# Major Tar Compounds in Raw Producer Gas and Deposits from a Small Downdraft Gasifier: Analysis and Comparison

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Tar is an undesirable product of biomass gasification. Tar analysis is a challenging task because it is a complex mixture. The objectives of this study are to identify and quantify the major tar compounds in raw producer gas and deposits from a 10 kW downdraft gasifier using cedar pellets. Gas chromatography-mass spectrometry (GC-MS) was used to analyze the 16 tar samples from raw producer gas under varying airflow rates and four tar samples from the deposit inside the suction pump after long-term operation. The results showed that tar in raw producer gas and tar deposits consisted of about 46 and 28 major chemical compounds, respectively. Tar in raw producer gas was found to contain three main groups of substances, including acids/ketones with 32.1 wt%, heterocyclics with 30.0 wt%, and light poly-aromatic hydrocarbons (light PAHs) with 31.8 wt%. Heterocyclic and light PAH compounds dominated in tar deposits and accounted for 58.6 wt% and 36.2 wt%, respectively. It was observed that the tar condensation problem was dominated by the components and the molecular weight of tar compositions instead of the tar concentration. These findings are useful for optimizing the gasification process and developing the gas cleaning system for a small downdraft gasifier.

*Keywords: Tar composition; Biomass gasification; Small downdraft gasifier; Producer gas; Deposit*

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## INTRODUCTION

Biomass is a promising renewable energy resource. Although it is abundant in nature, biomass resources are not concentrated; they are widely dispersed depending on geographical area. Therefore, the cost of collecting and transporting a large number of biomass materials to large power plants is expensive. Thus, the development of small capacity power generation is desirable for on-site use. These systems can be connected to the emergency power system, even in a disaster area or remote areas with no grid. Although there are various gasifier types (gasification reactors), which are different in design and operational characteristics, the small downdraft gasifier is the first candidate for small power generators because of its easy fabrication, favorable operation, and low tar content in producer gas (Martínez *et al*. 2012).

Gasification is the most effective process to convert biomass fuels into combustible gases, called producer gas, because it allows higher efficiency than combustion and pyrolysis. However, tar content in the producer gas is an unwanted side product. Tar formed during gasification is a complex mixture of various organic compounds (Morf *et al*. 2002). It condenses on the downstream equipment when cooling the producer gas for introducing into an internal combustion engine (ICE). The presence of tars in producer gas is a challenge because it causes serious operational issues, such as plugging or blockage in filter elements, suction pumps, and the various ICE devices (Rakesh and Dasappa 2018a). Thus, better insight into the tar composition of producer gas is necessary to optimize the gasification process and mitigate the tar problem.

Many previous studies have examined tar compositions obtained from biomass gasification (Kinoshita *et al.* 1994; Milne *et al.* 1998; Li and Suzuki 2009; Yu *et al.* 2014; Kuba and Hofbauer 2018; Rios *et al.* 2018; Zhang and Pang 2019). Most of these studies have been performed on the fluidized bed gasification system. Besides, several researchers have studied tar concentration in producer gas from a downdraft gasifier. Table 1 summarizes the tar concentration from this type of gasifier reported in the scientific literature. The results of tar concentration were presented by the gravimetric tar yield in these studies. Overall, tar concentration depends on several parameters, namely the initial feedstock, reactor temperature, fuel moisture content, equivalence ratio, and the gasifying medium. However, there is a significant variation in tar concentration analyzed by gravimetric method. This is due to the fact that numerous methods of tar sampling and analysis procedures were in use (Prando *et al.* 2016). Gravimetric tar only shows the total tar concentration, but it does not provide the individual components present in tar. Van Paasen and Kiel (2004) showed that the effect of tar on downstream process efficiency was not only related to the total tar concentration but also the specific tar fractions or tar components. Moreover, in most cases, the producer gas from a downdraft gasifier was combusted as fuel in ICE. The tar acceptance limit for ICE is less than 100 mg/Nm$^3$ (Milne *et al.* 1998). From literature results, it can be realized that the elimination of tar concentration to meet the required level is still a challenging task. Thus, the in-depth understanding of tar compositions could help in the design of the gas purification system (Rakesh and Dasappa 2018b).

**Table 1.** Tar Concentration of Downdraft Gasifier According to the Feedstock Type Using Air as an Agent

| Feedstock | Temperature | Tar Concentration | Reference |
|---|---|---|---|
| | °C | g/Nm$^3$ | |
| Black pine wood pellet | 900 | 32.3 | (Ueki *et al.* 2011) |
| Eucalyptus wood | 550-700 | 0.054 – 1.27 | (Galindo *et al.* 2014) |
| Softwood pellets | 800 - 850 | 3.31 | (Striūgas *et al.* 2014) |
| Poultry litter pellets | 800 - 850 | 1.11 | (Striūgas *et al.* 2014) |
| Rape straw pellets | 800 - 850 | 0.41 | (Striūgas *et al.* 2014) |
| Corn cobs | 780 | 1.77 – 5.97 | (Omar *et al.* 2017) |
| Waste wood | 840 | 1.61 – 5.02 | (Omar *et al.* 2017) |
| Rice husk | 680 - 820 | 5.8 – 53.3 | (Susastriawan *et al.* 2019) |
| Sawdust | 800 - 950 | 8.3 – 35.0 | (Susastriawan *et al.* 2019) |
| Wood | 750-800 | 11-16 | (Vonk *et al.* 2019) |
| Teak wood | 810-950 | 2.0 | (Upadhyay *et al.* 2019) |
| Sawdust briquette | 810-950 | 2.15 | (Upadhyay *et al.* 2019) |

Furthermore, tar condensation phenomena are concerned with the compositions and the properties of tar in producer gas (Li and Suzuki 2009; Prando *et al*. 2016). Therefore, the identification of major tar compounds is useful in efforts to eliminate the tar problem. Hernández *et al.* (2013) have studied the tar characteristics from a small scale drop-tube gasification pilot plant. The experiments were carried out at different temperatures ranging from 750 to 1200 °C using marc of grape as biomass fuel. Prando *et al.* (2016) gasified casuarina wood chip and coconut shell using a 1 kg/h open top gasifier to comprehend the individual tar compounds in the raw producer gas at the oxidation temperature of 950 °C. Zhou *et al.* (2018) conducted gasification experiments using *Camellia sinensis* branches to provide insights on the tar formation and tar compositions. Zubair Yahaya *et al.* (2020) examined the influence of temperature on the chemical composition of tars from a downdraft fixed bed reactor using coconut and palm kernel shells at temperatures between 700 and 900 °C. In these studies, the temperature of the reactor was high and fixed due to the use of the external heater with a controller system, and the experiments were conducted on simulated or lab-scale facilities. However, the small downdraft gasifiers usually entail autothermal operation with the small dimensions of the reactor; this leads to lower reactor temperatures because of the heat loss. Also, the reactor temperatures are various closely related to the fuel/air ratio based on the required load. The lower and variable temperature of the reactor makes it possible that the tar contents in producer gas could be different compared with lab-scale facilities or large-scale gasifier. Nevertheless, a detailed analysis of tar compositions in producer gas from a small downdraft gasifier under real operation conditions is scarce in the literature.

