Thermo-catalytic decomposition of biomass tar models through microwave irradiation

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Abstract. Producer gas from biomass gasification is tormented by the demeanour of tar which causes pipe blockages, plugging, corrosion, and catalyst deactivation. Thermo-catalytic tar models decomposition via microwave irradiation has been shown to be effective method in reducing tar from producer gas. This study, toluene and naphthalene were used as tar models with N2 as the carrier gas followed by the use of spurious producer gas. Thermal and catalytic decomposition of tar models with over a wide temperature range from 850 °C to 1,200 °C and 650 °C to 900 °C, respectively, at residence time of 0.24 - 0.5 s. In term of catalytic treatment, Ni/Mg/Al2O3 which the improved catalyst was used to remove both of tar models too. The results showed that the high tar removal efficiency both of thermal and catalytic cracking method. In addition, toluene was much easier to be reduced than naphthalene.

1. Introduction

Biomass is produced from both plant and animals, that usually calls clean energy due to it can be converted into the energy which low greenhouse gas emitted. For the gaseous fuel, biomass gasification is converted fossil or non-fossil fuels (solid, liquid, or gaseous) into useful gases. That process has taken biomass into gasifier which is controlled oxygen limited. So, the producer gas can be used as renewable fuel for electricity by steam engine, internal combustion engines for power generation and can be used as raw materials in industry [1].

The producer gas must be cleaned from dust contamination of inorganic substances including nitrogen compounds (NH3 and HCN) and sulfur compounds (H2S), ash and tar contain contamination before using in all applications as reported by Milne et al. [2]. Although, biomass gasification is largely accepted but the contaminants are released with the flue gas, especially biomass tar that is the more problem for biomass gasification because it is a mixture of hydrocarbon complex. That property
is a thick, black, highly viscous liquid which can condenses in the low temperature zones in the gasifier. So, tar is highly displeasing due to it can create many problems and it can be impacted to products gas as well [3] [4]. Usually, in biomass gasification system, the tar contamination in syngas is approximately 1, 10 and 100 g/m$^3$ which in downdraft, updraft and fluidized bed gasifiers respectively [2].

Generally, there are two types of tar removal method: 1) primary method which tar is removed in the gasifier and 2) secondary method which tar is removed outside the gasifier [4]. Although the primary methods can reduce the tar contamination in syngas but that cannot complete to removal tar without applying secondary measures [5]. The secondary methods can be divided in three ways: physical or mechanical method, catalytic cracking and thermal cracking, particularly thermo-catalytic decomposition which is thermal and/or catalytic cracking. That treatment is most sufficient for removal of tar and also more desirable due to tar transformation into useful gases such as H$_2$, CO or HCN gases which can be improved the producer gas energy content as mentioned by Anis and Zainal [6]. Previous researches have reported that thermal cracking is high tar decomposition efficiency with using the temperature of 1,200 °C and residence time shorter than 10 s. That also agrees with Zhang et al [7] who have mentioned about the toluene which is one of tar composition was hardly to decompose and should be up the temperature to 1,200 °C for removing. Only some researches were related for using the temperature at higher than 1,100 °C [7] [8] which provide high efficiency of tar removal. In term of catalytic cracking, many literatures showed that the catalytic removal of tar use several catalysts. Basically, there are catalysts of nickel based, non-nickel metal, alkali metal, basic, acid, and activated carbon that are the six groups of catalysts classified [3]. The most broadly used catalysts for cracking are nickel-based, acid and basic catalysts i.e. dolomite, olivine, zeolite and silica–alumina [6]. Some researcher were reported that zeolite catalyst has shown good catalytic activity but the main disadvantage is rapid deactivation due to coke formation [9][10]. Other case, nickel alumina (Ni/Al$_2$O$_3$) catalyst also showed the highest efficiency and activity for removing of tar [11] but it is unstable and lastly deactivate [12].

Anyhow, there is more usefulness of these catalysts as above-mentioned but the main disadvantages with these catalysts are faster deactivation and carbon deposit due to coke formation. So, many researched have been reported that nickel and/or, magnesium which load over catalysts have been good performed to catalytic activity and stability on tar cracking without carbon deposition and coke formation [9][13][14]. By the way, the thermo-catalytic decomposition of tar method is more effective, but this system must be required high energy demand which about 700-1,200 °C because of its treatment suggested at mechanism of conventional heating by using an external high electrical source where heat transfer arises from the surface into the material core as maintained by Salema and Ani [15]. Consequently, the heating for tar treatment is higher cost and uneconomical. While, there has been reported the microwave irradiation application can furnish intensive, rapid and localized heating for the materials. Besides, the microwave convenient for thermo-catalytic decomposition of tar system due to its application can be provide the high temperature range, ease to heating control and the reducibility of expenses on energy consumption [15].

