

Solar Thermochemical Conversion of CO₂ into C via SnO₂/SnO Redox Cycle: A Thermodynamic Study

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ABSTRACT

In this paper we report the computational thermodynamic modeling of the solar thermochemical SnO₂/SnO redox cycle for solid C production via CO₂ splitting. In this redox cycle, the first step corresponds to the solar thermal reduction of SnO₂ into SnO and O₂ in presence of inert atmosphere. The second step, which is a non-solar exothermic stage, is the reaction of SnO with CO₂ to produce solid C together with SnO₂ that is recycled back to the first step. Commercially available HSC Chemistry software and databases were used for the computational thermodynamic modeling of this process. The thermodynamic analysis was performed in two sections: 1) equilibrium composition analysis, and 2) exergy analysis. Results obtained via the computational thermodynamic modeling are presented in detail. The simulation results indicate that the solar thermochemical SnO₂/SnO redox cycle for solid C production via CO₂ splitting can achieve the solar to fuel conversion efficiency upto 12%.

Keywords–Solar Energy, Computational Thermodynamic Modeling, Exergy Analysis, SnO₂/SnO, CO₂ Splitting

I. INTRODUCTION

The concentration of CO₂ in atmosphere is increased upto 392 ppm as of 2011 and, according to the recent analysis, it is expected to increase upto 550 ppm by the end of the year 2050 [1]. The increase in the concentration of CO₂ has hostile effects on environment and daily life and hence significant efforts are underway towards minimization of the CO₂ discharge. For instance, physical adsorption [2], membrane separation [3], and closed loop chemical absorption-desorption methods (CADM) [4-5] are used regularly to inhibit the CO₂ release to the atmosphere.

In addition to the capture of CO₂, sequestration of CO₂ is also very important. Geological and oceanic storage are considered as few of the promising options for the sequestration of CO₂, however, the high process cost is one of the limitations associated with such storage. A promising alternative to the geological and oceanic storage is the metal oxide based solar thermochemical conversion of CO₂ into C, CO, and O₂. Solid C can be safely stored and C/CO can further be used as combustion fuels or can be converted into the syngas for the production of transportation liquid fuels such as gasoline, kerosene (jet fuel) [6].

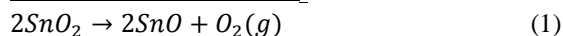
In past, several solar thermochemical metal oxide based redox cycles such as Fe₃O₄/FeO [7-8], ZnO/Zn [6, 9], SnO₂/SnO [10-14], ferrites [15-23], and ceria/doped ceria [24-27] were examined towards H₂O and CO₂ splitting reactions. Previous studies indicate that among the various metal oxide systems investigated, volatile metal oxide systems such as SnO₂/SnO redox cycle is very promising due to its higher chemical reactivity.

A two-step thermochemical H₂O splitting reaction based on SnO₂/SnO redox cycle was first investigated experimentally by Charvin et al. [10]. Chambon et al. [12] further investigated the reaction kinetics of the thermochemical water splitting reaction based on SnO₂/SnO redox cycle. The hydrolysis of different kinds of tin oxide powders at different experimental conditions were examined by Vishnevetsky and Epstein [13]. Recently, Abanades [11] investigated the reduction of CO₂ and H₂O by solar thermochemical looping using SnO₂/SnO redox reactions by performing thermogravimetric experiments.

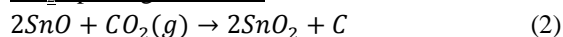
This paper reports the computational thermodynamic modeling of solar thermochemical SnO₂/SnO redox cycle for conversion of CO₂ into solid C. The production of solid C via solar thermochemical SnO₂/SnO based CO₂ splitting

cycle can be achieved according to the following reaction scheme.

Thermal Reduction of SnO₂:



CO₂ Splitting to solid C:



The computational thermodynamic modeling was performed with the help of commercial thermodynamic HSC Chemistry software and databases [28]. The equilibrium and exergy analysis was performed to determine the solar absorption efficiency of the solar reactor ($\eta_{absorption}$), solar energy input to the solar reactor (Q_{solar}), net energy absorbed in the solar reactor ($Q_{reactor-net}$), radiation heat losses from the solar reactor ($Q_{re-radiation}$), rate of heat rejected to the surrounding from the quench unit (Q_{quench}) and from the SnO oxidizer ($Q_{sno-oxd}$), and solar to fuel conversion efficiency ($\eta_{solar-to-fuel}$) and results are presented in detail. A typical SnO₂/SnO based two-step solar thermochemical CO₂ splitting process for the production of solid C is presented in Fig. 1.

