



Steam gasification of biomass in a conical spouted bed reactor with olivine and γ -alumina as primary catalysts



Aitziber Erkiaga, Gartzten Lopez, Maider Amutio, Javier Bilbao, Martin Olazar*

Department of Chemical Engineering, University of the Basque Country UPV/EHU, P.O. Box 644-E48080 Bilbao, Spain

ARTICLE INFO

Article history:

Received 25 April 2013

Received in revised form 28 June 2013

Accepted 17 July 2013

Available online 22 August 2013

Keywords:

Steam gasification

Tar cracking

Biomass

Spouted bed

Olivine

γ -alumina

ABSTRACT

Olivine and γ -alumina have been used as primary catalysts for tar elimination in the continuous steam gasification of pine wood sawdust in a bench-scale plant provided with a conical spouted bed reactor. A comparison of the performance of each catalyst with that observed for a bed made up of inert silica sand shows that both catalysts have a significant activity for tar cracking/reforming, given that the amount of tar obtained by operating with beds of inert sand is reduced by 79% and 84% when olivine and γ -alumina are used, respectively. The tar cracking reduces selectively the content of light and heavy PAHs, giving way to an increase in the concentration of light aromatics. Furthermore, both catalysts cause a positive effect on the gas composition by slightly enhancing the water–gas shift and reforming reactions.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The valorization of lignocellulosic biomass (available and widespread renewable source) by means of thermochemical and catalytic processes is one of the most promising alternative to fossil fuels, given that it does not contribute to a net rise in the level of CO₂ in the atmosphere [1]. The biomass gasification process takes place at high temperatures (generally in the 600–900 °C range or even higher) in the presence of a gasifying agent (air, oxygen, steam, CO₂, or mixtures of these components) and allows obtaining a gaseous stream composed mainly of permanent gases (CO, H₂, CO₂, CH₄, H₂O and N₂ when air is used as an oxidizing agent). This gas can be used as fuel (contains 70–80% of the original biomass energy) and/or feedstock for the production of liquid fuels and raw materials by means of catalytic processes of increasing industrial implementation such as Fischer Tropsch and DME synthesis [2–4]. In the DME synthesis the interest is centered on the incorporation of CO₂ in the feed with the biomass derived syngas [5–7].

However, a fraction of the biomass (around 10 wt.%, depending on gasification conditions and biomass type) remains as carbonaceous solid residue (char) or is transformed (mainly during the devolatilization process prior to gasification) into a complex mixture of volatile organic compounds (tar), which include aromatic and heterocyclic species as well polycyclic aromatic compounds (PAHs) [8]. Furthermore, ashes (derived from char gasification) and N, S and Cl containing compounds (such as NH₃, HCN, H₂S and Cl) are also formed. Consequently, the gas requires complex purification steps (accounting for 50% to 75% of the

overall cost) in order to meet specifications. These specifications become particularly restrictive for applications involving the catalytic conversion of syngas into fuels [9] and for highly efficient solid fuel cells (SOFCs) [10]. The main challenge for the valorization of syngas lies in its tar content, which condenses or polymerizes below 300 °C, leading to the fouling, corrosion and blocking of pipes, heat exchangers and particle filters, thus causing a reduction in the process efficiency. Moreover, tars are dangerous due to their carcinogenic nature and contain a significant amount of energy that may be transferred to the syngas.

Measures to avoid tar formation are essential and, accordingly, several reviews deal with the strategies for the production of a tar free syngas [11–16]. These strategies can be gathered into two groups: i) primary, by reducing or limiting the tar formation in the gasifier; ii) secondary, by cleaning the gaseous product at the outlet of the gasifier, which may involve physical (wet scrubbing, filtration, electrostatic precipitation), thermal and/or catalytic processes.

