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Effect of Fe–olivine on the tar content during biomass gasification in a dual fluidized bed

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ABSTRACT

The Fe/olivine catalyst effectiveness regarding tar primary reduction during biomass gasification in dual fluidized beds has been investigated. The use of Fe/olivine instead olivine leads to an important decrease in the amount of produced tar, which was reduced by up to 65% at 850 °C, naphthalene being the most stable molecule. It has been found that Fe/olivine materials have a double effect on tar destruction. On the one hand, they act as a catalyst for tar and hydrocarbon reforming. On the other hand, they can act as an oxygen carrier that transfers oxygen from the combustor to the gasifier, and part of the oxygen is used to burn volatile compounds. The catalyst was fairly stable because the result was confirmed during 48 h of continuous operation. The Fe/olivine material characterization (X-ray diffraction, Mössbauer spectroscopy, temperature programmed reduction and oxidation, etc.) revealed that the catalyst structure was maintained despite the large number of oxidizing–reducing cycles. The carbon that formed on the catalyst surface was low and easily oxidized in the combustion zone. Therefore, the inexpensive and non-toxic Fe/olivine catalyst is a material suitable for use as primary catalyst in a fluidized bed gasification of biomass.

1. Introduction

Biomass gasification is an interesting technology in future development of a worldwide sustainable energy system, which can help to decrease our current dependence on fossil fuels. Biomass gasification is a thermal process where solid fuel is converted into a useful gas using several gasifying agents such as air, and steam. The producer gas has a great number of applications. The most important being combustion for power and heat generation as well as raw gas for production of fuels or chemicals [1].

There are several designs of small and large scale gasifiers available for the use of biomass. Among them, those based on fluidized bed technology offer several advantages including the possibility of being scaled up to both medium and large scale, and temperature limitation to avoid bed agglomeration [2]. Moreover, the use of some specific designs can present additional advantages. For example, the use of a dual fluidized bed gasification system can be used to generate a high quality producer gas. The steam blown dual fluidized bed reactor located at Güssing is a well-known example of the successful industrial application of this technology [3]. The basic idea behind this gasification system is to physically separate the gasification and the combustion reactions, in order to obtain a largely nitrogen-free producer gas. Both reactors are thermally connected due to a circulating bed material. The gasification of biomass takes place in a steam fluidized bed. Together with the circulating bed material, ungasified char is transported to the combustion reactor and burned with air. Heat is delivered back to the gasifier by the bed material to satisfy the endothermic gasification reactions.

However, gasification produces not only useful fuel gases but also some unwanted byproducts. Among them, tar is recognized as one of the most problematic parameters in any gasification system [4,5]. Most of the tar removal technologies are based on low temperature gas cleaning processes located downstream to the gasifier [6]. Among hot gas conditioning systems, catalytic cracking and steam reforming of high molecular weight hydrocarbons offer several advantages, such as thermal integration and high tar conversion. A large number of investigations deal with biomass gasification in fluidized bed reactors utilizing nickel based catalysts, dolomite or olivine. Supported nickel-based catalysts with various supports and promoters have been the most widely studied class of materials. The high activity and selectivity of those reforming catalysts is well known [7,8] but they are susceptible to deactivation from contaminants. Olivine shows a slightly lower

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Table 1
Proximate and ultimate analysis of pine wood.

Property	Parameter value (wt%)
Total moisture	6.30
Ash	1.10
Volatiles content	77.30
Fixed carbon	15.40
C	46.60
H	6.00
N	0.20
S	0.004
Cl	0.002
High heating value (kJ/kg)	18,235

activity in biomass gasification and tar reforming, but higher attrition resistance than dolomite [9]. The addition of some metals to olivine can help to increase its tar reforming activity. In this sense, the tar abatement activity of a Ni/olivine catalyst was successfully demonstrated in the 100 kWth FICFB (dual fluidized bed steam blown biomass gasifier) pilot plant located in Vienna, with an order of magnitude reduction in the tar content of the product fuel gas [10,11]. The main drawback attributed to the use of Ni is the cost and the environmental and safety measures derived from its toxicity.

In addition, Rauch et al. [12] demonstrated that olivine activity, or more specifically olivine activation, depends on its iron oxide content. In fact, depending on olivine temperature treatment, iron can be present in the olivine phase, or as iron oxides. Thus, iron impregnation of natural olivine appears to be very interesting way to produce in-bed primary catalysts, for both economic and environmental reasons. Iron does not affect the catalyst cost due to its low price in comparison to noble metals and nickel thus markedly reducing catalyst pollution problems.

A global objective of this work was: (a) to develop a new material, the Fe/olivine prepared by impregnation; (b) to test its capacity for a primary in-bed reduction of heavy hydrocarbons (tar) in a dual fluidized bed gasification system; and (c) to characterize the material after the tests to determine its behavior during long term operation.

