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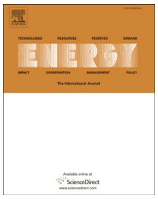

Low-cost catalysts for in-situ improvement of producer gas quality during direct gasification of biomass

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ABSTRACT

In this work, the concept of biomass direct (air) gasification was demonstrated in a pilot-scale bubbling fluidized bed and the influence of in-situ application of low-cost catalytic materials on the produced gas characteristics and gasifier performance was analyzed. Three different low-cost catalysts were tested: bottom bed ashes resulting from combustion of residual forest biomass derived from eucalyptus, char particles resulting from wood pellets direct (air) gasification, and synthetic fayalite (Fe_2SiO_4). Without using catalysts, the produced gas composition was 7.7–16.9%v CO, 3.2–8.3%v H_2, 0.5–3.4%v CH_4 and 9.5–14.6%v CO_2, with 2.4–4.3 MJ/Nm^3 lower heating value, specific dry gas production between 1.0 and 1.8 Nm^3 dry gas/kg biomass (dry basis), cold gas efficiency between 13.7 and 30.5% and carbon conversion efficiency between 30.7 and 50.9%. With the use of catalysts, the produced gas composition was 14.2–37.6%v CO, 9.5–14.7%v H_2, 2.6–3.5%v CH_4 and 3.6–14.8%v CO_2, with 3.9–6.3 MJ/Nm^3 lower heating value, specific dry gas production between 1.4 and 2.0 Nm^3 dry gas/kg biomass (dry basis), cold gas efficiency between 38.1 and 66.3% and carbon conversion efficiency between 56.8 and 86.6%. The highest increase in H_2 concentration (352% increase) was observed on experiments using wood pellets char as catalyst while the highest increase in CO (305% increase), lower heating value (123% increase), specific dry gas production (62% increase), cold gas efficiency (262% increase) and carbon conversion efficiency (174% increase), was observed on experiments using synthetic Fe_2SiO_4 as catalyst.

1. Introduction

Several thermochemical processes are available for heat and power production from biomass, amongst which combustion is the most widely used [1]. However, biomass gasification is gaining interest worldwide due to the process flexibility and the need of renewable fuels that can replace gaseous fossil fuels in distinct applications. Gasification is a promising alternative to direct biomass combustion due to the recognition that combustible gases have practical advantages over solid fuels, such as handling and application [2,3]. Different types of biomass can be converted by gasification into a fuel gas containing mainly hydrogen, carbon monoxide, carbon dioxide and methane and, from this gas, it is possible to produce heat, power, biofuels and chemicals [4,5]. Gasification of biomass is recognized as a partial solution to diverse environmental problems and societal needs, with emphasis on greenhouse gases accumulation in the atmosphere, fossil fuel depletion and waste disposal [6]. This process has the potential to partly replace the use of fossil fuels through liquid fuels/chemicals production, integrated gasification combined cycles for electricity/steam production, producer gas combustion in gas-fired kilns and furnaces and production of hydrogen-rich syngas and synthetic natural gas. Thus, biomass gasification technologies are expected to have an important role in future energy systems [2–4,7–14] and to be the basis of potential future biorefineries that will provide a variety of chemicals and energy products [14], including electricity and transportation fuels.

In addition to these advanced applications, which are

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particularly suitable for developed countries, biomass gasification can also meet the rural electrification and thermal needs of developing countries, mainly those with a high share of solid biofuels in their energy mix [5,15,16]. In fact, in developing countries with intense agricultural activities, and, consequently, strong potential for power generation from agricultural byproducts and wastes, such as rice husk [17], sugar cane bagasse [18] or almond shell [19], biomass gasification technologies have been considered of particular interest [15]. This interest is increased when considering integrated gasification combined cycles technologies which allow high efficiencies in electricity generation (about 40%) [20–22]. In developed countries, thermochemical conversion of biomass by gasification has been emerging as a suitable CO_2-neutral energy conversion process capable of providing distinct energy carriers [4,5]. This is important due to the imposed need to reduce CO_2 emissions from fossil fuels consumption [5], coupled to an increased necessity of biomass wastes valorization [23] and energy supply security. However, critical drawbacks associated to the use of biomass, such as its availability as energy resource and the impacts of energy crops [24,25], must also be taken in account. It has been argued that pressure on land will increase strongly under a growing biomass to energy demand, which can lead to adverse effects on biodiversity [24], and there exists resistance against the use of existing arable land to produce biomass instead of food, due to indications on endangerment of food security, especially in third world countries [26], as well as concerns regarding water scarcity [25]. Nonetheless, several studies propose that it is possible to sustainably increase biomass production if additional measures are provided, such as integrated policies for energy, land use and water management [25,27–30]. In fact, the European Union forest grew approximately 2% over the past decade [27]. Process efficiency and wastes valorization is also important in this context. For example, wood residues from industrial processes (e.g., small sawmills) can be efficiently used for power generation if integrated energy systems can be conceived [31], thus being an alternative to energy crops and respective land use needs. Another relevant drawback is related to the uncertainties regarding biomass stocks availability and prices and long-term national and European energy and climate policies. Unpredictable changes in energy policies or biomass availability can turn a current attractive biomass to energy conversion solution to a considerably expensive one in the future.

