



# Study of olivine supported copper sorbents performances in the desulfurization process in link with biomass gasification



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## ABSTRACT

In this study, a Cu/olivine system was prepared with different loading (3–10 wt.%) by wet impregnation method and calcined at different temperatures in order to raise and to optimize its performances in the presence and in the absence of hydrogen in desulfurization process during gasification of biomass. The Cu/olivine catalysts are as well characterized by XRD and H<sub>2</sub>-TPR experiments. XRD patterns are found to show formation of copper and iron oxides and mixed Cu–Fe oxides after calcination process. H<sub>2</sub>-TPR results revealed that the materials calcined in the 900–1000 °C temperature range were more difficult to reduce than those calcined at lower temperatures because of their strong interactions between copper and olivine material. Desulfurization over 3% Cu/olivine sorbent calcined in the 900–1000 °C temperature range has been considered to be the best materials offering the highest breakthrough times and the highest amounts of H<sub>2</sub>S removed in the presence or in the absence of hydrogen with low production of SO<sub>2</sub>. Regeneration/sulfidation cycles performed on 3% Cu/olivine sorbent calcined at 1000 °C revealed that the material is not deactivated and exhibits the same performances after 10 cycles.

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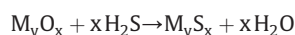
## 1. Introduction

Nowadays, the need of energy associated with the environmental challenge has increased dramatically. Indeed, during the recent decades, renewable energy research has highly grown in developing a clean energy alternative to fossil fuels. Biomass is considered as renewable energy sources from which gases can be produced by several processes (gasification, pyrolysis, and combustion). The gasification is currently the most interesting process for the thermochemical conversion of biomass. This process uses air, oxygen and/or steam as gasification agent and can be carried out in the Fast Internally Circulating Fluidized Bed (FICFB) gasifier [1,2]. The core of a FICFB (Fast Internally Circulating Fluidized Bed) reactor is formed by two inter-connected fluidized bed systems, namely gasification and regeneration zones. In the gasification zone the cut-down biomass is whirled up and gasified in anaerobic conditions at around 850 °C. While for the regeneration (combustion) zone, the spent material coming from gasification zone and containing tars and coke is heated up in aerobic conditions (air) in which temperature may reach 900 °C. The bed material mainly olivine (Mg,Fe)<sub>2</sub>SiO<sub>4</sub> has the function of a heat transfer medium and provides a stable temperature in the reactor. The resultant product gas is purified and cooled.

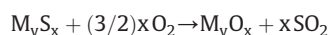
The syngas produced from the steam gasification process at 850 °C contains: H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and N<sub>2</sub>. Hydrogen and carbon monoxide could be used for methanol or Fischer–Tropsch synthesis, chemical production and hydrogen for electricity generation (turbine,

gas engine or fuel cells). However, the steam gasification process leads to the formation of undesired products such as particulates, tars, alkali oxides, heavy metals, hydrogen chloride, ammonia and sulfur compounds (mainly H<sub>2</sub>S in gasification reactor). Tars destruction [3,4], alkali oxide reactions and particulates [5,6] removal has been largely described in the literature, however sulfur compounds elimination constitute a major problem especially at the temperature of biomass gasification [7–9]. In the presence of H<sub>2</sub>S, the decrease in catalyst activities owing to the poisoning of catalytic active sites and the corrosion of metallic equipments leads to a decrease in the total efficiency and an increase in the cost of the process [10]. For further application in fuel cells, H<sub>2</sub>S has to be eliminated until attending allowable sub-ppm level to avoid poisoning of fuel cell catalysts or electrolytes [11].

