Tar Removal by Combination of Plasma with Catalyst

R. Cimerman, D. Račková, and K. Hensel

Division of Environmental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská Dolina F2, 842 48 Bratislava, Slovakia.

Abstract. Gasification of a biomass is an industrial process utilised to produce synthesis gas that can be used to generate electricity. The generated synthesis gas is however often polluted with tar and other pollutants, and thus cleaning before its further use is necessary. The objective of this paper is to investigate the potential of tar removal by non-thermal plasma generated by atmospheric pressure discharges in combination with TiO₂ catalyst in various operating conditions. Naphthalene was used as a model tar compound and its decomposition and by-products formation was analysed by means of the FTIR spectrometry. The results showed higher naphthalene removal efficiency in ambient air with the catalyst than without it (almost 80 % and 40 %, respectively, at 11 kV, 500 Hz).

Introduction

Biomass is one of the most available renewable energy sources around the world. It can be used directly in combustion processes or transformed by gasification processes into biomass derived fuel gas (mixture of CO, H₂, CH₄, etc.), also called synthesis gas or syngas. The process of gasification is defined as partial oxidation of carbonaceous feedstocks at elevated temperature to produce an energy carrier [*Devi et al.*, 2006]. The syngas has numerous industrial as well as energy production applications. It can be used in gas turbines or engines, fuel cells producing methanol, hydrogen as well as synthetic natural gas. However, the problem is that the syngas produced by the gasification is often polluted with NOx, SOx and especially tar compounds and this fact disqualifies the syngas from further utilization. Besides the environmental hazard, tar compounds have negative impact on the human health, constrain the heating value of the fuel gas, may cause operational problems due to aerosol and soot formation, and block particle filters and fuel lines. Thus, it is important to reduce or remove tar compounds from syngas as well as to investigate related processes to obtain their higher removal efficiencies at lower energy consumption.

Tar compounds are generally defined as a complex mixture of condensable hydrocarbons including singlering to multiple-ring aromatic compounds and other substituents. With respect to their structure they are classified as heterocyclic (e.g., phenols, pyridine), light aromatic (e.g., toluene, xylene), light polyaromatic (e.g., naphthalene, anthracene) and heavy polyaromatic (fluoranthene, pyrene) [*Devi et al.*, 2006].

State-of-the-art

Gas cleaning techniques

There are several techniques used to clean industrially polluted gases. Nowadays the most commercially used technique is a chemical catalysis. The role of the catalyst in the process is to lower the reaction activation energies in order to achieve desired chemical reactions. The catalyst activity leads to an increase in the chemical reactions rate responsible for decomposing of pollutant molecules by the processes of oxidation and reduction. Moreover, chemical catalysis is strongly selective, which means that the increase in the chemical reactions rate does not occur for all chemical reactions, but only for some of them. The ideal catalyst is expected to be chemically, mechanically and thermally stable. However, in real operating conditions, the catalyst lifetime is always limited because of its natural poisoning caused by exposure to a range of chemical compounds that lead to catalyst chemical deactivation. Another problem is the temperature dependence of catalytic activity because it may require high temperatures. In the case of tar catalytic removal, temperatures above 850 °C are often needed and the most used and studied catalytic materials are Ni-, dolomite- and olivine-based catalysts [*Devi et al.*, 2006].

In the last decades, polluted gas treatment by using non-thermal plasma has been extensively studied and tested for various environmental applications. Non-thermal plasma typically contains electrons with typical energies in the range of 1–25 eV that are not in thermal equilibrium with other particles [*van Durme et al.*, 2008]. Because of high-energy electrons, non-thermal plasma provides a high reactive environment. These electrons collide with other molecules present in the gas mixture, that can lead to formation of many other particles and species as well as highly reactive short-lived species, radicals (such as $\cdot O$, $\cdot OH$, O_3 , H_2O_2). Subsequent radical

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reactions with pollutant molecules in the gas mixture can lead to their decomposition [*Kim*, 2004]. Non-thermal plasma can be generated by atmospheric pressure discharges such as corona discharge, dielectric barrier discharge or spark discharge. Besides high chemical potential, non-thermal plasma techniques often possess high energy consumption as well as formation of undesired by-products limiting practical use.

