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Ilmenite as low-cost catalyst for producer gas quality improvement from a biomass pilot-scale gasifier

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Abstract

In this work, in-situ application of natural occurring ilmenite (FeTiO₃) for upgrading the producer gas from a pilot-scale bubbling fluidized bed gasifier was performed and its influence on the gas characteristics and gasifier performance was analyzed.

Without using ilmenite, the producer gas average composition (volumetric basis, dry gas) was 15.2% CO, 7.6% H_2 , 3.8% CH₄ and 15.6% CO₂, with 0.50 H_2 :CO molar ratio and 5.0 MJ/Nm³ lower heating value. For this condition, 1.6 Nm³ gas/kg biomass (dry basis) specific dry gas production, 44.5% cold gas efficiency and 68.4% carbon conversion efficiency were attained.

Using ilmenite as catalyst, the producer gas average composition (volumetric basis, dry gas) was 13.9% CO, 11.7% H_2 , 4.0% CH₄ and 17.9% CO₂, with 0.84 H_2 :CO molar ratio and 5.1 MJ/Nm³ lower heating value. For this condition, 1.7 Nm³ gas/kg biomass (dry basis) specific dry gas production, 49.8% cold gas efficiency and 75.5% carbon conversion efficiency were attained. Thus, in-situ application of ilmenite generally improved the gasifier performance and induced an increase of H_2 concentration and H_2 :CO molar ratio in the producer gas of 35.1% and 40.7%, respectively, improving its suitability for advanced gas applications that require high H_2 :CO ratios, such as liquid fuels and chemicals synthesis.

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Keywords: Biomass; Bubbling fluidized bed; Catalyst; Gasification; Ilmenite

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Nomenclature	
$V_{ m G}$	Dry gas volumetric flow rate (N m ³ /s, where N m ³ refers to m ³ at normal pressure (1.013 \times 10 ⁵ Pa) and temperature (273 K))
m _F	Biomass (dry basis) mass flow rate (kg dry basis/s)
LHV _G	Lower heating value of the dry gas produced (MJ/N m ³)
m _F	Biomass (dry basis) mass flow rate (kg dry basis/s)
LHV_F	Lower heating value of the biomass (MJ/kg dry basis)
P _G	Absolute pressure (Pa) of the dry gas
T _G	Absolute temperature (K) of the dry gas
R	Ideal gas constant (8.314 J mol ⁻¹ K^{-1})
M _C	Molar mass of Carbon $(12 \times 10^{-3} \text{ kg/mol})$
Index I	Gaseous compound CO ₂ , CO, CH ₄ , C ₂ H ₄
$\varepsilon_{\mathrm{C,I}}$	Molar fraction of Carbon in gaseous compounds containing Carbon ($\varepsilon_{C,CO2} = 1$, $\varepsilon_{C,CO} = 1$,
	$\varepsilon_{C,CH4} = 1, \ \varepsilon_{C,C2H4} = 2)$
yi	Molar fraction of CO ₂ , CO, CH ₄ , C ₂ H ₄ , in the dry gas produced
$w_{ m CF}$	Mass fraction of Carbon in the biomass (kg C/kg biomass dry basis).

1. Introduction

Energy plays a vital role in the modern society, being essential for economic development and life quality. However, the current worldwide energy supply mainly relies on fossil fuels, resulting in its excessive extraction and consumption. Furthermore, continuous industrialization, population growth and general increase of life quality, increased the worldwide energy supply necessities in the last decades. These behaviors led to negative economic and environmental consequences, being responsible for the depletion of underground carbon resources and emission of large amounts of greenhouse gases (e.g. CO_2) [1]. Thus, the search for alternative fuels that allow sustainable development has been growing, reflected by a significant increase in renewable energies production in the last years [2].

Bearing this, bioenergy is considered as one of the most important routes to mitigate greenhouse gas emissions and replace fossil fuels [3]. Biomass is considered an adjustable and sustainable renewable feedstock to produce energy and chemicals, with the capacity to increase the worldwide energy supply security.

Gasification, which is recognized as a key process for biomass conversion, provides high flexibility by using different kinds of feedstock materials to generate a gaseous product that can be used in distinct applications [3,4]. The process is defined as the thermochemical conversion of organic material (solid or liquid) into a combustible gas mixture, under reducing conditions.

The gaseous product from biomass gasification, after the required refinement and upgrading, can provide different kinds of chemicals and energy carriers [5]. For example, the gas can be applied in direct combustion systems, gas engines and turbines, fuel cells and combined heat and power processes. Methanol [6], dimethyl ether [7], methyl tertiary butyl ether, formaldehyde and acetic acid are commonly referred as obtainable products from this gas [8]. The Fischer–Tropsch process can also be employed to produce synthetic fuels from this gaseous product, such as gasoline and diesel [9].