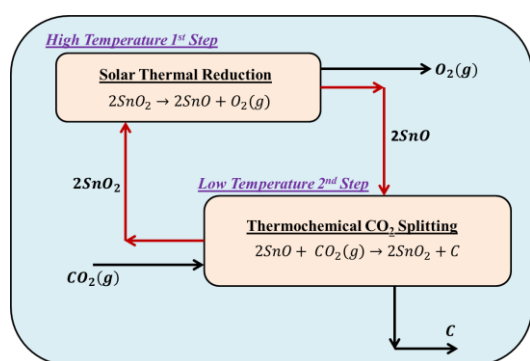


Fig. 1. A typical SnO₂/SnO based two-step solar thermochemical CO₂ splitting process.

II. EQUILIBRIUM ANALYSIS

The equilibrium composition of the solar thermal reduction of SnO₂ (in absence of inert Ar) is shown in Fig. 2a. According to the equilibrium composition analysis, in absence of inert Ar, the solar thermal reduction of SnO₂ started at 2080K and 100% thermal reduction into gaseous SnO and O₂ were achieved at or above 2380K. In contrast to this, if inert Ar = 45 mole/sec was used as the

carrier gas inside the solar reactor, the starting temperature of the thermal reduction of SnO₂ and the temperature required for the 100% conversion into gaseous SnO and O₂ was reduced to 1500K and 1900K, respectively (Fig. 2b).

Fig. 3 represents the equilibrium compositions associated with the thermochemical splitting of CO₂ to produce solid C using SnO₂/SnO redox cycle. This step was carried out in absence of Ar (as it is not required). According to the results reported in Fig. 3, the solid C production via thermochemical splitting of CO₂ via SnO oxidation was feasible from 298 K to 775 K. After 775K, the production of solid C decreased and production of gaseous CO increased. From 775K upto 990K, thermochemical CO₂ splitting via SnO oxidation yields into a product mixture of solid C and gaseous CO. Furthermore, above 990K, solid C production was not feasible and gaseous CO was the only product of thermochemical splitting of CO₂ via SnO oxidation.

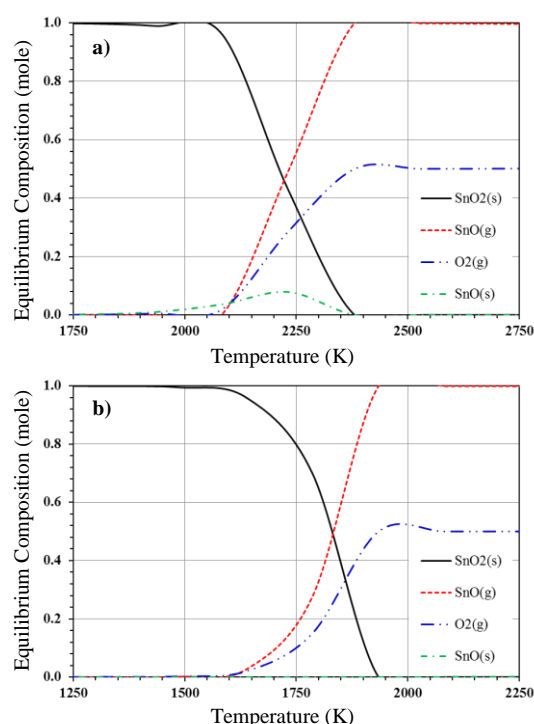


Fig. 2. Equilibrium compositions associated with the solar thermal reduction of SnO₂, a) Ar = 0 mole, b) Ar = 45 mole.

