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Research article

Co-production of syngas and potassium-based fertilizer by solar-driven thermochemical conversion of crop residues

F. Müller[a], H. Patel[b], D. Blumenthal[a], P. Poživil[a], P. Das[b], C. Wieckert[c], P. Maiti[b], S. Maiti[b], A. Steinfeld[a,*]

[a] Department of Mechanical and Process Engineering, ETH Zurich, 8092 Zurich, Switzerland
[b] CSIR-Central Salt and Marine Chemicals Research Institute, Bhavnagar, Gujarat 364002, India
[c] Solar Technology Laboratory, Paul Scherrer Institute, 5232 Villigen, Switzerland

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ABSTRACT

We report on the thermochemical conversion of inedible crop residues using concentrated solar energy as the source of high-temperature process heat. Experiments were performed using a 5 kW_{th} solar packed-bed reactor exposed to radiative fluxes up to 1788 suns. The waste biomass feedstock consisted of unprocessed batches of cotton boll, soybean husk, and black mustard husk and straw, which were pyrolysed and steam-based gasified at nominal temperatures in the range 879–1266 °C, yielding high-quality syngas with molar ratios in the range H_2:CO = 1.43–3.25, CO_2:CO = 0.28–1.40, and CH_4:CO = 0.03–0.28. The solar-to-fuel energy conversion efficiency, defined as the ratio of the heating value of the syngas produced to the solar radiative energy input and the heating value of the feedstock, reached 18%. The heating value of the feedstock was solar-upgraded by 7%, thus outperforming autothermal gasification that typically downgrades by at least 15%. The ash contained 23% potassium. The solar-driven thermochemical process offers a sustainable and efficient path for the conversion of agricultural wastes into valuable fuels and soil fertilizers.

1. Introduction

In developing countries, a large fraction of crop residues is disposed of by on-site burning, mainly to clear the fields for the subsequent cultivation cycle. Apart from the loss of potentially useful energy, such uncontrolled incineration has adverse impacts on soil properties and releases smoke and soot [1–3]. This prompted us to develop technologies that provide incentives for the collection and productive utilization of those inedible waste materials without depriving the soil of essential nutrients. A promising approach is the high-temperature thermochemical processing using concentrated solar process heat, which has the potential to convert crop residues into high-quality syngas – a mixture of mainly H_2 and CO that can be processes to liquid hydrocarbon fuels – while the residual inorganic matter provides the minerals for the production of potassium-based fertilizer [4–7]. The thermochemical conversion of carbonaceous matter into syngas involves two endothermic processes, namely: pyrolysis, favored at temperatures in the range 200–600 °C, and the gasification which becomes dominant at temperatures above 1000 °C [4]. Pyrolysis can be represented by the net reaction:

$$C_1H_xO_yS_uN_v \rightarrow C(s) + CO + CO_2 + H_2 + C_\chi H_\xi + \text{tars}, \quad (1)$$

where x, y, u, and v are the elemental molar ratios of H:C, O:C, S:C, and N:C in the feedstock, respectively, while $C_\chi H_\xi$ denotes hydrocarbons. Steam-based gasification is represented by the net reaction:

$$C(s) + H_2O = H_2 + CO \qquad \Delta H^\circ_{298K} = 131\frac{kJ}{mol}. \quad (2)$$

Beside Eq. (2), a number of intermediate competing reactions occur during gasification, such as the water-gas-shift and Boudouard reactions. Autothermal gasification of biomass has been investigated for various crop residues, e.g. rice husk [8], jatropha shell [9], sunflower and soya residues [10], hazelnut shells [11], and cotton stalk [11,12]. There are several technical challenges associated with such a process, including combustion of a large portion of the feedstock for process heat, syngas contamination by soot, tars and combustion byporducts, feeding of fibrous feedstock, and ash slagging, all of which are strongly dependent on the variant physiochemical characteristics of the feedstock, predominantly on the content of volatiles and ash and the fraction of fixed carbon and moisture [5,13–16]. In contrast, solar-driven allothermal gasification at elevated temperatures yields high-quality syngas that is free of combustion by-products and with little tar or soot

* Corresponding author.
E-mail address: aldo.steinfeld@ethz.ch (A. Steinfeld).

