Catalytic Treatment of Biomass Tar Models Over Upgraded Y-Zeolite Via Microwave Irradiation

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Hafnee Lateh[1], Juntakan Taweekun[1,*], Kittinan Maliwan[1], Zainal Alimuddin Zainal Alauddin[2], Sukritthira Rattanawilai[3]

[1] Department of Mechanical Engineering, Faculty of Engineering, Prince of Songkla University, 90112 Hat Yai, Songkhla, Thailand
[2] School of Mechanical Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 NibongTebal, Penang, Malaysia
[3] Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University, 90112 Hat Yai, Songkhla, Thailand

ARTICLE INFO	ABSTRACT
	Biomass tar is the major problem for biomass gasification that can create many problems in the system such as blockages, catalyst deactivation, and pipe corrosion can be impact to producer gas as well. The tar removal system is necessary to assure in economic cost and effective on fuel gas utilization. In this article, the catalytic activity of the Ni/Mg/Y-Zeolite as the upgraded catalyst was investigated in the removal of tar model compounds as toluene and naphthalene via microwave irradiation. The results founded that the tar treatment system via microwave irradiation which is low energy consumption, swiftly, and efficient has been successfully improved catalytic decomposition of tar models. The temperature of 900 °C can simply to assess within 20 minutes of irradiation under MW power at 0.7 kW, gas flow rate at 10 L/min and bed height of 12 cm. Ni/Mg/Y-Zeolite shows high catalytic activity due to lower coke deposited on catalyst surface compared with the previous study.

1. Introduction

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 that can condenses in the low temperature zones in the gasifier. So, Tar is highly unpleasing due to it can create many problems and be impact to producer gas as well [1, 2]. Normally tar contents within producer gas from downdraft gasifier, updraft and fluidized bed gasifiers are about 100 g/Nm^3, 1 g/Nm^3 and 10 g/Nm^3, respectively. While tar concentration of downstream use is stringent which tar contents less than 5 mg/Nm^3 and raise to 100 mg/Nm^3 are consented for gas turbines and internal combustion engines respectively [3]. The tar removal can be classified into three general methods: physical or mechanical treatment, catalytic cracking and thermal treatment. Particularly catalytic cracking which is the

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*Corresponding author.
E-mail address: juntakan2016@gmail.com (Juntakan Taweekun)*

method typically refers to a process of converting higher hydrocarbons into lower hydrocarbons in the presence of a set of catalysts with require temperature during 450-900 °C, such that the process can be carried out at lower temperatures than thermal cracking solely which use high temperature above 1,000 °C. So, that method is very interesting and the most effective for tar removal [1]. Many literatures regarding that the tar decomposition by catalytic cracking use several catalysts, the most broadly used catalysts are nickel-based, acid and basic catalysts i.e. olivine, dolomite, zeolite and silica–alumina. Corella *et al.,* [4] mentioned that the dolomite is a very renowned catalyst for tar decomposition which is low cost and aggregation defending. Meanwhile, zeolite is a commercial catalyst of catalytic cracking and that has been verified as active tar reduction catalyst, enhances the quality of gaseous and inexpensive. By the way, very limited research has been showed about the zeolites application specifically Y-Zeolite for tar model disposal such as benzene [5], 1-methylnaphthalene [6] and naphthalene underneath steam reforming at high temperature of 750 °C [7]. While, some researcher has been proven as Y-Zeolite is better activity of catalytic compared to dolomite for removing of biomass tar model compounds as reported in Anis *et al.,* [8]. Anyway, the main disadvantages with these catalysts are the rapid deactivation and carbon deposit caused by coke formation. At the same time, many data have been reported that nickel and/or, magnesium which load over above catalysts have been shown good catalytic activity and stability on hydrocarbon or tar cracking without carbon deposition and coke formation by several researchers [7, 9, 10, 11].

