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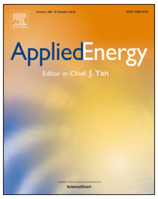

Energy and exergy analysis of concentrated solar supercritical water gasification of algal biomass

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HIGHLIGHTS

- Exergy destruction due to process heat recuperation (~12%) is not excessive.
- Optimal process exergy efficiency (45%) favours high pumped algae concentration of ~25%.
- High gasification temperature 605 °C is optimal, for product mix and low char levels.
- 0–35% of CSP heat input is used for reforming processes; varies need for make-up H_2.

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ABSTRACT

Solar supercritical water gasification (SCWG) of biomass has attractive advantages for liquid fuel production, but only very few system-level concepts have so far been investigated. Here, a solar SCWG reactor is integrated with a downstream solar reforming reactor and a supplementary hydrogen supply (assumed from photovoltaic-powered electrolysis), to produce syngas at the H_2:CO ratio required for liquid fuels synthesis. Three alternative reforming reactor options are considered. The overall process, excluding the liquid synthesis, is modelled as a steady-state process in Aspen Plus, with detailed heat transfer modelling for most process units. Reactors are modelled as idealised equilibrium reactors, due to the absence of kinetics data in the case of SCWG. Optimal process parameters are determined through parameter studies: algae concentration should be high (25% by mass, at the limit of pumping), as should the SCWG reactor temperature (605 °C, within pipework material limits, at 24 MPa pressure) and reformer temperature (1050 °C in the case of steam methane reforming). Overall exergy efficiency declines strongly at reduced algae concentrations, since lower concentrations necessitate greater recirculation of water, and cause consequently higher exergy destruction in heat exchangers and separators. Char production is another factor that greatly affects process efficiency, and the lack of good models and data mean that further work is required to understand and control this factor. Alternative reformer options (steam methane reforming, autothermal reforming and partial oxidation/dry reforming) had negligible affect on the overall process carbon, exergy or energy efficiency (88%, 71% and 45%, respectively, at the optimal design point), but greatly affected the amount of H_2 required from the supplementary photovoltaic-electrolysis system. This tradeoff offers interesting design choices for hybridised solar-thermal/photovoltaic solar-fuel systems, which should be the topic of future technoeconomic analysis.

1. Introduction

Carbon dioxide equivalent (CO_2-e) emissions from liquid-fuel consumption account for nearly one-third of the global anthropogenic greenhouse gas (GHG) emissions [1]. Sustainable carbon-neutral fuel production is imperative to meet the global GHG emissions reduction targets set by the Paris Agreement, assuming the highly likely scenario that alternative carbon-free fuels for long-range aviation and shipping, will not be adopted in the near-term. Thermochemical conversion of biomass can provide carbon-neutral high calorific-value fuels (hydrogen, methane and/or syngas) for manufacturing, fuel cells, or subsequent conversion to liquid fuels via commercially available technologies such as Fischer-Tropsch, methanol or dimethyl ether synthesis. Supercritical water gasification (SCWG) is one such conversion route for wet biomass and carbonaceous waste. Compared to conventional gasification, SCWG offers more flexibility in terms of feedstock, lower

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Nomenclature

ATR	autothermal reforming
BM	Boston–Mathias
CST	concentrated solar-thermal
HT Sep	high-temperature separator
HX	heat exchanger
MHV2	modified Huron–Vidal
Mix	mixer
PO/DR	partial oxidation and dry reforming
PREoS	Peng–Robinson equation of state
PV	photovoltaic
RGIBBS	equilibrium reactor
RP	raceway ponds
RR	reforming reactor
RSTOIC	stoichiometric reactor
SCWG	supercritical water gasification
SMR	steam methane reforming
SNG	synthetic natural gas
SRK	Soave–Redlich–Kwong
WGS	water–gas shift
WS	Wong–Sandler

