

Tire pyrolysis char as tar cracking catalyst for gasification of RDF in dual pyrolysis-gasification reactor

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Gasification is an alternative and efficient process for municipal solid waste (MSW) disposal. Approximately 1,300 Mt of MSW is produced every year worldwide, 10 % of which is incinerated, but most is disposed of in landfills which represents a serious environmental hazard. Compared to commercial MSW incineration, lower than stoichiometric amount of oxygen is used in gasification resulting in production of hydrogen and carbon monoxide rich gas which can be combusted for heat and electricity production. Furthermore, synthesis gas obtained by gasification can be utilized in production of organic compounds like methanol or dimethyl ether. By removal of components with low heating value like kitchen waste and metals, MSW can be turned into refuse-derived fuel (RDF) with a lower heating value of up to 23.7 MJ/kg (Zhao *et al.*, 2016). Thus, MSW can be turned into renewable and plentiful energy source. Gasification is more energy efficient process than incineration and provides more options in final product generation. Many scientific papers discuss gasification of biomass, but only a few focus on gasification of MSW or RDF.

Although synthesis gas is the main product, minor solid and liquid products are produced as well. Liquid products, also known as tar, leave the gasifier with the product gas in form of vapors. Tar is a mixture of condensable hydrocarbons and their derivatives. Tar condensation causes fouling and corrosion of downstream processing units, so it has to be removed from the product gas. Physical means like cold filtration, absorption and condensation and chemical means like catalytic and non-catalytic cracking are well known techniques of tar removal. Physical means are expensive and require disposal of separated tar. On the other hand, catalytic and non-catalytic cracking turn tar into desirable gaseous products. However, some coke and higher polycyclic aromatic hydrocarbons (PAH) are produced as well (Devi, Ptasiński and Janssen, 2002).

Commercial alumina and zeolite based catalysts with Ni, Fe, Co or noble metal content are suitable for tar decomposition but they are expensive and easily deactivated by coke formation and by the presence of sulfur and chlorine based compounds in the product gas. As a cheap alternative, natural minerals like dolomite, olivine, silica or easily prepared materials like pyrolysis char can be used as tar cracking catalysts. These raw materials possess low catalytic activity, so they require thermal or chemical activation. Their catalytic activity can be further increased by metal impregnation. Tar cracking capability of nickel loaded olivine and dolomite was proven by several authors (Kuhn *et al.*, 2008)(Zhang *et al.*, 2017). Some authors used biomass pyrolysis char as catalyst or catalyst support because of its large specific surface area (Park, Lee and Ryu, 2016)(Nestler *et al.*, 2016)(Lu *et al.*, 2017). However, just a few papers focus on application of tire pyrolysis char which contains beneficial metals, mostly zinc (Al-Rahbi and Williams, 2017).

In this work, tire pyrolysis char based catalyst was prepared and tested during decomposition of model tar compound, p-xylene, and during gasification of RDF in dual pyrolysis-gasification reactor. Firstly, pelletized char was carbonated in tubular steel reactor heated by electric furnace for 4 h under constant flow of CO₂. Secondly, carbonated pellets were impregnated with water solution of nickel nitrate to achieve 2 wt. % Ni loading. Thirdly, impregnated pellets were then dried in an oven at 105 °C for 6 h and thermally treated at 800 °C for 2 h after which a finalized catalyst was obtained. To observe the impact of catalyst preparation on its porous structure, specific surface area, specific pore volume and average pore diameter were measured by nitrogen adsorption and BET isotherm evaluation at each stage of the catalyst preparation. Values obtained by this analysis are shown in Table 1.

Finalized catalyst was used for decomposition of p-xylene, which served as model tar compound. This experiment was carried out in tubular steel reactor which was filled with an amount of catalyst which varied between 7 g and 20 g. The reactor was heated to a temperature which varied between 700 °C and 900 °C.