In addition, catalytic cracking is more desirable because of the tar transformation into beneficial gases such as H_2, CO or Ch_4 which can improve the producer gas quality and energy content [8]. Although, tar removal by catalytic treatment is more effective, but this process generally requires high energy demand (450-900 °C) due to it 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. Furthermore, Anis *et al.,* [8] reported that other blemishes are the lack of heat transfer resistance and heat losses to surrounding that can corrode to walls of rector by virtue of continuous electrical heating. Thus, in order to be economically feasible, catalytic tar treatment system need to be inexpensive, effective and highest tar removal. For these reasons, the microwave irradiation application can furnish intensive, rapid and localized heating for the materials. The microwave technology advantage for catalytic cracking system can be concluded as following: high temperature range, rapid heating, increase on chemical reactivity, flexibility and comfort to control for heating selectively, and lower cost energy consumption [12].

In this study, the upgraded catalytic and microwave irradiation were used to solve above problems of catalytic decomposition of tar models. The upgraded Y-zeolite, various temperatures was also examined by using tar model compounds which are toluene and naphthalene. While, the appropriate optimal conditions for the proposed microwave irradiation of catalytic treatment system concern with temperature evolution inside the reactor, various parameters consisting of microwave power, absorber particles size, gas flow rate and bed height and were tested.

2. Methodology
2.1. Material

Toluene and naphthalene were used as the tar model compounds which that are good example for tar from biomass gasification [12]. Toluene (C_7H_8) is a class 3 of tar which property is light aromatic hydrocarbon (LAH) with single ring compound. When, naphthalene ($C_{10}H_8$) is a class 4 of tar also which property is a light poly-aromatic hydrocarbon (LPAH) with two rings compound. The tar of biomass gasification both downdraft and fluidized bed gasifiers regularly is classified as class 3 and 4 of tar composition [3]. Nitrogen gas was used as a carrier gas to clear the evaporated of tar model.

The upgraded catalyst of Y-Zeolite which is nickel and magnesium impregnation over catalysts was used to decompose tar model compounds in this study.

2.2. Catalyst Preparation

The catalyst preparation for the impregnation and drying method includes the following steps: (1) The Y-Zeolite preheating in an oven at 120 °C for 12 hours to eliminate the moisture within the catalyst. (2) the dry Y-Zeolite immersion as supports in a magnesium nitrate solution at ambient temperature for impregnation about 24 hr. (3) Mg/Y-Zeolite is dried in an oven at a constant temperature at 80 °C for 2 hours and then it is calcined at 500 °C for 3hour, followed by impregnation with nickel nitrate with the same above method [13].

2.3. Experimental Apparatus and Procedures

The experimental apparatus features of a modified inside microwave oven, tar generator, mixing chamber, tar sampling train or tar collector, and measuring systems are presented in Figure 1. The thermal effect of various microwave (MW) powers (0.135–0.7 kW), N_2 gas flow rates (5–15 L/min), particle sizes of SiC or absorber material (F10 and F14) and bed heights (8–12 cm) on temperature profile within the reactor were examined. The N_2 gas was passed through the system from below of the microwave reactor and controlled using valves and flow meters. For catalytic treatment, the 3 layers: SiC, SiC+Ni/Mg/Y-Zeolite and SiC, of bed were prepared inside the reactor. In each experimental run 3 g of Ni/Mg/Y-Zeolite which mixed with 25 g of absorber material for preparing the bed height of 3 cm. The tar model initial concentration was fixed at 50 g/Nm3 and residence time also was fixed at 0.24 s [8]. The reactor temperature for toluene/naphthalene cracking was conducted and varied in the range of 450–900 °C [14]. Asbestos rope was used for insulating all tanks and pipes to keep up vapor temperature over 200 °C and toprotect vapor of tar condensation. The gas was passes through into a tar sampling train or tar collector which consists of 6 bottles which 100 mL capacity each. For before and after leaving the microwave reactor, first 2 bottles were placed at room temperature condition filled with 50 ml isopropanol solvent for tar condensation and absorption. The next 4 bottles (3 bottles were filled with 50 ml isopropanol, the last bottle was empty) were kept in an ice and saltmixture for maintaining the temperature about -22 °C which is able to condense the tar compounds in classes 3 and 4 as reported by Bergman *et al.*, [15].