The main advantages of using steam as gasifying agent lie in the production of a syngas with a high hydrogen concentration, nitrogen free and high heating value (>10 MJ m⁻³). Different reactor configurations are commonly used for the steam gasification of biomass, which according to their hydrodynamic behaviour can be classified as follows: fixed bed, fluidized bed, moving/downdraft and updraft [17,18]. Fluidized beds are the most commonly used [19–26], with their main advantages being: i) isothermal bed with a suitable temperature control (generally below 900 °C) and vigorous particle movement that avoids bed agglomeration due to ash melting; ii) high heat transfer rate (crucial for this endothermic process) enhanced in dual fluidized beds with heat recovery by external combustion of the char [21]; iii) suitable for scaling up the process and co-feeding the biomass with other materials (coal,

* Corresponding author. Tel.: +34 946012527; fax: +34 946 013 500.
E-mail address: martin.olazar@ehu.es (M. Olazar).

plastics and waste tyres) [25,27–30]. The main drawback is the incomplete conversion of biomass due to the solid mixing regime that needs a continuous char removal from the reactor, which limits the valorization of the carbon and hydrogen contained in the biomass.

A previous paper dealing with the biomass steam gasification in a conical spouted bed reactor (CSBR) in the 800 to 900 °C range reports the advantages of the gas–solid contact regime in the spouted bed reactor compared to the bubbling fluidized bed [31]. The vigorous cyclic movement of the particles in the CSBR allows handling solids of irregular texture, as is the case of biomass particles. Moreover, the sand/biomass ratio in the bed for suitable fluidization is lower than in fluidized beds and, therefore, the biomass mass flow rate per reactor volume unit is higher. Versatility in the gas flow rate is also noteworthy, which allows operating from the minimum spouting regime to a very dilute spouting regime [32,33]. The excellent performance of the CSBR has allowed the development of the biomass pyrolysis process up to a unit of 25 kg/h [34–37].

The solid circulation flow rate attained in these beds avoids agglomeration and defluidization problems caused by ash melting and allows handling mixtures of solids of different density and particle size [38,39]. This feature is especially interesting for operating with catalysts in situ, as has been proven in the catalytic pyrolysis of tyres [40,41] and polyolefins [42,43]. Furthermore, the CSBR has also been used in the steam gasification of polyolefins [44].

In order to gain knowledge on the possibilities of the CSBR for the steam gasification of biomass, this paper addresses this process on olivine and γ -alumina as primary catalysts. Given the high heat transfer rates between phases, steam gasification may be carried out using coarse sawdust (2–4 mm) without limitation in the syngas yield. However, the short residence time (centiseconds) gives way to high tar yields [31]. The use of primary catalysts instead of sand is the easiest way to reduce tar formation and improve process efficiency. The results presented are the basis for future studies aimed at the development of the CSBR technology for biomass gasification following more expensive and complex strategies, such as the application of reforming catalysts. Olivine (crystalline magnesium and iron silicate, $(\text{Fe}_x\text{Mg}_{1-x})_2\text{SiO}_4$) is regarded as a suitable primary catalyst because it is an inexpensive mineral with excellent mechanical properties (harder than dolomite) and with a significant reforming capacity [45–48]. γ -Alumina has also a considerable mechanical strength and a significant tar cracking capacity, mainly due to the presence of Lewis acid sites promoted by the use of steam as gasifying agent [49,50].

2. Experimental section

2.1. Biomass properties

The biomass used in this study is forest pine wood (*Pinus insignis*), which has been crushed and ground to a particle size below 4 mm. The sawdust has been sieved to obtain three different fractions, 0.3 to 1 mm, 1 to 2 mm and 2 to 4 mm. This material has been dried to a moisture content below 10 wt.%. Ultimate and proximate analyses have been carried out in a LECO CHNS-932 elemental analyzer and in a TGA Q500IR thermogravimetric analyzer, respectively. The higher heating value (HHV) has been measured in a Parr 1356 isoperibolic bomb calorimeter. The main characteristics of the raw biomass are summarized in Table 1.

