Nanocatalysts Used for Tar Cracking Present in the Syngas from Gasification of Municipal Solid Waste

Antonio Trinca[a,*], Valentina Segneri[a], Jean H. Ferrasse[b], Mariapaola Parisi[a], Daniele Patrizi[a], Nicola Verdone[a]

[a]"Sapienza" University of Rome, Department of Chemical Engineering Materials and Environment, via Eudossiana 18, 00184, Rome, Italy
[b]Aix Marseille Univ, CNRS, Centrale Marseille, M2P2, Marseille, France
antonio.trinca@uniroma1.it

Waste gasification is considered one of the most promising potential routes for the fuel gas production since it represents one of the most powerful and reliable approaches for the biomass conversion. Tar is the undesirable, but unavoidable, by-product of the gasification processes. not only does it lower the overall energy conversion efficiency, but it also leads to potential contamination and clogging problems, thus It is of paramount importance to remove it. Tar can be converted into gases by catalytic cracking, which has become a hot research topic in biomass pyrolysis and gasification technologies. Various tar cracking catalysts have been extensively studied and current advances in the study of nanomaterials have attracted wide interest for their catalytic properties compared to their bulk counterparts: in particular, the supported transition metal NanoParticles show the best catalytic characteristics for tar cracking. This work gives a comprehensive overview of the most promising nanocatalysts for tar removal reported in the litterature: it reviews the different synthesis methods and the catalytic properties of the produced nanocatalysts, thus providing useful information for the understanding of the most promising routes for an efficient conversion of biomass tar into combustible gas.

1. Introduction

As global economy rapidly expands and energy consumption increases, world is confronted with the growing dual difficulties of meeting both its energy supply and demand needs. To address the challenges posed by energy supply and demand, many nations around the world have turned their focus towards developing renewable and clean energy sources such as wind, solar, geothermal, nuclear, biomass energy and reuse of municipal solid waste (MSW) as a means of replacing some or all of their reliance on traditional fossil fuels (Trinca et al., 2023). Syngas production is seen as a highly promising and dependable method for converting biomass and waste, which has a wide range of applications in chemical synthesis, power generation, heating, hydrogen production, and biofuel manufacturing.

Syngas can be obtained from biomass through thermochemical conversion processes such as pyrolysis and gasification. MSW pyrolysis is an exothermic decomposition process that occurs at high temperatures in the absence of a gasifying agent, resulting in the production of syngas, tar, and char. During pyrolysis, the chemical bonds in biomass can be broken down to form gaseous products primarily composed of H_2, CO, CO_2, and CH_4. Gasification, on the other hand, occurs at high temperatures (typically between 600–900 °C) in an oxidative atmosphere with the use of a gasifying agent, such as air, steam, oxygen, CO_2, or a combination of these. Gasification offers several advantages over conventional solid waste combustion, largely due to the ability to adjust operating conditions, such as temperature and equivalence ratio, and the characteristics of the chosen reactor (fixed bed, fluidized bed, entrained bed, vertical shaft, moving grate furnace, rotary kiln, plasma reactor), to produce syngas that is suitable for various applications.

However, the pyrolysis and gasification of waste not only yields valuable fuel gas, but also generates some undesirable by-products such as tar, fly ash, alkali metals, nitrogen oxides (NO_x), and SO_2. Of these by-products, the production of tar is the most challenging issue limiting the widespread use of biomass gasification and as

such, it has received considerable research attention. Tar can be converted into gases through catalytic cracking, making it a major area of research in biomass pyrolysis and gasification technologies. In recent years, numerous tar catalysts have been studied, and current advancements in catalyst preparation and utilization have been reviewed in various publications, with a focus on both synthetic metal catalysts and natural ore-based catalysts (Chan & Tanksale, 2014).

Biochar, another by-product, has also been explored as a solid catalyst with significant potential for the conversion of biomass into biofuel, value-added chemicals, and other chemical processes (Cao et al., 2018). In particular, biochar can serve as a support for the synthesis of char-supported metal nanoparticles (NPs), also known as biochar-based nanocatalysts (BBNs). BBNs often display high catalytic activity due to the disordered distribution of metal NPs on the biochar support, making them a promising new type of catalyst that is both efficient and cost-effective (Gai et al., 2019).

