The Removal of Mixed Tar in Biomass Fuel Gas through the Thermal and Catalytic Treatment Methods: Review

Hafnee Lateh¹, Juntakan Taweekun², Kittinan Maliwan³ and Aulia Ishak⁴

¹,²,³Department of Mechanical Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, Songkhla, Thailand
⁴Department of Industrial Engineering, Faculty of Engineering, Universitas Sumatera Utara, Medan, Indonesia

E-mail: abuhaf_me@hotmail.com

Abstract. The global situation consumes enormous amount of energy while the energy sources are limited and decreasing. Alternative energy source is widely focused for compensating the main energy source. Thus, the finding of alternative resources particularly biomass energy is highly essential. Biomass gasification is a transforming process of solid biomass into the valued fuel gases. Although biomass fuel gas provides utility gases, the contaminant as tar that need to eliminate for evading the problems to engines and turbines. Hence, the treatment methods of tar are extremely important and challenge. This paper indicates the recent treatment researches for biomass tar removal. The problems of tar as well as the weakness and advantages of all tar treatment methods are discussed.

1. Introduction
Nowadays, the crisis of global warming, the crisis of lacking fossil fuels and energy, and the crisis of greenhouse gas emission have been apprehensive problems to our life [1]. These problems have been widely debated and promoted to quest for substitution the using of fossil fuels through green energy [2]. Currently, the energy is being considered to global issues due to the demand and supply of energy imbalance and the population augmentation.

The global situation consumes enormous amount of energy while the energy sources are limited and decreasing. Alternative energy source is widely focused for compensating the main energy source. Thus, the finding of alternative resources particularly biomass energy is highly essential. Biomass gasification is a transforming process of solid biomass into the valued fuel gases. Although biomass fuel gas provides utility gases, the contaminant as tar that need to eliminate for evading the problems to engines and turbines. Hence, the treatment methods of tar are extremely important and challenge. This paper indicates the recent treatment researches for biomass tar removal. The problems of tar as well as the weakness and advantages of all tar treatment methods are discussed.

In reference to the global status report of renewables 2019, the renewable energy supplied for estimation about 18.1% of final global energy consumption by the end of 2017 as displayed in figure 1. Among of renewable energies, biomass is the largest used of energy source around the world, while 7.5% of which derived from the traditional biomass utilized to cook and heat in developing countries. Besides, the modern renewable has increased approximately 4.4% from 2016. So, biomass energy is the most promising of research topic as above mentioned.
Biomass gasification, a thermo-chemical process, is the conversion process of biomass into useful gas basically called producer gas. Biomass producer gas (BPG) is the main product of that process, commonly consisting of \( \text{H}_2, \text{CO}, \text{CO}_2, \text{CH}_4, \text{N}_2, \text{and H}_2\text{O} \). The gas products can be applied for electricity generation via internal combustion engine and gas turbine [4],[5]. However, its process provides not only the useful products but also by products such as \( \text{NO}_x, \text{SO}_2, \text{particle and tar} \). Generally, byproducts can cause the metallic corrosion and erosion, especially the tar that can corrode the equipment, clog the valves and reduce the quality of biomass producer gas.

2. Tar and its removal method
Tar is the organic contaminants produced from gasification process, that tar also has a larger of molecular weight than which of benzene. Its characteristic is a black, thick, and high concentration that can condense at low temperature zone, can block pipeline system, can be stained the turbine and engines, and lastly, it led to disrupt of all systems as represented in figure 2.
Figure 2. The problems of tar with some equipment [10]

Usually tar concentration depending on the type in the process gasifiers which are approximately 1 g/Nm\(^3\) for downdraft gasifier, 10 g/Nm\(^3\) updraft gasifier, and 100 g/Nm\(^3\) respectively [5-7]. Tar components can be divided into 5 classes corresponded to their tar properties of chemical, solubility and condensability as given in Table 1. [8][9]