In this article, the characteristics of thermo-catalytic tar models decomposition with aid of a microwave irradiation application were examined. Besides, in order that the effectiveness of tar removal during thermo-catalytic treatment, the improved catalysts which is Ni/Mg/Al$_2$O$_3$ with various temperatures condition was also tested by using toluene and naphthalene as biomass tar models.

2. Methods

2.1 Material

The improved catalyst of Al$_2$O$_3$ which is nickel and magnesium impregnation over catalysts was used to decompose tar model compounds in this study. In term of tar models, toluene and naphthalene were used as the tar model compounds which are good tar representative in the producer gas by biomass gasification [13]. Toluene (C$_7$H$_8$) is a light aromatic hydrocarbon (LAH) with single ring compound which a class 3 of tar. As, naphthalene (C$_{10}$H$_8$) is a light poly-aromatic hydrocarbon (LPAH) with two rings compound which a class 4 of tar. Both of tar models (toluene and naphthalene) usually are occurred in downdraft and fluidized beds gasifiers [2]. Nitrogen gas was used as a carrier.
gas for carrying the evaporate tar models to the reactor thought insulated pipes system. In addition, SiC (F10) also was used as absorber materials that good irradiation material for absorption and converting the microwave energy into heat [16]

2.2 Catalyst Preparation

The catalyst in this study is a commercial of Al₂O₃. Catalyst was prepared by wetness impregnation and drying method with these steps: a) removing of the moisture within the catalyst by preheating the Al₂O₃ in an oven at 120 °C overnight. b) to immerse the dry Al₂O₃ with solution of magnesium nitrate at the room temperature for 24 h C) to dry the Mg/Al₂O₃ in an oven at 80 °C for 2 h and then it was calcined at500 °C for 3 h followed by impregnation with nickel nitrate with the same above method [17].

2.3 Experimental system

A schematic diagram of the experimental system is shown in Figure 1. The system features of a tar generator, tar removal system, tar collector and measuring systems. The fixed conditions consist of a microwave (MW) powers at 0.7 kW, particle sizes of SiC or absorber material of F10 and 12 cm of bed height. N₂ gas has used as a carrier gas for carrying the evaporate tar models to the reactor thought all pipes system. Whereas, asbestos rope was used to insulate all tanks and pipes which can keep the temperature over 200 °C and can maintain the tar vapour condensation.

2.4 Thermo-catalytic decomposition of tar model compounds

This study was focused on tar removal system through thermal and catalytic cracking process. The nitrogen gas was passed through the system from tar generator into the tar removal (microwave reactor) and controlled by valves and flow meters. In term of thermal decomposition of tar, the initial condition of concentration of tar models were fixed at 100 g/m³. While, the residence time through the microwave reactor was fixed at 0.5 s. The range of temperature for toluene and naphthalene removing in this study were operated during 850 - 1,050 °C and 900 - 1,200 °C, respectively followed by Evans and Milne [18]. In term of catalytic decomposition of tar, the 3 layers of bed which are SiC, SiC+Ni/Mg/Al₂O₃ and SiC, that were prepared within the reactor. In each experimental was set 3 g of Ni/Mg/Al₂O₃ which mixed together with 25 g of silicon carbide for preparing 3 cm of bed height. The initial concentration of tar models were fixed at 50 g/Nm³ and residence time also was fixed at 0.24 s.
The reactor temperature for toluene and naphthalene removing were various tested in the range of 700–900 °C [6].

