

The Effect of Mg Loading Over Ni/Al₂O₃ on Catalytic Cracking of Tar Model Compounds Via Heat Transfer of Microwave Irradiation

Hafnee Lateh¹, Juntakan Taweekun^{1,*}, Kittinan Maliwan¹, Zainal Alimuddin Zainal Alauddin², Sukritthira Rattanawilai³

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 Nibong Tebal, Penang, Malaysia

³ Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University, 90112 Hat Yai, Songkhla, Thailand

ARTICLE INFO

Article history:

Received 7 July 2021

Received in revised form 15 October 2021

Accepted 20 October 2021

Available online 8 November 2021

Keywords:

Tar model compounds; Catalytic cracking; Heat transfer; Microwave irradiation

ABSTRACT

The tar contamination along with the biomass producer gas needs to be removed for avoiding the tar problems to all systems of biomass gasification. In this paper, toluene and naphthalene were used as tar model compounds along with nitrogen gas as carrier gas. The conditions of catalytic cracking of tar models were fixed at temperature of 800 °C, residence time of 0.24 s, and gas flow rate of 3.8 LPM. The Ni/Mg/ Al₂O₃ catalyst has been good displayed on efficiency rate of tar removal through heat transfer of microwave irradiation with almost stable of differentiation rate. The results also found that the slight deactivation on the modified catalyst caused by the magnesium addition into catalyst performed as promoter for reduction of carbon deposit on catalyst surface. In order that, naphthalene was harder to destruct than toluene.

1. Introduction

Nowadays, the energy demand is a very important and necessary not only in the production system but also in the transportation and other activities. The energy consumption around the world is focused on commercial energy, such as oil, natural gas or coal. That energy, in addition to creating a very high amount of pollution, it has been used up causing the finding of new energy sources to replace energy from oil. Biomass energy is considered as an alternative energy that is interesting as a renewable energy source and high potential. Biomass is converted into useful gases that usually called biomass gasification process. That method is taken biomass to gasifier with controlling oxygen and produced the fuel gas or producer gas. Its gas is mainly consisted of hydrogen, carbon monoxide, carbon dioxide, methane and also by products such as sulfur compounds (H₂S), tar and particles. Among of all by products, tar content is the most problem both the system and the producer gas. The problems of tar content have widely reported in several literatures [1-6]. Thus, the raw producer gas must be cleaned to avoid the tar problems before utilization of producer gas [7,8]. The purified

* Corresponding author.

E-mail address: jantakan.t@psu.ac.th

<https://doi.org/10.37934/arfmts.88.3.110116>

producer gas (low contaminant) will be used as fuel for internal combustion engines to produce electricity and can be used as raw materials in industry [9].

There are several methods for removal of tar such as mechanical treatment, thermal treatment and catalytic cracking [1,7,10-13]. Among of these methods, catalytic cracking is extensively suggested as compared with other methods due to its ability to remove tar, to increase the gasification process efficiency and its swift the rate of reaction [6,14,15]. These catalysts consist of nickel based, non-nickel metal, alkali metal, basic, acid, and activated carbon [1]. All of catalysts, that have been mentioned by several studies previously in term of their advantages and some weaknesses on tar removal. It has suggested Ni-based catalysts have been extensively used and supported by alumina (Al_2O_3) as metal oxides, or dolomite, olivine as natural materials [16]. Sutton *et al.*, [17] were reported that Ni/ Al_2O_3 catalysts have provided the high efficiency of tar removal and high activity of catalysts. The tar conversion, Al_2O_3 was shown good catalytic cracking of tar compared with dolomite, activated alumina catalyst, silica-alumina catalyst and silicon carbide, respectively [18]. Besides, it has founded that the main problem of Ni-based catalysts is not stable and rapid deactivated [19]. Thus, Ni-based catalysts are the best capability for tar removal although that was often unstable and deactivated through coking at high temperatures [19-22]. Recently, some research was reported that the additives of magnesium (Mg) on catalysts can improve the stability and resistance the carbon deposition [23]. In addition, the tar removal by catalytic cracking is more effective but its method requires high energy demand about 400-900 °C. Salema and Ani [24] also mentioned that its treatment usually uses an external high electrical source where heat transfer arises from the surface into the core of material but the heat transfer resistance, heat losses to surrounding and the corrosion of wall reactor are the lack of this treatment because of continuous high electrical heating.