| Tar Class | Class Name | Tar Properties | Tar Elements |
|-----------|------------|----------------|--------------|
| 1         | GC-undetectable | Heavy tar and can’t be detected by GC | Gravimetric Tars |
| 2         | Heterocyclic Aromatics | Heterocyclic elements (like pyrrole, furan, pyridine, and thiophene). These are elements usually show high water solvability, in consequence of their polarity. | Pyridine, Phenol, Cresol, Quinolone |
| 3         | Aromatics (1 ring) | Aromatic elements. Light hydrocarbons that are not significant condensation and water solubility issues. | Xylene, Styrene, Toluene |
| 4         | Light PAH (2 - 3 ring) | Light poly aromatic hydrocarbons (2 - 3 rings PAH’s). These elements condense at relatively high concentrations and moderate temperatures | Naphtalene; Methyl-naphtalene; Biphenyl; Ethynlnaphtalene; Acenaphtylene; Acenaphtene; Fluorene; Phenanthrene; Anthracene Fluoranthene; Pyrene; Benzo-anthracene; Chrysene; Benzo-Fluoranthene; Benzo-pyrene; Perylene; Indenopyrene; Dibenzanthracene; Benzo-perylene |
| 5         | Heavy PAH (>3 - ring) | Heavy poly aromatic hydrocarbons (4 - 5 rings PAH’s). These elements condenses in a low concentration at a relatively high temperature. | |

Tar contaminant along with the producer gas is the main problem of gasification process as above mentioned and it needs to remove before using any applications of producer gas. In the last three decade, various methods of tar removal have been consistently studied, reported, and developed in several literatures. Generally, tar removal method is divided in two treatments: 1) primary treatment is that tar was decomposed inside the gasifier and 2) secondary treatment that the tar was eliminated outside the gasifier. Although mainly treatments were able eradicate the tar pollution in biomass producer gas, it seems that their method cannot be removed completely without applying the secondary measures such as mechanical treatment, thermal treatment, and catalytic cracking.

2.1 Physical treatment

Physical treatment is the mechanical tar trap method that usually divides into dry gas and wet gas reduction methods. Dry gas is trapped with this equipment such as ESB, cyclone, bag filter, baffle filter,
rotational particle separator (RPS), and esc. In case of wet gas, the equipment of tar trap includes wet scrubber, wet ESB, spray tower, and wet cyclone, etc. The efficiency of various tar elimination tools is shown in table 2.

### Table 2. The efficiency of various tar elimination tools

| Tools            | Particulates removal | Tar removal |
|------------------|----------------------|-------------|
| Sand bed filter  | 70-99                | 50-97       |
| Bag filter       | 70-95                | 0-50        |
| RPS              | 85-90                | 30-70       |
| Spray tower      | 60-98                | 10-25       |
| Venturi scrubber | -                    | 50-90       |
| Wet ESB          | >99                  | 0-60        |

Among of these tar cleaning techniques, thermal and catalytic cracking is appropriate approach because its method has been completely removed the tar and converted the tar into useful gases. That also can be improved the producer gas quality [2][8][9].

#### 2.2 Thermal treatment

Thermal cracking of tar denotes that tar is fractured from heavy aromatic to lighter non-condensable gases with high heating temperature and a definite of the residence time. The high-up of temperature reaction can be affected the heavy aromatic of tar and converted that tar into other gases species. It has been reported that this method can be decompose the tar at temperature of 900 °C [13] while Jess [14] informed that a high achievement of tar removal efficiency needs to operate with temperature at higher than 1,100 °C and less than 5 s of residence time. Based on Zhang et al. [15] reported, toluene, one of typical tar compounds, is hardly to decompose with low heating temperature and need to use the heating temperature more than 1,200 °C for complete the removal of tar. It is to be noted that the high heating temperature need to use the high energy that could be impacted to total energy consumption and efficiency that lead it to diseconomy of the tar removal process.

#### 2.3 Catalytic treatment

Catalytic cracking of tar, this treatment method has been interesting since 1980 because the catalyst assists the chemical reaction of which cracks the tar into useful gases. Basically, the fine catalysts for tar treatment should have the following characteristics: 1) The effectiveness on tar removal 2) The ability of reforming methane, if the product is to be used as a fuel gas 3) The resistant ability of coke deposition on catalyst surface and 4) Strong, durable and inexpensive. Several catalysts have been used and reported in many previous studies that were categorized in six groups of catalysts such as nickel based catalyst, non-nickel or transition metal catalysts (Rh, Ru, Pd – noble catalysts), alkali metal catalysts, acid catalysts (zeolite), and activated carbon catalysts [2][14].