2.5 Sampling and Analysis

2.5.1 Tar Sampling Train

Before and after pass into the microwave reactor, the gas was ran through into a tar sampling train or tar collector that includes 6 bottles with 100 mL capacity each. To content and absorb the tar, 5 bottles were filled with 50 ml of isopropanol solution and the last bottle was empty. First 2 bottles were set at room temperature condition and the next 4 bottles were kept in an ice bath with salt mixture to maintain the temperature about -22 °C which can condense the tar compounds in class 3 and 4 as reported by Bergman et al. [19]

2.5.2 Rotary Evaporator

The condensed tar models before and after removal that was detected the tar collector with isopropanol solution. Then its solution was filtered through a pre-weighed qualitative filter paper for dividing the solution and solid particle (soot). The filtered solution (isopropanol) was evaporated by BUCHI rotary evaporator to find out the gravimetric of tar. The tar models removal efficiency was calculated from Eq. (1):

\[
\text{Tar models removal Efficiency (\%)} = \left( \frac{\text{Tar mass in} - \text{Tar mass out}}{\text{Tar mass in}} \right) \times 100
\]

2.5.3 GC-TCD

The dry clean gas after the tar sampling train can be directly collated with gas sampling bag and then analysed by a gas chromatography (GC–TCD) to determine the amount of H\(_2\) and CH\(_4\).

2.5.4 TGA

The catalyst after used that was then to find the coke deposited yield on catalyst by using a thermogravimetric analyzer (TGA).

3. Results and Discussions

3.1 Thermal decomposition of tar models

In this study, the residence time was run constant at 0.5 s, following to a gas flow rate of 5 LPM. As reported by Han and Kim [20] that was achieved sufficiently high tar removal efficiency at high temperature and residence time of 0.5 s is necessary. In case of toluene decomposition, at several reaction temperatures of 850-1050 °C within the microwave reactor has tested by thermal cracking as shown in Figure 2. At temperature of 850 °C which is the minimum test temperature, the results showed that the grew steadily efficiency of toluene removal at about 9%, at temperature reaction of 1,000 °C, the activity of toluene conversion showed that Increased dramatically conversion activity which was reached at 78% of toluene conversion. As the graph, at maximum temperature reaction of 1,050 °C that graph was reached a peak of 88 % of toluene removal efficiency. Other products, soot was found at 24% of yield product and the gases also showed increase while the temperature increased. In case thermal decomposition of naphthalene, the result was shown as in Figure 2. The naphthalene removal efficiency was rose steadily in duration of temperature 900 – 1,050 °C, at temperature of 1,100 °C that removal was climbed dramatically and the highest naphthalene removal is about 88 %. In order that, both of tar models removal as conformed by the previous studies by Anis et al [6] and Aris et al [21] which that removal efficiency increases with temperature of reaction in reactor increase. Soot and H\(_2\) were appeared as the product by thermal decomposition of naphthalene and toluene due to those main reactions at thermal decomposition of tar models (C\(_x\)H\(_y\)) were produced those products.
3.2 Catalytic decomposition of tar models

The catalytic decomposition of tar models which both toluene and naphthalene by upgraded Al₂O₃ as a catalyst was tested at several temperatures as shown in Figure 3. In term of this study, the temperature of toluene and naphthalene removal were operated at 650-850 °C (toluene) and 700-900 °C (naphthalene) as to evade the thermal treatment effect which mentioned by Anis et al [6]. The graph show that toluene and naphthalene removal using Al₂O₃ as catalyst increase significantly where the temperature reach at 750 °C for toluene and 850 °C for naphthalene. The highest removal of both toluene and naphthalene are about 91 %, 87% respectively due to low coke deposit on catalyst as shown from the graph. In addition, coke product was gone down moderately and CH₄ appeared as the main product of this method decomposition.

![Figure 2. The removal efficiency and products yields while the thermal decomposition of biomass tar models : (a) toluene (b) naphthalene](image1)

![Figure 3. The removal efficiency and products yields while the catalytic decomposition of biomass tar models by using Ni/Mg/Al₂O₃: (a) toluene (b) naphthalene](image2)
4. Conclusions

Biomass gasification system is widely used in commercial for electrical generating and other applications. Although, it largely accepted but there has occurred several problem which is tar contaminated. That tar can cause the pipe blockages, plugging, corrosion, and catalyst deactivation. Thermo-catalytic tar model decomposition via microwave irradiation has been shown to be effective method in reducing tar from producer gas. This study, toluene and naphthalene were used as tar models. The system of thermal and catalytic decomposition of tar models were operated at over a wide temperature range from 850 °C to 1,200 °C and 650 °C to 900 °C, respectively, residence time at 0.24 - 0.5 s. In case of catalytic cracking, Ni/Mg/Al\textsubscript{2}O\textsubscript{3} which the improved catalyst was also used to remove both of toluene and naphthalene. The study showed the high tar removal efficiency both of thermal and catalytic cracking method with increase temperature. Moreover, the toluene was much easier to be reduced than naphthalene.

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