Unlike the large-scale biomass gasification, the small downdraft gasifier often undergoes the start/stop process with a low temperature of the reactor. Tar formation in this process for the long-term operation may be causing the clogging and fouling of downstream equipment. It is challenging to analyze the tar in start/stop duration because this process is not stable operation and changes the time duration based on the operating condition. Therefore, the analysis of tar deposits in long-term operation is necessary to identify correct tar compounds that caused the problem for downstream equipment in overall operation processing. The relationship between tar in raw producer gas and tar deposit is evaluated to elucidate the main tar components that passed the gas cleaning system. However, we have not found any previous research that analyzes and discusses in detail the major components of tar deposits in the downstream equipment of a small downdraft gasifier.

From the analysis above, it is believed that the exploration of the major tar components is of significant importance. The purpose of this study is to identify and quantify the major tar compounds in raw producer gas and tar deposits inside the suction pump from a 10 kW downdraft gasifier. From that, the major tar components pass the gas cleaning system were identified. This knowledge may lead to the optimization of the gasification process and improvement in the selection of the gas cleaning type and the design of the gas purification system. In this study, sixteen tar samples obtained from raw producer gas under varying airflow rates from 40 to 100 L/min and four tar samples of deposits after the long-term operation were analyzed.

## EXPERIMENTAL

### Biomass Feedstock

The biomass used in this work was cedar pellets with a relative homogeneity in size because it is popular and commercially available in Japan. They were provided by Meiwa Co., Ltd., Ishikawa, Japan. Cedar pellets had a diameter of 6 mm and a length between 12 and 15 mm. The moisture content of the cedar pellet was 8.5 ± 0.5 wt%. The moisture analyzer AND MF-50 (A&D Company, Tokyo, Japan) with 0.05% accuracy was used to analyze the moisture content of cedar pellets. The proximate and ultimate analyses of cedar pellets were analyzed by Forest Product Research Institute, Toyama, Japan. Table 2 summarizes the properties of cedar pellets.

**Table 2.** Ultimate and Proximate Analysis of Cedar Pellets

| **Ultimate Analysis (wt%, dry basis, JIS M8813)** | |
|---|---|
| C | 49.75 |
| H | 6.40 |
| O (balance) | 43.14 |
| N | 0.09 |
| S | 0.09 |
| Ash | 0.53 |
| **Proximate Analysis (wt%, dry basis, JIS M8812)** | |
| Fixed carbon | 17.65 |
| Volatile matter | 81.82 |
| Ash | 0.53 |
| Low heating value (LHV, MJ/kg) | 15.37 |

## Experimental Apparatus and Procedure

Figure 1 shows the schematic diagram of the 10 kW downdraft gasifier system. The 10 kW downdraft gasifier system consists of feedstock feeding, reactor, soot remover, gas cleaning, and cooling heat exchanger. The reactor was a downdraft throatless type, and it was made of stainless steel tube with an inner diameter of 120 mm and a total height of 500 mm. A grate at the bottom of the reactor used to support the pellet fuel and charcoal bed. A screw shaft with a height of 290 mm was installed above the grate to remove ash when the charcoal bed is stuck. This system was controlled by a pressure signal mounted after the reactor. A specified level sensor detects the level of pellets inside the reactor to start/stop the screw conveyor for controlling the feeding rate. The agitator was mounted at the top of the reactor to agitate the feeding pellets, avoiding the bridging.

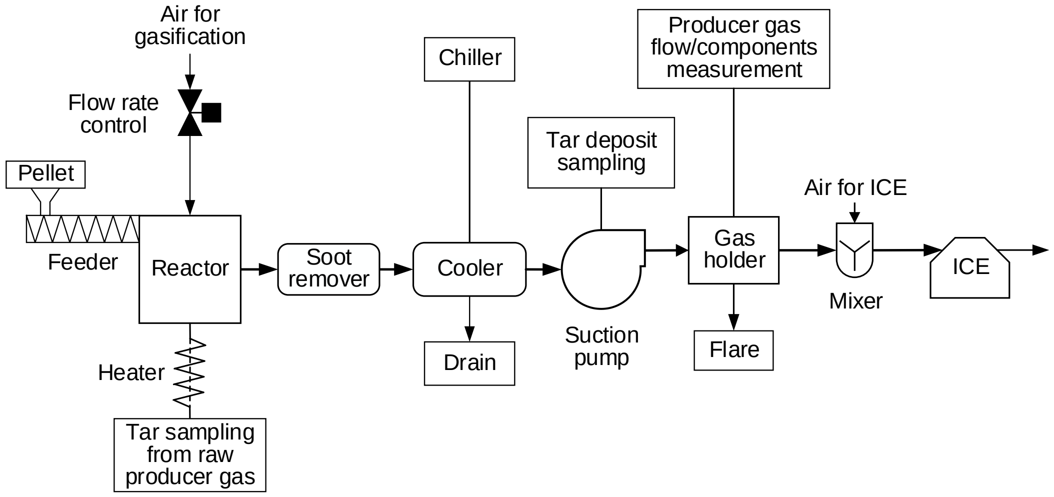

**Fig. 1.** Schematic diagram of the 10 kW downdraft gasifier system

In this study, the gasifier system used air as a gasifying agent. The airflow rate was 40, 60, 80, and 100 L/min. The experiments were performed four times for each airflow rate on different days to identify correct major tar compounds. Air entered the reactor from the top side through suction pump DA-120S (200W), which controlled by the inverter. An Azbil CMS200 mass flow meter (Azbil Corporation, Kanagawa, Japan) was used to measure the airflow rate into the reactor. The air supply system was controlled automatically using PLC and electronic valves based on the target value setup for each of the experiments. An ignition port located at the top of the reactor was used to ignite the gasifier using a gas pilot light. After igniting the pellet, the feeding system was started. The gasifier system was operated at least 1 h to reach a stable state. The charcoal bed height was kept constant in these experiments to avoid other additional variables being introduced in the process.

