Biomass and Bioenergy 100 (2017) 98–107

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe

Research paper

Catalytic conversion of residual fine char recovered by aqueous scrubbing of syngas from urban biomass gasification

Gnouyaro Palla Assima [a], Stefano Dell'Orco [a], Shahram Navaee-Ardeh [b], Jean-Michel Lavoie [a, *]

[a] Université de Sherbrooke, Chaire de Recherche Industrielle sur l'Éthanol Cellulosique et les Biocarburants (CRIEC-B), 4070, boul. de Portland, Sherbrooke, QC, J1L 2Y4, Canada

[b] CRB Innovations, 4070, boul. de Portland, Sherbrooke, QC, J1L 2Y4, Canada

ARTICLE INFO

Article history:
Received 8 December 2016
Received in revised form
6 March 2017
Accepted 17 March 2017
Available online 24 March 2017

Keywords:
Oxidation
Catalyst
Urban biomass
Tars reforming
Biochar

ABSTRACT

Conversion of carbon contained in the solid residues (tars + biochar) derived from urban biomass gasification named herein TC would allow enhancing the yield of carbon species (CO/CO_2) in synthetic gas. For this purpose, three low cost materials have been tested as possible catalysts: iron species (reduced Fe), bone meal (BM), and ashes (ash) recovered from biochar complete oxidation. The parametric study used the following as variables: air GHSV, onset of reaction temperature, reaction time to optimize CO/CO_2 molar ratio and tar content in the produced gas. Results showed an autocatalytic effect of biochar leading to the catalytic conversion of approximately 78% of tars by the native metals contained in TC. The catalytic effect was further enhanced by adding Fe, BM, and extra ash. Addition of Fe catalyst resulted in significant heat generation (temperature increase of ca. 500 °C) and a twofold decrease in reaction time to consume all the carbon. Use of ash and BM as catalysts exhibit heat generation comparable to Fe, along with an improved reaction time, complete tars conversion and a CO/CO_2 molar ratio to above 1.3 in the produced gas.

1. Introduction

Thermochemical conversion of renewable carbon-rich residues (such as biomass-containing residues) to gaseous fuel (biosyngas) is increasingly regarded as a promising, eco-efficient, and self-sustainable route for the production of energy, fuels, or various chemicals as it also offers a neutral carbon footprint on anthropogenic greenhouse gas emissions [1]. In Canada, the annual production of residual biomass (commercial harvest of forest and agricultural biomass) is estimated to ca. 1.43 × 10^8 metric tons carbon [2]. This residual biomass has a potential energy content of approximately 2.25 × 10^9 GJ which is tantamount to energy content of ca. 3.7 × 10^8 barrel of oil (on a LHV basis). As the daily production of Canadian Crude Oil is estimated to be around 3.9 × 10^6 barrels (National Energy Board, Government of Canada), the energy recoverable from the residual biomass annually is significant as it might account for 9.3 days of oil production [3]. The thermal conversion of biomass into biosyngas or biosynthetic gas (known as gasification) is a process where the conversion is made to produce CO, H_2, CO_2, CH_4, and minor quantities of other hydrocarbons, essentially low molecular weight alkanes/alkenes and aromatics. In some cases, steam is added to the feed to increase the level of H_2 in the produced gas [4]. Typically, the resulting biosyngas has a low calorific value (3.8–5.6 MJ/m^3 against 38 MJ/m^3 for natural gas) [5].

Various types of gasification technology were developed over the years and applied for biomass based feedstocks conversion. They usually fall in three main classifications: fixed-bed or moving-bed gasifiers (updraft or downdraft), entrained-flow gasifiers and fluidized-bed gasifiers [6,7]. The big challenge in the particular case of fluid beds is achieving total carbon conversion of the biomass into synthetic gas directly in the gasifier. This challenge comes from the very rapid formation of char when biomass is heated in an oxygen-limited environment. Generally, only 80–90% of the carbon in the biomass feed is converted into permanent gases at "normal" gasification temperatures, between 700 and 1000 °C [8]. The unconverted carbon ends up in (a) entrained fine particles of char which contain some of the ash and tars or (b) in larger particles that

---

Abbreviations: GHSV, Gas hourly space velocity; TC, Tar-char; BM, Bone meal; Ash, Ashes (inert) from TC complete oxidation.

* Corresponding author.

E-mail address: Jean-Michel.Lavoie2@usherbrooke.ca (J.-M. Lavoie).

http://dx.doi.org/10.1016/j.biombioe.2017.03.015
0961-9534/

are retrieved with the heat carrier through appropriate ducts. The larger particles are normally subjected to an oxidizing treatment to recover the heat from the carbon present, thus raising the temperature of the heat carrier that is then returned to the fluid bed. Regarding the fines particles, a possible approach to convert the entrained char and tars would be to raise the temperature along the gasifier (which implies adding O_2-containing mixtures or simply air) by oxidizing part of the C in the char and tars and have steam and CO_2 react with the remaining C. If the temperature is high enough, the C is consumed and permanent gases are produced in a time span that depends very much on the temperature at which the operation is carried out. Slag will be inevitably formed and its complexity will have to be appropriately handled.

