Quantification of Tars, Particulates, and Higher Heating Values in Gases Produced from a Biomass Gasifier

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Syngas from biomass gasifiers contains impurities such as tars and particulates, which can create difficulties for the downstream processes (e.g., internal combustion engines and the Fischer-Tropsch process). To design an efficient and effective gas cleaning system, it is important to accurately quantify the tars and particulates. The absence of an ASTM procedure for tars and particulates produced from a gasifier led to the development and testing of the protocol presented in this study. Syngas was generated from woodchips using a pilot-scale downdraft gasifier, which was designed and constructed in-house. The sampled impurities were analyzed using mass gravimetry, solvent evaporation, and weight differential methods. The higher heating value of the exiting gases was estimated from the syngas composition. The average tar and particulate concentrations of the sample runs were 1.8 to 3.1 g/m$^3$ and 5.2 to 6.4 g/m$^3$, respectively. The higher heating values of the syngas ranged between 4.38 and 4.55 MJ/m$^3$.

Keywords: Tars; Particulates; Protocol; Biomass gasification; Syngas; Higher heating values

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INTRODUCTION

The production of renewable energy through biomass gasification is essential because of the need to augment non-renewable fossil fuels, as well as environmental issues such as global warming, a consequence of net carbon addition to the atmosphere (Demirbas and Demirbas 2007; Pereira et al. 2012). Biomass gasification is a thermochemical process that converts solid biomass materials into a mixture of combustible gases comprising hydrogen, carbon monoxide, and methane through partial oxidation at elevated temperatures (Zhang et al. 2010; Akudo et al. 2012). The oxidants or gasifying agents can be air, pure oxygen, steam, carbon dioxide (CO$_2$), or their mixtures (Wang et al. 2008). Each of these gasifying agents has its own merits and limitations. The selection of a specific gasifying agent depends on the target application and the end use of the generated syngas. The abundance of air and the associated process simplicity makes it a widely used gasifying agent. However, air contains a high concentration of nitrogen, which lowers the heating value of the syngas produced. While pure oxygen increases the heating value of the syngas, the cost of operating a gasifier using oxygen for a long period of time may not be economically feasible (Wang et al. 2008).

The syngas generated from biomass gasification can either be directly used in a gas turbine for power generation or catalytically converted into Fischer-Tropsch oils and other chemical products (Nair et al. 2003; Han and Kim 2008). However, one of the most challenging issues involved with this technology is impurities, such as tar and particulates formed during the process. Tars are a complex mixture of the condensable fraction of organic gasification products and are largely aromatic hydrocarbons (Li and Suzuki 2009; Michel et al. 2011). Particulates are the solid impurities in syngas that can be separated by

filtration. Tars and particulates are problematic in integrated biomass gasification systems, as they may condense on valves and fittings, hampering the ability of the valves to function properly. They also clog fuel lines and injectors in internal combustion engines (Nair et al. 2003; Devi et al. 2005; Pereira et al. 2012). In spite of these problems, there are currently no specific ASTM protocols for determining the concentration of tars and particulates produced by biomass gasification. Reliable sampling and analysis of these impurities from biomass gasification is needed for an efficient process development and economical operation of gasifiers.

The higher heating value (HHV) is a measure of the energy content of a fuel and refers to the quantity of heat released during the combustion of the syngas with generated water in the condensed state (Sheng and Azevedo 2005). Higher heating values can be evaluated from the biomass feedstock, using an oxygen bomb calorimeter (Fassinou 2012), or from the syngas produced, by determining the fraction of each combustible gas (Guangul et al. 2012).

In this study, a pilot scale downdraft gasifier with an average throughput capacity of 6.6 kg/h was used to establish the characterization of tar and particulates from the gasification of woodchips. A simple and effective procedure for measuring the tar and particulates produced from biomass gasification was operated at atmospheric pressure using a modified EPA Method 5 and is presented in this paper. The syngas produced was analyzed using gas chromatography. The higher heating value was evaluated in terms of the syngas.

MATERIALS AND METHODS

Gasifier Setup

A 6.6-kg/h pilot scale downdraft gasifier was designed and constructed in the Biological and Agricultural Department of the Louisiana State University and LSU Agcenter. Cypress mulch woodchips dried to between 11% and 13% moisture content were used for this study.

The gasification process was carried out at atmospheric pressure, and air was used as the gasification agent. Temperature monitoring was achieved by attaching six K-type thermocouples at different positions on the inside wall of the gasifier. The gasifier operation and process details were not considered critical for this manuscript and were reported earlier (Akudo et al. 2012). The determination of tars and particulates in the syngas produced was carried out in two steps: sampling and analysis.

Syngas Sampling

The syngas sampling was performed during stable operation of the gasification process. This was indicated by a steady self-sustained flare from the burning of the generated syngas and a temperature of 800 °C or higher at the hearth of the gasifier (thermocouple #3).