Fig. 1. The experimental apparatus setup

The dry clean gas after the tar sampling train can be directly to collect into gas sampling bag and then analyzed by a gas chromatography (GC–TCD) to determine the amount of H_2 and CH_4, a thermo-gravimetric analyzer (TGA) was used for finding the coke deposited yield on catalyst. The filtered solvent (isopropanol) was evaporated by BUCHI rotary evaporator for determination of gravimetric of tar. The tar models removal efficiency was calculated from Eq. (1):

$$\text{Tar models Removal Efficiency (\%)} = \frac{(Tar\ mass\ in - Tar\ mass\ out)}{Tar\ mass\ in} \times 100 \qquad (1)$$

3. Results and Discussion

3.1. Microwave Tar Removal Reactor Characterization

3.1.1. Effect of microwave power

The temperature profiles inside the microwave reactor during 20 minutes with various microwave power levels are shown in Figure 2a. Other parameters were fixed constant such as SiC (absorber material) size of F10, bed height at 12 cm and gas flow rate at 10 L/min. The graph presents that the reactor temperature increased with the microwave power increase. The graph also shows the maximum temperatures were 287 °C and 746 °C to achieve at the microwave powers of 0.135 kW and 0.44 kW, respectively which were not sufficient for tar removal by catalytic cracking. Whereas higher microwave powers at 0.59 kW and 0.7 kW, the temperatures reached at 985 °C and 1,176 °C, respectively at 20 minutes of irradiation. For 0.7 kW of microwave power was selected due to its temperature achieved at 900 °C in short time.

3.1.2. Effect of absorber particles size

The SiC particles as absorber material was determined to study the effect of absorber particle size on the microwave thermal heating. Three sizes of SiC as absorber material such as F10, F12 and F14 were tested at constant microwave power at 0.7 kW, bed height at 12 cm and gas flow rate at 10 L/min. Figure 2b shows that F14 which smaller SiC particle size was achieved at higher temperature in reactor and heating rate. Although F14 SiC achieved at higher temperature but it will give high pressure drop within reactor because of the small SiC granulesand lower porosity formed followed Wu *et al*., [16] was mentioned that at constant velocity or flow rate condition, the pressure drop in reactor will increase with lower porosity of any porous medium. Thus, F10 was selected due to its low pressure drop.

3.1.3. Effect of gas flow rate

The purified nitrogen (N_2) gas flow rate was varied at 5 - 15 L/min, to study its effect on thermal heating in the microwave reactor system under constant variables such as microwave power at 0.7 kW, bed height at 12 cm, and F10 of absorber particle size. The result is shown in Figure 2c. That was noticed that the gas flow rate at 10 L/min is the highest rate of heating in reactor compared with the other gas flow rates. For 5 and 10 L/min of gas flow rate as shown in Figure 2c also, the temperature in reactor increased in the first 5 minutes of microwave irradiation. After that, the temperature inside the reactor increased slowly due to the rate of heat convection to heat up all the particles of SiC as absorber material was lower.