Point (a) has been studied and detailed in a previous paper [13], where the Fe/olivine catalyst preparation, characterization before testing and preliminary reaction of toluene steam reforming have been largely discussed. The aim of the present paper is focused on both points (b) the Fe/olivine efficiency in tar removal in a dual fluidized bed and (c) after testing characterizations.

2. Experimental

2.1. Biomass

The biomass feedstock consisted of crushed and sieved pine wood with average particle size of 0.5–2.0 mm. Proximate and ultimate analysis of the biomass is given in Table 1. The applied feedstock is characterized by low ash, nitrogen, sulfur and chlorine contents. Thus, possible undesirable effects on the in situ catalysts (deactivation caused by sulfur) might be avoided.

2.2. Preparation of Fe/olivine catalysts

The olivine used in this study came from Austria (Magnolithe GmbH) and its mechanical resistance has been improved by calcination at 1600 °C for 4 h. Olivine is a silicate mineral in which magnesium and some iron cations were embedded in the silicate tetrahedral. The elemental analysis performed by ICP-MS on this mineral allows the determination of its composition: 30.5 wt% Mg–19.6 wt% Si–7.1 wt% Fe. Mössbauer spectroscopy, associated to X-ray diffraction, revealed that half of the 7.1 wt% Fe is present as Fe(III) oxides (α-Fe_2O_3, $MgFe_2O_4$) and the other part is present as Fe(II) inside the olivine structure. The Fe(III)/Fe(II) ratio depends on the calcination conditions [13,14].

The Fe/olivine catalyst has been synthesized using an optimized method of impregnation. Iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), in an appropriate quantity to assure an additional iron content of about 10 wt%, was dissolved in an optimized amount of water by heating. About 25 kg of olivine (100–250 μm) was added to the iron aqueous solution and the water excess was evaporated under vacuum by heating at 90 °C. The sample was dried inside the tank, then overnight under an extractor hood, before being calcined at 1000 °C over 4 h (temperature heating rate of 3 °C min^{-1}). ICP-MS measurements performed after catalyst synthesis indicate a total iron weight percentage of 16 wt% corresponding to the iron initially present in olivine and the added iron.

2.3. Catalysts characterization

X-ray diffraction (XRD) patterns were acquired with a Bruker AXS-D8 advance using Cu Kα radiation, the diffraction spectra have been indexed in comparison to the JCPDS files (Joint Committee on Powder Diffraction Standards).

The Mössbauer spectra measurements were carried out in transmission mode with ^{57}Co diffused into an Rh matrix as a source moving with constant acceleration. The spectrometer (Wissel) was calibrated by means of a α-Fe foil standard, and the isomer shift was expressed with respect to this standard at 293 K. The fitting of the spectra was performed with the help of the NORMOS program.

Temperature programmed reduction (TPR) allows the evaluation of catalyst reducibility by a flow of 3.85% of hydrogen in argon (total flow of 52 mL min^{-1}) on a 50 mg sample. The temperature was increased at a rate of 15 °C min^{-1} from room temperature to 900 °C. A thermal conductivity detector was used to analyze the effluent gas for a quantitative determination of hydrogen consumption.

The amount of carbon deposited on catalyst after the reactivity tests can be determined by the quantification of the oxidation products (CO_2) observed during temperature programmed oxidation (TPO) by a mass spectrometer (Quadrupole Pfeifer Omnistar). This analysis was performed on a 50 mg sample. After desorption with helium at up to 900 °C with a slope of 15 °C min^{-1} then cooled, an oxidizing gas mixture of 10% oxygen in helium (total flow of 50 mL min^{-1}) passed through the catalyst heated up to 1000 °C with a slope of 15 °C min^{-1}. This technique allows to determine the carbon deposition stability depending on the carbon oxidation temperature.

2.4. Description of the bench scale unit

Continuous catalytic steam gasification of biomass has been performed using a bench scale unit based on the dual fluidized bed (DFB) reactor system (Fig. 1) in a temperature range between 750 °C and 850 °C. This process consists of two bubbling interconnected fluidized beds: the gasifier (0.05 m inner diameter and 0.2 m height) and the combustor reactor (0.08 m inner diameter and 0.1 m height). The gasifier and the combustor were externally heated by furnaces for the start-up of the plant, so as to avoid excessive heat loss and to control the temperature in the reactors more efficiently.

Interconnection of the reactors was made by two loop seals and solid materials circulating between the two reactors. Two different fluidized bed materials (olivine and Fe/olivine) with particle size in the range of 0.1–0.25 mm were used. A test with silica sand was