



# Highly abrasion resistant thermally fused olivine as in-situ catalysts for tar reduction in a circulating fluidized bed biomass gasifier

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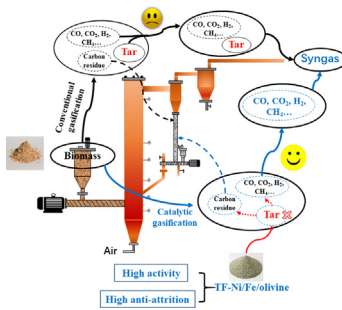
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## GRAPHICAL ABSTRACT



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## ABSTRACT

Olivine synthesized by wetness impregnation (WI) and thermal fusion (TF) methods were investigated as in-situ catalysts to reduce the tar content during air-blown biomass gasification in a circulating fluidized bed (CFB). The results showed that the tar content decreases with the increase of reaction temperature. Raw-olivine reduced tar content by 40.6% compared to non-active bed material (silica sand) experiments; after calcination, the catalytic activities of olivine catalysts were further improved due to the migration of Fe from olivine grain to the surface. 1100-WI-olivine could reduce the tar content by up to 81.5% compared with that of raw-olivine because of the existence of Fe<sub>2</sub>O<sub>3</sub>, NiO and NiO-MgO. For 1400-TF-olivine, due to the formation of NiFe<sub>2</sub>O<sub>4</sub>, the tar content decreased to 0.77 g/Nm<sup>3</sup>, an 82.9% reduction compared to raw-olivine. Moreover, the TF-olivine had a stronger anti-attribution performance and was more suitable for using in a circulating fluidized bed.

## 1. Introduction

With the depletion of fossil fuels, renewable energy has been attracting great attention (Zhang et al., 2010). As the only potential carbonaceous renewable energy, the development of biomass energy is

crucial to alleviate the shortage of fossil energy and reduce environmental pollution (Ahmad et al., 2016; Patel et al., 2016). Biomass energy can be converted into high value-added chemicals through thermal conversion processes, such as pyrolysis, gasification and combustion, etc (Hossain et al., 2016). Among the thermochemical conversion

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processes, biomass gasification is considered to be one of the most promising transformation pathways (Abdoulmoumine et al., 2015). The syngas generated by biomass gasification can be used as fuel for direct combustion to generate heat or power, as well as can be used as a raw material for producing liquid fuels through Fischer-Tropsch synthesis (Atsonios et al., 2013; Ruiz et al., 2013).

In the biomass gasification, the following reactions mainly occur: pyrolysis of biomass, gasification of char, combustion of carbon residues and cracking/reforming of tar, and some components can be both reactant and product because that multiple reactions may occur simultaneously (Chen et al., 2015), therefore, the design of the gasifier is also very important. At present, biomass gasifiers mainly include fixed bed gasifier, fluidized bed gasifier (including bubbling fluidized bed and circulating fluidized bed) and entrained flow gasifier (Ahmad et al., 2016). In the CFB, high heat and mass transfer rates and good mixing between the solid phase (biomass particles and bed material) with gas phase (gasification agent such as air, oxygen and steam) can form a uniform reaction zone, which is beneficial for the conversion of biomass (Calvo et al., 2012; Weerachanchai et al., 2009). Of course, CFB also has disadvantages, for example, it is not easy to operate stably for a long time, and it requires that the bed materials must have strong abrasion resistance.

In addition to the useful fuel gases (CO, H<sub>2</sub>, CO<sub>2</sub> and C<sub>2</sub>-C<sub>5</sub>), some unwanted by-product tar produced from biomass gasification is considered as the most problematic (Barman et al., 2012). Several approaches for eliminating tars economically have already become the focus of current research (Anis and Zainal, 2011; Shen and Yoshikawa, 2013). For a CFB system, tar removal methods can be classified into two categories: primary methodologies and secondary methodologies (Phuphuakrat et al., 2010). The secondary methodologies mainly include tar washing, electrostatic trapping, etc. (Materazzi et al., 2014). The primary methodologies mean that the tar is cracked inside the gasifier under the promotion of catalysts, which can reduce the tar content while promoting the full use of energy in tar (Christodoulou et al., 2014; Li et al., 2014). In addition to the catalyst, the optimization of experimental parameters, and the innovative design of gasifiers are also essential for the reduction of tar.

The main role of the catalyst is to increase the reaction rate at low-temperature inside the gasifier and facilitate the conversion of tar into valuable syngas via thermal cracking, steam reforming, dry reforming, char gasification and water-gas reaction (Gao et al., 2015; Hu et al., 2016). Currently, a large amount of catalysts have been studied, and the catalysts being studied can be decided into synthetic catalysts and mineral catalysts. Synthetic catalysts are synthesized by chemical approaches at a relatively high cost, such as noble metals-based catalysts (Oh et al., 2016; Wang et al., 2012), Ni-based catalysts (Tomishige et al., 2007), Fe-based catalysts (Huang et al., 2012; Zamboni et al., 2017). These catalysts generally have high catalytic activity. Mineral catalysts are much more cost-effective than synthetic catalysts, and the catalytic effect of mineral catalysts is usually not as good as those of synthetic catalysts. The typical examples of mineral catalysts are dolomite, olivine, zeolite and clay minerals (Buchireddy et al., 2010; Wang et al., 2005). Combining the advantages of synthetic catalysts and mineral catalysts to produce catalysts with low cost and high catalytic performance is becoming the focus of the current research (Quan et al., 2017).