The removal of the hydrogen sulfide (desulfurization) of gases produced during biomass gasification can be achieved with a metal oxide (MO<sub>x</sub>) through the reaction of sulfidation of MO<sub>x</sub> [7,8], following:



for which several mechanisms are proposed in the literature depending to the gas environment (presence or absence of hydrogen, or other gas like CO, CO<sub>2</sub> and H<sub>2</sub>O). The sulfided material can be regenerated in oxidative atmosphere and by thermal decomposition of the sulfates [7,8]:



Several works have been carried out to study the desulfurization process at low and high temperatures (400–1200 °C) using supported

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metal oxides and/or mixed metal oxides [8,11–13]. Among the investigated materials many have shown good potential for H<sub>2</sub>S removal. Westmoreland and coworkers [14,15] studied the thermodynamics and kinetics of the desulfurization reaction up to 1500 °C for many metal oxides. They concluded that the desulfurization potential of several candidates (iron, zinc, molybdenum, manganese, vanadium, calcium, strontium, barium, cobalt, copper and tungsten oxides) can be established for high temperature ranges. However, the use of zinc oxide is restricted to temperatures lower than 550 °C because of the formation of zinc vapor [15,16]. It can be used for the desulfurization of gases produced from the biomass gasification at 850 °C, only if associated with other metal oxides like Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CuO allowing an increase in its stability, efficiency and resistance against reduction at low temperatures. It was also reported that iron oxide might be an effective material at temperature up to 550 °C because at a temperature of reduction of about 700 °C, Fe<sub>2</sub>O<sub>3</sub> is reduced into FeO while its desulfurization capacity dropped significantly [7,9,12,17,18].

Calcium compounds continue to be of interest because of their utility under both oxidizing and reducing conditions and their low cost. Their limitations are linked to their poor reactivity and capability to absorb CO<sub>2</sub> at low temperatures, the pore closure during sulfidation and difficult regenerability [19].

Copper oxides and copper mixed oxides were developed and considered to be the best materials for the desulfurization process because of their sulfidation equilibria, sulfidation reactivity (H<sub>2</sub>S reduction from several thousand ppm to levels below the ppm), absence of volatilization (low vapor pressure of copper oxide and copper metal) and regenerability at a temperature between 650 °C and 900 °C [20–24]. However, CuO, in an uncombined form, is reduced by H<sub>2</sub> and CO decreasing hence the desulfurization efficiency. In fact, copper oxides (CuO and Cu<sub>2</sub>O) have higher sulfidation equilibrium constants compared to copper metal [25]. Therefore, the aims of improving the copper-based material by retaining copper at its oxidation state (Cu<sup>+2</sup> and Cu<sup>+1</sup>), mixed binary oxides of copper were studied. Yasyerli et al. [12] studied the activities of copper oxide and Cu–V and Cu–Mo mixed oxides for H<sub>2</sub>S removal in presence and in absence of hydrogen. They observed a real competing in the reduction of CuO and the two mixed oxides by H<sub>2</sub> and H<sub>2</sub>S. Furthermore, they found that vanadium and molybdenum oxides provide strong interactions with copper oxides which prevent the reduction of these oxides by hydrogen at high temperature compared to the pure copper oxides. Kyotani et al. [22] investigated desulfurization abilities of pure CuO and CuO supported on SiO<sub>2</sub>. It was found that the supported CuO materials

have high reactivity in both desulfurization and regeneration steps and shows no loss of reactivity during cyclic reactions.

Regarding the effects of iron oxide, Lee et al. [26] reported that the addition of various amounts of Fe<sub>2</sub>O<sub>3</sub> in CuO material tends to increase the H<sub>2</sub>S removal. The same results were found by Tamhankar et al. [8]. The former work tested three mixed oxides (CuO–Fe<sub>2</sub>O<sub>3</sub>, CuO–Al<sub>2</sub>O<sub>3</sub>, and CuO–Fe<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub>) and showed the positive effect of the association of copper oxide with iron oxide in copper ferrite and alumina in copper aluminates. These phases permit the stepwise reduction of copper from Cu<sup>2+</sup> to Cu<sup>1+</sup> then to Cu<sup>0</sup> during the sulfidation process and stabilize an intermediate compound with better sulfidation equilibria than Cu<sup>0</sup> [27].