Seventeen K-type thermocouples were installed at various locations to measure the reactor temperature. The thermocouples were located near the walls of the reactor to not interfere with the pellet movement. Datalogger GL 820 (Dataq Instruments Inc., Ohio, USA) used to measure and store all data in the experimental process every 60 seconds. The main gas compositions after the gas holder were analyzed by gas chromatography Agilent 490 Micro GC (Agilent Technologies Inc., CA, USA).

## Tar Sampling Method

The diagram layout of the tar sampling system is shown in Fig. 2. The tar sampling system was designed based on tar protocol (Neeft *et al.* 2002) and was set up based on the Japanese patent number JP2009040885A "Tar collecting method and device" (Matsuzawa and Ohara 2009). Tar in the raw producer gas was trapped by condensation on the cold surfaces of the glass beads that called a solvent-free condensation method. A similar approach for tar sampling was shown by Norisada *et al.* (2017) and Amini *et al.* (2019). Tar in raw producer gas was sampled at the exit of the reactor after the gasifier system operated with a steady-state condition.

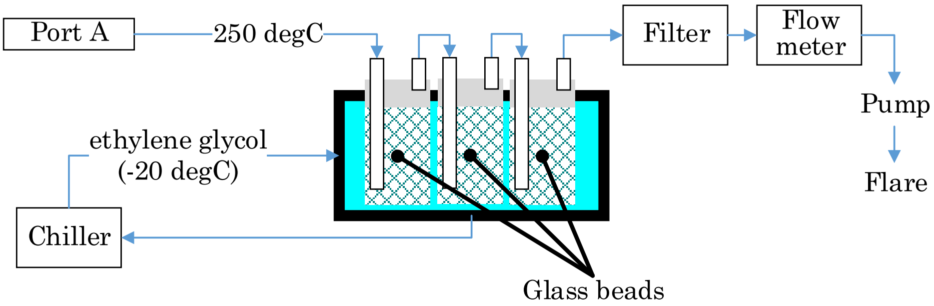

**Fig. 2.** The diagram layout of the tar sampling system

The tar sampling train included three bottles with a length of 300 mm and an inner diameter of 24 mm. The tar amount and compositions from initial testing were almost the same in three-bottles case, four-bottles case, and six-bottles cases. Hence, three bottles were used in this study. All three bottles put in the dewar vessel with a mixture of ethylene glycol and water. Each bottle was filled with 30 mL of glass beads (AS ONE BZ – 2, Φ 1.5 to 2.5 mm) after getting almost the same of tar results between 30, 40, and 50 mL of glass beads. These bottles were kept in a cold bath, which maintained the temperature of -20 °C to facilitate the tar compound condensation on the glass beads. Besides, in the initial testing, one bottle contained three cotton balls that were connected after the last bottle of tar collection system to check tar compounds passed three bottles in tar sampling process. After the experiment, the acetone was used to extract tar from three cotton balls. The GC-MS analysis result indicated that only a very small amount of tar compounds was detected. Thus, the bottle containing cotton balls was not used in the tar sampling process to reduce the time required for extraction.

In the tar sampling processing, the sampling line was kept less than 20 mm, and the inside diameter of the sampling line was 5 mm to prevent plugging problems. The temperature of the inlet sampling pipe was maintained 250 °C to prevent the particle adhering and tar condensation on the pipe wall. The volumetric flow rate was measured by a flow meter. The vacuum pump was used to draw the producer gas. The sampling flow rate was 8 L/min and the sampling time was 20 min. These settings were appropriate with the recommendation from the tar protocol (Neeft *et al.* 2002). They suggested that the sampling flow rate should range from 2 to 10 L/min and the minimum sample volume was 100 L in the tar sampling process. Moreover, in this experiment, water vapor was frozen in the bottle if the flow rate was small.

After each experiment, the sampling bottles and sampling pipes were washed with 50 mL of fresh acetone to dissolve the tar. Although isopropyl alcohol was often used to absorb and extract tar samples in tar protocol, the distillation temperature was often more than 100 $^{o}$C in gravimetric tar analysis. Thus, moisture content and light tar in producer gas could not be measured. In this study, therefore, the acetone was used as the extraction solvent to reduce the distillation temperature in gravimetric tar analysis for preventing the evaporation of some light tar. The mixture of acetone and tar was denoted as the "tar sample". The tar sample was filtered using a mixed cellulose-ester filtration with pore size 0.45 μm to remove the particles for subsequent measurement and analysis. All tar sample accessories were cleaned carefully by fresh acetone and ultrasonic cleaning machine after each sampling.

The samples of tar deposits were taken from inside the suction pump after the long-term operation. Four deposit samples were obtained from different days. 200 mg tar deposits were dissolved with 50 mL fresh acetone as solvent. The tar samples were filtered using a mixed cellulose-ester filtration. After that, the tar samples were poured into a 1mL vial bottle for GCMS analysis.

## Tar Analysis Method

The collected tar samples were analyzed with Shimadzu GCMS-QP2010 Plus using the RTX-5MS column with an internal diameter of 0.25 mm, a length of 60 m, and a thickness of 0.25 μm. The column oven temperature initiated at 40 °C for 2 min after the temperature was increased to 300 °C at a rate of 3 °C/min, and the final temperature was kept for 40 min. The injector and interface temperatures were 300 °C, the sample size was 3 µL, and the injection mode was split. High purity helium (99.999 vol%) served as the carrier gas and flowed at 3.9 mL/min with pressure 106.1 kPa. The National Institute of Standards and Technology (NIST) library was used to compare the mass spectra of tar compounds.

Tar is a complex organic mixture, including many different compounds. Although the usage of internal standard is a simple method to quantify tar concentration, the result generated by this method will be too low if the sample contains significant amounts of oxygenated compounds such as tar samples. Also, if the analysis sample contains a considerable high number of different compounds, calibration using external standards should be applied (Neeft *et al.* 2002). Therefore, the external standard calibrations method was used in this study. However, it is challenging to predict tar candidate compounds to prepare enough external standards for calculating the tar concentration in tar samples. Thus, in this study, the effective carbon number (ECN) method was used to quantify the candidate tar compounds, which did not have an external standard calibration, as previously described (Szulejko *et al*. 2013; Kim *et al*. 2014; Szulejko and Kim 2014). The fifteen external standard calibrations were used to calculate the concentration of tar compounds and estimate the response factor for the ECN method. The list of external standards includes acetic acid, propanoic acid, benzene, toluene, phenol, styrene, o-xylene, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, acenaphthene, fluorene, phenanthrene, pyrene, and fluoranthene.

