The paper represents the thermal treatment on co-product tar compounds that allow the establishing conditions under tar reduction was investigated. Due to the thermal effect, the functional groups were reduced that was confirmed by FTIR analysis. Moreover, this analysis indicated the most prominent functional groups of O-H stretching (methanol, acid), C=C stretching (aromatic skeleton mode) and C-C(H) stretching that was reduced due to the rising of temperature from 700 °C to 1000 °C. The morphological changes were occurred, and the roughness was increased with increasing the temperature up to 1000 °C. It was also found that tar reduction efficiency (wt.%) was increased from 81.87% to 97.25% at the thermal treatment temperature ranges from 700 °C to 1000 °C, respectively.

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