Demonstration of a prototype molten salt solar gasification reactor

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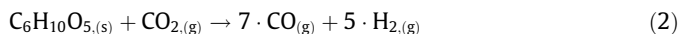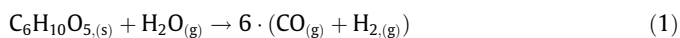
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ABSTRACT

In the present work, a prototype molten salt solar gasification reactor was demonstrated at the 2.2 kW scale using simulated concentrated solar radiation. The molten alkali carbonate salt offers the benefits of improved heat transfer, catalysis of gasification, reduced production of tars, and thermal stability for transient solar input. Utilizing cellulose as feedstock and carbon dioxide as oxidizer, the reactor achieved a solar efficiency of 30% and converted 47% of the carbon in a continuous process at 1218 K. Based on an energy balance on the reactor, we project efficiencies approaching 55% with future improvements to the reactor.

1. Introduction

Solar thermochemical processes offer several routes to providing fuels and chemicals traditionally obtained from petroleum at a greatly reduced carbon footprint. Among the various solar thermochemical processes, the use of solar energy to drive the gasification of carbonaceous materials is considered a near-term option given the relatively mild process temperatures involved and the potential for solar to fuel efficiency above 50%.

Considering cellulose as a surrogate feedstock representative of biomass, the ideal stoichiometric gasification reactions are given in Eqs. (1) and (2) for steam and carbon dioxide oxidizers, respectively.

$$C_6H_{10}O_{5,(s)} + H_2O_{(g)} \rightarrow 6 \cdot (CO_{(g)} + H_{2,(g)}) \tag{1}$$

$$C_6H_{10}O_{5,(s)} + CO_{2,(g)} \rightarrow 7 \cdot CO_{(g)} + 5 \cdot H_{2,(g)} \tag{2}$$

The solid feedstock is converted into a gaseous blend of carbon monoxide and hydrogen, which is referred to as synthesis gas due to its potential for subsequent synthesis of chemicals and fuels. The process is endothermic, effectively allowing storage of solar energy in the upgraded energy content of the synthesis gas relative to the feedstock.

Based on chemical thermodynamics, all of the biomass is converted to useful synthesis gas by supplying the required thermal energy at approximately 1200 K from a concentrated solar source. By avoiding partial combustion of the feedstock, the product is not diluted by excess CO_2 and N_2 nor contaminated by other combustion by-products, and there is no need for an economically and energetically expensive oxygen plant.

With these motivating benefits, a number of solar gasification reactors have been developed. Recent reviews of these efforts are reported by Puig-Arnavat et al. (2013) and Piatkowski et al. (2011) The assessment of solar gasification reactors is conventionally reported in terms of solar to fuel efficiency and carbon conversion. In the present work, we define the reactor efficiency in rate form as the ratio of the lower heating value (LHV) of the useful products to the energy input, which is the sum of the solar input and the LHV of the carbonaceous feedstock:

$$\eta_{reactor} = \frac{\sum_{i=\{CO,H_2,CH_4\}} \dot{n}_i LHV_i}{\dot{Q}_{solar} + \dot{n}_{feed} LHV_{feed}}. \tag{3}$$

Carbon conversion is given by the ratio of the net gaseous carbon released from the reactor to the feedstock carbon delivered to the reactor.

$$X_C = \frac{n_{CO} + n_{CO_2} + n_{CH_4} - n_{CO_2,in}}{n_{C,feed}} \tag{4}$$

Reactors can be categorized generally by batch or continuous fuel production. The packed bed reactors developed at Lawrence Livermore Laboratory (Gregg et al., 1980; Taylor et al., 1983) and the Paul Scherrer Institute and ETH Zurich (Piatkowski et al., 2009; Wieckert et al., 2013) are batch reactors. These reactors achieved efficiencies from 15% to as high as 35% (Wieckert et al., 2013) but exhibited issues with condensable tars or other secondary products in the product gas stream which, in addition to unreacted material remaining within the reactor, resulted in

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Nomenclature

A	area [m^2]		actual	measured value
C	flux concentration ratio [–]		ap	pertaining to the reactor aperture
h	molar enthalpy [J mol^{-1}]		cav	pertaining to the reactor cavity
I	standard insolation [1000 W m^{-2}]		C	carbon
LHV	lower heating value [J mol^{-1}]		CH_4	methane
n	number of moles [mol]		CO	Carbon Monoxide
$\dot{n}$	molar flow rate [mol s^{-1}]		CO_2	Carbon Dioxide
$\dot{Q}$	heat transfer rate [W]		feed	pertaining to the solid feedstock
T	temperature [K]		(g)	gaseous phase
X	carbon conversion [–]		i	general index variable
y	volume or mole fraction [–]		in	inlet mass flow
			loss	convection and conduction losses to the ambient
Greek			N_2	nitrogen
ε	emissivity [–]		out	outlet mass flow
η	efficiency [–]		rad	radiative losses to the ambient
ϕ	stoichiometric oxidizer ratio [–]		reactor	thermal efficiency of the solar reactor
σ	Stefan-Boltzman constant [5.67 × 10^{-8} W m^{-2} K^{-4}]		residual	carbon remaining within the reactor
			(s)	solid phase
Subscripts			stoich	amount of oxidizer predicted for stoichiometric reaction
a	apparent value			
abs	absorption efficiency			