This paper aims to provide a systematic review of the synthesis methods, catalytic performance, and main applications of BBNs.

2. Catalytic tar cracking/reforming

The use of catalysts can significantly decrease the energy required to break down the chemical bonds in tar molecules. Consequently, catalytic cracking or reforming offers a highly effective solution for removing biomass-derived tar and is widely considered as the most feasible method for converting tar into flammable gases at relatively low temperatures.

2.1 Metal nanocatalysts

The nanoscale metal catalysts that are being developed for tar cracking are currently receiving a lot of attention. Nanoscale Particles (NPs) show exceptional dispersion properties when placed on the support materials, enhancing the interaction between the metal catalysts and the reactants.

Guo et al. (2019) studied copper nanocatalysts supported on activated char production in a single step by pyrolyzing a mixture of $CuCl_2$-impregnated biomass and $ZnCl_2$ as the activation agent. These catalysts were then utilized in a dual-stage reactor for cracking primary tar gasification. Characterization techniques showed that the $CuCl_2$ was reduced to active Cu^0 nanoparticles and the addition of $ZnCl_2$ significantly increased the surface area of the char, resulting in improved dispersion of the copper nanoparticles. The synthesis process also created a large number of micropores and mesopores, which helped to adsorb tar molecules and extend catalyst life. The combination of $CuCl_2$ and $ZnCl_2$ resulted in excellent catalytic activity for the cracking of primary tar, with a conversion efficiency of 94.5% achieved using RHC-1.0Cu1·0Zn at 800°C. The yields of H_2, CH_4, CO, and the total gas product increased significantly due to the tar reforming reactions using the activated char supported catalysts. GC-MS analysis revealed that the primary tar was mainly decomposed into oxygenated aromatic compounds and light tar compounds over char supported copper nanocatalysts.

In another study (L. Wang et al., 2014), Co-Fe/Mg/Al catalysts were synthesized from hydrotalcite-like compounds containing Co, Fe, Mg, and Al and were used for the steam gasification of biomass-derived tar. The characterization through techniques showed that after reduction, the Co-Fe/Mg/Al catalysts had a nanocomposite structure composed of Co-Fe bcc alloy particles and oxide particles of $MgAl_2O_4$-based solid solution. The Co metal atoms partially substituted Fe metal sites in the bcc Fe metal regarding the Co-Fe bcc alloy particles. The composition of the Co-Fe/Mg/Al catalysts was optimized on the basis of the activity test results. The optimized Co-Fe/Mg/Al catalyst demonstrated superior performance compared to other catalysts such as Co-Fe/α-Al_2O_3, Co/Mg/Al, and Ni-Fe/Mg/Al in terms of activity and resistance to coke deposition. This behavior can be attributed to the formation of Co-Fe bcc alloy nanoparticles with a relatively uniform composition on the $MgAl_2O_4$-based solid solution.

Ashok et al. (2015) described the synthesis of Ni/SiO_2 and $Ni-Cu/SiO_2$ catalysts from phyllosilicate structures (Ni/SiO_2P and $Ni-Cu/SiO_2P$, respectively) for tar conversion. The influence of the steam-to-carbon ratio and reaction temperature was also explored. The results show that the catalysts synthesized via the phyllosilicate structures give better performance compared to the impregnation method. The optimum composition of 30Ni-5Cu/SiO_2P shows superior stability and activity with 78% of the tar being converted to gaseous products at 600°C. The TEM and XPS analysis confirmed the formation of a unique layered structure and uniform distribution of alloy species in the catalysts. The stronger metal-support interaction in Ni/SiO_2P compared to the conventional impregnation method is also indicated by temperature-programmed reduction results.

The effectiveness of nanoscale catalysts is significantly impacted by the characteristics of the support material, including surface area, pore size, functional groups, and mechanical strength (Guo et al., 2019). Various types of support materials have been investigated for the synthesis of nanoscale metal catalysts, such as SiO_2. Recently, biochar has gained attention as a support material for the synthesis of nanoscale catalysts due to its porous structure, high surface area, and favorable pore size distribution.