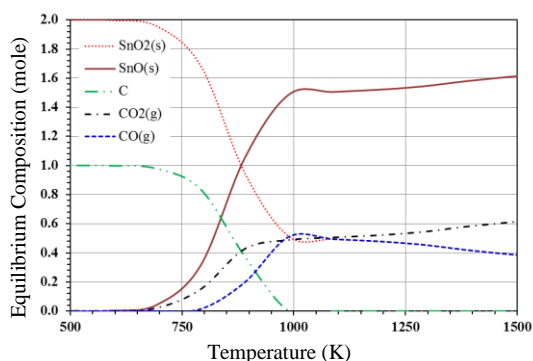


Fig. 3. Equilibrium compositions associated with the thermochemical splitting of CO₂ to produce solid C using SnO₂/SnO redox cycle.

III. EXERGY ANALYSIS

To determine the maximum possible solar to fuel conversion efficiency, we performed the second law exergy analysis of the SnO₂/SnO based two-step solar thermochemical CO₂ splitting process used for solid C production. The process flow configuration of this solar thermochemical cycle is shown in Fig. 4. The continuous SnO₂/SnO based solid C production via thermochemical CO₂ splitting process consists of a solar reactor, a quench unit, a CO₂ reducer, a gas separator and a theoretical C/O₂ ideal fuel cell. The molar flow rates of SnO₂ and inert Ar gas entering the solar reactor were fixed to 2 mole/sec and 45 mol/sec.

This process was assumed to be operated at

total pressure equal to 1 atm and at steady state conditions. Some aspects of this process have been omitted from the calculations such as the heat exchangers used for recovering sensible latent heat. Furthermore, several assumptions were made which includes: 1) a perfectly insulated solar reactor, 2) no convective/conductive heat losses, 3) kinetic and potential energies are neglected, and 4) all reactions proceed to completion. Thermodynamic properties were extracted from HSC software and databases and the analysis is normalized to the SnO₂ molar flow rate (2 mole/sec) entering the solar reactor as shown in Fig. 4.

Solar energy absorption efficiency

The solar energy absorption efficiency ($\eta_{absorption}$) is defined as the net rate at which the solar energy is absorbed by the reactor performing thermal reduction of SnO₂ divided by the solar energy input through the aperture of the solar reactor. By assuming the solar reactor as a perfectly insulated blackbody cavity-receiver (no convection or conduction heat losses; effective absorptivity and emissivity equal to 1), the solar energy absorption efficiency for solar thermochemical SnO₂/SnO redox cycle for solid C production via CO₂ splitting was calculated as:

$$\eta_{absorption} = \frac{Q_{reactor-net}}{Q_{solar}} = 1 - \left(\frac{\sigma T_H^4}{IC} \right) \quad (3)$$

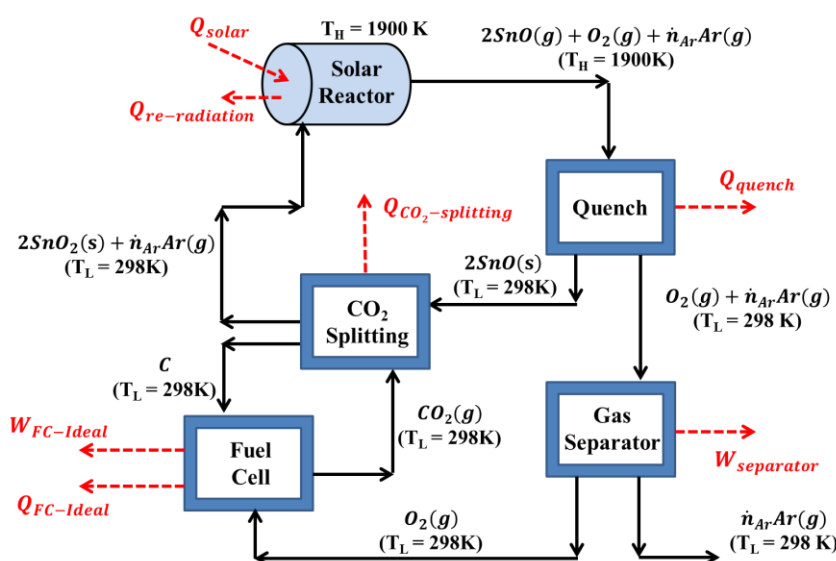


Fig. 4. Process flow configuration of solar thermochemical SnO₂/SnO redox cycle for solid C production via CO₂ splitting.