carbon conversions from 27 to 73% (Wieckert et al., 2013). Additionally, the presence of residual ash retarded gasification of the remaining feedstock in the case of the directly absorbing reactors (Gregg et al., 1980). The entrained flow (Melchior et al., 2009), vortex flow (Z'Graggen et al., 2007, 2006), and fluidized bed (Cho et al., 2015; Taylor et al., 1983) reactors are continuous reactors. At 1500 K, these reactors yielded a low-tar product stream and achieved rapid rates of conversion. However, they require significant amounts of carrier/fluidization gases to deliver the feedstock and maintain the feed entrainment or bed fluidization. Thus, efficiencies were low, 0.5–10%, despite high levels of conversion. Most recently Kruesi et al. (2014) demonstrated a new two-zone reactor design consisting of a drop-tube pyrolysis zone and a trickle bed gasification zone. The reactor achieved efficiencies up to 21% with carbon conversion near 90%.

In the present work, we characterize a new solar reactor in which the pyrolysis and gasification reactions of Eq. (2) are carried out in a ternary blend of molten alkali carbonate salts and operation is continuous. The molten salt offers several advantages over operation in a gaseous environment. The relatively high effective thermal conductivity of the salt (0.87 W m^{-1} K^{-1}) allows for rapid transfer of heat to the feedstock. The thermal capacity of the salt (1840 J kg^{-1} K^{-1}) provides stable operation through solar transients (Hathaway et al., 2013b), and the catalytic activity of the alkali metal cations accelerates carbon gasification and encourages tar cracking reactions (Adinberg et al., 2004; Iwaki et al., 2004; Jin et al., 2005; Ratchahat et al., 2015). Improved rates and yields from gasification reactions have been demonstrated at the bench-scale for coal (Matsunami et al., 2000; Yoshida et al., 1999) and a variety of biomass materials, including wastepaper, wood waste, corn stover, switchgrass, and perennial blends (Adinberg et al., 2004; Hathaway et al., 2011, 2013a; Iwaki et al., 2004; Jin et al., 2005). In a crucible heated in an electric furnace, gasification in the molten salt increased the overall gas yield from cellulose by up to 25%, doubled the rates of pyrolysis rates, and increased the rates of carbon gasification tenfold compared to gasification in a gaseous media (Hathaway et al., 2011). The reactivity index, defined as the inverse of twice the time needed to reach 50% carbon conversion, increased by as much as 600% for corn stover. Condensable tar

was reduced by 77% (Hathaway et al., 2013a). Additionally, the improved reaction rates have been found to be insensitive to the presence of ash in the melt at concentrations up to 20 wt.% (Trilling, 1977).

The performance of the molten salt reactor is demonstrated in an indoor high-flux solar simulator for carbon dioxide gasification of cellulose at 1218 K. Data include temperatures within the reactor, product gas composition, carbon conversion, and solar efficiency. The data are interpreted to identify areas for future improvement in the reactor.

2. Experimental

2.1. Reactor prototype

The nominal 3 kW prototype reactor (Fig. 1), absorbs concentrated radiation to drive steam or CO_2 gasification of biomass in a ternary eutectic blend of molten alkali-carbonate salts at 1200 K and near-atmospheric pressure. The reactor is a concentric cylinder arrangement. The inner cylinder is a cavity receiver with a front aperture. The outer cylinder bounds an annular volume which contains the molten salt and reacting biomass. It is constructed of Inconel X-750 alloy to provide strength and resistance to creep as well as resistance to corrosion by the molten alkali carbonate salts (Coyle et al., 1986).

The receiver cavity is cylindrical with a 150 mm length, 100 mm inside diameter and 3 mm wall thickness. Concentrated solar radiation enters the cavity through an open aperture of 50 mm diameter (left side of Fig. 1(a)). The aperture was sized to intercept 3 kW of incident thermal radiation at a nominal average flux of 1500 kW m^{-2}. Based on Monte-Carlo ray tracing radiative exchange simulations of the cavity and accounting for the spectral variations of reflectance of Inconel X-750 (Touloukian and DeWitt, 1979), the apparent absorptivity of the cavity receiver is 98% at 1200 K (Hathaway et al., 2012). The far end (right side in Fig. 1(a)) of the cavity is not in contact with the molten salt. To minimize absorption on this surface, the rear end-cap is coated with alumina, applied using a plasma spray, to achieve a diffuse solar weighted hemispherical reflectivity of 80% as measured by UV–VIS