Solar Energy 141 (2017) 91–102

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

Vacuum pumping options for application in solar thermochemical redox cycles – Assessment of mechanical-, jet- and thermochemical pumping systems

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ARTICLE INFO

Article history:
Received 31 August 2016
Received in revised form 7 November 2016
Accepted 11 November 2016

Keywords:
Solar fuels
Vacuum pump
Thermochemical pump
Pumping efficiency

ABSTRACT

Solar powered two step thermochemical redox cycles are often investigated as a pathway to producing renewable fuels, via the splitting of water and carbon dioxide. These processes require a high temperature step for the reduction of the redox material. The reduction thermodynamics also critically depend on the oxygen partial pressure. In generic process assessments, purge gases and mechanical vacuum pumps have been considered for removing the released oxygen. Even though both alternatives are expected to have a significant impact on the overall process efficiency, little effort has been made so far in providing a detailed analysis of the implementation of the related components - especially in the case of vacuum pumps. In this study models are developed for assessing the energy requirements of mechanical vacuum pumps as well as for jet pumps. The models are validated and compared to data provided by manufacturers. In addition, a novel thermochemical pumping concept is introduced and a first thermodynamic assessment is presented. The energy demands of the different pump options are discussed in the context of the targeted application. By comparison with the energy stored in the produced fuel, limitations for the implementation of these systems can be identified. Furthermore, the costs for mechanical and jet pumps have been taken into account for the assessment. While mechanical pumps are energetically favored and could be reasonably applied for pressures down to 150 Pa, jet pumps are the more economic option and can make direct use of waste heat, which should be vastly available in the process at the required temperature level. The concept of thermochemical pumps is energetically very interesting and might shift the limit of realistic operational pressures to lower values, especially when combined with conventional systems.

1. Introduction

Solar driven thermochemical cycles are studied as promising production paths of renewable hydrogen, syngas and liquid fuels. The considered processes were first discussed in combination with nuclear power plants providing the high temperature heat (Yalcin, 1989). In recent years concentrating solar power systems have received a lot more interest as heat source for the endothermic reactions of thermochemical cycles (Fletcher and Moen, 1977; Nakamura, 1977; Steinfeld, 2005). Since the conversion of light to heat is very efficient, in high level process assessments the efficiency is mainly determined by the ratio of the heating value of the fuel to the energy required for reactivating the material – which can result theoretically in overall process efficiencies of >60% (Kodama and Gokon, 2007). For this reason these cycles have attracted considerable attention in the research community.

There are several approaches for such solar driven thermochemical cycles. One promising approach - the production of syngas from water and CO_2 - considers the use of a redox material in a two-step process operated in a temperature swing mode. In a first high temperature step given in Eq. (1), the redox material becomes reduced in an endothermic reaction. The required high temperature heat for the reduction is provided by a concentrated solar power system. In a second step at lower temperatures the reduced redox material is brought into contact with steam and CO_2. While the redox material gets re-oxidized, H_2 and CO are produced in the reactions given in Eqs. (2) and (3). The redox material can then be heated again for reduction and the cycle repeated.

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http://dx.doi.org/10.1016/j.solener.2016.11.023
0038-092X/

Nomenclature

C	conductance value (m^3/h)
C_p	heat capacity (J/(kg K))
$f_{Entrainment}$	multiple of water loading (–)
G	Gibbs free energy (J)
H	molar enthalpy (J/mol)
K	compression rate (–)
K_0	zero delivery compression rate (–)
$\dot{m}$	mass flow (kg/s)
MO_x	metal oxide/redox material (–)
n	amount of substance (mole)
p	pressure (Pa)
P	power (W)
PEM	polymer electrolyte membrane (–)
PV	photo voltaic (–)
R	gas constant (J/(mol K))
S	pumping speed (m^3/h)
T	temperature (K)
Q	heat (J)
V	volume (m^3)
W	work (J)
$X_{H2O/O2}$	water loading of oxygen at 30 °C (–)
δ	reduction extent (–)
γ	heat capacity ratio (–)
η	efficiency (–)
ϑ	temperature (°C)
τ	correction factor