In this work, the modified catalyst and microwave reactor were used to resolve the problems of catalytic cracking of tar models. The stabilities and catalytic activities of catalyst on tar removal were investigated.

2. Methodology

2.1 Material

The modified of alumina (Al_2O_3), which is impregnated by nickel and magnesium, was used as catalysts for removal of tar. Toluene and naphthalene, the tar models compounds, are usually used as the representative of biomass tar which contaminated with biomass producer gas and both of them also are occurred in biomass gasification on downdraft and fluidized beds gasifiers [7,25]. Nitrogen gas, carrier gas, was used to deliver the evaporated tar models to the microwave reactor through insulated pipes system. In addition, silicon carbide (SiC-F10), absorber materials, were used for absorption and conversion of microwave energy into heating source [16].

2.2 Catalyst Preparation

The catalyst, Al_2O_3 , is a commercial grade catalyst. It was prepared by wetness impregnation and drying methods. Al_2O_3 was dried in an oven at 120 °C for 12 h for removing the moisture and impurities inside the catalyst. Then, the dry Al_2O_3 was immersed with magnesium nitrate (solution- $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) at room temperature 24 h, dried at 80 °C for 2 h and calcined in a furnace at 500 °C for 3 h. The catalyst ($\text{Mg}/\text{Al}_2\text{O}_3$) was finally followed impregnation with nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) as the same above processes [26].

2.3 Experimental Equipment and Catalytic Activity Tests

The activity tests were operated in the experimental equipment that is shown in Figure 1. This apparatus was consisted of a modified microwave reactor, tar generator, tar mixing tank and tar collection. In this process, the catalytic cracking of tar model compounds was conducted using the modified catalyst (Ni/Mg/ Al₂O₃). The experimental parameters of this study are listed in Table 1. Inside the reactor, SiC was used as absorber material; three layers of bed with total length 12 cm were prepared by SiC, SiC+ catalyst and SiC, respectively. In each run of experiment, the model tar compounds were put into the tar generator with 3 g of catalyst mass. The carrier gas (nitrogen) was passed through the system from below of microwave reactor into other parts with gas flow rate of 3.8 LPM which was controlled by flow meter. The temperature for tar model compounds removal was fixed at 800 °C. To prevent tar condensation, asbestos rope was used to insulate all tanks and pipes.

Before and after departing the microwave reactor, the gas was flowed through the tar collection for condensing the tar. The tar collection system consists of six bottles which first five bottles were filled 50 ml of isopropanol and last bottle was empty. The first two bottles were put at room temperature and next four bottles were dipped into an ice box filled with ice and salt that were mixed together to keep temperature about -22 °C. Its temperature is sufficient to condense the tar compounds (class 3,4 of tar) as reported by Bergman *et al.*, [27]. The tar samples were captured in the isopropanol solution in tar collection and then were filtered through the whatman filter paper to separate soot (solid particles). The filtered solution of isopropanol (tar content) was sent into BUCHI rotary evaporator to evaporate and determine the gravimetric of tar. The tar removal efficiency was calculated as the follow equation [28]

$$\text{Tar removal efficiency (\%)} = [(\text{Tar}_{\text{mass in}} - \text{Tar}_{\text{mass out}})/(\text{Tar}_{\text{mass in}})] \times 100 \quad (1)$$

The purified gas was sent into the gas sampling bag and then investigated with GC-TCD to analyze the quantification of H₂ and CH₄. All the activity tests of catalyst cracking were analyzed every 10 min for 5 times. The thermogravimetric analyzer (TGA) was used to determine the carbon deposited on catalyst (coke).