##### 2.3.1 Nickel based catalysts

Nickel is such effective catalysts that are the most used for tar elimination and also support the water gas shift reaction. These catalysts can crack the tar and contribute the producer gas on improving its quality [17]. Miyasawa et al. [18] were mentioned that Ni/Al₂O₃ showed high efficiency on tar elimination, while its weakness is rapid deactivation from the coke formation.

##### 2.3.2 Non-nickel metal catalysts

Non-nickel metal catalysts or transition metal catalysts, these catalysts such as Rh, Ru, Pd (noble catalysts) are investigated for tar reduction. There gave the results in the highest efficiency and long thermal stability on tar decomposition. Among of Non-nickel metal group,
rhodium (Rh) is founded that has the best tar removal compared with other catalysts of this groups as follows: Rh > Pt > Pd > Ni = Ru. In addition, the performance of this group is not only the high tar removal but also good resistance the coke formation too, while the price of these catalysts are very high [17-19].

2.3.3 Alkali metal catalysts. Several researches have proven that these catalysts improved the quality of producer gas and effected on tar reduction. The main weakness of alkali metal catalysts is rapid deactivated of tar from sintering inside structure of catalyst. It is also informed that some effect of this catalyst shows the ash content increase after char gasification and it can be problem to the process of tar removal [18][20].

2.3.4 Natural catalysts. The catalysts of this group such as dolomite and olivine, are widely used in tar reduction. The advantages of these catalysts are inexpensive and able to reduce tar but the activity of catalytic reduction of tar is lower than other groups.

2.3.5 Acid catalysts. These catalysts such as silica-alumina, zeolite, etc. have been many studied that give more efficient on reduction of tar and producer gas improvement. The previous study of Dou et al. [23] that focused on tar removal with using several catalysts such as Y-zeolite, alumina, silica, Ni/Mo, and lime were examined. The results presented that Y–zeolite and Ni/Mo are the best effectiveness catalysts on which removal of tar. Anis et al. [24] were studied that toluene and naphthalene as model tar content of biomass tar are removed about 79% - 83% through Y-zeolite cracking both of their model tar at temperature reaction of 700 °C and residence time of 0.5 s. Anyhow, the strange of zeolite is low price, high surface area, and high capacity of adsorption, while the important weakness is catalysts deactivated rapidly. Silica–alumina catalysts also have been tested for tar removing of biomass gasification. It is found that silica-alumina can remove the tar notwithstanding the activity of that catalysts lower than others [9][25].

2.3.6 Activated carbons catalysts. Activated carbons catalysts, or char catalysts, are also widely used in tar removal process due to its high surface area of catalyst. Many papers present that activated carbons or chars can reduce the amount of tar. The remarkableness of this catalyst are inexpensive cost, whereas the coke formation of this catalysts is the main problem because it can reduce the catalyst surface area [19].

The above mentioned, among of six groups catalysts, nickel based and acid are the most attractive catalysts to reduce the tar and transform tar into useful gas. Nevertheless, the rapid catalyst deactivation from the deposition of coke formation inside the catalysts structures remains weakness that needs to be improved. Thermal and catalytic cracking are the promising methods to reduce among of biomass tar that also can be converted the tar into useful gas. However, these cracking methods usually operate at high heating temperature during 650 – 1,200 °C. To achieve the high temperature, both methods require a higher of external electrical source which heat transfer arises from the surface into material core. While, heat transfer resistance, heat loss to the surrounding along with the corrosion of reactor wall are the lack of these treatment due to the continuous high electrical heating, that also must be solved those weaknesses for complete and worth on tar removal process.

3. Conclusions
The challenge issue on biomass gasification is the tar contaminant. Several problems of tar directly impact to production system of biomass producer gas. The completely removal method of tar is necessary to reduce the tar contaminant and improve quality biomass fuel gas. In addition, the cost and stability of removal process need to be considered. Thermal and catalytic cracking method that seems concerned because of completion on tar removal. While, the rapid of catalyst deactivation on catalytic
cracking and a higher heating energy requirement of both methods should be adjusted as well.