The individual density of tar compounds $ID_i$ (expressed in mg/Nm$^3$ product gas) was calculated as follows,

$$ID_i = \frac{[C]_i \, x \, V_{total}}{\dot{V}_{pg} \, x \, t_m} \qquad (1)$$

where $[C]_i$ is the individual compounds concentration from GCMS (ppm), $V_{total}$ is the measured volume of total tar sample (mL), $\dot{V}_{pg}$ is the producer gas flow rate in the tar sampling process (L/min), and $t_m$ is the measured duration of tar sampling (min).

Gravimetric tar analysis was conducted in this work to evaluate the tar concentration in the producer gas and verify the GC-MS analysis result. Tar samples obtained from raw producer gas were evaporated at 65 °C in 5 h using a microprocessor-controlled heater (Minic-100 Mini Dry Bath, Zhengzhou, China). The residue weight was measured by a high precision balance with an accuracy of 0.1 mg.

## RESULTS AND DISCUSSION

### Evaluation of Tar Components from GC-MS Results

Tar compound identification is often obtained from GC-MS data analysis. The tar target compounds are achieved by matching the mass spectra of experimental data with the mass spectra in a reference library based on the similarity index (Wei *et al.* 2014). From the similarity index, the search function in GCMS Postrun Analysis provides a list of the best matches found in the library records. The higher the similarity index, the higher is the probability of correct identification. Thus, the chosen similarity index is important, as it has an effect on the correct identification of tar compounds. Also, the appearance ratio of tar components in all tar samples should be evaluated to identify the correct compounds. In this study, the sixteen tar samples obtained from raw producer gas with varying airflow rates were analyzed and the effect of the similarity index and appearance ratio on the number of tar components was evaluated. Figure 3 shows the relationship between the number of tar compounds and the appearance ratio of sixteen tar samples when similarity index changes from 60 to 90%.

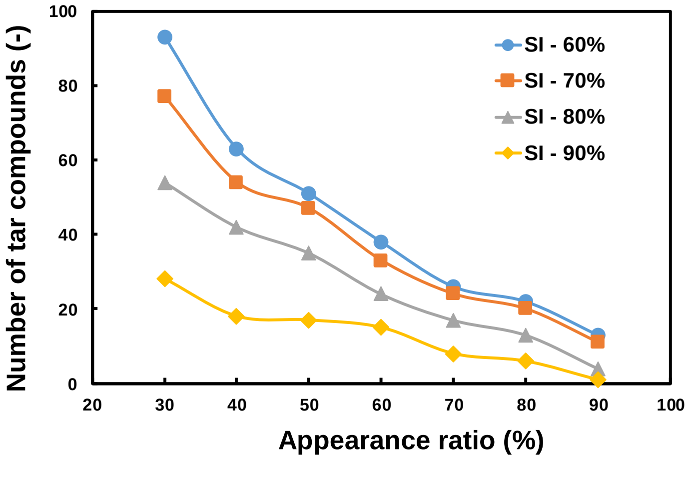

**Fig. 3.** The relationship between the number of tar compounds and the appearance ratio of sixteen tar samples when the similarity index change from 60 to 90%

Horvat *et al.* (2016) indicated that the chromatography analysis was the main source of uncertainty in tar analysis process. They showed that although about 100 species were detected from the chromatogram data, only 20 of the most abundant tar compounds were identified. Therefore, as mentioned above, the evaluation of chromatogram data based on the similarity index and appearance ratio is necessary to identify the major tar compounds correctly. The results from Fig. 3 indicate that the similarity index and the appearance ratio increase, the number of tar compounds decreases. The highest tar compounds were 93 compounds in the case similarity index of 60% and appearance ratio of 30%, and the lowest tar compounds were only one compound in case similarity index of 90% and appearance ratio of 90%. The main indication from this result is that the similarity index and appearance ratio had substantial effects on the number of tar compounds. The similarity index of 70% and the appearance ratio of 50% was chosen for further analysis of tar compositions in this study to identify correct tar compositions. This threshold of similarity index gives high identification for the comparison of the mass spectra from the NIST library (Hübschmann 2015).

## Major Tar Compounds in Raw Producer Gas and Deposits

The identification and quantification of tar compounds from GC-MS analysis of tar in raw producer gas and tar deposits inside the pump are shown in this section. The molecular weight, boiling point temperature, and chemical formula of several tar compounds have been searched in available online databases (ChemicalBook; PubChem). In this study, tar components are classified based on chemical structure, properties, and solubility behavior. The tar compounds were divided into different categories such as heterocyclics, light aromatics (1 ring), light polyaromatic hydrocarbons (2-3 rings; light PAHs), and heavy polyaromatic hydrocarbon (4-6 rings; heavy PAHs) compounds following the method reported by Anis and Zainal (2011). However, in this classification method, the low molecular weight tar compounds such as acids or ketones were ignored. To deepen the discussion in tar compositions, the group of substances related to low molecular weight, namely: acids/ketones, was added into the tar classification in this study.

Table 3 presents the major tar compounds and the density of each component of sixteen tar samples obtained from raw producer gas. The average density of sixteen tar samples was 831.8 mg/Nm$^3$. This result is in good correlation with gravimetric analysis. The average value of tar density using gravimetric analysis was 760.5 mg/Nm$^3$. Gravimetric analysis result is lower than GC-MS result may be due to the lighter tar compounds will disappear during the solvent evaporation process. The density of gravimetric tar determined in this study was smaller than the results reported by Upadhyay *et al.* (2019) and Vonk *et al.* (2019) for downdraft gasifier using wood as fuel.

