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Research paper

Combined gas conditioning and cleaning for reduction of tars in biomass gasification

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ABSTRACT

Tar production in a biomass gasification process is one of the biggest issues for this technology and, thus, gas conditioning represents a key role in its development. The aim of this work is to evaluate the removal efficiency, besides the stability during the time, of a gas conditioning and cleaning section in a combined configuration. In particular, the primary treatment step consists in a secondary bed reactor of dolomite, before of an exhausted vegetable oil scrubber. They were analysed for several hours of operation (12 h), coupled to a bench-scale gasification reactor. It was obtained that the combined system provides reduction of total tars (MW > C_7H_8) equal to 97%, leading to a producer gas dew point temperature of 17 °C. On the contrary, when only cleaning action of scrubber media is considered, saturation of oil occurs after only 1.5 working hours. In the same time, when only conditioning system of dolomite guard bed is considered, tars reduction is still high, even after 14 working hours, but dew point temperature is 56 °C. The combined gas conditioning and cleaning system resulted to be the best solution in terms of removal efficiency and stability.

1. Introduction

Biomass gasification is a thermo-chemical process to convert biomass into producer gas containing gaseous species. In particular, steam fluidized bed gasification produces a fuel gas rich in hydrogen and carbon monoxide, with a significant content of methane and carbon dioxide [1–3]. However, also organic impurities (tar) are present [4–6]. As defined in Ref. [7], the organic compounds produced under thermal or partial-oxidation regimes (gasification) of any organic material are called tars. Generally, it is assumed that tars are aromatic hydrocarbons. They are undesirable and noxious by-products, known for their toxic and carcinogenic properties. The tar concentration in gas produced in a fluidized bed gasifier, as reported in Ref. [7], has a relative order of magnitude of 10 g m^{-3} in standard conditions of 103.5 kPa and 298 K. Moreover, corrosive and pollutant characteristics of tar compounds prohibit direct utilization of the produced gas. Therefore, tar reduction strategies are actively pursued [8,9]. Syngas produced by a biomass gasification system can be used, after proper cleaning and pretreatments, for different purposes: synthesis of other chemicals and liquid bio-fuels [10,11], production of pure hydrogen [12–14] or high-efficient power and heat production by means of gas engines, as ICE or CHP [15–17], or gas turbine [18,19]. The water scrubber is at the moment the most used technique in many gasification plants to remove contaminants and tar [20–22]. In the scrubbing process, or gas absorption process, the contaminants of gas stream are physically absorbed into an absorbent media. In order to have an efficient absorption, the contaminant in the gas phase must have some solubility in the scrubbing liquid [23]. Tar is a mixture of several organic compounds having low or no water-solubility characteristics (hydrophobic substances), water is thus not appropriate to be used as a scrubbing medium for tar removal in efficient way. Therefore, use of other kinds of absorbents, especially hydrophobic absorbents, should be more effective for tar absorption. In the work of Pfeifer et al. [24] rape seed oil methyl ester was used in their scrubber unit, but no information on performance was showed and a nickel-enriched catalytic bed material was tested for primary reduction of tar in a dual fluidized bed biomass steam gasifier with 100 kW of thermal energy. Könemann and Van Paasen [25] reported that the scrubbing oil had an efficiency of 98.8% for total tar removal, but no detail of scrubbing oil was published. In the work of Phuphuakrat et al. [26] several kinds of scrubbing liquids (water, diesel fuel, biodiesel fuel, vegetable oil, and engine oil) have been investigated for their absorption performances as a medium against real biomass tar. The results showed that only 31.8% of gravimetric tar was removed by the water scrubber, whereas the highest

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removal of gravimetric tar was obtained by a vegetable oil scrubber with a removal efficiency of 60% while for lighter PAH efficiency was higher than 90%. These results were obtained for 100 min of operation, further studies should be carried out to evaluate saturation of oil and tar concentration in the gas after longer period.

A different approach to remove tar could be the thermal or catalytic cracking of tar at high temperature. Phuphuakrat et al. [27] demonstrated that the reduction of the gravimetric tar mass was 78% in the case of the thermal cracking, whereas it was in the range of 77%–92% in the case of the steam reforming. Catalytic steam reforming/cracking seems to be the best way to eliminate tar compounds, converting these into syngas, and thus recovering their energy content whilst reducing pollution. An effective catalyst for this scope is nickel as shown in different works [28–32] but further works are necessary in the medium-long period to reduce their production and management costs (deactivation, sulphur poisoning.). A low cost and available catalyst would be preferable at the moment for this reason, like natural catalyst as calcined dolomite. Different works showed [33–37] that calcined dolomite is an efficient and cheap natural catalyst at least to reduce tar before any further treatments.

The aim of this work is to investigate the utilization of waste vegetable oil as scrubber media with or without an upstream guard bed of calcined dolomite to remove tar from syngas for energy production by means of an internal combustion engine. In fact, an evaluation of the maximum tar absorption capacity of the bio-oil is not available in literature and the theoretical evaluation of it is not an easy task due to the complex interactions between solvent and solute species and the lack of experimental data to choose and implement an appropriate thermodynamic model (Henry/Raoult Law, UNIFAC, NRTL, etc.). In particular, experimental tests on a bench scale steam gasifier coupled with dolomite bed and vegetable oil scrubber were carried out in order to verify the removal efficiency and to evaluate the stability of these two coupled gas conditioning and cleaning systems for several hours of operation.

