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Fe/olivine catalyst for biomass steam gasification: Preparation, characterization and testing at real process conditions

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ABSTRACT

Continuous steam gasification of biomass is carried out in a fluidized bed reactor with the utilization of 10 wt%Fe/olivine catalyst. The volume composition of the product gas is analyzed by means of IR, UV and TCD for online detection of CO, CO_2, CH_4, H_2, NH_3 and H_2S.

The results obtained have been evaluated with reference to a blank test (olivine bed inventory) performed with the same experimental rig: when 10 wt%Fe/olivine is utilized in the gasifier, the gas yield increases on average by 40% and the hydrogen yield by 88%. Correspondingly, the methane content in the syngas is reduced by 16% and tar production per kg of dry ash free (daf) biomass by 46%.

10 wt%Fe/olivine characterization after test shows that the catalyst is fairly stable.

1. Introduction

Among different ways technically feasible for biomass energy conversion, gasification is considered a valid process option, to obtain a fuel gas composed of hydrogen and carbon monoxide usable for different applications. More than 70% by weight of biomass produces volatile compounds when it is pyrolysed, and this in fact makes convenient its thermal conversion in a valuable fuel gas that can generate electric power by means of internal combustion engines or fuel cells, with overall process efficiencies ranging from 25% to 40%, in addition to heat.

To increase the efficiency of the utilization of thermal and chemical energy of the produced gas, it is necessary to reform the high molecular weight hydrocarbons (tar), since the presence of tar means lower gas yields. Tar deposition could also block gas coolers, filter elements and engine suction channels, and interferes with catalysts performance [1]. In addition, tar separation is sometimes not as effective as it should be, and originates waste streams difficult to dispose or recycle properly.

The yield of these undesirable gas contaminants can be reduced by careful control of the operating conditions, appropriate reactor design and a suitable gas conditioning system [2].

A large number of investigations deals with biomass gasification in fluidized bed reactors utilizing dolomite ((Ca, Mg)CO_3) or olivine ((Mg, Fe)$_2$SiO$_4$) [3,4]. Olivine, a natural occurring mineral, demonstrates tar conversion activity similar to that of calcined dolomite, with the advantage of higher mechanical strength, and it has been applied as a primary catalyst to reduce the output tar levels form fluidized bed gasifiers [5,6].

The application of Ni/olivine catalysts in steam gasification has been largely investigated, as they are very effective in terms of tar conversion to hydrogen-rich gas [7–9]. The same synthesis methodology can be applied to other transition metals like cobalt, copper or iron.

It has been recently demonstrated that olivine activity, or more specifically olivine activation, depends on its iron oxides content [10]. In fact, depending on olivine temperature treatment, iron can be present in the olivine phase, or as iron oxides [11]. Thus, iron impregnation of natural olivine appears as a 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 lower price in comparison to nickel. Moreover, the fines particles separated from the product gas, can be easily disposed due to the absence of carcinogenic metals such as nickel compounds. A Fe/olivine catalyst has been developed and its activity evaluated in comparison to olivine in steam reforming of toluene (as tar model compound) [12].

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In the present work, a Fe/olivine catalyst with relative high metal content (10 wt%) has been tested at real fluidized bed gasification conditions [12].

Tests with 10 wt%Fe/olivine in the gasifier bed inventory have been carried out to check the gas purity resulting from the effect of cleaning and conditioning the syngas. Comparison with blank tests allows the assessment of 10 wt%Fe/olivine performance against olivine. Instantaneous gas yield and composition, tar content, carbon conversion, etc., have been monitored to characterize each test. Mass balances have been utilized to verify the compatibility and reliability of measured data. The influence of operating parameters has been explored. 10 wt%Fe/olivine has been characterized before and after the gasification tests by X-ray Diffraction (XRD), Temperature Programmed Reduction (TPR) and Temperature Programmed Oxidation (TPO).

2. Materials and methods

2.1. Experimental apparatus and gasification method

Continuous catalytic steam gasification of biomass has been performed using a bubbling fluidized bed gasifier with an internal diameter of 0.10 m, in a temperature range of 800–830 °C.

A sketch of the laboratory gasification plant is reported in Fig. 1. Details concerning the plant configuration have been provided in a previous publication [13].

The gas quality is monitored in terms of gas yield and composition (H_2, CO, CO_2, CH_4, and H_2S) as functions of the operating time, and average tar content.