Furthermore, even though biomass gasification advantages are widely recognized and research on biomass gasification is not recent, being that industrial biomass gasifiers and commercial/demonstration plants have been developed in the past decades [1,6,8,32–34], it is acknowledged that some barriers must still be overcome in order to allow a commercial breakthrough of biomass gasification technologies. Gasification technologies for heat production are commercially available and deployed but their current application is scarce [35]. CHP gasification exists in the market, but its deployment is limited due to high costs and critical operational demands [35]. Gasification using integrated combined cycles, namely biomass integrated gasification/combined cycle (BIG/CC) for electricity production, has potential but is currently at a demonstration phase [35,36]. Several specific applications are also under demonstration/research phase, for example, integration in the pulp and paper industry [37–39], production of biofuels to offer small communities means to cover their energy demand for public transport by using local biomass feedstocks [16], production of electricity in agricultural intensive countries [15], production of oxymethylene ethers for blending with conventional diesel fuels [40–42], production of biomethane [43], solar-biomass power generation integrated with a gasifier [44], bio-oil gasification to act as bridge between bio-oil and transportation fuels [45], among several others [4,9,16,46–49]. Biomass gasification is a complex process in nature, with many reactants and many possible reaction paths, leading to difficult operation and variable gas composition. Thus, biomass gasification technologies are limited by diverse technological and operational aspects and are dependent on public and policy support [4,5,50]. Recognized drawbacks that need to be solved are related to difficulties regarding the control of the composition of the produced gas, heterogeneous composition and availability of biomass [10,51,52], environmental and safety questions [8,53], inorganics effect on the process performance, including agglomeration, fouling and corrosion problems [20], and, most importantly, the tars present in the produced gas [4,5,8,10,12,51,54–58] and the uncertainties regarding its cleaning and upgrading for downstream applications [5,8,10,11,51,59]. These issues, regardless of the current availability of vast literature on biomass gasification and the technological advances made [34], have not been overcome and are the reason behind the lack of commercial biomass gasification designs with economic competitiveness [5,11,54]. Thus, the application of this process at industrial scale is difficult [54,57], and, therefore, it is currently confined to specific applications and niche markets [5].

Tars present in the produced gas are recognized as the main technological barrier to the development and implementation of biomass gasification at industrial scale [2,4,10,12,49,54–58]. Tars are mainly aromatic compounds (e.g. phenol, toluene, naphthalene, oxygenated hydrocarbons) formed during biomass pyrolysis whose amount depend on diverse conditions, such as the type of gasifier. For sufficiently long reaction times, chemical equilibrium is reached and the products are mostly limited to light gases, however, gasifier temperatures and residence time are usually not enough to attain chemical equilibrium, and, therefore, the produced gas contains large amounts of tars [14]. In fluidized beds, which are a technology recognized as capable to offer a good performance in biomass gasification, average tar concentration is usually around 1–30 g/Nm^3 [60]. Unfortunately, this concentration is too high for most raw gas applications [61–63] because tar condenses at relatively high temperatures [64]. Tar removal technologies can be broadly divided in primary measures (inside the gasification reactor) and secondary measures (downstream the gasification reactor) [61]. Several types of these measures have been developed and are under research in order to improve the raw gas quality through the decrease of the tar content [1,4,12,61,62,65–68]. Primary measures are interesting because they eliminate the need of downstream clean-up, however, they are not fully understood and still lack commercial implementation [61]. Primary measures consist mostly in changes in the operating parameters, such as the equivalence ratio, changes in the reactor design and in the usage of bed additives/catalysts [61].

Catalysts can be used as primary measure, when for example mixed with the biomass feed prior to gasification [69] or used as bottom bed material [70], and as secondary measure when placed in a post gasification reactor [12,68]. When the produced gas passes over catalyst particles, tar can be reformed on the catalyst surface with either steam or carbon dioxide, thus producing additional hydrogen and monoxide carbon [71]. Even though primary measures for tar removal are considered more promising, research has been more focused on applying catalysts as secondary measure [1,4,12,61,62,65–67], due to the catalysts tendency to deactivate by carbon deposition, contamination (sulphur, chlorine, alkalis, etc.), microstructural changes, erosion related problems, etc., when inserted inside the gasification reactor [68].

In this work, an alternative configuration for studying primary tars destruction measures using catalysts is proposed and analyzed. A small fixed bed reactor filled with catalyst materials was integrated on the high temperature region of the bubbling fluidized bed (BFB) freeboard, just above the bottom bed. The raw gas was