2.2. Catalytic materials

The γ - Al_2O_3 has been provided by Alfa Aesar and the olivine by Minelco. Both materials have been ground and sieved to the desired particle diameter, 0.4–0.8 mm in the case of γ - Al_2O_3 and 0.35–0.4 mm the olivine. Olivine has been calcined at 900 °C for 10 h prior to use in the gasification reaction to enhance its reactivity for tar cracking. The conditions mentioned for olivine calcination have been determined as optimum by Devi et al. [45] in order to maximize tar cracking activity.

Table 1
Pine wood sawdust characterization.

<i>Ultimate analysis (wt.%)</i>	
Carbon	49.33
Hydrogen	6.06
Nitrogen	0.04
Oxygen	44.57
<i>Proximate analysis (wt.%)</i>	
Volatile matter	73.4
Fixed carbon	16.7
Ash	0.5
Moisture	9.4
HHV (MJ kg ⁻¹)	19.8

The BET surface area has been measured by N₂ adsorption–desorption (Micromeritics ASAP 2010). Calcined olivine has a limited porosity, with a surface area of only 0.18 m² g⁻¹. However, γ - Al_2O_3 has a much higher porous development, reaching a surface area of 159 m² g⁻¹.

2.3. Equipment

Steam gasification runs have been carried out in a bench scale plant, whose scheme is shown in Fig. 1. The main element of the plant is the conical spouted bed reactor (CSBR) whose design is based on previous hydrodynamic studies [51] and on the application of this technology to the pyrolysis of different solid wastes, such as biomass [35,36], plastics [52] and waste tires [53].

The reactor is located within an oven which is in turn placed in a forced convection oven maintained at 270 °C to avoid the condensation of steam and tars before the condensation system. This forced convection oven contains a high-efficiency cyclone and a sintered steel filter (5 μm) for retaining the fine sand particles entrained from the bed and the soot or char particles formed in the gasification process.

The plant is provided with a system for continuously feeding biomass. The system for solid feeding consists of a vessel equipped with a vertical shaft connected to a piston placed below the material bed. The sawdust is fed into the reactor by raising the piston at the same time as the whole system is vibrated by an electric engine. A very small nitrogen flow rate introduced into the vessel stops the volatile stream entering the feeding vessel. The sawdust feed rate can be varied from 0.2 to 3 g min⁻¹. The pipe that connects the feeding system with the reactor is cooled with tap water to avoid the degradation of the biomass and blocking the system.

Water has been fed by means of a Gibson 307 pump that allows a precise measuring of the flow rate. The water stream has been vaporized by means of an electric cartridge (not plotted in Fig. 1) placed inside the forced convection oven and prior to the entrance of the reactor. Moreover, N₂ is used as fluidizing agent during the heating process and its flow rate is controlled by a mass flow controller that allows feeding up to 20 L min⁻¹. The plant is also equipped with an additional mass flow meter (20 L min⁻¹) for measuring air flow rate.

The gases leaving the forced convection oven circulate through a volatile condensation system consisting of a condenser, Peltier cooler that reduces the temperature to approximately 0 °C and a coalescence filter. The condenser is a double-shell tube cooled by tap water. The coalescence filter and the Peltier cooler ensure the total condensation and retention of the tars.

2.4. Reactor

Fig. 2 shows the dimensions of the reactor. The bed is stable in a wide range of gas flow rates, from the regime of incipient spouted bed to the vigorous regime of jet spouted bed (or dilute spouted bed) [51]. Despite the endothermic nature of the steam gasification process, the isothermicity of the bed is ensured by the vigorous solid circulation of the sand that is characteristic of the CSBR, which also

Download English Version:

<https://daneshyari.com/en/article/6657390>

Download Persian Version:

<https://daneshyari.com/article/6657390>

[Daneshyari.com](https://daneshyari.com)