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Hot treatment and upgrading of syngas obtained by co-gasification of coal and wastes

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ABSTRACT

Nowadays there is a great interest in producing energy through co-gasification of low grade coals and waste blends to increase the use of alternative feedstocks with low prices. The experimental results showed that the viability of co-gasification to process such blends and that by the right manipulation of coal and biomass or waste blends, syngas treatment and upgrading may be simplified and the cost of the overall process may be reduced. Blends of three different coal grades (sub-bituminous coal from Puertollano mines, South African bituminous coal and German brown coal) with two different types of biomass (pine and olive oil bagasse) or polyethylene (PE) were co-gasified. Blend co-gasification showed to be beneficial to reduce the negative characteristics of some coals, such as the high ash and sulphur contents, especially of Puertollano coal. Syngas obtained by these blends was hot cleaned and undesirable syngas components (tar, NH_3 and H_2S) were measured along the hot treatment tested, which proved to be suitable to treat syngas produced by a wide range of feedstocks. Different routes for syngas cleaning were analysed to reduce unsuitable components to values required by most common end-uses. The results obtained showed that the type of feedstock to be gasified is a key outcome on initial syngas composition, affecting greatly syngas cleaning needs, its application and the economic viability of the overall process.

1. Introduction

Gasification is an effective process to obtain a synthetic gaseous fuel from carbonaceous materials. This gas is usually named as syngas, because besides being used for energy production, it may also be converted into synthetic fuels either liquids (ethanol, methanol, gasoline, gasoil) or gaseous such as: dimethyl ether and SNG (synthetic natural gas). Gasification may also act as a pre-combustion carbon capture technology, as syngas may be converted into a CO_2 stream ready for storage and into a hydrogen rich fuel. Gasification has high efficiency, low negative environmental impact and produces a gas with a wide range of applications [1].

Gasification was first developed for coal and it has also been widely studied for biomass conversion into syngas. The need of using low grade coals and wastes for energy production has led to the study of carbonaceous material co-gasification, especially blends of coal with biomass and wastes, with the aim of using existing installations to process coal with diversified feedstocks.

Besides the feedstock diversification, co-gasification of coal and biomass has the advantage of decreasing the use of fossil fuels and of reducing CO_2 emissions, due to biomass carbon bio origin [2]. Biomass or other wastes with lower mineral contents than coal might also dilute the negative characteristics of some coals, like lower volatile matter contents, high ash content and high contents of S, N, halogens and heavy metals. Hence, the technical and economic viability of low grade coal gasification might be increased. However, the choice of the wastes to use should be carefully done, to decrease the negative bearing of some coals and avoid additional problems during syngas cleaning and upgrading processes.

The formation of undesirable compounds like: H_2S, HCl, NH_3, alkali metals, particulates and tar has been studied by several authors during gasification and co-gasification processes [1–11]. Syngas desulphurization, both during gasification and during syngas cleaning procedures was reviewed by Meng et al. [2] and Cheah et al. [5] who analysed several types of sorbents based on zinc, copper, iron, calcium, manganese, and ceria for syngas desulfurization. Mid- to high-temperature sulphur sorbents for desulphurization of biomass and coal-derived syngas were also studied by Ohtsuka et al. [6], namely TiO_2-supported $ZnFe_2O_4$ sorbent. Different sorbents have also been studied by Dooley et al. [7] and Cheah et al. [8]. Xu et al. [9] reviewed recent developments on catalysts for tar and ammonia abatement and Ohtsuka et al. [6] also studied new catalysts for the decomposition of 2000 ppm NH_3 in a syngas at 750 °C. Ni-based catalysts have shown high activities for tar and ammonia decomposition, especially when used as secondary catalysts [3,10]. However, better performances in ammonia conversion have been obtained with several precious metal catalysts on modified zirconia (Rh, Ni, Pd, Ir, Ru, and Pt) as reported by Rönkkönen et al.

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[11]. But the high cost of some of these catalysts makes their use at large scale prohibitive. Another option is the use of multifunctional catalyst or sorbents that allow the reduction of several adverse components in syngas, though the technical advantages of such materials, the economic viability of the overall process still needs to be proven.

The use of efficient catalysts inside the gasifier is usually prohibitive, because of the high catalyst cost and its fast deactivation, due to the adverse conditions inside the gasifier. Thus, the best option is to use such catalysts outside the gasifier for syngas cleaning and upgrading. Syngas may be cleaned by cold processes and there are several well-known ones, but though being efficient in contaminant removal and largely employed, they are not environmentally friendly, as large volumes of liquid effluents need to be further treated, which is very expensive. Besides, syngas has to be cooled down, which decreases the overall energy efficiency of the process, whenever syngas needs to be heated afterwards, for its upgrading, for H_2 production through steam reforming and water–gas and shift reactions, or for heat and power generation in a high-temperature fuel cell. For these applications the overall energy efficiency of hot cleaning processes is improved and the operational costs are lower. Hot gas cleaning processes may have a lower environmental impact and are normally safe [12].

However, high temperatures and some expensive catalysts are needed for hot syngas cleaning processes to ensure the thermal catalytic decomposition of tar, S and N compounds. Besides syngas desulfurization of organic compounds, such as COS and S-organics, is quite difficult to achieve. The study of hot syngas cleaning processes has shown an increasing interest and several authors have developed and tested different sorbents and/or catalysts for syngas cleaning, focusing on syngas desulphurization, tar and NH_3 abatement [1–11,13–17]. Despite the capability and efficiency of some catalysts, they are still too expensive to be used at large scale. Syngas cleaning still needs further development especially to treat syngas produced by low grade coals and wastes with undesirable elements. It is important to use sorbents and/or catalysts with low cost, high efficiency and regeneration capacities and without negative environmental impact.