Fig. 1. The photograph of catalytic cracking set up (1. nitrogen gas; 2. flow meter; 3. tar generator; 4. tar tank; 5. microwave reactor; 6. absorber material; 7. asbestos insulation; 8. tar collection; 9. gas bag)

Table 1

The experimental parameters for catalytic cracking of tar model compounds

Condition	Parameter	Unit
Catalyst mass	3	G
Carrier gas flow rate	3.8	LPM
Catalyst bed height	3	Cm
Initial mass concentration of model tar	50	g/Nm ³
Residence time	0.24	S
Temperature	800	°C
Microwave power	0.7	kW

3. Results and Discussion

The problem of catalyst deactivation, structural damage of the catalyst, was mainly from coke deposit or the deposition of carbon on the catalyst surface. The carbon mentioned is caused by the reaction of boudouard and from methane decomposition reactions. The deactivation of the catalyst due to carbon deposit is a very important problem for the cleaning process of biomass producer gas. Since that gas is composed of light hydrocarbons and tar. Therefore, the opportunity to generate carbon is increasing especially from thermal cracking, catalytic cracking as reported by Wang *et al.*, [25].

In this work, the tar model compounds (toluene and naphthalene) removal with Ni/Mg/Al₂O₃ as the modified catalysts, the catalysts were tested continuously for 5 times in microwave reactor. Figure 2 performs the removal efficiency and tar concentration during Ni/Mg/Al₂O₃ cracking of tar model compounds with the testing temperature at 800 °C, 0.24 s of residence time and 3.8 LPM of gas flow rate. The modified catalysts have been shown good tar removal rate efficiency in first two times of run number at 90% , 83% for removal of toluene and naphthalene respectively. Then, the rate of tar removal efficiency has slightly declined. The graphs also show the results conform with Buchireddy *et al.*, [15] and Anis *et al.*, [29] that were reported the removal of naphthalene more difficult than toluene. It can be seen that, the phenomena in efficiency of tar removal by adding with nickel and magnesium on catalyst has shown small reduction rate with trends to almost stable rate. The main reason, it may explain that the magnesium which was added to the catalyst performs as promoter for reduction of carbon deposit on catalyst surface. Thus, the modified catalyst showed excellent on tar removal and stability activity test of catalyst. The products yields during Ni/Mg/Al₂O₃ cracking of tar model compounds are showed similar trends of slightly reduction after testing for 5 times. Coke deposit on catalyst also shows small differentiation that led to the high tar removal efficiency because of lower coke deposit as mentioned by Fakeeha *et al.*, [30].