3.1.4. Effect of bed height

The constant variables: 0.7 kW of MW power, gas flow rate at 10 L/min and F 10 of SiC particle size were tested with difference two bed heights at 8 and 12 cm. As showed in Figure 2d, it can be seen that the temperature inside reactor increased directly variation with the bed height increase. That is because of the higher of bed height has higher absorption on microwave power and lead to higher reactor temperature.
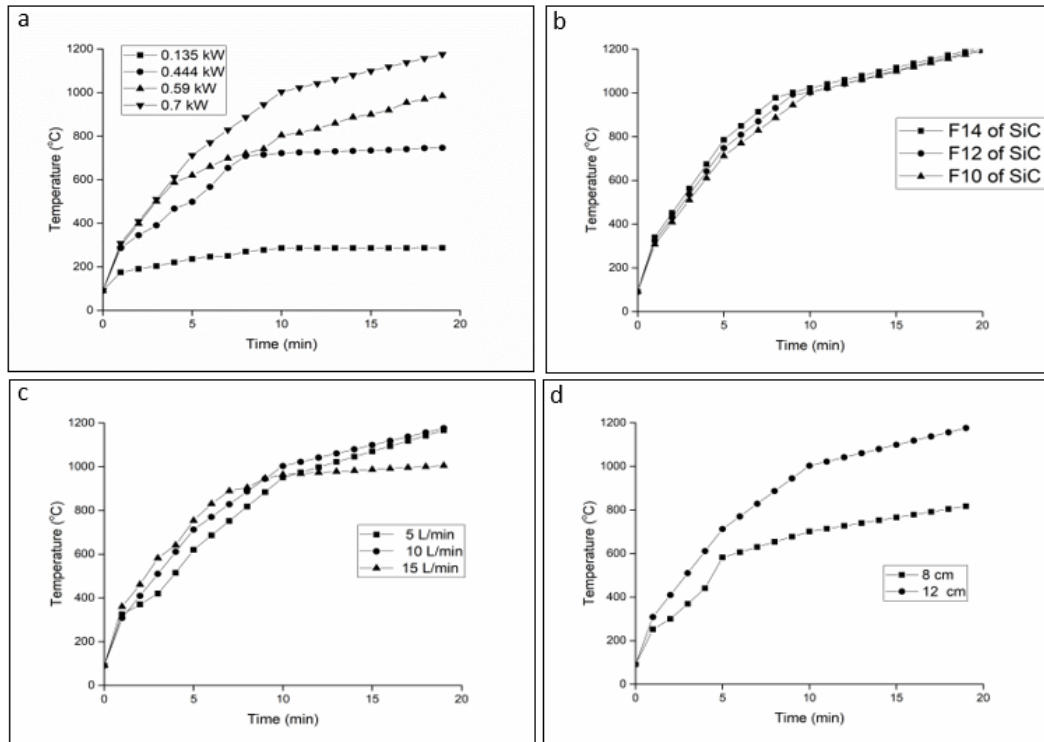

Fig. 2. Temperature profiles with various: a) effect of MW power, b) effect of absorber particle size, c) effect of gas flow rate and d) effect of bed height

3.2. Catalytic Treatments of Tar Models

The tar models, toluene and naphthalene removal testing Ni/Mg/Y-Zeolite as a catalyst which various investigated temperatures are shown in Figure 3. The graph also shows that toluene and naphthalene removal increase significantly where the temperature achieve at 550 °C, 650 °C for toluene and naphthalene respectively. Under the same temperature reaction condition at temperature range of 450 – 700 °C, toluene is easier to disposal than naphthalene that agrees with the previous studies by Buchireddy *et al.,* [7]. The highest removal efficiency of tar models was 90% for toluene and 86% for naphthalene at temperature of 700 °C. Coke deposited on the Ni/Mg/Y-Zeolite surface gradually increased with the increase of temperature reaction both naphthalene and toluene removal.

