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Increasing tar and hydrocarbons conversion by catalysis in bubbling fluidized bed gasifiers

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ABSTRACT

The paper reports on the catalytic gasification of biomass (lignocellulosic) in bubbling fluidized beds. A review of the influence of operating conditions influencing the effectiveness of the catalytic bed is proposed. The concept of a partitioned fluidized bed by introduction of screens in the middle is also introduced and analyzed for its advantages in increasing the contact between tar and catalyst. An experimental test with a partitioned bed proved that the presence of an intermediate screen could affect the tar yield and composition. The catalyst can be present in the bed only partly, as demonstrated by a test with a bed composed of 25% catalyst and 75% inert materials giving similar tar conversion with respect to the 100% catalytic bed. The results obtained during biomass gasification are reported for a bed composed of a novel iron based catalyst. It proved to be a good substitute of Ni-oxide as catalyst for in-bed tar conversion. Furthermore, the novel catalyst is harmless and easily disposable. The iron based catalyst also preserves the content of hydrocarbons in the syngas.

1. Introduction

Gasification processes are widely considered as an effective option for the energetic valorization of biomass and waste at small (<1 MWth) and medium scale (<50 MWth). Different destinations can be envisaged for the producer gas, depending on its characteristics such as: combined heat and power (CHP) generation in IC engines [1], conversion to gaseous fuels (e.g. synthetic methane) for intake into the grid [2], synthesis of liquid fuels via Fisher–Tropsch process [3] and, finally, synthesis or separation of chemicals, like hydrogen and methanol [4]. Tar and heavy hydrocarbons produced during biomass gasification are undesired and dangerous for typical post-process applications (e.g. fuel cells, engines, chemical synthesis). Their cracking or catalytic conversion into H_2, CO and light hydrocarbons is the alternative to wet scrubbing methods.

Fluidized beds (FB) are often preferred for accomplishing biomass gasification, thanks to the flexibility and robustness of this technology [5]. It is also reported that the integration of several functionalities into suitable fluidized bed gasifiers, such as catalytic tar cracking/reforming as well as CO_2 capture is a promising strategy for developing cost-effective high quality syngas, particularly for small to medium-scale installations [6]. In this concern, the research is still looking for effective and reliable materials and plant configurations (e.g. multistage gasifiers).

Nickel is one of the most diffused catalysts for tar and hydrocarbons reforming, and is also used inside FB gasifiers for biomass [7] and plastic/waste [8], although its toxicity calls for use of safer materials. Iron base catalysts could represent an alternative to nickel catalyst. In fact, it is generally accepted that the activity of olivine, a natural catalyst, in tar reforming can be associated with the presence of iron on the surface of the materials [9,10]. It is also reported that the dispersion of iron on olivine improves the performance of olivine [11,12]. Metallic iron and iron oxide catalytically crack the tar produced, resulting in active syngas cleaning [13,14].

Bypass and segregation phenomena [15] affect the contact between syngas and catalyst in the bed. Comparing the performance of the same catalyst in a fixed bed and a bubbling fluidized bed, the result on effectiveness is around 80% [16] in the former, while it deteriorates down to 50% in the latter case [7]. Furthermore, biomass particles (e.g. wood pellets or rods) have a devolatilization time of some dozens [17] that are much higher than their rising time in a bubbling bed [15]. As a consequence, the gaseous species evolving upon fuel devolatilization do not undergo sufficient contact with catalytic particles and the reactor performance declines.

The present paper reports on the influence that operating conditions and some measures can have on the tar conversion in a catalytic fluidized bed. Both theoretical and experimental results are reported and commented on, in particular on the catalyst dilution in the bed, the presence of a screen in the middle, as well as the use of a novel iron based catalyst.

2. Experimental

The experimental activity has been carried out in an atmospheric fluidized bed gasifier. The fluidization column is formed by two vertical

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Table 1
Properties of the fuel (spruce wood pellets).

Fuel	Commercial spruce pellets
Pellets dimensions (diameter x length), mm	6 × 20
Moisture, wt.%	8.5
Volatiles, wt.%	74.1
Fixed carbon, wt.%	17.1
Ash, wt.%	0.3
Carbon, wt.% on dry and ash free basis	49.4
Hydrogen, wt.% on dry and ash free basis	5.9
Nitrogen, wt.% on dry and ash free basis	0.1
Oxygen, wt.% on dry and ash free basis	44.5
Low heating value, MJ/Kg	18.5

stainless steel tubes having different sizes and connected by means of a conical adapter. The lower tube has internal diameter of 140 mm and height of 1010 mm, whereas the upper tube has 200 mm ID and is 1800 mm high. A reverse-cone distributor is installed at the bottom for the fluidization of the bed materials, having certain advantages in bed mixing. The fuel was fed under-bed into the reactor, by means of a screw conveyor, 130 mm above the conical distributor. The fuel flow rate was regulated by means of an additional screw feeder, rotating at changeable rate and directly connected to a sealed fuel hopper. An auxiliary nitrogen stream was used for inertizing the fuel feeding devices and was passed into the gasifier together with the fuel. Further details about the experimental facility can be found elsewhere [7].

Continuous analyzers (ABB) are used for measurements of CO, CO_2, CH_4 and H_2 concentration, upon sampling, filtering and drying. Samples in bags are also taken during a test for further gas-chromatographic analysis. Tars are isokinetically sampled inside the reactor, by means of a probe connected to a volumetric pump (Zambelli PF 12000-02). The tars are collected in three bottles at −20 °C. The collected samples are treated with dichloromethane for water separation; the separated water fraction is weighed and, in turn, the amount of the tar fraction is calculated by difference. Finally, the tars are subjected to gas-chromatographic characterization. Due to a chain of steps the precision of the gravimetric determination of tar is ±10%.