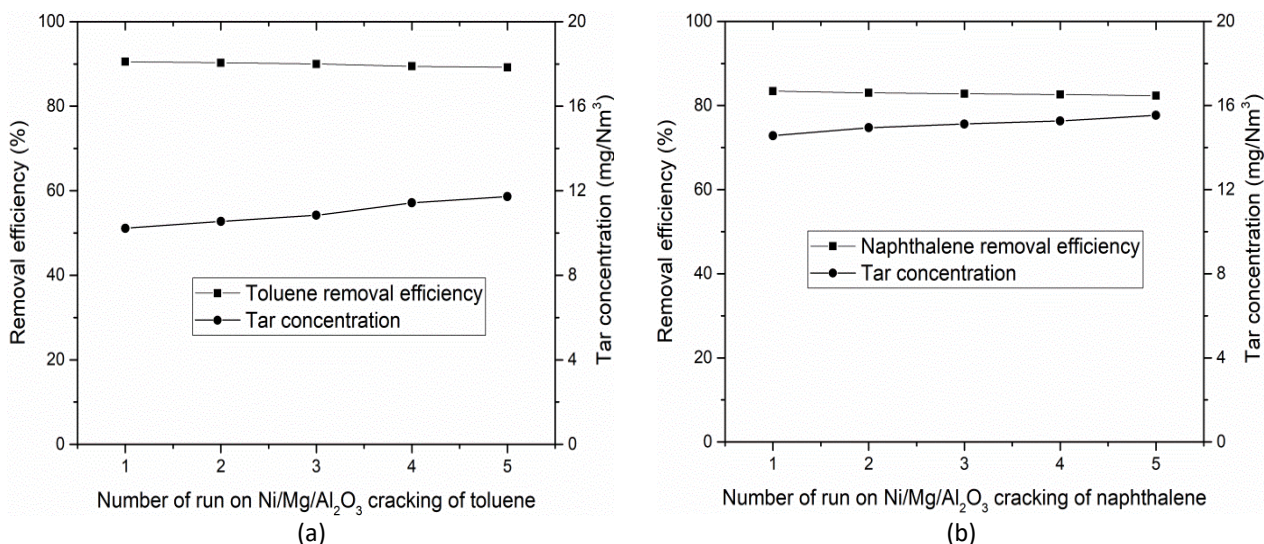


Fig. 2. Removal efficiency and tar concentration during Ni/Mg/Al₂O₃ cracking of tar model compounds: (a) toluene (b) naphthalene

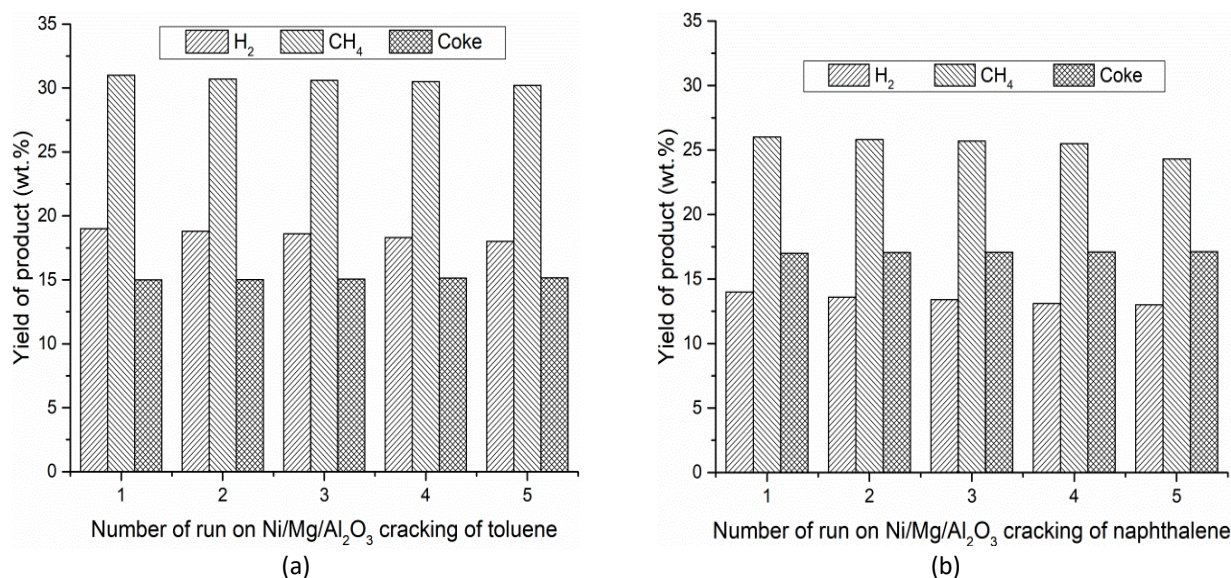


Fig. 3. Products yields during Ni/Mg/Al₂O₃ cracking of tar model compounds: (a) toluene (b) naphthalene

4. Conclusions

The main problem of catalyst deactivation is the structural damage of catalyst due to coke deposit or the deposition of carbon on the catalyst surface. The performance of Ni/Al₂O₃ with the addition of Mg on tar removal has been studied. Toluene and naphthalene were used as the representative of biomass tar. The reaction temperature of 800 °C, the residence time of 0.24 s and 3.8 LPM of gas flow rate were fixed as the conditions of this study. The Ni/Mg/ Al₂O₃ catalysts have been shown good on tar removal efficiency with almost stable differentiation rate. This paper found that the addition of magnesium into the catalyst has been performed as the promoter for reduction of carbon deposit on catalyst surface. Besides, the result also displays that the toluene was facile to remove than naphthalene.

Acknowledgements

The authors would like to thank the 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.