Net solar energy absorbed by the solar reactor

As per the process configuration shown in Fig. 4, the molar flow rate of the continuous stream of SnO₂ and inert Ar gas entering in the solar reactor is equal to 2 mole/sec and 45 mole/sec, respectively. By utilizing solar energy, these streams were heated up to 1900K and SnO₂ then undergoes 100% thermal reduction. Hence the net solar energy absorbed by the solar reactor was calculated as:

$$Q_{reactor-net} = \dot{n}\Delta H|_{\substack{2SnO_2(s)+45Ar(g)@298K \rightarrow \\ 2SnO(g)+O_2(g)+45Ar(g)@1900K}} \quad (4)$$

Solar energy input to the solar reactor

After obtaining the solar absorption efficiency and the net solar energy absorbed by the solar reactor, the total solar energy input needed to operate the solar reactor (Q_{solar}) for the production of solid C via solar thermochemical CO₂ splitting using SnO₂/SnO based redox reactions was determined by following equation:

$$Q_{solar} = \frac{Q_{reactor-net}}{\eta_{absorption}} \quad (5)$$

Irreversibility associated with the solar reactor

Irreversibility in the solar reactor arises from the non-reversible chemical transformations and re-radiation losses to the surroundings at 1900K, which was estimated by using Eq. (6):

$$Irr_{reactor} = -\left(\frac{Q_{solar}}{T_H}\right) + \left(\frac{Q_{re-radiation}}{T_L}\right) + \dot{n}\Delta S|_{\substack{2SnO_2(s)+45Ar(g)@298K \rightarrow \\ 2SnO(g)+O_2(g)+45Ar(g)@1900K}} \quad (6)$$

Re-radiation losses from the solar reactor

Radiation heat losses from the solar reactor conducting the thermal reduction of SnO₂ can be calculated by Eq. (7).

$$Q_{re-radiation} = Q_{solar} - Q_{reactor-net} \quad (7)$$

Heat rejected to the surrounding by quench unit

The solar thermal reduction of SnO₂ at 1900K resulted into a gaseous mixture containing SnO(g), O₂(g) and inert Ar(g) at 1900K. At such a high

temperature, the gaseous SnO will try to recombine with the O₂ to form SnO₂. To avoid this recombination, a quench unit was used just after the solar reactor (to quench the gaseous product mixture to room temperature = 298K). It is also assumed that the chemical composition of the products remain unchanged upon cooling. The sensible and latent heat rejected by the quench unit to the surrounding was determined by Eq. (8).

$$Q_{quench} = -\dot{n}\Delta H|_{\substack{2SnO(g)+O_2(g)+45Ar(g)@1900K \rightarrow \\ 2SnO(s)+O_2(g)+45Ar(g)@298K}} \quad (8)$$

Irreversibility associated with the quench unit

In addition to the heat rejected by the quench unit, the irreversibility associated with the quench unit was also determined according to the Eq. (9).

$$Irr_{quench} = \left(\frac{Q_{quench}}{T_L}\right) + \dot{n}\Delta S|_{\substack{2SnO(g)+O_2(g)+45Ar(g)@1900K \rightarrow \\ 2SnO(s)+O_2(g)+45Ar(g)@298K}} \quad (9)$$

Heat rejected to the surrounding by CO₂ splitting reactor

After quenching, the products were assumed to separate naturally without expanding work. The solidified SnO leaving the quench was sent to the CO₂ splitting reactor where it was reacted with a stream of CO₂ to produce solid C at 298K. For this step, complete conversion of SnO to SnO₂ was assumed and the rate of heat rejected to the surrounding from the CO₂ splitting reactor was calculated as:

$$Q_{CO_2-splitting} = -\dot{n}\Delta H|_{2SnO(s)+CO_2(g) @298K \rightarrow 2SnO_2(s)+C@298K} \quad (10)$$

Irreversibility associated with the CO₂ splitting reactor

Similar to the solar reactor and quench unit, the irreversibility associated with the CO₂ splitting reactor was estimated as per Eq. (11).

$$Irr_{CO_2-splitting} = \left(\frac{Q_{CO_2-splitting}}{T_L}\right) + \dot{n}\Delta S|_{2SnO(s)+CO_2(g) @298K \rightarrow 2SnO_2(s)+C@298K} \quad (11)$$