To overcome disadvantages of chemical catalysis and non-thermal plasma processes, it is possible to combine these two techniques in one stand-alone system. In such a case, we talk about plasma catalysis. The combined system brings together individual benefits of the two techniques. The plasma catalysis maintains high plasma reactivity along with high catalytic selectivity that is very important for its practical use. In the plasma catalysis catalytic system, not only plasma is affected by the presence of catalyst, but also catalytic activity is affected by the presence of plasma. The catalyst causes the enhancement of local electric field that may result in a change of discharge type, or it can change the energy distribution of accelerated electrons and formation of reactive species. Vice versa, the plasma can activate surface of catalyst material by either heat radiation (known as thermal activation of catalyst) or by sufficiently high energy light radiation (known as plasma light emission triggering photocatalysis) and even the plasma can also affect the adsorption processes and thus gas residence time. As a result, we can talk about plasma catalysis system synergy and plasma catalytic processes [*van Durme et al.,* 2008].

Tar removal

Tar removal processes by non-thermal plasma have been studied in recent years by several research groups. Pemen et al. [2003] and Devi et al. [2006] operated a cylindrical corona discharge reactor in the streamer discharge mode and powered by pulse high voltage power supply was used. The effect of temperature (in range of 200–500 °C) and gas composition (various ratios of synthetic syngas mixture components, such as CO, CO₂, H₂, CH₄, H₂O, and N₂) on tar removal processes were mainly investigated. Naphthalene, toluene and phenol were chosen as model tar compounds with concentrations in range of 500–700 ppm. It was found, that in the reducing atmosphere of syngas mixture, the presence of CO_2 and H_2O played a crucial role in tar removal processes. In the presence of CO₂, tar removal is mainly governed by oxidation processes by O radicals generated by CO₂ dissociation. In the presence of H₂ the tar is removed by cracking mechanisms by H radicals, and in the presence of H₂O by a combination of both H and OH radicals formed by H₂O dissociation [Pemen et al., 2003]. In general, an admixture of H_2O and CO_2 enhances the tar removal processes, while addition of CO suppresses it by scavenging O and OH radicals. Moreover, experiments with addition of air into a gas mixture of $N_2 + CO_2 + CO$ were also studied and resulted in a slight decrease of the energy density requirements. The other works of naphthalene removal processes used dielectric barrier discharge at atmospheric pressure alone [Wu et al., 2016] or filled with a bed of glass beads with and without addition of char particles in N2 + H2 + CO2 + CO mixtures at a temperature of 350°C [Hübner et al., 2015]. Other research groups studied naphthalene decomposition by a surface dielectric barrier discharge in air-like mixture at room temperature [Abdelaziz et al., 2014] as well as by gliding arc discharge in $N_2 + H_2O$ mixture at 300°C [Liu et al., 2017]. The gliding arc was also used by Chun et al. [2012], where a pyrene was chosen as a surrogate of biomass tar compounds.

Combination of the plasma with catalysis on tar removal processes has been studied less frequently than plasma alone. However, in these works, toluene was mostly chosen as a model tar compound. For example, in Tao et al. [2013], plasma enhanced catalytic steam reforming over Ni/SiO₂ catalyst was comparatively studied with other tar removal techniques in He + H₂O mixtures at 500 °C, while in Liu et al. [2017] the effect of Ni/Al₂O₃ catalysts with different nickel loadings on plasma-catalytic gas cleaning process was evaluated in Ar + H₂O mixtures at 160 °C. To our best current knowledge, there are the only two works [Nair, 2004 and Gao et al., 2008] in which plasma-catalytic removal of the naphthalene, as a target tar compound, has been investigated. Nair investigated naphthalene removal by corona discharge, but also by a combination of corona discharge with cordierite monolith with yAl₂O₃ catalyst washcoat. He observed synergetic effect of plasma catalysis on naphthalene at a temperature of 300°C in N₂ + CO₂ + CO mixture and clearly showed that plasma catalysis is a promising method for tar removal because it can reduce energy requirements in comparison with plasma alone. Gao et al. studied the naphthalene decomposition by corona radical shower system with MnO_2 catalyst in air-like mixture at 25°C and concluded that low initial concentration of naphthalene is helpful to naphthalene decomposition. In addition, in Blanquet et al. [2017] real small pyrolysis reactor of wood pellets was used as a source of tars and their decomposition was studied in dielectric barrier discharge along with Ni/Al₂O₃ catalyst at 250°C. The results showed that the plasma-catalytic system produced less liquid, more gas and the lowest coke deposition level on the catalyst compared to systems using either catalyst or plasma alone.