Nonetheless, even though this conversion process potential is recognized for several applications, some barriers must still be overcome for the general commercialization of biomass gasification technologies, such as the subpar quality of the producer gas (obtained by direct gasification with air), which is diluted in nitrogen and may contain high amounts of tars and low H_2 :CO molar ratios [10].

In this regard, catalysts can be applied as primary measures (inside the gasification reactor) or secondary measures (in a post-gasification reactor), to improve the producer gas quality by reforming tar on the catalyst surface, leading to higher contents of hydrogen in the gas.

In this work, natural occurring iron-titanium mineral (FeTiO₃, ilmenite) is applied as primary measure to upgrade the raw gas quality in a novel reactor configuration developed here and previously described [10] and its impacts

on the producer gas quality and gasification process efficiency analyzed. Ilmenite is recognized as interesting for this application due to its mechanical and thermochemical properties at high temperature, catalytic activity for tar reforming and high water-gas shift reaction (Eq. (1)) activity [11,12].

$$CO + H_2O \leftrightarrow H_2 + CO_2$$
 (1)

2. Experimental work

The experimental infrastructure used in this work was previously described [10,13] and includes a pilot-scale bubbling fluidized bed (BFB) reactor with 80 kW_{th}. For testing the ilmenite mineral, a fixed bed reactor was installed in the freeboard of the BFB reactor, just above the bottom bed and biomass feeding location [10]. The operating conditions of the performed experiments are detailed in Table 1. The fuel used was wood pellets, which was characterized in previous works [13].

The effect of the ilmenite mineral in the producer gas properties and gasification efficiency parameters was evaluated based on a comparison between the composition of the gas sampled after passing the fixed bed reactor filled with ilmenite particles and sampled without passing the fixed bed. The experiments were performed during steady-state conditions of operation, in terms of temperature at different locations of the reactor and exhaust gas composition, as previously described in other experimental work performed in this facility [10,13]. An indication of the raw gas quality improvement is obtained by assuming that any increase in the concentration of combustible light gases, such as H_2 , may result from tar destruction reactions promoted by the catalyst [10,14].

Table 1. Pilot-scale gasification experiments and respective operating conditions.

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Experiment	Fuel	Equivalence ratio	Average bed	Biomass feed rate	Air feed rate
reference			Temperature [°C]	[kg/h]	[L NPT/ min]
Without catalyst	Wood pellets	0.26	809	11	200
With catalyst	Wood pellets	0.26	801	11	200

The lower heating value (LHV) of the dry gas produced during the gasification experiments was determined based on the relative abundance of combustible gases components (H_2 , CO, CH₄ and C₂H₄) and their respective LHV (at reference conditions, 273 K and 101 kPa).

The gasification efficiency parameters, namely specific dry gas production (Y_{gas}), cold gas efficiency (CGE) and carbon conversion efficiency (CCE), were determined according to the methodology described in [13], through the following equations [15–17]:

$$Y_{gas} = \frac{V_G}{m_F}$$
(2)

$$CGE [\%] = \frac{V_G \times LHV_G}{m_F \times LHV_F} \times 100$$
(3)

$$CCE[\%] = \frac{V_G \times \frac{P_G}{R \times T_G} \times M_C \times \sum_i \epsilon_{C,i} \times y_i}{m_F \times w_{CF}} \times 100$$
(4)

The crystalline phases of fresh Ilmenite were assessed by powder X-ray diffraction (XRD) (BrukerD8 Advance DaVinci). Diffraction patterns were analyzed using ICDD (International Centre of Diffraction Data, PDF 4). Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) measurements were performed to determine the specific surface area and average pore diameter of the particles.

The XRD patterns indicate ilmenite as the main phase (FeTiO₃) and alumina (α -Al₂O₃), rutile (TiO₂) and mayenite (Ca₁₂Al₁₄O₃₃) as residual phases (Fig. 1). Other relevant characteristics of the fresh ilmenite and the conditions of the catalytic test are shown in Table 2.

3. Results and discussion

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The results presented in this section include the composition of the producer gas in terms of CO₂, CO, CH₄, C₂H₄, C₂H₆, C₃H₈, N₂ and H₂, and determined gasification efficiency parameters, namely LHV, Y_{gas} , CGE and CCE, during direct (air) biomass gasification experiments without and with ilmenite applied as in-situ catalyst (inside the gasifier).



Fig. 1. XRD patterns for ilmenite (α -Al₂O₃ — \bigstar ; SiO₂ — \blacklozenge ; TiO₂ — X; FeTiO₃ — \blacklozenge ; Ca₁₂Al₁₄O₃₃ — \blacksquare).

Table 2. Ilmenite characteristics and test conditions for the fixed bed reactor.