Work done by the gas separator

It was previously assumed that the SnO after quenching separates naturally (without requiring work) from the gaseous mixture of O₂ and Ar. However, to split and separate the O₂ and Ar gases, a gas separator was needed. The minimum work done by the gas separator at 298K was also determined according to Eq. (12).

$$W_{separator} = \dot{n}_{SnO_2} RT_L \left[0.5 \ln \left(\frac{1}{y_{O_2}} \right) + \frac{\dot{n}_{Ar}}{\dot{n}_{SnO_2}} \ln \left(\frac{1}{y_{Ar}} \right) \right] \quad (12)$$

Rates of theoretical work performed and heat rejected by the ideal fuel cell

An ideal fuel cell was added to the process configuration in Fig. 4 in order to complete the SnO₂/SnO based solid C production cycle and calculate the maximum possible theoretical work that can be extracted from this cycle. The ideal fuel cell operates in the presence of C/O₂, and the rates of theoretical work performed and the heat rejected by the fuel cell was calculated by using following equations in which the efficiency of the fuel cell was assumed to be 100%.

$$W_{FC-ideal} = -(\eta_{FC}) \times \dot{n} \Delta G|_{C+O_2(g) \rightarrow CO_2(g)} @ 298K \quad (13)$$

$$Q_{FC-ideal} = -(T_L) \times \dot{n} \Delta S|_{C+O_2(g) \rightarrow CO_2(g)} @ 298K \quad (14)$$

Process efficiency

Cycle efficiency of the solar thermochemical process is defined as the ratio of net work performed by the cycle to the solar energy input:

$$\eta_{cycle} = \frac{W_{net}}{Q_{solar}} \quad (15)$$

Where,

$$W_{net} = W_{FC-ideal} - W_{separator} \quad (16)$$

Furthermore, the solar-to-fuel conversion efficiency of this process is defined as the ratio of higher heating value (HHV) of the C produced to the solar energy input:

$$\eta_{solar-to-fuel} = \frac{HHV_C}{Q_{solar}} \quad (17)$$

Heat recuperation

The η_{cycle} and $\eta_{solar-to-fuel}$ for the solar thermochemical SnO₂/SnO redox cycle for solid C production via CO₂ splitting can be enhanced further if the heat rejected by the quench unit and CO₂ splitting reactor was recuperated and utilized to operate this cycle.

$$Q_{recuperable} = Q_{quench} + Q_{CO_2-splitting} \quad (18)$$

Furthermore, the solar energy input required for the operation of this cycle after heat recuperation can be estimated as:

$$Q_{sol-recuperation} = Q_{solar} - (\% recuperation \times Q_{recuperable}) \quad (19)$$

The η_{cycle} and $\eta_{solar-to-fuel}$ after heat recuperation can be determined as:

$$\eta_{cycle} = \frac{W_{net}}{Q_{sol-recuperation}} \quad (20)$$

$$\eta_{solar-to-fuel} = \frac{HHV_C}{Q_{sol-recuperation}} \quad (21)$$

The results of the exergy analysis for the solar thermochemical SnO₂/SnO redox cycle for solid C production via CO₂ splitting are listed in TABLE I. The baseline parameters are, molar flow rate of SnO₂ = 2 mole/sec, molar flow rate of inert Ar = 45 mole/sec, thermal reduction temperature = 1900K, CO₂ splitting temperature = 298K, I = 1 kW/m², C = 1000 suns. According to the obtained results, the η_{cycle} and $\eta_{solar-to-fuel}$ of the investigated solar thermochemical cycle was observed to be equal to 3.47% and 3.57%, respectively.

The η_{cycle} and $\eta_{solar-to-fuel}$ of this solar thermochemical cycle can be further improved by using higher value of C and by employing heat recuperation. For instance, as the concentration ratio (C) increased from 1000 to 5000 suns, the η_{cycle} and $\eta_{solar-to-fuel}$ was increased upto 11.33% and 11.65%, respectively. Likewise, if 50% heat recuperation was applied (with C = 1000 suns), the η_{cycle} and $\eta_{solar-to-fuel}$ was increased upto 3.91% and 4.02%, respectively.