Table 1. Specific surface area, specific pore volume and average pore diameter of catalyst during its preparation

	S_{BET} [m ² /g]	v_{pore} [cm ³ /g]	d_{pore} [nm]
Raw char	45.0	0.394	43.14
Carbonated char	72.4	0.328	33.78
Impregnated and dried char	66.9	0.315	36.76
Finalized catalyst	88.4	0.330	32.59

During the experiment, a mixture of nitrogen, carbon dioxide, steam and p-xylene vapors were continuously fed into the reactor. Condensable reaction products and unreacted p-xylene leaving the reactor were removed from permanent gases by absorption into isopropanol. Permanent gases and products captured in isopropanol were analyzed by gas chromatography. Each experiment took 3 hours. Deactivation of the catalyst was estimated according to the time dependence of p-xylene conversion. The results of these experiments suggest that higher temperature in the reactor leads to higher hydrogen yield. Studied catalyst ensured nearly complete conversion of p-xylene independently of catalyst amount in the first hour of every experiment. However, p-xylene conversion decreased overtime as the catalyst became more and more deactivated by coke formation.

Catalytic activity of studied catalyst was then tested during gasification of RDF in dual pyrolysis-gasification reactor. This experimental apparatus consisted of two reactors. 10 g of dried RDF was pyrolyzed in lower reactor at 550 °C under a nitrogen flow of 15 L/h. Volatiles released from pyrolyzed RDF was fed through a connector into upper reactor, gasifier, which contained 10 g of the catalyst. Air was fed into the system through the connector and its flowrate varied between 0 L/h and 15 L/h. The temperature of the gasifier varied between 700 °C and 900 °C. Every RDF gasification experiment lasted 2 hours. Gaseous products leaving the upper reactor were passed through series of isopropanol scrubbers to remove any tar compounds. Composition of the product gas was analyzed by gas chromatography and the amount of produced tar was obtained as the residual weight of isopropanol mixture from scrubbers after evaporation and removal of isopropanol and water. One experiment was carried out without any catalyst in the upper reactor. Goal of RDF gasification experiments was to find optimal air flow and gasifier temperature at which the hydrogen content in the product gas was the highest and total tar yield was the lowest. Air flow had negligible impact on the amount of produced tar or hydrogen. The lowest amount of tar (45.7 mg) was produced at the temperature of 750 °C, but the highest H₂ content of 33.8 vol. % in the product gas was at the gasifier temperature of 850 °C. Comparing experiment with and without the catalyst, the presence of the catalyst decreased the overall tar yield by 65 % at air flow of 10 L/h and gasifier temperature of 800 °C.

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References:

- Al-Rahbi, A. S. and Williams, P. T. (2017) "Hydrogen-rich syngas production and tar removal from biomass gasification using sacrificial tyre pyrolysis char," *Applied Energy*. Elsevier Ltd, 190, pp. 501–509.
- Devi, L., Ptasinski, K. J. and Janssen, F. J. J. G. (2002) "A review of the primary measures for tar elimination in biomass gasification processes," *Biomass and Bioenergy*, 24(2), pp. 125–140.
- Kuhn, J. N. *et al.* (2008) "Ni-olivine catalysts prepared by thermal impregnation: Structure, steam reforming activity, and stability," *Applied Catalysis A: General*, 341(1–2), pp. 43–49.
- Lu, P. *et al.* (2017) "Preparation of high catalytic activity biochar from biomass waste for tar conversion," *Journal of Analytical and Applied Pyrolysis*. Elsevier B.V., 127, pp. 47–56.
- Nestler, F. *et al.* (2016) "Catalytic decomposition of biomass tars: The impact of wood char surface characteristics on the catalytic performance for naphthalene removal," *Fuel Processing Technology*. Elsevier B.V., 145, pp. 31–41.
- Park, J., Lee, Y. and Ryu, C. (2016) "Reduction of primary tar vapor from biomass by hot char particles in fixed bed gasification," *Biomass and Bioenergy*, 90, pp. 114–121.
- Zhang, B. *et al.* (2017) "An experiment study of biomass steam gasification over NiO/Dolomite for hydrogen-rich gas production," *International Journal of Hydrogen Energy*. Elsevier Ltd, 42(1), pp. 76–85.
- Zhao, L. *et al.* (2016) "Characterization of Singapore RDF resources and analysis of their heating value," *Sustainable Environment Research*, 26(1), pp. 51–54.