This makes it an ideal support for stabilizing metal nanoparticles. Furthermore, biochar can be easily produced through the biomass pyrolysis process, making the preparation methods flexible and cost-effective.

2.2 Biochar-supported metal NPs

Char is defined as a product derived by the thermal decomposition of carbon-hydrogen compounds, including detonation or incomplete combustion, with a distinct morphology. Biochar is a carbonaceous material with valuable applications. It can be synthesized from a wide range of organic wastes, including digestate (Cavali et al., 2022). Biochar-Based Nanocatalysts are typically created through oxygen-limited thermal conversions of biomass materials, such as pyrolysis and gasification (Gao et al., 2019). The form and content of metals, surface area, and chemical structure of the char are influenced by the impregnation method, type of biomass material, pyrolysis temperature and time. For tar cracking and reforming, nickel (Ni), iron (Fe), and other transition metals are commonly used due to their excellent catalytic performance. The synthesis of BBNs is based on the type of metals employed.

Ni-based catalysts have been extensively researched for the removal of biomass tar and secondary gas reforming during biomass pyrolysis and gasification. Different metal and non-metal oxides, such as Al_2O_3, MgO, SiO_2, and natural materials, such as dolomite, olivine, and zeolite, have been explored as supports for Ni-based catalysts. Among these, porous supports have been found to enhance the distribution of Ni-based active substances, leading to improved catalytic activity. For example, D. Wang et al. (2011) studied Ni-based catalysts synthesys by blending NiO and char particles in varying ratios. The catalytic performance of Ni/char catalysts was evaluated and compared to that of wood char and coal char without Ni, for syngas cleaning in a laboratory-scale biomass gasifier. The parameters of the reforming reaction studied included the temperature (650-850°C), the NiO loading (5-20% of the weight of the char support), and the gas residence time (0.1-1.2s). The Ni/coalchar and Ni/woodchar catalysts were able to remove more than 97% of tars from the syngas at 800°C, with 15% NiO loading, and 0.3 s gas residence time. The analysis of the syngas composition showed significant increases in the concentrations of H_2 and CO. Additionally, the performance of the Ni/coalchar catalyst was continually tested for 8 hours, and it showed a slight decrease in activity in the early stages of tar/syngas reforming but stabilized soon after. The results showed that chars, particularly coal char, can be an effective and low-cost support material for NiO in removing tars and cleaning syngas in gasification.

Fe, another metal with strong catalytic ability for cracking tars, has gained significant attention in recent years for its potential in creating biochar supported Fe NPs to effectively convert biomass tars (Cahyono et al., 2018). Several approaches for the synthesis of biochar supported Fe nanocatalysts have been explored. Yu et al. (2006) presented a new type of nano iron catalyst supported by char, which is made from Victorian brown coal that has been loaded with iron and then undergone pyrolysis and gasification. Analysis using X-ray diffraction and TEM showed that iron is well-dispersed in the char as magnetite, with particle sizes smaller than 50 nm. Testing revealed that the catalyst is highly effective in the water-gas shift (WGS) reaction, even at low temperatures of 300°C. The authors proposed a process that utilizes the char-supported nano Fe catalyst in a moving-bed reactor to simultaneously achieve chemical heat pumping, hot gas cleaning, pollutant control (especially for NH_3 and H_2S), and water-gas shift reaction catalysis.