The results in Figure 4 show that the models removal tar removal in this study by using Ni/Mg/Y-Zeolite were higher removal efficiency than using Y-Zeolite from the study of Anis *et al.,* [8]. Both toluene and naphthalene removal that because of lower coke deposited on catalysts surface that correspond with the study by Fakeeha *et al.,* [17] and Wang *et al.,* [9] which high activity of catalyst assign to lower coke formation.
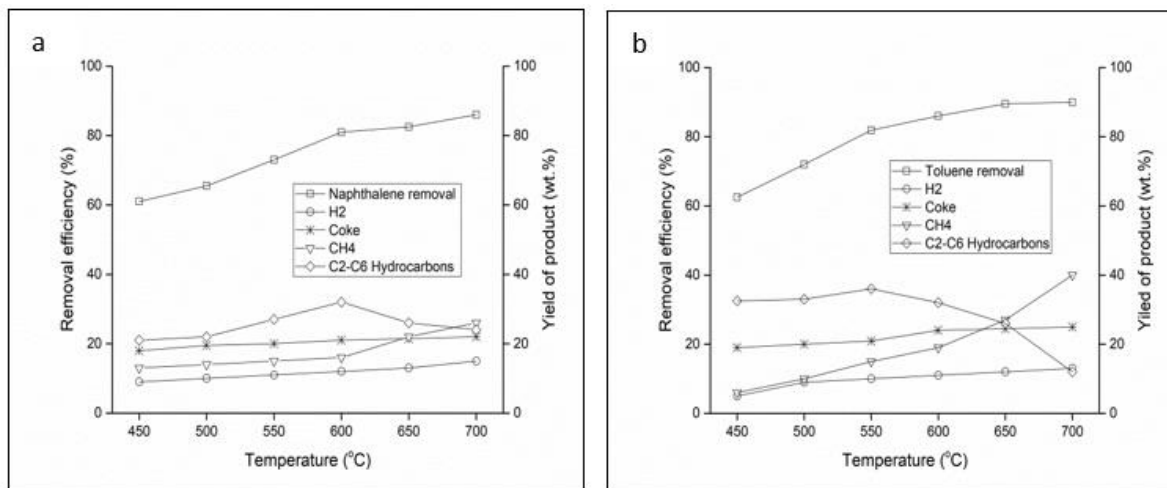
Fig. 3. Removal efficiency and products yields during catalytic cracking of tar models by using Ni/Mg/Y-Zeolite: (a) toluene (b) naphthalene
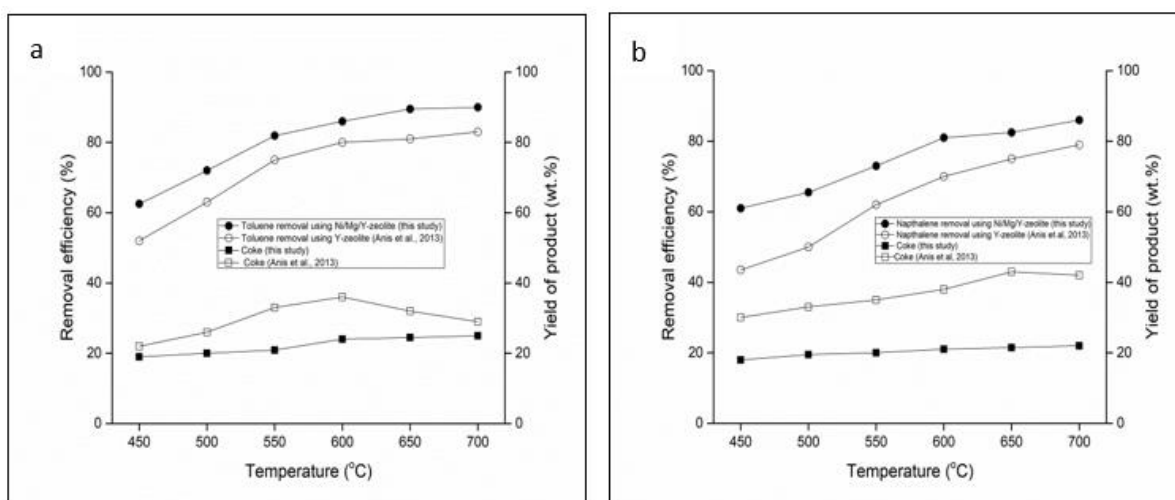

Fig. 4. The comparison of tar removal efficiency and products yields by using Ni/Mg/Y-Zeolite and Y-Zeolite: (a) toluene and (b) naphthalene

4. Conclusions

The tar models removal system via microwave irradiation which is less energy consumption, rapid heating and effective operation has been successfully improved with catalytic decomposition of tar models. The temperature within reactor at 900 °C can simply be achieved within 20 minutes of irradiation under MW power at 0.7 kW, purified N_2 gas flow rate at 10 L/min bed height at 12 cm and F 10 of SiC particle size. Ni/Mg/Y-Zeolite in this study as upgraded catalyst shows better catalytic activity due to lower coke deposited on catalyst surface compared to Y-zeolite.

References

[1]   Anis, Samsudin, and Z. A. Zainal. "Tar reduction in biomass producer gas via mechanical, catalytic and thermal methods: A review." *Renewable and Sustainable Energy Reviews* 15, no. 5 (2011): 2355-2377.