To obtain reliable data, it was important that the sampling conditions were maintained at defined values during the experiment. The sample gas flow rate decreased from 94.4 cm³/s at the start of the sampling to 78.7 cm³/s due to the partial plugging of the glass fiber filter in the filter assembly and small depositions of tars on the inner walls of the insulated tubing.
**Preparation of sampling equipment**

It was necessary to ensure that all of the sampling equipment was in good operational condition before the startup. The sampling line was kept as short as possible, and a leak test was performed on the sampling train to ensure airtight connections.

**Syngas Sampling Setup**

A sketch of the gas sampling process is shown in Fig. 1. It was based on the EPA Method 5 for measuring particulate matter emissions from stationary sources, but it was adapted to measure gravimetric tar and particulate matter generated during biomass gasification. Unlike the EPA standard, it did not include the determination of moisture content in the gas. Also, the probe and Pitot tube assembly was not used in this protocol to measure the gas velocity. However, the gas flow analysis was performed using a flow regulator and flow meter. Copper tubes (1/8” or 3.175 mm dia.) and brass compression fittings were used for the lines between the gasifier and the acetone bottles. The copper tubes were insulated with insulation wraps to minimize condensation in the lines. However, use of electrically heated tapes is a preferred alternative to insulation. The lines after the first acetone bottle were not insulated as gas temperatures were lowered during the bubbling.

![Fig. 1. Tar and particulates sampling train. Syngas from the gasifier was first passed through a glass-fiber filter for particulate quantification. The filter was held in a stainless steel filter assembly, which was kept inside a heated oven (250 °C) to prevent tar condensation. The tar component was collected in a series of impinger bottles containing acetone.](image)

The measurement principle of this procedure is based on the discontinuous sampling of a gas stream containing tar and particulates under isokinetic conditions. The sampling of tar and particulates is performed simultaneously, and the impurities are collected and quantified as described below.

**Particulate collection**

The particulates were collected on a 90-mm-diameter glass microfiber filter (Whatman™, GF/F 0.7-μm pore size), which was held in a stainless steel pressure filter holder (Millipore, Billerica, MA). The filter assembly was placed in an oven and heated to 250 °C to prevent the condensation of tars in the filter and copper tubing. Prior to the start of the sampling, the filter paper was heated to 250 °C for 15 min before the gas stream was drawn through the filter.
Tar collection

Tar sampling was accomplished using a sampling train comprising four impinger glass bottles (Fig. 1) containing 50 mL of acetone, which were connected in series using Teflon tubing. The syngas sample was bubbled through the acetone, and the dissolved tars were then recovered after the evaporation of the acetone. To facilitate the bubbling of the syngas through the acetone bottles and to assist in proper tar dissolution, the impinger bottle caps were fitted with brass push-to-connect fittings (1/8” NPTM, 1/8” tubing OD) and bubbling tube, as shown in Fig. 2.

Fig. 2. The tar dissolving-impinger bottle setup comprised 4 standard glass media bottles (80 mL). The caps were drilled and tapped to accept brass push-to-connect fittings with 1/8” NPT male threads. A short section of PTFE tubing (1/8” OD) was fixed to the back of the inlet port to facilitate bubbling in the acetone column.

Duration of sampling

The amount of time needed to collect a representative quantity of tars and particulates can be varied based on the concentration of the impurities in the gas stream, which has a major influence on the filter clogging and gas flow rates. For the sample runs in this study, the sampling period was initiated after the gasifier temperatures had reached steady state and was terminated after the syngas had been sampled for approximately one hour.

Sample Analysis

An analysis was performed within 24 h after sampling. Two basic techniques are traditionally used for tar analysis, depending on the need for tar investigation and characterization.

One of the analytical methods involves gas chromatography, where individual tar compounds are separated in a heated column and a positive identification of the chemical compounds is made.

The second method involves gravimetric analysis, which is used to quantify the tar yield during gasification and treats the tar as a collective substance. In most applications, gravimetric tar and particulate quantification data are needed for designing a cleaning
system. The procedure described below provides a gravimetric method for analyzing both the tars and particulates in the syngas.

**Determination of gravimetric tar**

The tars collected in the acetone impinger bottles were combined with 20 mL of high purity acetone collected from washing all of the condensed tar particles from the transfer lines (e.g., copper tubing). Approximately 220 mL of acetone (with tars) was reduced to 10 mL in a rotovap (for evaporation and recovery of acetone). The final 10 mL of acetone was evaporated under a fume hood in a pre-weighed aluminum pan that was dried in an oven at 50 °C. This temperature, which is slightly less than the boiling point of acetone (56 °C), was specifically selected to ensure a safe and controlled evaporation process. Both the initial pan weight (pan alone) and the pan weight with the tar residues were recorded with an analytical balance. Gravimetric tar was calculated using Eq. 1,

\[
C_t = \frac{W_t}{V_g}
\]

where \( C_t \) is the concentration of the tar in the syngas (g/Nm\(^3\)), \( W_t \) is the weight of the tar (g), and \( V_g \) is the volume of the sampled gas (Nm\(^3\)).