In addition to Ni and Fe, other metals like copper (Cu), cobalt (Co), and molybdenum (Mo) can also form nanoparticles on carbon materials, leading to the study of their use in BBNs. For instance, biomass char supported copper NPs can be made by impregnating fir sawdust with contaminated wastewater containing copper ions, then undergoing fast pyrolysis of the impregnated material, which has shown good activity in many reduction reactions and chemical stability over a long period of use (Liu et al., 2014). Yang et al. (2019) prepared, characterized, and evaluated Ni, Co, and Ni-Co catalysts supported on acid washed Shengli lignite for catalytic reforming at a low temperature of 450°C. The focus was on the production and selectivity of hydrogen. The bimetallic Ni-10%Co/AWSL catalyst showed the best results. This catalyst also altered the composition of the gas and had the highest selectivity of hydrogen, with H_2 accounting for 50.3% and 63% under argon and steam atmospheres, respectively. The superiority of the Ni-Co based catalysts, despite the loss of specific surface area, was due to better reducibility and electronic properties, as well as high metal dispersion. The combination of Ni and Co also contributed to enhanced catalytic reforming and improved selectivity for hydrogen-rich syngas under moderate conditions. (Kaewpanha et al., 2013) documented the formation of Mo_2C NPs supported biochar through the following steps: First, dried cedar was impregnated with an aqueous solution of ammonium heptamolybdate with a concentration range of 5-30 wt%. The impregnated mixture was then dried overnight at 110°C. Finally, the solid mixture was carburized from room temperature to a desired temperature between 600-800°C under an Argon atmosphere for 2 hours.

Table 1: Summary of NPs, support, and brief description of their properties

NPs	Support	Brief Description
CuCl$_2$ ZnCl$_2$	Activated Char	Long life, High conversion efficiency
Co-Fe	Mg/Al	High activity and resistance to coke deposition
Ni Ni-Cu	SiO$_2$	High stability and activity
NiO	Char	Low cost, High yields
Fe	Char (Vitcorian Brown coal)	Highly effective in WGS
Ni-Co	Biochar	Good electronic properties, High reducibility and metal dispersion

To better understand the behavior of nanocatalysts, kinetic models based on the shrinking core model have been developed, allowing to estimate the kinetic and diffusional model parameters (Vilardi, 2018, 2019). Another useful model for description is the Langmuir-Hinshelwood mechanism, fitting the apparent kinetic constant and thermodynamic parameters with the Eyring equation (Vilardi, 2020).

2.3 Catalytic approaches for tar reduction

The synthesis of catalysts shows that NPs supported on porous biochar have an abundance of pores that can effectively absorb tar molecules, creating a series of nanoreactors. These metal NPs serve as active sites, enhancing the catalytic activity. Currently, the methods for reducing tar in biomass pyrolysis and gasification systems are divided into two categories, based on where the catalyst is placed in the process.

The first approach to reducing tar consists in synthesizing the catalyst or mixing it with biomass directly in the reactor, known as the "in situ reforming method". The second approach involves the use of a secondary reactor for tar cracking or reforming downstream of the pyrolysis or gasification reactor, known as the "ex situ reforming method" (Shen & Fu, 2018).

"In situ catalytic cracking" is an efficient method for removing biomass tar that also carries out biomass catalytic pyrolysis, nanocatalyst formation, tar catalytic cracking, and gasification reactions. This method simplifies the steps of biomass pyrolysis or gasification without requiring additional equipment, but it is difficult to control the reactions at different stages, making it challenging for long-term applications. Currently, the in situ catalytic performance of BBNs is mainly studied in laboratory experiments, such as the study by Richardson et al. (2013) which found that Ni NPs supported on char were generated during the biomass pyrolysis process and had high catalytic activity for tar cracking. Du et al. (2019) successfully decomposed biomass tar using biochar supported Ni NPs at a low reforming temperature of 600°C. The in situ generating process of metallic Ni nanoparticles via carbothermal reduction was manipulated to modulate the Ni particle size. The possible decomposition pathway of toluene on the catalysts' surface is described as follows: first, adsorption in a parallel configuration on the porous surface, followed by gradual dehydrogenation of the methyl groups, then breaking of the C-H bond in the aromatic ring and the opening of the aromatic ring through cleavage of the C1-C2 bond. Lastly, the ring opened aliphatic C7 hydrocarbons are decomposed into C3 and C4 fragments.