During the gas conditioning downstream the gasifier, a common practice in biomass gasification processes is to subject the primary gas, to one or several scrubbing treatments. The conditioning encompasses cleaning tar and other contaminants as well as downstream reforming processes. The cleaning step enables the removal of particulates, tars, alkali compounds, nitrogen, and sulfur-containing compounds, while reforming processes are generally meant to achieve a desired composition of syngas for a specific usage. The scrubbing step(s) generate sludge which is often recovered as a tar-char cake typically containing 50 wt% moisture [9]. If desired, it can be further dried to lower moisture contents (20 wt% being relatively easy). The presence of tars, typically PAHs, makes it difficult to transport and use the recovered tar-char cake in burners (such as those in cement kilns) due to fouling issues. Also, careful control of emissions in the flue gas following combustion to recover the heat is required. To achieve full carbon conversion in such processes, the tar-char cake needs to be reprocessed whilst ensuring to convert all the carbon it contains (tars + char). The char content is readily converted into gas at temperature $\geq$500 °C while the tars conversion or destruction can only be achieved either under severe temperatures (temperature above 1000 °C) [10] or catalytically (use of catalyst at temperature below 1000 °C) [11]. Processing at temperature above 1000 °C especially in autothermal process tantamount on the one hand sacrificing the tar-char indigenous carbon under enriched oxygen environment while producing elevated amounts of CO_2 at the expense of the desired CO. Moreover, such severe temperatures might trigger the amalgamation of heavy metals enclosed in the tar-char matrix which typically start to melt, agglomerate and/or vaporize above 1000 °C [12,13].

In this work, the <1000 °C catalytic oxidation of the tar-char cake into synthetic gas has been explored to avoid complications related to slagging and minimize CO_2 production. The catalytic conversion of tars and char is in fact widely covered in the open literature while the recent trend is to use cheap non-metallic compound for char and tars conversion. The common features with catalysts reported as effective for tars reforming such as dolomite ($CaMg(CO_3)_2$), calcium oxide (CaO), calcium carbonate ($CaCO_3$), calcium hydroxide [$Ca(OH)_2$], magnesium oxide (MgO) and potassium carbonate (K_2CO_3), olivine (Mg_2SiO_4), chrysotile ($Mg_3Si_2O_5(OH)_4$) were their contents in Ca, K, and Mg and Fe that were held liable for their catalytic behavior [14–22]. One of the main targets of this work is to gain additional knowledge of the catalytic effects on tars and char conversion using three additives: iron species (Fe), calcium phosphates (bone meal -BM) and ashes produced from the gasification of the feed material. Experimental investigations have been performed in a bench scale allothermal semi-batch reactor, controlling the partial pressure of O_2 so that the produced gas would have a CO/CO_2 molar ratio of ~1 (such as in the case of autothermal gasifier using O_2 and steam). The gasifier was operated as a fixed bed reactor and the main parameters monitored were temperature in the reaction zone as well as in the free zone above the fixed bed, reaction time, residual PAHs, and carbon conversion into synthetic gas. Special consideration was also given to the heat generated during the oxidation reaction since achieving an autothermal mode of operation while minimizing the production of CO_2 was targeted.

2. Material and methods

2.1. Materials characterization

The tar-char cake (TC), iron species (Fe), bone meal (BM) which was rich in calcium and phosphorus, and ashes from combusted tar-char cake (ash) samples consisted of fine powder with $D_{80} \leq 90$ μm. TC was received from Enerkem Alberta Biofuels, a commercial gasification plant located in Alberta (Canada), processing urban biomass such as sorted Municipal Solid Waste (MSW), Institutional Commercial and Industrial Waste (ICI), Construction, Renovation & Demolition Waste (CRD) and treated wood (railway ties, spent power and telephone poles). Fe (grade $\geq$ 99%) was purchased from Sigma-Aldrich as fine powder and BM was purchased from ECOlogical FERTILIZERS, while ashes (ash) were produced from TC following calcination at 750 °C overnight. The tars, char, and water content of TC were determined using soxhlet extractions, Karl Fischer titration and gravimetric measures. Water as well as some of the tars were extracted using isopropyl alcohol while the remaining tars were extracted using toluene. Water content was quantified using a Karl Fischer titration on the extracts. The residual solid was considered as composed of char (fixed carbon and ash). The ash content was thereafter determined following a complete combustion of the char. The organic content of BM was determined by weight difference between the initial mass and the one obtained after its complete combustion.

TC and BM samples were analyzed using a Perkin-Elmer inductively coupled plasma–optical emission spectrometry (ICP-OES 43000DV) to quantify the following elements: Al, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Hg, Ni, P, K, Se, Si, Ag, Tl, U, V, Zn, and Zr. CHNOS analysis was also carried out on TC and ash samples using a TruSpec Micro (LECO Corporation) to determine their respective contents in C, H, N, O and S. The sample's crystalline phases were identified using X-ray diffraction (XRD) spectra registered on a PANalytical X'Pert Pro MPD, powered by a Philips PW3040/60 X-ray generator and fitted with a PIXel 1D. X-rays were generated from a Cu anode supplied with 40 kV and a current of 50 mA. Diffraction data was acquired by exposing powder samples to Cu-Kα X-ray radiation at 1°/min (0.02° step size) over the 5–70° scattering angle range and at characteristic wavelengths of 1.5418 Å. Results were compared to those compiled in the Joint Committee on Powder Diffraction Standards library. The unconverted carbon and entrained metal levels were analyzed by Groupe EnvironeX using a GC-6890A MS-5973A (Agilent), a GC-7890A MS-5975C (Agilent) and a Q ICP-MS (Thermo Scientific) after concentrating the solution to identify and/or quantify the metals, PAHs and phenols, at each cleaning step of the produced gas. The metals were thereafter computed versus their initial amounts in the feed. Finally, an infrared gas monitor (Guardian Plus) was used to follow the production of CO and CO_2 online. H_2 was not monitored in this study as its production was negligible in the current steam-free process.

2.2. Oxidation setup and procedure

TC conversion was performed in a vertical-electrically-heated Inconel alloy 600 reactor (ID = 2.54 cm and H = 93.98 cm) presented in Fig. 1. The experimental setup was mainly composed of (1) a gasifier where the reaction occurs, (2) a controlled air and N_2 feed (3) a water scrubber to remove fine particles and phenols from