An iron catalyst (Fe-cat) was prepared by wet impregnation by dissolving the given amount of iron nitrate $Fe(NO_3)3°9\ H_2O$ (98 +%, Sigma-Aldrich) in aqueous solution and adding a suitable amount of high mechanical resistance γ-alumina (PURALOX SCCA-150/200, Sasol). The particle size is 150 μm, the particle density is 1800 kg/m^3, the minimum fluidization velocity U_{mf} and the terminal velocity U_t, calculated with standard correlations of fluidization [18], are 0.006 and 1.1 m/s, respectively. The impregnation process did not significantly alter such properties of the support. The metallic iron content in the catalyst was 2.9 wt.%, as determined by ICP-MS analysis carried out by using an Agilent 7500CE instrument after dissolving the sample in HCl/HNO_3 solution at 80 °C. The redox behavior of the catalyst has been determined by performing H_2 temperature programmed reduction (TPR) tests with a Micromeritics 2900 TPD/TPR analyzer. The TPR measurements consisted in the reduction of the catalyst with a 2% H_2/Ar mixture (25 ml min^{-1}) at 10 °C min^{-1} up to 800 °C. The catalyst was pre-treated 1 h in air (100 ml/min) at the calcination temperature before the experiment.

Table 2
Effect of the operating conditions on tar removal by in-bed catalysis.

Temperature	High
Equivalence ratio	High
Steam/fuel ratio	Moderate (asymptotic)
Fluidization velocity	High
Bed height	Moderate (asymptotic)
Bed dilution	Low
O-bed vs. U-bed	High/moderate

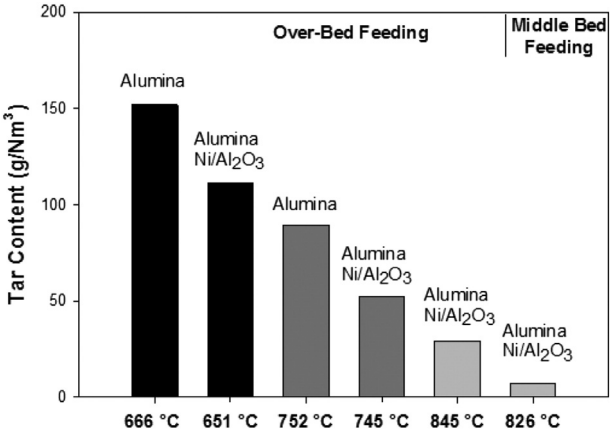

Fig. 1. Tar content at different temperatures, bed feeding position and bed material composition.
Courtesy of Brachi et al. [4].

Commercial pellets (spruce wood) were used as fuels for steady state gasification tests with feeding rate in the range 3–5 kg/h. The properties of the fuel are reported in Table 1. The other operating conditions were: bed temperature 780–810 °C; equivalence ratio 0.17; steam/fuel ratio 0.65; fluidization velocity 0.17–0.40 m/s, static bed height 0.16 m (above the cone).

3. Effect of operating conditions and reactor design

Table 2 summarizes the effect of the operating conditions on tar catalytic tar conversion in a bubbling fluidized bed containing a suitable catalyst, e.g. NiO. The qualitative trend are derived by reviewing the results on catalytic gasification obtained in the same experimental facility [7]. Tar conversion is strongly enhanced by increasing the bed temperature T, as clearly shown in Fig. 1, where results of different tests are compared for a non catalytic and catalytic bed. At temperatures higher

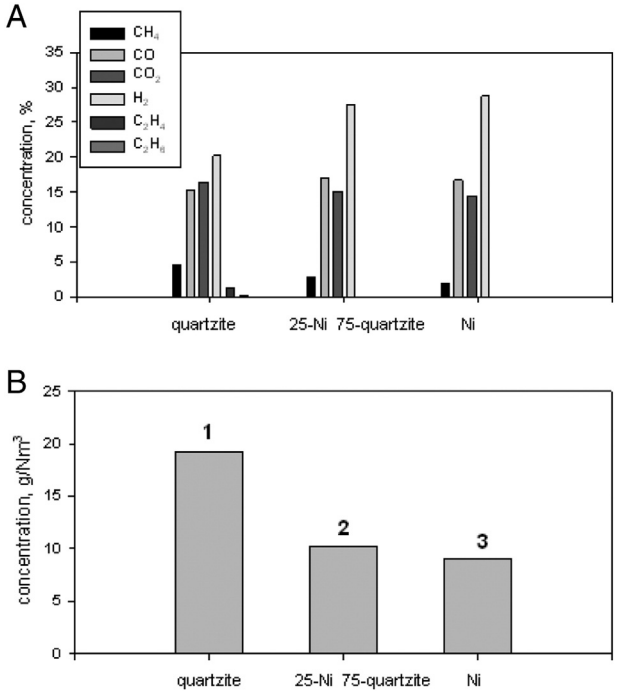

Fig. 2. Comparison of gas composition (A) and tar concentration (B) for three tests carried out at the same operating conditions with: 1) quartzite bed (Miccio et al. [7]), mixed bed (75% quartzite–25% Ni catalyst by mass), 3) Ni catalyst (Miccio et al. [7]). Fuel = wood pellets; T=780 °C; U = 0.3 m/s; ER = 0.17; steam/fuel ratio = 0.64.