4. References

[1] REN 21, 2015 Renewables 2015 global status report (Paris, France: REN21 Secretariat)
[2] Anis S and Zainal Z A 2011 Tar reduction in biomass producer gas via mechanical, catalytic and thermal methods: A review, Renew Sustain Energy Rev 15 (5) pp 2355–2377
[3] REN 21, 2019 Renewable 2019 Global Status Report (Paris, France)
[4] Han J and Kim H 2008 The reduction and control technology of tar during biomass gasification/pyrolysis: An overview, Renew Sustain Energy Rev 12 (2) pp 397–416
[5] Basu P 2018 Biomass gasification, pyrolysis and torrefaction: practical design and theory (Third Edition) Academic Press pp 189–210
[6] Devi L, Ptasinski K J and Janssen F J J G 2003 A review of the primary measures for tar elimination in biomass gasification processes Biomass Bioenergy 24 (2) pp 125–140
[7] Ahrenfeldt J 2005 Handbook biomass gasification H Knoef (Ed.) (The Netherlands: BTG biomass technology group) pp 1755-1768
[8] Devi L, Ptasinski K J, Janssen F J J G, van Paasen S V B, Bergman P C A and Kiel J H A 2005 Catalytic decomposition of biomass tars: use of dolomite and untreated olivine, Renew Energy 30 (4) pp 565–587
[9] Abu El-Rub Z, Bramer E A and Brem G 2004 Review of Catalysts for Tar Elimination in Biomass Gasification Processes Ind Eng Chem Res 43 (22) pp 6911–6919
[10] Thersites [Online] Available: http://www.thersites.nl/ [Accessed: 18-Sep-2019]
[11] Hasler P and Nussbaumer T 1999 Gas cleaning for IC engine applications from fixed bed biomass gasification Biomass Bioenergy 16 (6) pp 385–395
[12] Wang D, Yuan W and Ji W 2011 Char and char-supported nickel catalysts for secondary syngas cleanup and conditioning Appl Energy 88 (5) pp 1656–1663
[13] Qin Y, Huang H, Wu Z, Feng J, Li W and Xie K 2007 Characterization of tar from sawdust gasified in the pressurized fluidized bed, Biomass Bioenergy 31 (4) pp 243–249
[14] Jess A 1996 Mechanisms and kinetics of thermal reactions of aromatic hydrocarbons from pyrolysis of solid fuels Fuel 75 (2) pp 1441–1448
[15] Zhang Y, Kajitani S, Ashizawa M and Oki Y 2010 Tar destruction and coke formation during rapid pyrolysis and gasification of biomass in a drop-tube furnace Fuel 89 (2) pp 302–309
[16] Guan G, Kaewpanha M, Hao X and Abudula A 2016 Catalytic steam reforming of biomass tar: Prospects and challenges Renew Sustain Energy Rev 58 pp 450–461
[17] De Lasa H, Salaices E, Mazumder J and Lucky R 2011 Catalytic Steam Gasification of Biomass: Catalysts, Thermodynamics and Kinetics Chem Rev 111 (9) pp 5404–5433
[18] Miyazawa T, Kimura T, Nishikawa J, Kado S, Kunimori K and Tomishige K 2006 Catalytic performance of supported Ni catalysts in partial oxidation and steam reforming of tar derived from the pyrolysis of wood biomass, Catal Today 115 (1) pp 254–262
[19] Anis S and Zainal Z A 2011 Tar reduction in biomass producer gas via mechanical, catalytic and thermal methods: A review Renew Sustain Energy Rev 15 (5) pp 2355–2377
[20] Sutton D, Kelleher B, Doyle A and Ross J R H 2001 Investigation of nickel supported catalysts for the upgrading of brown peat derived gasification products Bioresour Technol 80 (2) pp 111–116
[21] Asadullah M, Miyazawa T, Ito S, Kunimori K, Koyama S and Tomishige K 2004 A comparison of Rh/CoO2/SiO2 catalysts with steam reforming catalysts, dolomite and inert materials as bed materials in low throughput fluidized bed gasification systems Biomass Bioenergy 26 (3) pp 269–279
[22] Hu M, Laghari M, Cui B, Xiao B, Zhang B and Guo D 2018 Catalytic cracking of biomass tar over char supported nickel catalyst Energy 145 pp 228–237
[23] Dou B, Gao J, Sha X, and Baek S W 2003 Catalytic cracking of tar component from high-temperature fuel gas Appl Therm Eng 23 (17) pp 2229–2239
[24] Anis S, Zainal Z A and Bakar M Z A 2013 Thermocatalytic treatment of biomass tar model compounds via radio frequency *Bioresour Technol* 136 pp 117–125