The biomass feedstock consisted of crushed and sieved almond shells with average particle size of 1054 μm. The elemental analysis of the biomass has been reported elsewhere [13]. The fluidized bed consisted of 3 kg of 10 wt%Fe/olivine catalyst, with an average diameter of 393 μm, and particle density of 2500 kg/m^3. The catalyst particle density has been measured by comparing the bulk densities of the olivine and catalyst particles, assuming the same bulk void fractions.

The overall gasification conditions are reported in Table 1. The fluidizing gas consists of a nitrogen/steam mixture. Nitrogen is supplied to help a smooth feeding of biomass particles and to stabilize the flow. In test IV, nitrogen is supplied at the minimum possible rate (compatible with that needed to assure a smooth biomass feeding rate), in order to obtain the greatest possible concentration of reactants in the gasifier bed.

The biomass feeding rate is kept constant during each test to avoid pressure fluctuations.

At the end of each test, the quantity of char produced by gasification is determined by the analysis of CO_2 and CO in the exit gas obtained by burning under air stream the whole carbonaceous residue trapped into the gasification rig.

2.2. Preparation and characterization of Fe/olivine catalyst

2.2.1. Catalyst synthesis

A sufficient quantity of 10 wt%Fe/olivine catalyst has been synthesized by using an optimized method of impregnation. Iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), in an appropriate quantity to assure an iron content of 10 wt%, was dissolved in an optimized amount of water by heating. About 25 kg of olivine was added to the iron aqueous solution and the water excess was quickly evaporated under vacuum by heating at 90 °C. The sample was dried inside the tank, then overnight inside an extractor hood, before to be calcined at 1000 °C over 4 h (temperature heating rate of 3 °C/min).

In order to validate the synthesis method, characterizations have been performed on the catalyst prepared from large scale synthesis and the results compared to those obtained with the catalyst synthesized at laboratory scale (10 g) [14].

2.2.2. Methods of characterizations

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

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 50 mg of sample. The temperature was increased at a speed of 15 °C min^{-1} from room temperature to 900 °C. A thermal conductivity detector is used to analyze the effluent gas for a quantitative determination of hydrogen consumption.

The amount of carbon deposited on catalyst after 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 50 mg of sample. After desorption with helium until 900 °C with a slope of 15 °C.min^{-1} then cooling, an oxidizing gas mixture of 10% oxygen in helium (total flow of 50 mL min^{-1}) passed through the catalyst until 1000 °C with a slope of 15 °C min^{-1}.

2.3. Characterization and quantitative analysis of tars

At the end of each gasification run, a representative sample of the condensate fraction (tar + water) was filtered using a 0.45 μm pore sizes filter and diluted with high purity distilled water. The Total Organic Carbon (TOC) content was measured injecting the sample in a Shimadzu TOC-VCPN analyzer operating the complete catalytic oxidation at 680 °C. The tar content was then calculated using naphthalene as key component.

In addition, tars condensed in 2-propanol (HPLC grade) according to technical specification CEN/TS 15439 were characterized by means of HPLC technique. The system was equipped with an UV detector (Hitachi UV-detector L2400) set at 254 nm. The chromatographic column used was a reversed phase C18, 150 mm × 4.6 mm (Alltech "Apollo C18 5 μm"), protected with a guard column. Pure standard compounds were used to confirm the identification and also to quantify tars by external calibration. Standards of phenol (ph-OH), toluene (Tol), styrene (Sty), indene (Ind), naphthalene (Naph), byphenyl (Bph), diphenyl ether (DphE), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla) and pyrene (Pyr) were provided from Acros Organics (Geel, Belgium). Additional details of the method used are reported in a previous publication [15].

3. Results and discussion

3.1. Characterization of Fe/olivine catalyst

Fig. 2 compares the X-ray diffraction patterns of 10 wt%Fe/olivine catalyst synthesized at laboratory scale (10 g) with three different 10 wt%Fe/olivine catalysts synthesized in large scale (25 kg). Olivine ($(Mg,Fe)_2SiO_4$) structure is the major crystalline phase for the iron catalysts. The presence of iron is indicated by the spinel phase rays (meaning Fe_3O_4 and $MgFe_2O_4$ at $2\theta = 30.19°$, $35.59°$ and $43.22°$) and iron oxide phase Fe_2O_3 at $2\theta = 33.11°$ and $40.82°$. These phases are already present in the olivine mineral (about 7 wt% of iron), and appear here amplified due to the addition of 10 wt% of iron and calcination at 1000 °C. Distinction between iron oxide phase Fe_2O_3 and $MgFe_2O_4$ has been performed by Mössbauer spectroscopy [16]. The presence of an enstatite phase ($MgSiO_3$) at $2\theta = 31.1°$ is due to the reaction of amorphous silica with MgO [11]. Those phases are observed for