TABLE I

Exergy analysis of solar thermochemical SnO₂/SnO redox cycle for solid C production via CO₂ splitting.

Net Reaction Cycle	CO ₂ Splitting to C
Q_{solar} (kW)	11028.5
$Q_{re-radiation}$ (kW)	8150.06
$Q_{reactor-net}$ (kW)	2878.44
$Irr_{reactor}$ (kW/K)	24.06
Q_{quench} (kW)	2284.6
Irr_{quench} (kW/K)	5.374
$Q_{splitting}$ (kW)	200.34
$Irr_{splitting}$ (kW/K)	0.4479
$Q_{FC-Ideal}$ (kW)	-0.858
$W_{FC-Ideal}$ (kW)	394.48
$W_{separator}$ (kW)	11.936
W_{net} (kW)	382.544
$\eta_{absorption}$ (%)	26.1
η_{cycle} (%)	3.47
$\eta_{solar-to-fuel}$ (%)	3.57

IV. SUMMARY

Solar thermochemical SnO₂/SnO redox cycle for solid C production via CO₂ splitting was thermodynamically investigated using HSC Chemistry software and databases. First of all the thermodynamic equilibrium compositions associated with the solar thermal reduction of SnO₂ and thermochemical CO₂ splitting via SnO oxidation for solid C production were identified. It was observed that the 100% thermal reduction of SnO₂ can be achieved at 1900K by using Ar as an inert gas (45 mole/sec). It was also observed that the solid C production via thermochemical CO₂ splitting reaction was favorable below 775K and the CO production was suitable above 990K. The exergy analysis performed indicate that the

η_{cycle} and $\eta_{solar-to-fuel}$ of this process (at molar flow rate of SnO₂ = 2 mol/sec, molar flow rate of inert Ar = 45 mol/sec, thermal reduction temperature = 1900K, CO₂ splitting temperature = 298K, I = 1 kW/m², C = 1000 suns) equal to 3.47% and 3.57%, respectively. Furthermore, η_{cycle} and $\eta_{solar-to-fuel}$ of this process can be increased by a factor of 3.25 if the concentration ratio was increased from 1000 to 5000 suns. Similarly, η_{cycle} and $\eta_{solar-to-fuel}$ of this process can also be increased by 11% if 50% heat recuperation was applied.

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NOMENCLATURE

C	Solar flux concentration ratio, suns
HHV	Higher heating value
I	Normal beam solar insolation, W/m ²
$Irr_{reactor}$	Irreversibility in the solar reactor (kW/K)
Irr_{quench}	Irreversibility in the quench (kW/K)
$Irr_{splitting}$	Irreversibility in the splitting reactor (kW/K)
MO	Metal oxide
\dot{n}	Molar flow rate, mole/sec
\dot{n}_{Ar}	Molar flow rate of Ar, mole/sec
$Q_{Ar-heating}$	Energy required for heating of Ar, kW
Q_{quench}	Heat rejected to the surrounding from quench unit, kW
$Q_{FC-Ideal}$	Heat rejected to the surrounding from ideal fuel cell, kW
$Q_{CO_2-splitting}$	Heat rejected to the surrounding from CO ₂ splitting reactor, kW
$Q_{reactor-net}$	Net solar energy absorbed by the solar reactor, kW
$Q_{re-radiation}$	Radiation heat loss from the solar reactor, kW
$Q_{recuperable}$	Total amount of heat that can be recuperated, kW
Q_{solar}	Solar energy input, kW

$Q_{sol-recuperation}$	Solar power input after heat recuperation, kW
T_H	Thermal reduction temperature, K
T_L	Water splitting temperature, K
$W_{FC-ideal}$	Work output of an ideal fuel cell, kW
W_{net}	Net work output of the cycle, kW
$W_{separator}$	Work output of the separator, kW
$\eta_{absorption}$	Solar absorption efficiency, %
η_{cycle}	Cycle efficiency, %
$\eta_{solar-to-fuel}$	Solar to fuel conversion efficiency, %
ΔG	Gibbs free energy change, kJ/mol
ΔH	Enthalpy change, kJ/mol
ΔS	Entropy change, J/mol·K
σ	Stefan – Boltzmann constant, 5.670×10^{-8} (W/m ² ·K ⁴)

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