The objective of this study was to investigate tar removal by non-thermal plasma generated by atmospheric pressure dielectric barrier discharge in combination with photocatalyst TiO_2 . The effects of the amplitude and frequency of the applied voltage (11 and 14 kV, 200 and 500 Hz) and the effects of carrier gas (N₂, O₂, air) on naphthalene removal efficiency and gaseous and solid by-products were investigated.



Figure 1. Experimental setup.

Experiment

The experimental setup is illustrated in Fig. 1. Non-thermal plasma was generated by dielectric barrier discharge reactors of cylindrical geometry operated in the streamer discharge mode. The reactors consisted of quartz glass tube of 1.5 cm inner diameter and 10 cm length. Tungsten wire of 0.2 mm diameter placed in the axis of the tube was used as a high voltage electrode, while an aluminium foil sheet was wrapped around outer surface of the quartz tube and served as a ground electrode. In order to evaluate and compare the plasma catalytic effect with the effect of plasma alone, one reactor was without catalyst (*plasma reactor*) and the other one with catalyst (*plasma-catalytic reactor*). The plasma-catalytic reactor was filled with 2–3 mm diameter pellets of titanium dioxide TiO_2 , one of the most common types of photocatalysts.

Naphthalene was used as a model tar compound because of its stability and difficulty of being decomposed. At ambient temperature, the naphthalene is white solid crystalline compound with very low saturated vapour pressure. To increase the naphthalene concentration in the gas, the whole experimental system was heated by electric oven and ribbon heaters and its temperature maintained at about 100 °C. Pressure tanks of oxygen, nitrogen or ambient air were used and the gas flow rate was controlled by flow meters and subsequently was led into the oven. In the oven, the gas mixture was preheated, enriched with naphthalene vapours and subsequently fed into the reactor. An initial concentration of naphthalene in the gas mixture was approximately 0.5 vol.%.

The both reactors were powered by AC high voltage power supply equipped with function generator (*GwINSTEK SFG-1013*) to vary the frequency of the applied voltage. The waveform of the applied voltage was measured by high voltage probe (*Tektronix P6015A*) and current pulses by current probe (*Pearson Electronics 2877*) connected to a digital oscilloscope (*Tektronix TDS2024*). Gas composition as well as solid by-products of naphthalene decomposition were analysed by means of the FTIR spectrometry (*Shimadzu IR-Affinity 1S*).

Results and Discussion

Figures 2 and 3 show the naphthalene removal efficiency ('NRE') and CO production in plasma (Fig. 2) and plasma-catalytic (Fig. 3) reactors as functions of the frequency and amplitude of the applied voltage. The removal efficiency is defined as a ratio $(c_{in} - c_{out})/c_{in}$ multiplied by 100%, where c_{in} and c_{out} represent input and output naphthalene concentration, respectively. Out of the main naphthalene decomposition by-products (i.e., CO, CO₂, and H₂O), the CO concentration is presented as an indicator of naphthalene decomposition. In both reactors, NRE and CO production increased with the increase in the frequency of the applied voltage. However, when the amplitude of the applied voltage increased, significant increase in the NRE was observed only for the plasma-catalytic reactor. In general, NRE was always significantly higher in plasma-catalytic reactor in contrast to plasma reactor for all applied frequencies and amplitudes of the applied voltage. These results show the plasma-catalytic synergistic effects as well as potential of tar removal by plasma catalytic processes as was also confirmed by [*Nair*, 2004].

Figure 4 shows the effect of carrier gas mixtures on NRE in both plasma and plasma-catalytic reactor. In the nitrogen gas mixture in both reactors, NRE was very poor (below 25 %) in comparison with the ambient air gas mixture. In ambient air, the highest NRE in plasma-catalytic reactor reached values of approximately 77 % and 95 % at 500 Hz, 11 kV and 14 kV, respectively. Moreover, lower yield of solid by-products was also observed for plasma-catalytic reactor in contrast to plasma reactor. Therefore, more effective and complete oxidation of naphthalene to desired by-products (i.e., CO_2 and H_2O) can be attributed to plasma-catalytic system. Our results



Figure 2. Naphthalene removal efficiency and CO production for plasma reactor (ambient air, 11 and 14 kV, 200 and 500 Hz).



Figure 3. Naphthalene removal efficiency and CO production for plasma-catalytic reactor (TiO₂ catalyst, ambient air, 11 and 14 kV, 200 and 500 Hz).