[25] Buchireddy P R, Bricka R M, Rodriguez J and Holmes W 2010 Biomass Gasification: Catalytic Removal of Tars over Zeolites and Nickel Supported Zeolites *Energy Fuels* 24 (4) pp 2707–2715

[26] Liu X, Khinast J G and Glasser B J 2014 Drying of Ni/Alumina Catalysts: Control of the Metal Distribution Using Surfactants and the Melt Infiltration Method *Ind Eng Chem Res* 53 (14), pp 5792–5800

[27] Din Z U and Zainal Z A 2018 Tar reduction mechanism via compression of producer gas, *J Clean Prod* 184 pp 1–11

[28] Evans R J and Milne T A 1997 Chemistry of tar formation and maturation in the thermochemical conversion of biomass. In *Developments in thermochemical biomass conversion* (Dordrecht: Springer) pp 803–816

[29] Gates B C *Catalytic chemistry* 1992 (Singapore: Wiley & Son, Inc)

[30] Zainal Z A, Rifaiu A, Quadir G A and Seetharamu K N 2002 Experimental investigation of a downdraft biomass gasifier *Biomass and bioenergy* 23(4) pp 283-289

[31] Bergman P C, van Paasen S V and Boerrigter H 2002 The novel “OLGA” technology for complete tar removal from biomass producer gas In *Pyrolysis and gasification of biomass and waste*, expert meeting 30 pp 347–356

[32] Waldheim L and Nilsson T 2001 Heating value of gases from biomass gasification *Rep Prep IEA Bioenergy Agreem* 20

[33] Cherbański R and Molga E 2009 Intensification of desorption processes by use of microwaves—An overview of possible applications and industrial perspectives *Chem Eng Process Process Intensif*, 48 (1) pp 48–58

[34] Anis S and Zainal Z A 2014 Study on kinetic model of microwave thermocatalytic treatment of biomass tar model compound, *Bioresour Technol*, 151 pp 183–190

[35] Tang J, Hao F and Lau M 2002 microwave heating in food processing in *Advances in Bioprocessing Engineering* 1 pp 1–44

[36] Din Z U 2018 *Producder gas cleaning process from biomass gasification and its impact on solid oxide fuel cells performance* (Malaysia: Universiti Sains Malaysia)

[37] Wu C, Huang Q, Sui M, Yan Y and Wang F 2008 Hydrogen production via catalytic steam reforming of fast pyrolysis bio-oil in a two-stage fixed bed reactor system *Dimethyl Ether Spec Sect*, 89 (12) pp 1306–1316

[38] Anis S 2013 *Tar removal from producer gas via thermal and catalytic means* (Malaysia: Universiti Sains Malaysia)

[39] Radwan A M, Kyotani T and Tomita A 2000 Characterization of coke deposited from cracking of benzene over USY zeolite catalyst, *Appl Catal Gen.*, 192 (1) pp 43–50

[40] Milne T A, Evans R J and Abatzoglou N 1998 *Biomass gasifier“Tars”*: their nature, formation, and conversion* (No NREL/TP-570-25357 ON: DE00003726) (CO (US): National Renewable Energy Laboratory)

[41] Chiang K Y, Chien K L and Lu C.H 2012 Hydrogen energy production from disposable chopsticks by a low temperature catalytic gasification *Int J Hydrog Energy* 37(20) pp 15672–15680

**Acknowledgments**

The authors would like to thank The Department of Mechanical Engineering, Faculty of Engineering, Prince of Songkla University (PSU) and School of Mechanical Engineering, Universiti Sains Malaysia (USM), Engineering Campus, Malaysia for the laboratory facilities; The PSU Ph.D. scholarship grant from the Graduate School; The financial support through the Thailand government research grant no. ENG 600608S; and the Research Grants for Higher Education Student 2017 through the Energy Conservation Promotion Fund, Ministry of Energy.