As shown in Table 3, the major tar compounds in raw producer gas are about 46 substances, which include acids/ketones, heterocyclics, light aromatics, light PAHs, and heavy PAHs. Nitrogen compounds were not detected. Acids/ketones compounds were the most abundant group substances, accounting for 32.1% of mass fraction (wt%) of tar, in which acetic acid was the most abundant component in this group, accounting for 27.7 wt%. This group substance also contained the acetol (1-hydroxy-2-propanone) with 2.7 wt%. These results were in correlation with findings from Morf *et al*. (2002) and Atnaw *et al.* (2014). In addition, heterocyclic (mainly phenolics) compounds accounted for 30 wt%. Zhou *et al*. (2018) indicated that the phenolic compounds were the main tar components (> 80%) produced from lignin in the temperature range of 500 to 800 °C. A similar trend of heterocyclics was also observed by Chang *et al.* (2016). They showed that lignin-rich fuel generated higher heterocyclic compounds at temperatures ranging from 660 to 850 °C. The chemical analysis of Japanese cedar pellets, used in this work, had 53.4 wt% of lignin and 21.8 wt% of cellulose (Umemura *et al*. 2014). This explains the reason for the high percentage of heterocyclic compounds in tar compositions. Moreover, the average temperature of the reactor ranging from 550 to 750 °C in this study discouraged the thermal cracking of acids/ketones and heterocyclic compounds to form aromatic compounds (Milne *et al*. 1998).

**Table 3.** Major Tar Compounds from Raw Producer Gas

| Substance group | Compound name | Chemical formula | Molecular weight | Boiling point | Density |
|---|---|---|---|---|---|
| | | | g/mol | °C | mg/Nm$^3$ |
| Acids/ Ketones | Acetic acid | $C_2H_4O_2$ | 60 | 117.9 | 230.5 |
| | 2-Propanone, 1-hydroxy- | $C_3H_6O_2$ | 74 | 146 | 22.4 |
| | Propanoic acid | $C_3H_6O_2$ | 74 | 141.7 | 13.9 |
| Σ | | | | | **266.8** |
| Heterocyclics | Phenol | $C_6H_6O$ | 94 | 181.7 | 72.6 |
| | Phenol, 2-methyl- | $C_7H_8O$ | 108 | 191 | 20.7 |
| | Phenol, 3-methyl- | $C_7H_8O$ | 108 | 202.2 | 65.1 |
| | Benzofuran | $C_8H_6O$ | 118 | 174 | 7.3 |
| | Benzofuran, 2,3-dihydro- | $C_8H_8O$ | 120 | 188.5 | 8.3 |
| | Benzofuran, 2-methyl- | $C_9H_8O$ | 132 | 197.5 | 3.3 |
| | Phenol, 2,3-dimethyl- | $C_8H_{10}O$ | 122 | 210 | 17.4 |
| | Phenol, 2,4-dimethyl- | $C_8H_{10}O$ | 122 | 210.9 | 11.1 |
| | Phenol, 4-ethyl- | $C_8H_{10}O$ | 122 | 219 | 23.4 |
| | Phenol, 2-ethyl-4-methyl- | $C_9H_{12}O$ | 136 | 214.9 | 5.1 |
| | Dibenzofuran | $C_{12}H_8O$ | 168 | 287 | 10.0 |
| | 9H-Fluoren-9-ol | $C_{13}H_{10}O$ | 182 | 367.5 | 4.4 |
| | Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl- | $C_{23}H_{32}O_2$ | 340 | 428.6 | 1.4 |
| Σ | | | | | **249.9** |
| Light aromatics | Benzene | $C_6H_6$ | 78 | 80 | 11.5 |
| | Toluene | $C_7H_8$ | 92 | 110.6 | 7.8 |
| | Styrene | $C_8H_8$ | 104 | 145 | 6.7 |
| | Indene | $C_9H_8$ | 116 | 182 | 11.8 |
| | 2-Methylindene | $C_{10}H_{10}$ | 130 | 205.6 | 5.9 |
| Σ | | | | | **43.6** |
| Light PAHs | Naphthalene | $C_{10}H_8$ | 128 | 218 | 84.1 |
| | Naphthalene, 1-methyl- | $C_{11}H_{10}$ | 142 | 241 | 8.1 |
| | Naphthalene, 2-methyl- | $C_{11}H_{10}$ | 142 | 239.9 | 24.5 |
| | Acenaphthylene | $C_{12}H_8$ | 152 | 280 | 33.1 |
| | Acenaphthene | $C_{12}H_{10}$ | 154 | 279 | 9.7 |
| | Biphenyl | $C_{12}H_{10}$ | 154 | 255 | 10.2 |
| | Naphthalene, 2-ethenyl- | $C_{12}H_{10}$ | 154 | 270.9 | 13.9 |
| | Naphthalene, 1,3-dimethyl- | $C_{12}H_{12}$ | 156 | 268 | 4.8 |
| | Naphthalene, 1,8-dimethyl- | $C_{12}H_{12}$ | 156 | 270.6 | 5.1 |
| | Naphthalene, 1-ethyl- | $C_{12}H_{12}$ | 156 | 259 | 5.7 |
| | Naphthalene, 2,6-dimethyl- | $C_{12}H_{12}$ | 156 | 264.4 | 5.3 |
| | 1H-Phenalene | $C_{13}H_{10}$ | 166 | 316.4 | 4.6 |
| | Fluorene | $C_{13}H_{10}$ | 166 | 295 | 9.7 |
| | 1,1'-Biphenyl, 4-methyl- | $C_{13}H_{12}$ | 168 | 267.5 | 4.0 |
| | 1-Isopropenylnaphthalene | $C_{13}H_{12}$ | 168 | 257 | 2.4 |
| | Naphthalene, 2-(1-methylethenyl)- | $C_{13}H_{12}$ | 168 | 281.2 | 5.6 |
| | Naphthalene, 2-(1-methylethyl)- | $C_{13}H_{14}$ | 170 | 268.2 | 1.8 |
| | Phenanthrene | $C_{14}H_{10}$ | 178 | 336 | 17.7 |
| | 9H-Fluorene, 9-methyl- | $C_{14}H_{12}$ | 180 | 311 | 2.8 |
| | 4H-Cyclopenta(def)phenanthrene | $C_{15}H_{10}$ | 190 | 353 | 3.3 |
| | Anthracene, 2-methyl- | $C_{15}H_{12}$ | 192 | 353.5 | 2.8 |
| | 1,1'-Biphenyl, 3-(1-methylethyl)- | $C_{15}H_{16}$ | 196 | 300.5 | 2.4 |
| | Phenanthrene, 1-methyl-7-(1-methylethyl)- | $C_{18}H_{18}$ | 234 | 392 | 2.7 |
| Σ | | | | | **264.4** |
| Heavy PAHs | Fluoranthene | $C_{16}H_{10}$ | 202 | 375 | 3.7 |
| | Pyrene | $C_{16}H_{10}$ | 202 | 404 | 3.5 |
| Σ | | | | | **7.1** |

The light PAHs and heavy PAHs compounds accounted for 31.8 wt% and 0.9 wt%, respectively. Naphthalene was the most abundant compound in the light PAHs group, accounting for 10.1 wt% in total tar and 31.8 wt% in light PAHs. This result was in good correlation with previous work from Madav *et al.* (2019). They showed that naphthalene accounted for 5 to 9% in total tar from a 35 kW downdraft gasifier. Horvat *et al.* (2019) indicated that lignin was a tar precursor, leading to the production of more kinds and a larger amount of PAHs than cellulose and hemicellulose. As mentioned earlier, cedar pellets are lignin-rich fuel. This could be the reason for a considerable proportion of PAHs in tar compositions.