**Determination of particulates**

The particulate concentration was calculated from the difference in weight between the tare weight of the filter and the dry particulate-containing filter obtained after drying in an oven set at 105 °C for approximately 30 min and allowed to acclimatize in a desiccator. The equation below was used to quantify the particulates in the gas stream,

\[
C_p = \frac{W_p}{V_g}
\]

where \( C_p \) is the concentration of particulates in the syngas (g-dry/Nm\(^3\)), \( W_p \) is the weight of particulates collected on the filter (g-dry), and \( V_g \) is the volume of sampled gas (Nm\(^3\)).

**Determination of syngas higher heating value (HHV)**

A gas chromatography analysis (SRI Instruments, Multiple Gas Analyzer #1 with 8610C chassis) was conducted to determine the amount of methane (CH\(_4\)), hydrogen (H\(_2\)), and carbon monoxide (CO) in the syngas, and the higher heating value was calculated as shown below,

\[
HHV = \%H_2 \times HHV(H_2) + \%CH_4 \times HHV(CH_4) + \%CO \times HHV(CO)
\]

where HHV (H\(_2\)), HHV (CH\(_4\)), and HHV (CO) are the higher calorific values (MJ/Nm\(^3\)) of hydrogen, methane, and carbon monoxide gases, respectively.
RESULTS AND DISCUSSION

Sample results from the experimental runs showing the gravimetric quantification of tars and particulates are presented in Fig. 3.

![Graph showing tar and particulates concentration from a sample gasification run using three similar batches of woodchips.](image)

**Fig. 3.** Tar and particulates concentration from a sample gasification run using three similar batches of woodchips. Three different samples were collected and analyzed for each run. The concentrations shown are raw values, and the exiting gas was not passed through any gas cleaning or tar cracking components. The error bars represent the sample standard deviations.

The amount of tar and particulates in the syngas presented above was obtained after the gasifier temperatures had reached steady state and a continuous gas flare was observed. This was to ensure that the syngas being sampled contained sufficient combustible gases to be used as fuel. For each run, three separate sets of samples (filter papers and acetones solutions) were collected, and the tar and particulate concentrations were analyzed independently. The average tar concentrations from three experimental runs were $3.1 \pm 0.2$ g/m$^3$, $1.8 \pm 0.2$ g/m$^3$, and $2.7 \pm 0.1$ g/m$^3$. A relatively lower tar concentration was observed in the second experimental run; however, statistical analysis did not show any significant differences between the three runs (ANOVA; p > 0.05). The average particulate concentration corresponding to the tar values above were, respectively, $6.4 \pm 0.3$ g/m$^3$, $5.8 \pm 0.2$ g/m$^3$, and $5.2 \pm 0.2$ g/m$^3$. The particulate concentrations decreased after each run without tar cracking or particulate filtration processes. Statistical analysis showed that the particulate concentrations were not significantly different between the three experimental runs (ANOVA; p > 0.05).

Figure 4 shows a representative gasification temperature profile as the process approaches steady state. Temperature data were collected from the six thermocouples installed at the wall of the gasifier and connected to a PC-based data acquisition system, where the data were continuously recorded. Temperature data from each thermocouple
were collected by a USB-based data logger every 30 seconds (USB-TC, Measurement Computing Corp., DASYLab software).

Table 1 shows the syngas composition and heating values. The average concentrations of the combustible gases obtained were within the limits reported in previous studies (Heesch et al. 1999). The relatively high percentage of nitrogen (N2) in the gas mixture could be explained by the fact that air, which contains a high concentration of nitrogen, was used as the gasification medium.

Table 1. Summary of Gas Chromatography Syngas Analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO (%)</td>
<td>15.74</td>
<td>16.11</td>
<td>16.04</td>
</tr>
<tr>
<td>H2 (%)</td>
<td>15.05</td>
<td>18.69</td>
<td>14.37</td>
</tr>
<tr>
<td>CH4 (%)</td>
<td>1.93</td>
<td>2.24</td>
<td>1.89</td>
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<tr>
<td>CO2 (%)</td>
<td>15.48</td>
<td>13.45</td>
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<tr>
<td>N2 (%)</td>
<td>52.8</td>
<td>49.61</td>
<td>52.79</td>
</tr>
<tr>
<td>HHV (MJ/m³)</td>
<td>4.43</td>
<td>5.03</td>
<td>4.38</td>
</tr>
</tbody>
</table>
Figure 5 shows a sample gas chromatogram obtained after an analysis of the syngas for the major constituents. The peaks shown below are H₂, N₂, CO, CH₄, and CO₂, respectively, from left to right.

![Gas Chromatogram](image)

**Fig. 5.** Gas chromatogram showing syngas components. The peaks were identified and calibrated using calibration gases.

**CONCLUSIONS**

1. This manuscript describes a viable and easy-to-duplicate protocol for quantifying tars and particulates in syngas from a biomass gasifier. A sample of tar and particulate testing data is shown. Sample calculations of the higher heating value of the syngas from a given set of gas composition values were also presented.

2. The authors believe that these protocols can be used effectively by other researchers to optimize their gasifiers by lowering the particulate concentrations and improving the higher heating values.

**REFERENCES CITED**


Article submitted: April 13, 2013; Peer review completed: August 3, 2013; Revised version received: July 21, 2014; Accepted: July 22, 2014; Published: July 29, 2014.