The "ex situ cracking" method requires a special reaction zone with catalysts and a reforming reactor that is designed and connected behind the gasifier, or a separate reaction area set at the outlet of the gasifier. An external heating device is usually designed, or a certain amount of oxygen/air is introduced to regulate the temperature in the reforming zone. This method allows for better regulation of reaction conditions such as temperature and atmosphere during the tar cracking/reforming process, leading to higher tar conversion and improved selectivity of the product gas. However, it requires additional reaction equipment, increasing the complexity and cost of the gasification or pyrolysis system, and the catalyst bed creates additional resistance to gas flow during operation. Gai et al. (2017) utilized hydrochar-supported Fe NPs to perform ex situ reforming of biomass tar with phenol as a model. When the reforming temperature was set at 600°C, the conversion rate of phenol using pure hydrochar as a catalyst was 67.6%. However, when hydrochar-supported Fe NPs were used, the conversion rate significantly increased to 85.4-98.4%. Additionally, the hydrochar-supported Fe NPs exhibited remarkable selectivity in generating CO and H$_2$ yields. It is important to note that the catalytic cracking of phenol may result in carbon deposition sintering of Fe NPs, which can potentially impact the catalysts' structure and activity.

3. Challenges and perspectives

To further advance the synthesis methods and practical use of BBNs, it is recommended that efforts be focused on some key areas which will be briefly summarised.

Fine-tuning the size of metal particles at the nanoscale, precisely controlling the formation of NPs, and embedding the metal particles onto the biochar matrix remain significant challenges in the synthesis of BBNs. The weak interaction between metals and biochar matrix makes it easy for metal NPs with non-homogeneous particles to peel off from the surface, especially under harsh reaction conditions, causing a decrease in catalyst activity. Furthermore, uncoated metal NPs tend to agglomerate during the tar reforming process, reducing the dispersion of active sites, and blocking the pore structure, which can result in carbon deposition and deactivation. To advance the development and application of these catalysts, optimizing the pore structure of the biochar matrix, improving the particle size and dispersion uniformity of metal NPs, and preventing metal particles from peeling off and agglomeration are critical.

The inefficiency and instability of most BBNs in cracking biomass tar is mainly attributed to two factors. Firstly, the chemical bonding between carbon and metal NPs remains underexplored. Secondly, the use of raw carbon materials results in low stability and a short lifespan of the char-supported catalysts. Hence, it is crucial to discover appropriate carbon sources and catalyst preparation methods and investigate new metal-carbon nanocomposites with consistent and high catalytic performance.

It was discovered that biochar supported metal nanoparticles not only have a catalytic effect on the cracking and reforming of tar, but also on various gas reforming reactions. This leads to a significant increase in the concentration of specific gases such as hydrogen (H_2), carbon monoxide (CO), and methane (CH_4), which is generally referred to as the catalyst's selectivity. However, the exact selective catalytic mechanism of biochar-based nanocatalysts for different reactions is still not well understood. If the selectivity of biomass pyrolysis and gasification processes can be improved by manipulating the structure of the catalysts and optimizing the operational conditions, it could significantly increase the value of the produced gases and boost the commercial viability of these technologies.

The use of biochar-supported metal nanoparticles (BBNs) in catalytic cracking/reforming of tar may lead to changes in the pore structure and functional groups of the biochar support, potentially causing loss or deactivation of the BBNs over time. An important challenge in their long-term application is to find ways to effectively recover the metals and regenerate the catalyst in a cost-effective manner.

Currently, the development and testing of BBNs mostly takes place in laboratory settings, and the catalysts have shown promising results under controlled conditions. However, the application of the technology in large-scale biomass pyrolysis and gasification systems is much more complex and there are still numerous challenges to be addressed, such as optimizing the equipment design, dealing with high pressure drops, maintaining catalyst stability over time, and ensuring the technology can be successfully implemented in real-world commercial applications.

4. Conclusions

This review focuses on the use of metal nanocatalysts and biochar-based nanocatalysts as a solution to the tar problem in biomass pyrolysis and gasification technologies. It provides an in-depth understanding of the formation, synthesis, and catalytic properties of biochar-based nanocatalysts, and offers valuable insights into the conversion of waste tar into combustible gas.

Despite the potential benefits of biochar-based nanocatalysts, such as high efficiency and low cost, there are still many challenges to be addressed in terms of efficiency, stability, selectivity, and scalability, and further research and optimization are needed.

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