Moreover, the reactor temperature is considered as an essential parameter for the formation and maturation of tar. Weidemann *et al.* (2018) have performed pyrolysis experiments with softwood and wheat straw pellets using a lab-scale reactor in the temperature range from 550 to 700 °C. Their results indicated that the PAHs from both feedstocks consisted mainly of light PAHs compounds, regardless of the pyrolysis temperature. Zubair Yahaya *et al.* (2020) gasified coconut and palm kernel shells using the batch type downdraft gasifier at a temperature between 700 °C and 900 °C. They showed that the heavy PAHs were only detected at a temperature of 900 °C with a negligible amount. From this analysis, it can be realized that the reactor temperature range from 550 to 750 °C in this study prevented the formation of heavy PAHs compounds. However, PAHs compounds have a significant influence on tar condensation issues, although with low concentration. Thus, it is crucial to remove PAHs when designing the gas cleaning system. Besides, the presence of a high percentage of acids/ketones and PAHs in tar compositions could indicate the non-uniform conditions inside the reactor such as channeling and bridging (Evans and Milne 1997).

Additionally, the tar in raw producer gas contains 5.2 wt% of light aromatic compounds. This finding agrees well with the results obtained by Zubair Yahaya *et al.* (2020). Their results showed that the light aromatics accounted for 3.45% and 1.11% for coconut and palm kernel shells, respectively. Moreover, Amini *et al.* (2019) carried out experiments in a pyrolyzer apparatus under temperature ranging from 400 to 800 °C with 15 different biomass feedstocks. They indicated that light aromatics such as benzene and toluene accounted for a negligible proportion of tar compositions compared with acids/ketones or heterocyclics. However, this result was quite different compared with the results of Yamazaki *et al.* (2005). They showed that one-ring aromatics and naphthalene were abundant components of tar from the downdraft gasifier operated with reaction temperature from 900 to 1000 °C. Also, Hernández *et al.* (2013) and Prando *et al.* (2016) indicated that light aromatic compounds are the most abundant compounds in their results. Hernández *et al.* (2013) performed the experiments on a small scale drop-tube gasification pilot plant using mars of grape as fuel at a temperature range of 750 to 1200 °C. Prando *et al.* (2016) carried out the gasification of casuarina wood chip on a small scale drop-tube gasification pilot plant at the oxidation zone temperature of 950 °C. These analyses indicated that the high temperature of the reactor could be the reason for obtaining a high ratio of light aromatic components. Besides, Morf *et al*. (2002) examined tar production from fixed bed gasification using wood chips at a different temperature from 500 to 1000 °C. They showed that the conversion of primary tars such as acids/ketones to aromatic compounds becomes increasingly prevalent at temperatures higher than 750 °C.

Furthermore, Qin *et al.* (2015) have investigated the effect of different chemical compositions in biomass feedstock on tar formation. The experiments were carried out on the bench-scale spout fluidized bed reactor at a temperature between 700 and 900 °C. Their results showed that the lignin-rich fuel such as sawdust needs a higher temperature to generate light aromatics. Zubair Yahaya *et al.* (2020) indicated that lignin-rich palm kernel shell generated less light aromatics compared to cellulose and hemicellulose-rich coconut shell. Notably, benzene and toluene were not detected in their results when gasifying lignin-rich palm kernel shell. It can be realized that the formation of light aromatics is strongly affected by a higher temperature of the reactor and the lignin chemical composition of the feedstock. Thus, the small number of light aromatics in this work could be explained by the reactor temperature from 550 to 750 °C and the lignin-rich cedar pellets. A similar trend of light aromatics was also observed by Zhou *et al.* (2018).

The main compounds of tar deposits with 28 species are shown in Table 4. The average values of density were calculated from four tar deposit samples. Tar deposits of a small downdraft gasifier have complex components include many functional groups such as heterocyclics, light aromatics, light PAHs, and heavy PAHs. However, the acids/ketones and the nitrogen compounds are not detected in this study.