Figure 4. Naphthalene removal efficiency for plasma and plasma-catalytic reactor with TiO₂ catalyst in various carrier gas mixtures N₂, O₂ and ambient air at 11 kV, 200 and 500 Hz.

can be well compared with results of other authors. For instance, *Gao et al.* [2008] obtained NRE approximately 70 % at 14 kV, while *Nair* [2004] got NRE approximately 90 % at specific energy density 125 J/L. Others investigated naphthalene removal by non-thermal plasma only. For example, in *Hübner et al.* [2015], NRE did not exceed 35 % (at 400 J/L) and 60 % (at 220 J/L) for glass bed filling without and with char particles, respectively. Further, *Pemen et al.* [2003] achieved NRE at the level of approximately 80 % at 200 J/L, while *Wu et al.* [2016] obtained NRE almost 97 % at 85 J/L and *Liu et al.* [2017] at a level of approximately 70 % at 5 kV.

In the oxygen gas mixture, the NRE reached almost 100% in plasma reactor that confirms the dominant role of O radicals as was also reported by *Pemen et al.* [2003] and *Wu et al.* [2016]. The reason why in the oxygen NRE is higher in plasma reactor than in plasma-catalytic reactor at the same conditions can be explained by higher yield of ozone produced in plasma reactor. The ozone is great oxidizing agent and its lower production in plasma-catalytic system is attributed to higher energy dissipation in plasma-catalytic reactor. Because of the presence of catalyst, the onset voltage in plasma-catalytic reactor is smaller and therefore at the same applied voltage the discharge current as well as discharge power is much higher in plasma-catalytic system. Higher power

means higher energy dissipation resulting in higher temperature in the zone of discharge resulting in ozone decomposition.

Figures 5 and 6 show IR spectra of gas products as well as solid by-products of naphthalene decomposition in the case of plasma reactor and plasma-catalytic reactor. In both systems, the main gas products of naphthalene decomposition were CO, CO₂ and H₂O. In air and oxygen, the formic acid (HCOOH) was observed as well. The spectra show a significant difference between by-products of the plasma reactor and plasma-catalytic reactor. Higher concentration of H₂O vapours in the spectrum of plasma-catalytic system (Fig. 6) can be explained by more intensive by-products formation as well as by the desorption of water vapours pre-adsorbed on the pellets. On the other hand, in the plasma reactor besides gaseous by-products, there are also many solid by-products identified in the spectra. These solid by-products were found on the body of the gas cell and also on the IR windows. The result indicates that plasma-catalytic reactor chemistry is governed by completely other processes responsible for naphthalene decomposition in comparison to plasma reactor.

Identification of the exact solid by-products of naphthalene decomposition using FTIR spectroscopy is not trivial. We compared our spectra with the spectra of compounds found by the others [*Nair*, 2004, *Pemen et al.*, 2003, *Abdelaziz et al.*, 2013 and *Socrates*, 1994], however we have not found any match. Therefore, we excluded phthalic anhydride, naphthalenedione, naphthol, benzaldehyde, acetophenone, benzoic acid, phenylethyne or phenyl-naphthalene as potential by-products of naphthalene decomposition. Despite not being able to identify specific by-product, we identified several characteristic IR absorption bands of organic functional groups (such as C=O, C=C, C–O or O–H) in the spectra. The presence of these functional groups in IR spectra indicates the presence of lighter hydrocarbons formed as a result of naphthalene decomposition.

Conclusion

We investigated the effect of non-thermal plasma and its combination with the catalyst on tar removal. We used dielectric barrier discharge reactors of cylindrical geometry with and without TiO_2 catalytic pellets. The effects of the applied voltage and carrier gases were investigated on naphthalene removal efficiency and byproducts formation. The removal efficiency increased with the increase of the amplitude and frequency of the applied voltage. The naphthalene decomposition efficiency in air in plasma-catalytic reactor reached value of



Figure 5. IR spectrum of gas and solid by-products of naphthalene decomposition by plasma reactor in three different gas mixtures (14 kV, 500 Hz, 10 min treatment).



Figure 6. IR spectrum of gas and solid by-products of naphthalene decomposition by plasma-catalytic reactor in ambient air (11 kV, 500 Hz, 80 min treatment).