[2]   Basu, P. "Torrefaction." Biomass gasification, pyrolysis and torrefaction: Practical design and theory (2013): 87-145.

[3]   Milne, Thomas A., Robert J. Evans, and N. Abatzaglou. Biomass gasifier''Tars'': their nature, formation, and conversion. No. NREL/TP-570-25357; ON: DE00003726. National Renewable Energy Laboratory, Golden, CO (US), 1998.

[4]   Caballero, Miguel A., Jose Corella, María-Pilar Aznar, and Javier Gil. "Biomass gasification with air in fluidized bed. Hot gas cleanup with selected commercial and full-size nickel-based catalysts." *Industrial & Engineering Chemistry Research* 39, no. 5 (2000): 1143-1154.

[5]   Radwan, Aly Moustafa, Takashi Kyotani, and Akira Tomita. "Characterization of coke deposited from cracking of benzene over USY zeolite catalyst." *Applied Catalysis A: General* 192, no. 1 (2000): 43-50.

[6]   Dou, Binlin, Jinsheng Gao, Xingzhong Sha, and Seung Wook Baek. "Catalytic cracking of tar component from high-temperature fuel gas." *Applied Thermal Engineering* 23, no. 17 (2003): 2229-2239.

[7]   Buchireddy, Prashanth Reddy, R. Mark Bricka, Jose Rodriguez, and William Holmes. "Biomass gasification: catalytic removal of tars over zeolites and nickel supported zeolites." *Energy & Fuels* 24, no. 4 (2010): 2707-2715.

[8]   Anis, Samsudin, Z. A. Zainal, and M. Z. A. Bakar. "Thermocatalytic treatment of biomass tar model compounds via radio frequency." *Bioresource technology* 136 (2013): 117-125.

[9]   Wang, Tiejun, Jie Chang, Xiaoqin Cui, Qi Zhang, and Yan Fu. "Reforming of raw fuel gas from biomass gasification to syngas over highly stable nickel–magnesium solid solution catalysts." *Fuel Processing Technology* 87, no. 5 (2006): 421-428.

[10] Srinakruang, Jumluck, Kazuhiro Sato, Tharapong Vitidsant, and Kaoru Fujimoto. "Highly efficient sulfur and coking resistance catalysts for tar gasification with steam." *Fuel* 85, no. 17-18 (2006): 2419-2426.

[11] Wang, Chenguang, Tiejun Wang, Longlong Ma, Yan Gao, and Chuangzhi Wu. "Steam reforming of biomass raw fuel gas over NiO–MgO solid solution cordierite monolith catalyst." *Energy conversion and management* 51, no. 3 (2010): 446-451.

[12] El-Rub, Ziad Abu. "Biomass char as an in-situ catalyst for tar removal in gasification systems." (2008).

[13] Liu, Xue, Johannes G. Khinast, and Benjamin J. Glasser. "Drying of Ni/Alumina catalysts: control of the metal distribution using surfactants and the melt infiltration method." *Industrial & Engineering Chemistry Research* 53, no. 14 (2014): 5792-5800.

[14] Gates, B. C. 1992. Catalytic chemistry. Wiley & Sons, Inc., Singapore.

[15] Bergman, Patrick CA, Sander VB van Paasen, and Harold Boerrigter. "The novel "OLGA" technology for complete tar removal from biomass producer gas." In Pyrolysis and gasification of biomass and waste, expert meeting, Strasbourg, France, vol. 30. 2002.

[16] Wu, C., Q. Huang, M. Sui, Y. Yan, and F. Wang. "Hydrogen production via catalytic steam reforming of fast pyrolysis bio-oil in a two-stage fixed bed reactor system." *Fuel Processing Technology* 89, no. 12 (2008): 1306-1316.

[17] Fakeeha, Anis H., Ahmed S. Al-Fatesh, and Ahmed E. Abasaeed. "Stabilities of zeolite-supported Ni catalysts for dry reforming of methane." *Chinese Journal of Catalysis* 34, no. 4 (2013): 764-768.