**Table 4.** Major Compounds of Tar Deposits

| Substance group | Compound name | Chemical formula | Molecular weight | Boiling point | Density |
|---|---|---|---|---|---|
| | | | g/mol | °C | mg/g |
| Heterocyclics | Phenol | $C_6H_6O$ | 94 | 181.7 | 17.9 |
| | Phenol, 2-methyl- | $C_7H_8O$ | 108 | 191 | 4.5 |
| | Phenol, 3-methyl- | $C_7H_8O$ | 108 | 202.2 | 16.8 |
| | Benzofuran, 2,3-dihydro- | $C_8H_8O$ | 120 | 188.5 | 2.7 |
| | Phenol, 4-ethyl- | $C_8H_{10}O$ | 122 | 218 | 4.0 |
| | Phenol, 2-methoxy- | $C_7H_8O_2$ | 124 | 266 | 6.3 |
| | Phenol, 2-ethyl-5-methyl- | $C_9H_{12}O$ | 136 | 218.3 | 2.0 |
| | Phenol, 4-ethyl-2-methoxy- | $C_9H_{12}O_2$ | 152 | 235 | 4.6 |
| | Phenol, 2-methoxy-4-(1-propenyl)- | $C_{10}H_{12}O_2$ | 164 | 266.6 | 4.3 |
| | Phenol, 2-methoxy-4-methyl- | $C_8H_{10}O_2$ | 164 | 221 | 8.9 |
| | Dibenzofuran | $C_{12}H_8O$ | 168 | 287 | 3.5 |
| | Phenol, 2,4-bis(1,1-dimethylethyl)- | $C_{14}H_{22}O$ | 206 | 269 | 1.0 |
| | 3-benzyloxy-1,2-diacetyl-1,2-propanediol | $C_{14}H_{18}O_5$ | 266 | 360.9 | 2.3 |
| Σ | | | | | **78.9** |
| Light aromatics | Benzene | $C_6H_6$ | 78 | 80 | 5.2 |
| Σ | | | | | **5.2** |
| Light PAHs | Naphthalene | $C_{10}H_8$ | 128 | 218 | 9.6 |
| | Naphthalene, 2-methyl- | $C_{11}H_{10}$ | 142 | 214.1 | 4.6 |
| | Biphenylene | $C_{12}H_8$ | 152 | 255 | 11.1 |
| | Acenaphthene | $C_{12}H_{10}$ | 154 | 279 | 2.5 |
| | Biphenyl | $C_{12}H_{10}$ | 154 | 255 | 3.0 |
| | Naphthalene, 1-ethyl- | $C_{12}H_{12}$ | 156 | 259 | 1.5 |
| | 1H-Phenalene | $C_{13}H_{10}$ | 166 | 316.4 | 1.4 |
| | Fluorene | $C_{13}H_{10}$ | 166 | 295 | 2.6 |
| | 1,1'-Biphenyl, 4-methyl- | $C_{13}H_{12}$ | 168 | 267 | 1.5 |
| | Anthracene | $C_{14}H_{10}$ | 178 | 178 | 5.8 |
| | Phenanthrene | $C_{14}H_{10}$ | 178 | 336 | 2.4 |
| | 4H-Cyclopenta(def)phenanthrene | $C_{15}H_{10}$ | 190 | 353 | 1.4 |
| | Anthracene, 2-methyl- | $C_{15}H_{12}$ | 192 | 347.2 | 1.4 |
| Σ | | | | | **48.7** |
| Heavy PAHs | Pyrene | $C_{15}H_{12}$ | 192 | 347.2 | 1.8 |
| Σ | | | | | **1.8** |

Heterocyclic and light PAHs are the most abundant components, representing approximately 58.6 wt% and 36.2 wt%, respectively. Light aromatics and heavy PAHs account for only a small percentage of tar deposit compositions with 3.9 wt% and 1.3 wt%, respectively.

## Comparison of Tar in Raw Producer Gas and Tar Deposits

From Table 3 and Table 4, it can be realized that although acids/ketones components have a high concentration in raw producer gas, such compounds do not exist in the tar deposit compositions. This result may be due to the condensation of acids/ketones compounds, even though the temperature of the condenser was above the boiling point (Sui *et al*. 2014). Thus, acids/ketones compounds did not cause deposit problems in downstream equipment. They could be removed with a ceramic filter or heat exchanger in the gas cleaning system of the small downdraft gasifier used in this study. There are several heterocyclic compounds found in tar deposits, but they could not be detected in tar from raw producer gas. This situation may be because these compounds have a very small density in raw producer gas compositions, making them difficult to detect by GC-MS. However, through long-term operation, these compounds were fouling in the pump lead to it exists in tar deposit compositions.

The comparison of the percentage composition of tar components between tar deposit and tar in raw producer gas is shown in Fig. 4. Heterocyclics, which are mainly phenolics compounds, are the primary components that caused the deposit for downstream equipment in a small downdraft gasifier system. This result could be due to the fact that heterocyclic compounds are water-soluble substances. Hence, they might be absorbed into condensed water on the surface of the downstream devices. Demirbas (2007) showed that tar obtained from biomass pyrolysis at low temperature (500 to 550 °C) mainly consisted of heterocyclic and acids/ketones components that easily dissolved these fractions in condensed water. Al-Rahbi *et al*. (2016) indicated that the water fraction was about 15 to 20 weight-percent of tar yield. Besides, Susanto and Beenackers (1996) showed that water vapor accounted for 8.3% to 13.8% by volume in the producer gas from the downdraft gasifier. Due to the temperature of the producer gas is different from the inner wall temperature of the downstream equipment; hence, water vapor was condensed on the wall.

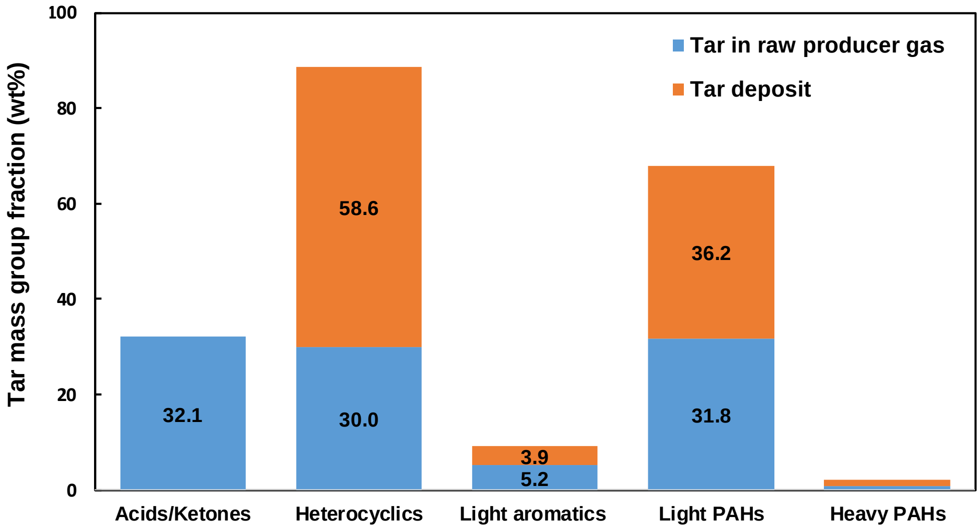

**Fig. 4.** The comparison of the percentage composition of tar components between tar deposit and tar in the raw producer gas

Furthermore, Anis and Zainal (2011) revealed that heterocyclic and PAHs compounds in producer gas might have become the primary cause of condensation, although at a low concentration of the substances. Figure 4 shows that the heterocyclic and light PAHs compounds were dominant in tar deposits, which accounted for 58.6 wt% and 36.2 wt%, respectively. These results have identified that heterocyclic and light PAHs compounds are the main cause of tar deposition for a small downdraft gasifier system. Therefore, the selectivity of the tar treatment method to remove the heterocyclic and light PAHs compounds need to be considered when designing the gas cleaning system for this type of gasifier. Additionally, the small downdraft gasifier usually has a low temperature of the reactor because of the heat loss. Hence, insulation issues should be considered to increase the temperature of the reactor for cracking heterocyclics to aromatic compounds.

