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# Solar co-production of samarium and syngas via methanothermal reduction of samarium sesquioxide

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ABSTRACT

This paper reports the thermodynamic analysis of the solar methanothermal reduction of $Sm_2O_3$ for the co-production of Sm and syngas in (a) Sm–Syngas open cycle, and (b) Sm–Syngas closed cycle. As per the chemical thermodynamic equilibrium modeling, the conversion of $Sm_2O_3$ into Sm increase with the increase in the $CH_4/Sm_2O_3$ ratio and 100% conversion is possible at 2528 K if $CH_4/Sm_2O_3$ ratio is equal to 3 is used. Exergy efficiency analysis of both open and closed cycles indicate that the $Q_{Sm_2O_3\text{-}reduction}$, $Q_{solar}$, $Q_{re\text{-}radiation}$, and $Q_{quench}$ increases with the increase in the $CH_4/Sm_2O_3$ ratio. Likewise, $W_{FC\text{-}Ideal\text{-}1}$, $Q_{FC\text{-}Ideal\text{-}1}$, and $HHV_{syngas\text{-}1}$ also increases with the upsurge in the $CH_4/Sm_2O_3$ ratio. Similar observations were realized in case of Sm–Syngas closed cycle. The $\eta_{exergy}$ (33.91%) and $\eta_{solar\text{-}to\text{-}fuel}$ (45.93%) of the Sm–Syngas open cycle was observed to be maximum in case of $CH_4/Sm_2O_3$ ratio = 3. As one of the applications, Sm was utilized toward splitting of $H_2O$ and $CO_2$ together for the production of syngas via Sm–Syngas closed cycle. At similar operating conditions, the $\eta_{exergy\text{-}closed}$ (45.22%) and $\eta_{solar\text{-}to\text{-}fuel\text{-}closed}$ (61.24%) of the Sm–Syngas closed cycle was observed to be higher as compared to the Sm–Syngas open cycle. Furthermore, it was observed that, these efficiency values can be increased significantly due to the utilization of higher values of C and recycling of the heat rejected by the quench unit and $H_2O/CO_2$ splitting reactor.



## 1. Introduction

Solar Samarium (Sm) production is very favorable as this metal can be used in various applications. One of the most vital applications of Sm is in samarium-cobalt magnets [1–3]. These magnets have higher permanent magnetization as compared to other magnets. These magnets also show higher resistance to demagnetization. Samarium based magnets can be used in small motors, headphones, guitars and related music instruments. Another important application of Sm and its compounds is as a catalyst and a chemical reagent [4–7]. Sm based catalysts and reagents are useful for the decomposition of plastics, dechlorination of pollutants, dehydration and dehydrogenation of ethanol, halogen-promoted Friedel–Crafts reaction with alkenes, organic synthesis via desulfonylation reactions, annulation, strychnine total synthesis, Barbier reaction, and etc.

Radioactive samarium-153 is used to kill cancer cells in the treatment of lung cancer, prostate cancer, breast cancer, and osteosarcoma [8,9]. Samarium-149 has high cross-section for neutron capture and stability of absorption, and therefore used in the control rods of nuclear reactors [10]. Samarium-doped calcium fluoride crystals can be used in solid state lasers and X-ray lasers which further can be utilized for applications in holography, high-resolution microscopy of biological specimens, deflectometry, interferometry, and radiography of dense plasmas related to confinement fusion and astrophysics [11,12]. Samarium monochalcogenides are used in commercially developed pressure sensors or in a memory devices triggered between a low-resistance and high-resistance state by external pressure. Samarium–Neodymium dating (Sm–Nd Dating) is a technique generally employed to determine the age and origin of rocks and meteorites by using the samarium and neodymium isotopes $^{147}Sm$, $^{144}Nd$, and $^{143}Nd$, respectively [13].

Recent studies reported that the solar syngas (a mixture of $H_2$ and CO) can be produced via metal oxide based two-step $H_2O/CO_2$ splitting process. Although, production of $H_2$ is possible via gasification and reforming of fossil fuels [14–17], pyrolysis and