2. Experimental activities

2.1. Experimental apparatus

The experimental apparatus used for experimental tests is shown in Fig. 1.

The fuel gas production is ensured by the cylindrical bubbling fluidized bed gasifier, continuously fed with fuel (biomass) and gasification agents. The fluidized bed gasifier (1) consists of an austenitic stainless steel (AISI 310) cylindrical vessel of 80 mm internal diameter and 860 mm height, containing olivine sand as bed inventory and a sintered stainless steel (AISI 310) porous distribution plate, which provides pressure drops higher than 40% of those through the fluidized bed yet at ambient temperature: this characteristic and the reactor design guarantee a uniform gas distribution at every temperature. The whole reactor is heated by a cylindrical electric furnace, equipped with two thermocouples, one immersed in the bed and the other located under the distributor, used for temperature and heating rate control. The electric furnace is used to maintain the temperature of the bed at the desired value of 800 °C, permitting in this way to operate the reactor as a steam gasifier similarly in the dual fluidized bed gasifier operating system. The biomass feeding (2) is set at the top of the reactor and is ensured by an endless screw system powered by an electric motor. The fuel feeding is supported by a constant nitrogen flow, continuously sent to the biomass inlet pipe in order to avoid problems of agglomeration and choking. The fluidization of the bed material inside the gasifier is guaranteed by right amounts of air, nitrogen, steam or their mixes (3) feeding the reactor. Steam is generated by an electrically heated boiler (6) fed by means of a dosing pump (5), which takes distilled water from a tank (4) at a constant flow rate. During the start-up, air is injected in the gasifier in order to enhance the fluidization and the heating of the bed material. During this phase the total amount of gas produced by gasification is completely burned in a torch (8). When steady state condition is established, steam is used as gasifying agent, in proper amounts depending on the steam to biomass ratio (SB). Since steam flow could not be sufficient to activate and support fluidization, nitrogen also is injected as inert in the reactor. During the gasification at steady state condition, only a part of the total produced gas feeds the torch and is burned, since the remain quantity is sent to the secondary reactor (10) and the scrubber (11) by means of a vacuum pump (13).

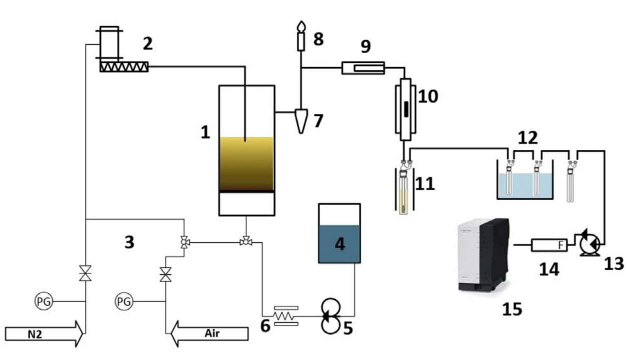

Fig. 1. Scheme of the experimental system.

Before reaching the secondary reactor, gas produced by gasification has to pass through a gas cleaning section, consisting in a cyclone (7) and in a heated ceramic filter (9) in series, having the aim of remove ashes and fine particles.

The tar removal section of the system consists in two components: dolomite bed and oil scrubber for gas conditioning and cleaning respectively. The stainless steel secondary reactor (10) contains an upstream guard bed of calcined dolomite and is located in an electrical furnace, having temperature and heating rate control systems based on the thermocouple sited inside the catalyst bed. The scrubber unit is, instead, simulated by an impinger bottle (11) filled with vegetable exhaust oil, inserted in a water bath and continuously heated by a hot plate and thermally controlled by means of a thermocouple. The hot water bath is necessary, at lab-scale, to avoid that gas and scrubber will drop to the ambient temperature, thus emulating a real scrubber behaviour in which the temperature is surely higher. 50 °C was chosen as scrubber unit operating temperature: this temperature is in line with that obtained with a real scrubber [38] in a 8 MW scale gasification power plant and with the operation temperature declared in the work of Anis and Zainal [39].

Syngas coming out from the scrubber passes through other different impingers (12), filled with 2-propanol and placed in a thermostatic bath maintained at −10 °C by a chiller-thermocouple system, in order to condensate the remaining tars and the excess water, according to the tar guideline provided by the European Committee for Standardization [40]. The vacuum pump (13) exhausts syngas, free from tars and water, which is then analysed using a volumetric gas-chromatograph (15) (VARIAN CP-4900 micro-GC Varian Inc, Middelburg, the Netherlands). A Bronkhorst-El flow regulator (14) (Bronkhorst High-Tech B.V., Ruurlo, The Netherlands) controls the slipstream of the raw gas. The 2-propanol mixed with tars is collected at the end of each test and successively analysed by means of a gas-chromatograph with mass spectrometry (Agilent GC-MS 5975C, Agilent Technologies, Santa Clara, CA, USA).

2.2. Experimental test

Biomass used for gasification tests was hazelnut shells, with a constant flow rate of 300 g h^{-1}. Preliminary and elemental analyses were carried out. In particular, preliminary analysis, was carried out by means of a TGA (Mettler-Toledo International Inc., Columbus, OH, USA) and, for LHV, a Parr 6200 oxygen bomb calorimeter (Thermo Fisher Scientific Inc., Waltham, MA, USA), while elemental analysis was