Experiment reference	Catalyst	Particle size [µm]	Apparent density [kg m ⁻³]	Surface specific area $[m^2 g^{-1}]$	Pore diameter [nm]	Bed mass [g]	Average contact time [s]
With catalyst	Ilmenite	<355	2570	0.52	3-4	200	4.7

The produced gas sampled before passing the fixed bed of ilmenite presented the following average composition (volumetric basis, dry gas): 15.2% CO, 7.6% H₂, 3.8% CH₄, 15.6% CO₂, 1.6% C₂H₄, 0.1% C₂H₆ and 0.1% C₃H₈, and a molar ratio H₂:CO equal to 0.50 (Fig. 2). Based on this gas composition, the following process efficiency parameters were determined:



Fig. 2. Composition of the dry gas (H₂, CH₄, CO, CO₂, C₂H₄) for the gasification experiments performed without catalyst and with catalyst.

- LHV = 5.0 MJ/N m^3 ;
- $Y_{\text{gas}} = 1.6 \text{ N m}^3 \text{ dry gas/kg dry biomass};$
- CGE = 44.5%;
- CCE = 68.4%.

The produced gas sampled after passing the fixed bed of ilmenite presented the following average composition (volumetric basis, dry gas): 13.9% CO, 11.7% H₂, 4.0% CH₄,17.9% CO₂, 1.1% C₂H₄ and 0.2% C₂H₆, and a molar ratio H₂:CO equal to 0.84 (Fig. 2). During this experiment, C_3 H₈ was below the detection limit (0.1% volume). Based on this gas composition, the following efficiency parameters were determined:

- LHV = 5.1 MJ/N m^3 ;
- $Y_{\text{gas}} = 1.7 \text{ N m}^3 \text{ dry gas/kg dry biomass};$
- CGE = 49.8%;



Fig. 3. Influence of the ilmenite mineral on the composition (H₂, N₂, CH₄, CO, CO₂, C₂H₄ and C₂H₆) of the dry gas sampled above the surface of the bed, H₂:CO molar ratio, LHV, Y_{gas} , CGE and CCE.

• CCE = 75.5%.

Thus, it can be observed that the ilmenite in-situ application caused a H_2 , CH_4 and CO_2 concentration and H_2 :CO molar ratio increase of 35.1%, 4.6%, 12.8% and 40.7%, respectively, while decreasing CO concentration by 9.4% (Fig. 3). Therefore, the producer gas was refined, presenting higher suitability for advanced gas applications, such as synthetic liquid fuels production through Fischer–Tropsch synthesis, which requires a H_2 :CO molar ratio of at least 0.6 [9]. The observed increase of CO_2 is not desirable; however, it is a minor inconvenient in the face of the higher H_2 :CO ratios attained [9]. In fact, other advanced applications require even higher H_2 :CO molar ratios, for example methanol production (molar ratio equal to 2) and dimethyl ether (DME) production (molar ratio equal to 1) [9,18]. This increase in H_2 :CO molar ratio, as well as the CO_2 increase, can be related to an increase in water-gas shift activity (Eq. (1)) induced by the ilmenite particles. This phenomenon was previously observed in other gasification processes involving ilmenite [12] and is typically associated to iron-based catalysts [11]. Accordingly, significant H_2 :CO molar ratio increases and wood pellets chars, performed in other works here [10].

The ilmenite mineral in-situ application also caused a general increase of approximately 10% for all determined efficiency parameters, except for LHV, which was similar for both experiments (Fig. 3). This similarity is related to the decrease of CO concentration observed in the experiments using ilmenite as catalyst, which accounts for a significant part of the energy content of the producer gas.

4. Conclusions

In this work, the application of ilmenite as low-cost catalyst for the improvement of the producer gas quality was evaluated. The research was focused on the impact of this mineral on the composition of the producer gas, and, consequently, on the efficiency of the gasification process.

The evaluation of the proposed catalytic material was performed by sampling the gas before and after passing a fixed bed of ilmenite inserted 0.2 m above the surface of the bottom bed of the pilot-scale BFB.

The results show that the in-situ application of ilmenite caused a significant H₂ production increase (35.1%) and a slight CO decrease (-9.4%), thus increasing the H₂:CO molar ratio from 0.50 to 0.84. It is also observed a general increase (~10%) in the determined efficiency parameters, such as Y_{gas} , CGE and CCE. The LHV remained almost unchanged, and this can be explained as a result of CO concentration decrease in the producer gas. Thus, it can be concluded that the in-situ appliance of this mineral for the improvement of the producer gas quality was successful. The increase in H₂:CO molar ratio is a promising result, which was not observed during the application of other low-cost catalysts in other works performed here [10], and can be associated to increased water-gas shift activity induced by the ilmenite. This is interesting because several advanced applications, such as liquid fuels and chemicals synthesis, require H₂:CO molar ratios higher than 0.6 [9].

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