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**Nomenclature**

| | |
|---|---|
| $C$ | solar flux concentration ratio, suns |
| $HHV$ | higher heating value |
| $HHV_{syngas\text{-}1}$ | higher heating value of syngas produced by Sm–Syngas open cycle, kW |
| $HHV_{syngas\text{-}1}$ | higher heating value of syngas produced by Sm–Syngas closed cycle, kW |
| $I$ | normal beam solar insolation, W/m$^2$ |
| $\dot{n}$ | molar flow rate, mol/s |
| $Q_{quench}$ | heat rejected to the surrounding from quench unit, kW |
| $Q_{FC\text{-}Ideal\text{-}1}$ | heat rejected to the surrounding from ideal fuel cell – 1, kW |
| $Q_{FC\text{-}Ideal\text{-}2}$ | heat rejected to the surrounding from ideal fuel cell –2, kW |
| $Q_{Sm\ \ oxidation}$ | heat rejected to the surrounding from $H_2O/CO_2$ splitting reactor, kW |
| $Q_{Sm_2O_3\text{-}reduction}$ | energy required for the methanothermal reduction of $Sm_2O_3$, kW |
| $Q_{re\text{-}radiation}$ | radiation heat loss from the solar reactor, kW |
| $Q_{recuperable}$ | total amount of heat that can be recuperated in case of Sm–Syngas open cycle, kW |
| $Q_{recuperable\text{-}closed}$ | total amount of heat that can be recuperated in case of Sm–Syngas closed cycle, kW |
| $Q_{solar}$ | solar energy input, kW |
| $Q_{solar,with\ \ recuperation}$ | solar power input after heat recuperation in case of Sm–Syngas open cycle, kW |
| $Q_{solar,with\ \ recuperation\text{-}closed}$ | solar power input after heat recuperation in case of Sm–Syngas closed cycle, kW |
| $T_H$ | thermal reduction temperature, K |
| $W_{FC\text{-}Ideal\text{-}1}$ | work output of an ideal fuel cell in case of Sm–Syngas open cycle, kW |
| $W_{FC\text{-}Ideal\text{-}2}$ | work output of an ideal fuel cell in case of Sm–Syngas closed cycle, kW |
| $\eta_{absorption}$ | solar absorption efficiency |
| $\eta_{exergy}$ | exergy efficiency in case of Sm–Syngas open cycle |
| $\eta_{exergy\text{-}closed}$ | exergy efficiency in case of Sm–Syngas closed cycle |
| $\eta_{solar\text{-}to\text{-}fuel}$ | exergy efficiency in case of Sm–Syngas open cycle |
| $\eta_{solar\text{-}to\text{-}fuel\text{-}closed}$ | exergy efficiency in case of Sm–Syngas closed cycle |
| $\sigma$ | Stefan–Boltzmann constant, $5.670 \times 10^{-8}$ (W/m$^2$ K$^4$) |

reforming of biomass [18–22], ethanol and methanol decomposition [23–27], etc.; lately, the researchers are attracted more toward $H_2$ generation via solar water splitting reaction. Likewise, the CO can be produced via solar thermochemical $CO_2$ splitting reaction. Various metal oxide systems such as ZnO/Zn, $SnO_2$/SnO/Sn, $Fe_3O_4$/FeO, undoped and doped ceria, mixed ferrites, and perovskites were investigated in past toward production of solar $H_2$, CO, or syngas via thermochemical splitting of $H_2O/CO_2$ in multiple cycles [28–51].

In the present study, the thermodynamics of the methanothermal reduction of samarium sesquioxide ($Sm_2O_3$) for the co-production of Sm and syngas via solar thermochemical Sm–Syngas cycle is studied. Thermodynamic data required for the calculations is collected from HSC Chemistry 7.1 software and databases. Effects of ratio of $CH_4/Sm_2O_3$ and reaction temperature on thermodynamic equilibrium compositions, $Sm_2O_3$ conversion, syngas production, solar energy input, radiation heat losses, heat rejected by quench unit, exergy and solar-to-fuel conversion efficiency are explored and presented in detail.

## 2. Materials and methods

To perform the thermodynamic calculations in a traditional way, we need to bank on the experimental or assessed data (which utilizes stability functions) published in different thermodynamic books or scientific journal papers. This approach is time consuming due to the difficulty in searching the thermodynamic data in published literature and also the calculations involved are very complicated. Furthermore, the inconsistencies arising from different selections of standard and reference states make the final results unreliable. HSC Chemistry software and its databases make the conventional thermodynamic calculations fast and easy to carry out with personal computers. It offers commanding calculations procedures for investigating the influence of different variables on a chemical system at equilibrium. In addition to the thermodynamic calculations, with the help of HSC Chemistry software and its databases, heat and material balance calculations of different processes can be carried out much more easily as compared to the manual method. The dissolution and corrosion behavior of different materials can also be studied in an expedite way by using the Eh-pH-diagrams available in HSC Chemistry software. One of the limitations associated with the HSC Chemistry software is that it cannot solve all chemical problems as it does not take into account the kinetics of the chemical reactions. Nevertheless, it can be used to find the optimal reaction conditions and yields of experiments (without carrying out actual expensive experiments) in an economical and effective manner. The name of the software is decided based on the fact that the calculations can be done by utilizing thermochemical database related to enthalpy (H), entropy (S), and heat capacity (Cp) for more than 28,000 chemical species (equivalent to more than twenty thick data books). Due to all these advantages, HSC has a wide range of applications in scientific education, industry and research.

In this study, HSC Chemistry software and its database (version 7.1) is used to perform the thermodynamic calculations. The thermodynamic analysis is performed in two sections: Section 1 – thermodynamic equilibrium analysis, and Section 2 – exergy efficiency analysis. In Section 1, the equilibrium compositions associated with the methanothermal reduction of $Sm_2O_3$ are identified (at different $CH_4/Sm_2O_3$ molar ratios). In Section 2, the exergy and solar to fuel conversion efficiency of the examined cycle is determined. The exergy efficiency analysis is performed by using the methodology developed in this investigation and reported in the results and discussion section. This methodology is developed by considering the previous publications associated with the thermodynamics analysis of different metal oxide based solar thermochemical $H_2O$ and $CO_2$ splitting cycles as a basis [29,31,52–54]. This study is purely based on the computational thermodynamics modeling and hence no experiments are performed (no chemicals or materials used). To perform the thermodynamic calculations, few fix parameters are used such as:

1. $CH_4/Sm_2O_3$ molar ratios from 0.5 to 3.
2. Direct-normal solar irradiance (normal bean insolation), $I$ = 1000 W/m$^2$.
3. Solar flux concentration ratio, $C$ = 5000 suns.