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content [4]. Furthermore, an upstream air-separation unit is not required as steam is the oxidant, and the specific throughput of syngas per unit feedstock is larger as no portion is combusted [4]. Comprehensive reviews on solar-driven gasification are given in [4,17]. It has been experimentally demonstrated with various solar reactor concepts, including those based on entrained flows [18–20], drop tubes [21–23], fluidized beds [24–26], molten salts [27], and packed beds [28–33]. Entrained-flow, drop-tube, and fluidized-bed reactors are limited by the particle size, requiring feedstock pre-processing such as shredding and/or pyrolyzing. In contrast, packed-bed reactors can accommodate a wide range of feedstock sizes and morphologies, as experimentally demonstrated at laboratory [30] and pilot scales [31]. Molten salts provide efficient heat transfer, but solid residues merge with the molten salt and accumulate.

The cultivation of crops depends on nitrogen and potassium-based minerals obtained from the soil [34]. The cycle of these minerals is closed in a natural way as the plants decompose on-site. If, however, further utilization of the crop residues is considered, these minerals are inherently extracted from the soil and have to be supplied through fertilizers. This open cycle can be closed by extracting potassium-based fertilizer (KNO_3) from the inorganic solid residues (ash) left after gasification [6,7]. Three Indian crop residues are considered for the co-production of syngas and fertilizers: cotton boll (COB), soybean husk (SBH), and black mustard husk and straw (MHS). These inedible crop residues are considered wastes, have a high potassium content, and their surplus accumulates in India to a yearly amount of 56.4 Mt., equivalent to 871 PJ of thermal energy [35–38].

This paper reports on the experimental investigation of the solar thermochemical conversion of the three Indian crop residues (namely: COB, SBH, and MHS) using a 5-kW solar packed-bed reactor. The performance of the solar reactor for the three feedstocks is compared in terms of the syngas quality, carbon-gas yield, energy efficiency, energetic upgrade factor, and ash properties pertinent to the production of KNO_3.

2. Feedstock

The characterization of cotton boll (COB), soybean husk (SBH), and mustard husk and straw (MHS) is summarized in Table 1. The ultimate (on a dry and ash free basis (daf), Elementar vario MICRO cube and LECO CHNS -932 & RO-479) and the proximate analyses (Advance Research Instruments Co APA 2 and Netzsch 409STA) were repeated five times to account for the variant properties of the feedstock. The ash composition was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer Optima 2000 DV) in combination with X-ray diffraction (XRD, PANalytical Empyrean). The ash-fusion temperatures (Advance AFT) were determined according to ASTM standards, the fiber analysis by applying the method of Van Soest [39] (Tulin equipments FibroTRON), and the heating values by an encapsulated calorimeter (Parr 6200 Calorimeter). The mean equivalent sphere diameter d and the characteristic particle shape were evaluated optically (ImageJ [40]). The specific surface area (SSA) was determined by the Brunauer–Emmett–Teller theory (BET, micromeritics TriStar).