Symbols

$\bar{x}^{\circ}_{\mathrm{ch}}$	standard molar chemical exergy, $\mathrm{kJ\,kmol^{-1}}$
$\bar{c}_p$	molar heat capacity, $\mathrm{kJ\,kmol^{-1}\,K^{-1}}$
$\bar{f}$	fugacity, Pa
$\bar{h}$	molar enthalpy, $\mathrm{kJ\,kmol^{-1}}$
$\bar{h}^{\circ}_{\mathrm{f}}$	molar enthalpy of formation at reference state, $\mathrm{kJ\,kmol^{-1}}$
$\bar{R}$	universal gas constant, $\mathrm{kJ\,kmol^{-1}\,K^{-1}}$
$\bar{s}$	molar entropy, $\mathrm{kJ\,kmol^{-1}\,K^{-1}}$
$\bar{s}^{\circ}_{\mathrm{f}}$	molar entropy of formation at reference state, $\mathrm{kJ\,kmol^{-1}\,K^{-1}}$
$\bar{x}$	molar exergy, $\mathrm{kJ\,kmol^{-1}}$
$\dot{E}$	total energy supplied to the system, kW
$\dot{I}$	exergy destruction (irreversibility), kW
$\dot{n}$	molar flow rate, $\mathrm{kmol\,s^{-1}}$
$\dot{Q}$	heat transfer rate, kW
$\dot{X}$	exergy, kW
μ°	chemical potential at reference state, $\mathrm{kJ\ kmol^{-1}}$
$\overline{\mathrm{HHV}}$	higher heating value, $\mathrm{kJ\ kmol^{-1}}$
C	geometric solar concentration ratio
f°	fugacity at reference state, Pa
G	Gibbs free energy, $\mathrm{kJ\ kmol^{-1}}$
G_{d}	direct normal irradiance, $\mathrm{W\,m^{-2}}$
n	number of moles
R^2	statistical coefficient of determination
T	temperature, K
y	mole fraction
z	mass fraction

Greek symbols

β	correlation factor defined in Eq. (21)
η	solar reactor thermal (energy) efficiency
η_{carbon}	carbon efficiency
η_{I}	energy efficiency
η_{II}	exergy efficiency
μ	chemical potential, $\mathrm{kJ\ kmol^{-1}}$
σ	Stefan-Boltzmann constant, $\sigma = 5.67 \times 10^{-8}$, $\mathrm{W\,m^{-2}\,K^{-4}}$

Subscripts

i	of component i
0	environmental condition
algae	algae
C	carbon
c	cooling
ch	chemical
H	hydrogen
h	heating
in	input
loss	loss
min	minimum
N	nitrogen
O	oxygen
out	output
ph	physical
r	reactor
rad	radiative
recov	heat recovery
ref	reference state
sun	solar
syngas	syngas
tot	total

char/tar formation, higher yield, and lower cost associated with drying of feedstock [2]. It can be argued that algae are the ideal feedstocks for the SCWG process. Algae, as renewable biomass sources, are not seasonal crops, have high growth rate, can be cultivated even in brackish water, and contain high fixed carbon and low volatile matter [3]. Even if the high-value products are extracted from algae (such as algae oil), the residual material is still desirable for SCWG.

Several lab-scale demonstrations and thermodynamic models of the SCWG process with different biomass feedstocks, including algae, have been reported in literature [4,5]. However, very few studies have focused on the system-level design. Process optimisation for producing fuel and/or electricity through thermochemical conversion of waste streams, such as, black liquor (using conventional gasification [6] and SCWG [7]) and sugarcane bagasse [8] have been reported. Similarly, design of fuel/electricity production pathways with real-biomass [9] and coal-water slurry [10] via SCWG have also been studied previously. Brandenberger et al. [11] investigated the production of synthetic natural gas (SNG) via SCWG and evaluated three different algae farming techniques, namely, raceway ponds (RP), tubular photobioreactors, and flat-panel-airlift photobioreactors, and found RP-SCWG to be the most cost-effective route with an optimistic SNG production cost of 53–90 €/GJ. In some of the more recent studies on the system design of a gasification process using algal biomass, *Chlorella vulgaris* [12,13], seaweed *Fucus sp.* [14,15], and *Spirulina sp.* [16], the authors focused on two primary aims: exergy recovery and process integration; most of these studies focussed on generation of hydrogen and/or electricity as the final product. A system-level analysis with algae as feedstock and with the view of producing syngas for downstream conversion to liquid fuels is not available.

An important observation from the aforementioned studies is partial consumption of the product gas, needed to power the endothermic SCWG reactor, which results in lower process efficiency. Integration of a concentrated solar-thermal (CST) collector presents an opportunity to design a renewable and carbon-neutral alternative to conventional fuel production routes, offering higher syngas yield from constrained biomass feedstock [17]. However, the integration of concentrated solar-thermal energy with SCWG and the feasibility of a solar-SCWG reactor for fuel production are relatively unexplored. Ganani et al. [18] combined a SCWG reactor with a supercritical Rankine turbine and designed a co-generation system for solar power and fuel production with