Different coal grades with dissimilar compositions were blended with different biomasses (pine and bagasse) or with PE (polyethylene) and co-gasified with oxygen and steam to show the viability of co-gasifying such blends, taking profit of the suitable characteristics of each feedstock that increased syngas yield and decreased its content in undesirable compounds. The amount of coal in the blend was higher than that of other carbonaceous materials, because these materials still face some problems related with limited and seasonal variations of quantities, low energy density, physical properties and chemical composition in opposition with stable and market-ready supplies of coal. Though, the use of renewable energy resources is advisable, coal content in the blend was always higher than that of other carbonaceous materials, as the objective was to integrate these materials in conventional industrial processes. The syngas obtained by fluidized bed co-gasification of coal blends was hot cleaned in two fixed bed reactors, the first one with dolomite for some reduction of undesirable syngas components. The second fixed bed reactor contained a Ni-based catalyst to achieve effective reduction of tar, H_2S and NH_3. Some good results obtained with such hot syngas cleaning procedure were reported previously [18,19] when studying the effect of using air or oxygen during gasification.

This paper aims to confirm previous results and to prove that the hot syngas cleaning process is suitable to treat different syngas compositions obtained by oxy-gasification of a wider range of feedstocks. In the previous papers only silica sand was used in gasification bed. In the present work dolomite was also used inside the gasifier and the results obtained were compared to those obtained in absence of dolomite. The benefits, if any, of using dolomite in the gasification bed when syngas is cleaned with dolomite followed by a Ni-based catalyst were also analysed. The main critical syngas components were monitored and controlled along the syngas cleaning process and different options for syngas cleaning were analysed, considering several applications for the final syngas: heat and power generation, chemical synthesis and hydrogen rich fuel production with CO_2 capture.

2. Experimental part

2.1. Gasification installation and gas sampling and analysis

In Fig. 1 is presented a schematic diagram of the installation where co-gasification tests were done. The gasifier was a bubbling fluidised bed made of refractory steel and operating at atmospheric pressure. The reactor was 0.2 m square in cross-section, it was 3.7 m high and was located inside an electrical furnace, which may provide the heat for the process. The gasifier is electrically heated with a total of 30 kW.

Feedstock is fed inside the bed by a continuous feeding system, composed by a screw feeder and a variable speed motor. The feeder is previously calibrated for the mixture to be studied. The raw materials were mixed in the required proportions before being loaded into the hopper. The amount placed inside the hopper was measured before the experiment and after each test the remaining feedstock was also measured and analysed to check the feeding rate and to identify any serious segregation. A nitrogen flow is used to help the fuel feeding and to avoid a back flow of the gas. The feed system is water cooled to prevent clogging, that may be caused by pyrolysis of the feedstock, prior to the entry into the gasifier. The gasifying/fluidising agent was a mixture of steam and oxygen, introduced through a gas distributor located at the base of the reactor. Steam is produced in an electrical generator. Its flow rate was controlled by a system, including: orifice plate, transmitter and measuring unit.

The gasification gas (syngas) went through a cyclone to remove particulates. Afterwards, the gas was filtered, before it was injected into CO and CO_2 on-line analysers. Syngas samples were also collected in bags to be analysed by GC (gas chromatography) to determine the contents of CO, CO_2, H_2, CH_4, N_2, O_2 and other heavier gaseous hydrocarbons, referred as C_nH_m. Gas composition was presented on dry basis. Gas yield was calculated as the ratio between the volumetric inert free gas flow measured during the experiment and the feedstock mass flow fed into the gasifier, expressed in a dry and ash free basis. Gas higher heating value (HHV) is defined as the gross calorific value of the inert-dry-free gas on a volumetric basis. HHV was calculated by the gas molar composition, as the sum of the heating value of each component of the gas. Energy conversion was determined as the ratio between the energy present in the produced gas and the energy contained in the gasified feedstock. After each experiment, solid bed residue, containing silica sand (or silica sand and dolomite), ashes and unconverted carbon, was collected and analysed.

Gas was also sampled for tar, H_2S and NH_3 determination. Isopropanol (2-propanol or isopropyl alcohol) was used for tar collection, using the CEN/TS 15439:2006 procedure [20]. The amount of tar obtained in g/Nm^3 was determined by gravimetry. NH_3 was analysed according to the method CTM-027 of EPA (Environmental Protection Agency). Ammonia was retained in an acidic absorbing solution of H_2SO_4 0.1 N and then analysed potentiometrically with a specific ion electrode. H_2S was analysed by method 11 of EPA. Sulphide was retained in an absorbing solution of $CdSO_4$ and then analysed by iodometry. Sulphur held in the condensation system was also analysed, as SO_4^{2-}, using Capillary Ion Electrophoresis.

2.2. Experimental gasification conditions

Three different coals were gasified, whose elemental and proximate analyses are shown in Table 1. The sub-bituminous coal from Puertollano mines had very high ash content. The bituminous coal from South Africa had lower ash content, though the lowest value was presented by German coal that also showed the highest volatile content. These coals were also co-gasified in blends with different