## The Molecular Weight Distribution of Major Tar Compounds

Figure 5 shows the relationship between the number of tar compounds and the molecular weight of tar deposit and tar in raw producer gas. The tar components in raw producer gas have the molecular weight focus on the range of 60 to 210 g/mol. There is one compound with a high molecular weight that is phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl- (340 g/mol). Tar deposit components have molecular weights mainly in the range of 90 to 210 g/mol. The highest molecular weight compound in the tar deposits was found to be 3-benzyloxy-1,2-diacetyl-1,2-propanediol (266 g/mol). The major tar compounds in raw producer gas with molecular weight from 60 to 90 g/mol were mainly acids/ketones compounds. Although these compounds had a high concentration, they did not cause the condensation problems. Additionally, it can be realized that the heavy-weight tars, which consist of components with high vapor pressure, could be decomposed or removed by the gas cleaning and cooling facilities installed in the gasifier system. However, the light-weight tars (except carboxylic acids and ketones), which consist of components with low vapor pressure, could not be removed by the gas purification facilities and could flow into the downstream equipment along with producer gas.

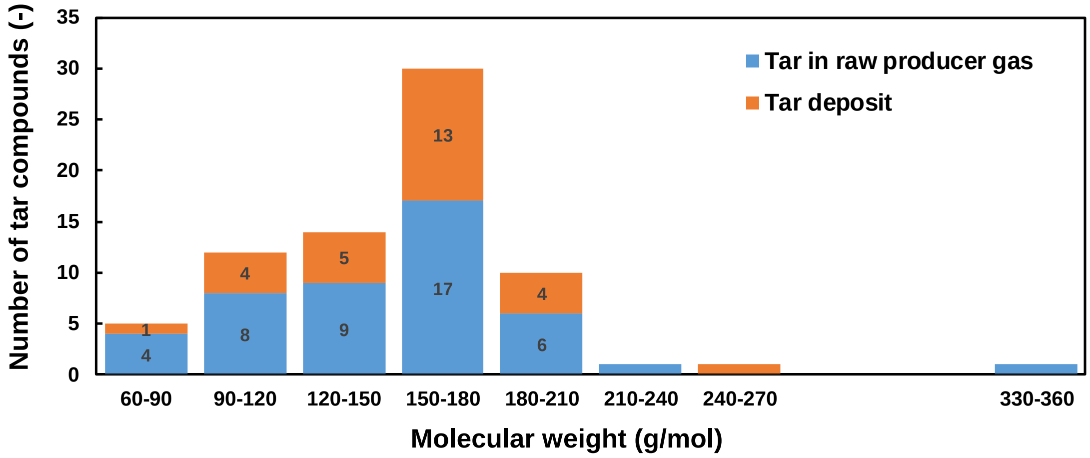

**Fig. 5.** The relationship between the number of tar compounds and the molecular weight of tar deposit and tar in the raw producer gas

Figure 6 presents the relationship between the tar mass group fraction and the molecular weight of tar deposit and tar in raw producer gas. The tar components with the molecular weight range from 60 to 150 g/mol were found to have a high concentration in raw producer gas, which accounted for 79.5 wt%. However, the molecular weight of tar deposit components was focused mostly in the range of 90 to 120 g/mol, and 150 to 180 g/mol accounted for 70.6 wt%. This result indicated that the condensation problem was dominated by the molecular weight of tar and not by the tar concentration. A similar trend was observed by Kiel *et al*. (2004).

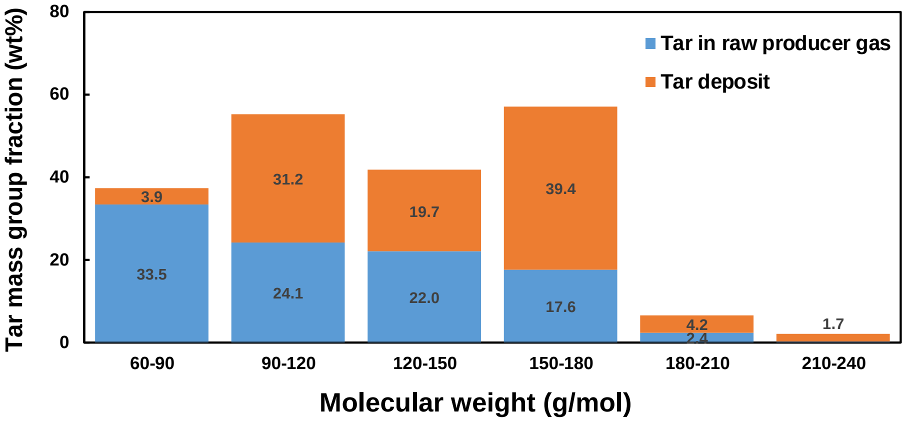

**Fig. 6.** The relationship between the tar mass group fraction and molecular weight of tar deposit and tar in the raw producer gas

## CONCLUSIONS

1. About 46 and 28 major chemical compounds from tar in raw producer gas and tar deposits were identified in detail, respectively. However, the number of tar candidate compounds was affected strongly by the chosen similarity index and the appearance ratio.
2. Tar in raw producer gas contained mainly acids/ketones, heterocyclic, and light PAH compounds, accounting for 32.1 wt%, 30.0 wt%, and 31.8 wt%, respectively. Besides, the main components of tar deposits were heterocyclic, and light PAH compounds which accounted for 58.6 wt%, and 36.2 wt%, respectively. These results revealed that heterocyclic and light PAHs compounds need to be considered when selecting types and designing the gas purification facilities for the small downdraft gasifier system.
3. The number of compounds in both tars was concentrated between 90 and 210 g/mol, where the majority of tar compounds had the molecular weight from 150 to 180 g/mol. Additionally, while tar components in raw producer gas were the group of 60 to150 g/mol, which accounted for 79.5 wt%, tar deposits had the components focusing on the group of 90 to 120 g/mol and 150 to 180 g/mol, accounting for 70.6 wt%. These results showed that the condensation issue was influenced by the molecular weight of tar compounds instead of the tar concentration.
4. GC-MS and gravimetric analysis showed that tar concentration in raw producer gas from a 10 kW downdraft gasifier using cedar pellets was 831.8 mg/Nm$^3$ and 760.5 mg/Nm$^3$, respectively. This result indicated a good correlation between both methods. When compared with previous studies, the lower concentration of tar was observed in the present study.

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