In the FICFB reactor, olivine is the solid material mixed with wood biomass. Olivine is a silicate of magnesium and iron (around 7 wt.% of iron) in which a variable part of the iron is out of the structure as hematite due to the calcination process [28]. It has also been discussed that foreign ions (Ni<sup>2+</sup> or Fe<sup>2+</sup>) could be included inside the structure [29,30]. Taking advantage of these properties and of the opportunity to obtain Cu–Fe oxides in the structure of olivine, the objective of the present investigation is to develop and evaluate a novel copper-based material (copper–olivine compared to olivine) for the removal of hydrogen sulfide from gases produced during biomass gasification at 850 °C. The interactions between copper oxides and olivine were studied by XRD and H<sub>2</sub>-TPR before and after sulfidation to understand their efficiency in the presence and in the absence of hydrogen in reactor feed and their regenerability during successive sulfidation–regeneration cycles.

## 2. Experimental

### 2.1. Materials preparations

The natural olivine is used as a reference and catalyst support in this study. It was pre-calcined at 1600 °C during 4 h and provided by Magnolithe GmbH company with the following characteristics: 315–400 μm particle size, very low specific surface area (< 1 m<sup>2</sup>/g) and composition (30.5 wt.% of Mg, 7.1 wt.% of Fe and 19.6 wt.% of Si) obtained by atomic absorption leading to the mean formula (Mg<sub>0.92</sub>Fe<sub>0.08</sub>)<sub>2</sub> SiO<sub>4</sub>. Moreover, about 50% of iron is in free iron oxide form (Fe<sup>3+</sup>) and about 50% is in olivine structure as Fe<sup>2+</sup>. This olivine will be named “initial olivine”. It was also studied as H<sub>2</sub>S removal material because of its iron oxide content and was calcined at the same temperature than the copper impregnated materials in order to evaluate the sorption capacity of this support.

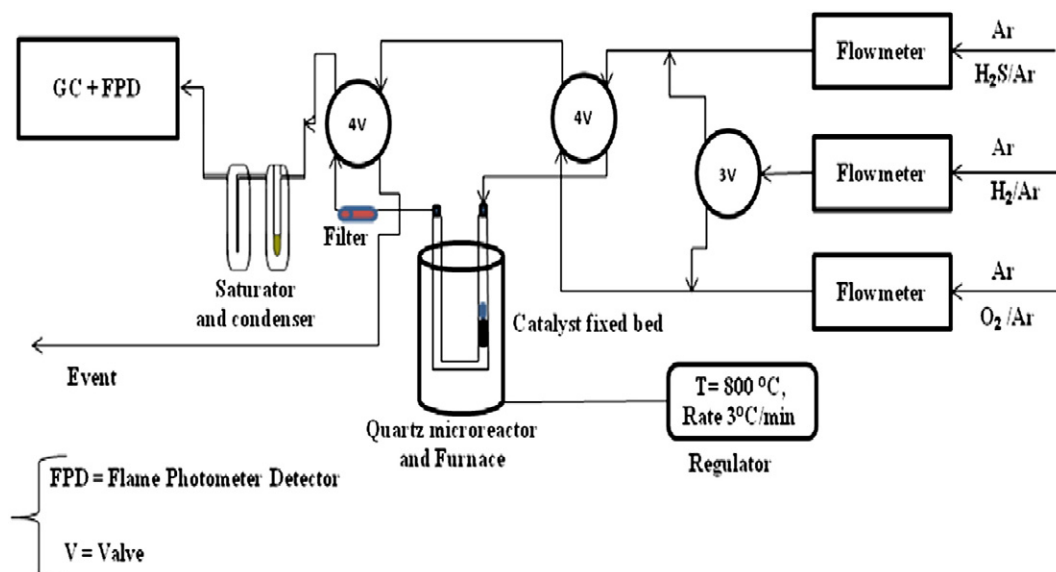


Fig. 1. Schematic diagram of the experimental apparatus.

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