Literatures show that dolomite has a good catalytic activity, but it has poor mechanical properties and is easily crushed, so it is not suitable for using in the CFB (Makwana et al., 2015; Rapagna et al., 2018). In contrast, olivine is mainly composed of (Mg, Fe)<sub>2</sub>SiO<sub>4</sub>; after calcination, olivine shows a comparable catalytic activity to that of dolomite, and its catalytic performance is further improved after loading active metals (such as Fe, Ni, Co, Ce, etc.). In addition, the strong abrasion resistance of olivine make it more suitable as a fluidized bed material. (Virginie et al., 2010) synthesized an iron/olivine for a use in fluidized bed gasifier, toluene conversion and hydrogen yield were

three times higher than that of olivine. (Świerczyński et al., 2007) has reported that Ni/olivine has higher activity, higher selectivity to H<sub>2</sub> and CO and lower carbon deposition compared with olivine alone, the lower carbon deposition might be attributed to the Ni-Fe/MgO/olivine system formed in the Ni/olivine. (Xu et al., 2015) used Ni/olivine as a support with CeO<sub>2</sub>/MgO as promoters to synthesize a series of Ni-Ce-Mg/olivine catalysts. The 6%Ni-3%Ce-1%Mg/olivine exhibited approximately 100% carbon conversion and 75% hydrogen yield and sustained for 70 h without deactivation. The olivine catalysts in the above literatures are all synthesized by wetness impregnation (WI). The olivine catalysts synthesized by this method is easy to attrite and the preparation steps are cumbersome. For the loading method of the active metal, in our previous studies (Meng et al., 2018b), it was found that different metal loading methods resulted in different combinations of metal and olivine support, which led to a different catalytic performance for the tar (Kuhn et al., 2008).

Above all, in this study a visualized biomass circulating fluidized bed gasifier was designed to ensure stable operation of the circulating fluidized bed. Aiming at the high requirement of circulating fluidized bed for the anti-attrition ability of the catalyst, a relatively new method, thermal fusion (TF), was performed to synthesize an in-situ olivine catalyst. In addition, the tar cracking ability, the attrite property and the combination of the active metal and the olivine support of the catalysts prepared by the TF method and the conventional method (wetness impregnation) were compared.

## 2. Methods

### 2.1. Biomass analysis

The feedstock pine sawdust was obtained from a wood treatment plant (Guangzhou, China), and the pine sawdust was prepared by sieving it with the mesh size of 180–380 μm and drying at the temperature of 105 °C for 7 h before used as a feedstock. The proximate (air-dry base) and ultimate analyses (dry-ash-free base) of the pine sawdust sample were conducted in a muffle furnace (SX-11-4, China) and an elemental analyser (Vario EL cube, Elementaranalyse, Germany), respectively. The Volatile matter, Fixed carbon and Ash content of the pine sawdust was 84.03%, 14.98% and 0.99%, respectively; and the content of Carbon, Hydrogen, Oxygen, Nitrogen and Sulfur in pine sawdust was 49.60%, 6.46%, 42.86%, 0.05% and 0.04%, respectively.

### 2.2. Catalyst preparation

The olivine ore was obtained from Shanxi Province (China). The olivine particles were sized between 180 and 380 μm (40–80 mesh) by screening, the olivine ore was marked as raw-olivine. The raw-olivine was calcined at 900 °C and 1100 °C for 4 h, which was marked as 900-olivine and 1100-olivine, respectively. Preparation of Ni-Fe bimetallic (the load of Fe and Ni were both 5%) olivine-based catalysts by WI has been described in previous study (Meng et al., 2018b). The catalysts prepared by WI method using 900-olivine and 1100-olivine as raw materials were recorded as 900-WI-olivine and 1100-WI-olivine, respectively. In addition, the Ni-Fe bimetallic (the load of Fe and Ni were both 5%) catalysts supported on 1100-olivine using TF method at 1100 °C and 1400 °C were designated as 1100-TF-olivine and 1400-TF-olivine, respectively. The specific steps of TF method were also introduced in previous study (Meng et al., 2018b).

### 2.3. Catalysts characterization techniques

The crystal phase of the olivine samples were characterized by XRD (X'Pert-PRO MPD). X-ray fluorescence (AXIOSmAX-PETRO) was used to analyse the chemical compositions of the olivine. And the H<sub>2</sub>-TPR was performed to evaluate the reductive ability of the olivine catalysts;

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