Subscripts

A20	air at 20 °C
ad	adiabatic
atm	atmospheric
ch	isochoric
D	discharge
f	friction
G	gas
in	inlet
iso	isothermal
MS	motive steam
n	stage n
pump	pump
tc	thermochemical
th	theoretical

$$MO_x \xrightarrow{heat=\Delta H^\circ_{rd}} MO_{x-\delta} + \frac{\delta}{2} O_2 \tag{1}$$

$$MO_{x-\delta} + \delta H_2O \rightarrow MO_{x-\delta} + \delta H_2 \tag{2}$$

$$MO_{x-\delta} + \delta CO_2 \rightarrow MO_{x-\delta} + \delta CO \tag{3}$$

The development of suitable redox materials is challenging and an ongoing task. While other promising materials have been identified, ceria (Abanades and Flamant, 2006) is mostly considered as redox material in related process and reactor development studies. The cyclability of ceria has been experimentally demonstrated with good structural stability. As a drawback of its stability ceria is only partially reduced within a reasonable operational temperature and pressure window. Typically less than 5% of oxygen atoms per cerium atom are removed from the crystal structure during the reduction. As a result, large amounts of redox material are cycled through the process inertly. The reduction extent can be increased by increasing the reduction temperature - which is often assumed to be limited to about 1500 °C due to sublimation of the oxide - and by reducing the oxygen partial pressure in the surrounding atmosphere.

More generally, the reduction reaction given in Eq. (1), will proceed spontaneously if the change in Gibbs free energy for the reaction is less than zero. The change in Gibbs free energy for the reduction is given by

$$\Delta G_{rd} = \Delta H^\circ_{rd} - T\Delta S^\circ_{rd} + \frac{1}{2} RT \ln\left(\frac{p_{O_2}}{p^\circ}\right), \tag{4}$$

where ΔH°_{rd} is the change in enthalpy of reduction at standard pressure, ΔS°_{rd} is the change in entropy at standard pressures, and the final term corresponds to change in Gibbs free energy due to reducing the oxygen partial pressure. Interestingly, both the enthalpy and entropy changes are material dependent, but provided the reaction only produces oxygen gas the pressure term is material independent. Therefore, the efficient reduction of the partial pressure will have benefits for all thermochemical cycles of the form given in Eqs. (1)–(3).

In order to reduce the oxygen partial pressure in the reactor one can purge the reactor with a sweep gas. In this case, large energy penalties have been identified related to the provision or recycling of sweep gas with low oxygen content and to the imperfect heat recovery when heating the sweep gas to the reduction reaction temperature. Due to the required large volumetric flow rates and the energy penalties the process efficiencies drop significantly when this method is considered (Brendelberger and et al., 2015; Ermanoski et al., 2013; Lin and Haussener, 2015; Bader and et al., 2013).

Another possibility is the reduction of the total pressure using vacuum pumps. This method has been considered in several process models and in general more promising process efficiencies than in the purge case have been predicted (Ermanoski et al., 2013; Lin and Haussener, 2015; Brendelberger and Sattler, 2015; Bulfin and et al., 2015; Jarrett and et al., 2016). A common shortcoming of these process models is that quite rough assumptions about the pump efficiencies are used mainly based on pump data for systems which are not optimized for large scale applications or on heuristics. The resulting high uncertainty of the pump efficiency has a significant effect on the derived process efficiency predictions.

In this work, a detailed analysis of pump performances considering pumps which are used in large scale industrial applications with similar requirements is conducted and the results are discussed in the context of the targeted redox cycles. An analytical expression for the best case pumping efficiency is provided as a function of pressure, allowing the results to be easily utilized by other researchers investigating such thermochemical redox cycles, as shown in Eqs. (1)–(3). In addition to mechanical vacuum pumps, jet pumps are also considered which might be beneficial, since they can be operated using waste heat of the process directly. Another novel approach presented here is the combined use of vacuum pumps and chemical binders which can be recycled using waste heat. With the information provided in this paper, the implications of reducing the oxygen partial pressure using a vacuum can be realistically assessed.

2. Mechanical pumps - displacement and turbo molecular pumps

Mechanical vacuum pumps are used in a wide range of applications with diverging requirements (Hablanian, 1997; Jousten,