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. <https://doi.org/10.1016/j.rser.2011.02.018>
- [2] Basu, Prabir. *Biomass gasification, pyrolysis and torrefaction: practical design and theory*. Academic Press, 2018. <https://doi.org/10.1016/B978-0-12-812992-0.00007-8>
- [3] Lateh, Hafnee, Juntakan Taweekun, Kittinan Maliwan, Zainal Alimuddin Zainal Alauddin, and Sukritthira Rattanawilai. "Catalytic Treatment of Biomass Tar Models Over Upgraded Y-Zeolite Via Microwave Irradiation." *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* 54, no. 1 (2019): 37-43.
- [4] Devi, L., K. J. Ptasinski, F. J. J. G. Janssen, S. V. B. van Paasen, P. C. A. Bergman, and J. H. A. Kiel. "Catalytic decomposition of biomass tars: Use of dolomite and untreated olivine." *Renewable Energy* 30, no. 4 (2005): 565-587. <https://doi.org/10.1016/j.renene.2004.07.014>
- [5] Han, Jun, and Heejoon Kim. "The reduction and control technology of tar during biomass gasification/pyrolysis: an overview." *Renewable and Sustainable Energy Reviews* 12, no. 2 (2008): 397-416. <https://doi.org/10.1016/j.rser.2006.07.015>
- [6] Wang, Duo, Wenqiao Yuan, and Wei Ji. "Char and char-supported nickel catalysts for secondary syngas cleanup and conditioning." *Applied Energy* 88, no. 5 (2011): 1656-1663. <https://doi.org/10.1016/j.apenergy.2010.11.041>
- [7] Milne, Thomas A., Robert J. Evans, and N. Abatzaglou. "Biomass gasifier" Tars": their nature, formation, and conversion." *National Renewable Energy Laboratory, United States*, 1998. <https://doi.org/10.2172/3726>
- [8] Abu El-Rub, Ziad, Eduard A. Bramer, and Gerrit Brem. "Review of catalysts for tar elimination in biomass gasification processes." *Industrial & Engineering Chemistry Research* 43, no. 22 (2004): 6911-6919. <https://doi.org/10.1021/ie0498403>
- [9] Hasler, P. H., and Th Nussbaumer. "Gas cleaning for IC engine applications from fixed bed biomass gasification." *Biomass and Bioenergy* 16, no. 6 (1999): 385-395. [https://doi.org/10.1016/S0961-9534\(99\)00018-5](https://doi.org/10.1016/S0961-9534(99)00018-5)
- [10] Jansen, J. la C., Karin Jönsson, and Marinette Hagman. "Biological detoxification of tar-water." *Water Science and Technology* 46, no. 4-5 (2002): 59-65. <https://doi.org/10.2166/wst.2002.0551>
- [11] Warsita, Aris, K. A. Al-Attab, and Z. A. Zainal. "Effect of water addition in a microwave assisted thermal cracking of biomass tar models." *Applied Thermal Engineering* 113 (2017): 722-730. <https://doi.org/10.1016/j.applthermaleng.2016.11.076>
- [12] Fagbemi, L., L. Khezami, and R. Capart. "Pyrolysis products from different biomasses: application to the thermal cracking of tar." *Applied Energy* 69, no. 4 (2001): 293-306. [https://doi.org/10.1016/S0306-2619\(01\)00013-7](https://doi.org/10.1016/S0306-2619(01)00013-7)
- [13] Kastner, James R., Sudhagar Mani, and Ankita Juneja. "Catalytic decomposition of tar using iron supported biochar." *Fuel Processing Technology* 130 (2015): 31-37. <https://doi.org/10.1016/j.fuproc.2014.09.038>
- [14] Shen, Yafei, and Kunio Yoshikawa. "Recent progresses in catalytic tar elimination during biomass gasification or pyrolysis-A review." *Renewable and Sustainable Energy Reviews* 21 (2013): 371-392. <https://doi.org/10.1016/j.rser.2012.12.062>
- [15] 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. <https://doi.org/10.1021/ef901529d>
- [16] Pompeo, Francisco, Nora N. Nichio, Osmar A. Ferretti, and Daniel Resasco. "Study of Ni catalysts on different supports to obtain synthesis gas." *International Journal of Hydrogen Energy* 30, no. 13-14 (2005): 1399-1405. <https://doi.org/10.1016/j.ijhydene.2004.10.004>
- [17] Sutton, David, Brian Kelleher, Aidan Doyle, and J. R. H. Ross. "Investigation of nickel supported catalysts for the upgrading of brown peat derived gasification products." *Bioresource Technology* 80, no. 2 (2001): 111-116. [https://doi.org/10.1016/S0960-8524\(01\)00086-4](https://doi.org/10.1016/S0960-8524(01)00086-4)
- [18] Simell, Pekka A., and JB-son Bredenberg. "Catalytic purification of tarry fuel gas." *Fuel* 69, no. 10 (1990): 1219-1225. [https://doi.org/10.1016/0016-2361\(90\)90280-4](https://doi.org/10.1016/0016-2361(90)90280-4)