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approximately 80 %, compared with only 40% in the plasma reactor at 11 kV, 500 Hz. In the oxygen gas mixture, the naphthalene removal efficiency reached almost 100% that confirms the dominant role of O radicals. By-products of naphthalene decomposition were mostly CO, CO_2 , and H_2O , although several solid by-products were found as well. Our results proved, that combination of the non-thermal plasma with catalysis is a promising method for tar removal in contrast to the most papers focused on the only non-thermal plasma treatment of naphthalene.

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References

- Abdelaziz, A. A., T. Seto, M. Abdel-Salam and Y. Otani, Influence of nitrogen excited species on the destruction of naphthalene in nitrogen and air using surface dielectric barrier discharge, *Journal of Hazardous Materials*, vol. 246–247, p. 26–33, 2013.
- Abdelaziz, A. A., T. Seto, M. Abdel-Salam and Y. Otani, Influence of N₂/O₂ Mixtures on Decomposition of Naphthalene in Surface Dielectric Barrier Discharge Based Reactor, *Plasma Chemistry and Plasma Processing*, 34, 1371–1385, 2014.
- Blanquet, E., M. A. Nahil and P. T. Williams, Reduction of tars from real biomass gasification by a non-thermal plasmacatalytic system, in: *Book of Extended Abstracts of 23rd International Symposium on Plasma Chemistry* in Montréal, 1084–1085, 2017.
- Chun, Y. N., S. Ch. Kim and K. Yoshikawa, Destruction of Biomass Tar Using a Gliding Arc Plasma Reformer, *International Journal of Environmental Protection*, vol. 2, 12, 1–8, 2012.
- Devi, L., S. A. Nair, A. J. Pemen, K. Yan, E. J. M. van Heesch, K. J. Ptasinski and F. J. J. G. Janssen, Tar removal from biomass gasification processes, in: *Biomass and Bioenergy: New Research*, ed. by: Michael D. Brenes, 249–274, 2006.
- van Durme, J., J. Dewulf, Ch. Leys and H. van Langenhove, Combining non-thermal plasma with heterogeneous catalysis in waste gas treatment: A review, *Applied Catalysis B: Environmental*, 78, 324–333, 2008.
- Gao, X., X. Shen, Z. Wu, Z. Luo, M. Ni and K. Cen, The Mechanism of Naphthalene Decomposition in Corona Radical Shower System by DC Discharge, in: *Electrostatic Precipitation*, ed. by: Keping Yan, 713–717, 2008.
- Hübner, M., R. Brandenburg, Y. Neubauer and J Röpcke, On the Reduction of Gas-Phase Naphthalene Using Char-Particles in a Packed-Bed Atmospheric Pressure Plasma, *Contributions to Plasma Physics*, vol. 55, 10, 747–752, 2015.
- Kim, H. H., Nonthermal Plasma Processing for Air-Pollution Control: A Historical Review, Current Issues, and Future Prospects, *Plasma Processes and Polymers*, 1, 91–110, 2004.
- Liu, S. Y., D. H. Mei, M. A. Nahil, S. Gadkari, S. Gu, P. T. Williams and X. Tu, Hybrid plasma-catalytic steam reforming of toluene as a biomass tar model compound over Ni/Al₂O₃ catalyst, *Fuel Processing Technology*, 166, 269–275, 2017.
- Liu, S., D. Mei, Y. Ma and X. Tu, Plasma gas cleaning process for the removal of model tar compound from biomass gasification, poster presentation at 23rd International Symposium on Plasma Chemistry in Montréal, 2017.
- Nair, S. A., Corona plasma for tar removal, PhD thesis, Technische Universiteit Eindhoven, 2004.
- Pemen, A. J., S. A. Nair, K. Yan, E. J. M. van Heesch, K. J. Ptasinski and A. A. H. Drinkenburg, Pulsed Corona Discharges for Tar Removal from Biomass Derived Fuel Gas, *Plasmas and Polymers*, vol. 8, 3, 209–224, 2003.

Socrates, G., IR Characteristic Group Frequencies — Table and Charts, John Wiley and Sons Inc, 1994.

- Tao, K., N. Ohta, G. Liu, Y. Yoneyama, T. Wang and N. Tsubaki, Plasma enhanced catalytic reforming of biomass tar model compound to syngas, *Fuel*, 104, 53–57, 2013.
- Wu, Z., J. Wang, J. Han, S. Yao, S. Xu and P. Martin, Naphthalene Decomposition by Dielectric Barrier Discharges at Atmospheric Pressure, *IEEE Transactions on Plasma Science*, vol. 45, 1, 1–8, 2016.