The mean molar ratios x and y of Eq. (1) varied in the range 1.51–1.66 and 0.74–0.86, respectively, while the volatile matter accounted for > 64 wt%. The moisture content varied in the range 6.8–9.3 wt%, which was low compared to other biomass sources (e.g.: switchgras: 13–15 wt% and bagasse: 40–50 wt% [41]) due to the on-sun drying after harvesting. The ash content was in the range 4.5–5.5 wt%, while the concentration of potassium oxide (K_2O) in the ash was in the range 10–45 wt%. The elemental composition, the ash content, and the high concentration of K-minerals indicated that the three crop residues belonged to the group of herbaceous biomasses [41,42]. The ash-fusion temperatures for COB were found to be below 635 °C, which eventually would lead to sintering of the ash during experiments. SBH and MHS exhibited low bulk densities of 113 and 62 kg/m^3, respectively, which limited the amount of biomass load per batch. Thus, shredding was executed for selected samples. The particle size distribution is shown in Fig. 1 for COB, SBH, shredded SBH, MHS, and shredded MHS. In general, all samples had rectangular particle shapes with large aspect ratios because of the fibrous structure. The SSA of the three unprocessed samples were in the range 0.86–1.75 m^2/g. Shredding increased the SSA to 1.52 and 1.80 m^2/g for the shredded SBH and MHS, respectively.

3. Experimental

3.1. Solar reactor

The 5 kW solar reactor is schematically shown in Fig. 2. Its engineering design was previously described in detail [30]; only the main features are highlighted here. It is designed for beam-down incident radiation and features two cavities in series, the upper and the lower cavity, separated by a 5 mm-thick emitter plate made of SiC-coated graphite. The upper cavity functions as solar absorber and contains a 65 mm-diameter aperture sealed with a 3 mm-thick fused quartz disk for the access of concentrated solar radiation. A compound parabolic concentrator (CPC) is incorporated at the aperture to reduce re-radiation losses and further boost the incident solar flux by a factor 1.67 [43]. The lower cavity functions as the reaction chamber and consists of a 14.3 cm-diameter, 16.0 cm-height cylindrical enclosure, lined with SiC tiles, that contains the packed bed of initial height h_{PB} on top of a Al_2O_3-SiO_2 grid for the distribution of the steam injected from below. A thin layer (~0.5 mm) of ceramic felt was placed on the distribution grid to avoid the blockage of the grid by small particles. With this arrangement, incoming high-flux solar radiation is efficiently absorbed by the upper cavity, re-emitted by the emitter plate towards the lower cavity, and transferred by radiation-conduction-convection to the reacting packed bed. The reactor is operated in batch mode, with the packed bed shrinking as the gasification progresses. Gas products exit through a lateral outlet port in the lower cavity, just below the emitter plate.

3.2. Experimental set-up

The experimental setup is schematically shown in Fig. 3. Experimentation was carried out at PSI's High-Flux Solar Simulator (HFSS). An array of 10 high-pressure Xenon arcs, each close-coupled to ellipsoidal reflectors, provided an external source of intense thermal radiation, mostly in the visible and infrared spectra, that closely approximated the radiative heat transfer characteristics of highly concentrating solar systems [44]. The solar radiative power input, $\dot{Q}_{solar}$, was controlled by the number of Xe arcs and a mechanical Venetian-blind shutter, and it was measured with a calibrated CCD camera focused on a refrigerated Al_2O_3 plasma-coated Lambertian (diffusely reflecting) target and verified by a water calorimeter. The maximum $\dot{Q}_{solar}$ entering the reactor's aperture was 5.54 kW, for which 6 of the 10 Xenon arcs were used, while the shutter was fully open (shutter transparency = 100%). This corresponds to a mean solar concentration ratio over the aperture of 1788 suns (1 sun = 1 kW/m^2). Temperatures were measured in the upper cavity, $T_{absorber}$, in the lower cavity above the packed bed, T_{top}, and at the bottom of the packed bed, T_{bottom}, using type-K thermocouples at locations indicated in Fig. 2. The upper and lower cavities were purged with argon (purity: ≥ 99.9999%) flow rates of 3 L_N/min* and 1 L_N/min, respectively. A steam-argon mixture was injected at the bottom of the lower cavity at excess steam flow rates, $\dot{n}_{H2O}$, and at an Ar flow rate of $\dot{m}_{Ar}$ = 1 L_N/min. The gas mass flow rates were controlled by electronic flow controllers (Bronkhorst HI-TEC,

* L_N denotes normal liters; mass flow rates are calculated at 273.15 K and 1 atm.