- [19] 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. <https://doi.org/10.1016/j.fuel.2006.04.026>
- [20] Liu, Haibo, Tianhu Chen, Xianlong Zhang, Jinhu Li, Dongyin Chang, and Lei Song. "Effect of additives on catalytic cracking of biomass gasification tar over a nickel-based catalyst." *Chinese Journal of Catalysis* 31, no. 4 (2010): 409-414. [https://doi.org/10.1016/S1872-2067\(09\)60061-9](https://doi.org/10.1016/S1872-2067(09)60061-9)
- [21] Michel, Rudy, Agata Łamacz, Andrzej Krzton, Gérald Djéga-Mariadassou, Philippe Burg, Claire Courson, and Rene Gruber. "Steam reforming of α -methylnaphthalene as a model tar compound over olivine and olivine supported nickel." *Fuel* 109 (2013): 653-660. <https://doi.org/10.1016/j.fuel.2013.03.017>
- [22] Hu, Mian, Mahmood Laghari, Baihui Cui, Bo Xiao, Beiping Zhang, and Dabin Guo. "Catalytic cracking of biomass tar over char supported nickel catalyst." *Energy* 145 (2018): 228-237. <https://doi.org/10.1016/j.energy.2017.12.096>
- [23] Nakamura, Kazuya, Tomohisa Miyazawa, Takuya Sakurai, Toshihiro Miyao, Shuichi Naito, Noorjahan Begum, Kimio Kunimori, and Keiichi Tomishige. "Promoting effect of MgO addition to Pt/Ni/CeO₂/Al₂O₃ in the steam gasification of biomass." *Applied Catalysis B: Environmental* 86, no. 1-2 (2009): 36-44. <https://doi.org/10.1016/j.apcatb.2008.07.016>
- [24] Salema, Arshad Adam, and Farid Nasir Ani. "Microwave induced pyrolysis of oil palm biomass." *Bioresource Technology* 102, no. 3 (2011): 3388-3395. <https://doi.org/10.1016/j.biortech.2010.09.115>
- [25] 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. <https://doi.org/10.1016/j.fuproc.2005.10.006>
- [26] 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. <https://doi.org/10.1021/ie500099c>
- [27] Bergman, P. CA, S. VB Van Paasen, and Harold Boerrigter. *The novel'OLGA'technology for complete tar removal from biomass producer gas*. CPL Press, Netherlands, 2002.
- [28] Josuinkas, F. M., C. P. B. Quitete, N. F. P. Ribeiro, and M. M. V. M. Souza. "Steam reforming of model gasification tar compounds over nickel catalysts prepared from hydrotalcite precursors." *Fuel Processing Technology* 121 (2014): 76-82. <https://doi.org/10.1016/j.fuproc.2014.01.007>
- [29] 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. <https://doi.org/10.1016/j.biortech.2013.02.049>
- [30] Fakeeha, Anis H., Ahmed S. Al-Fatesh, and Ahmed E. Abasaheed. "Stabilities of zeolite-supported Ni catalysts for dry reforming of methane." *Chinese Journal of Catalysis* 34, no. 4 (2013): 764-768. [https://doi.org/10.1016/S1872-2067\(12\)60554-3](https://doi.org/10.1016/S1872-2067(12)60554-3)