STOICHIOMETRIC OPERATION OF THE SYNMET REACTOR

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The thermodynamic implications of conducting the solar combined ZnO-reduction and CH₄-reforming under stoichiometric and non-stoichiometric conditions are examined. For a solar flux concentration ratio of 5000 and for a solar cavity-receiver operating at 1300 K, the solar thermal conversion efficiency is 55 % for a stoichiometric molar ratio of ZnO and CH₄, and decreases by 50 % when using excess methane by a factor 10 over the stoichiometric molar amount. A technical solution for operating a gas-solid vortex-flow solar reactor under stoichiometric conditions was established by using a pulsed-feed of methane to carry out the particles of ZnO. Using this technique, nearly stoichiometric operation was demonstrated with a prototype reactor in a high-flux solar furnace, thereby opening up a means for efficient conversion of sunlight into chemical fuels.

1 INTRODUCTION

Zinc and synthesis gas (syngas), besides being important material commodities, are attractive as energy carriers. Zinc finds applications in Zn/air fuel cells and batteries, and it can also be reacted with water to form hydrogen. Syngas is the building block of a wide variety of synthetic liquid fuels, including methanol - a promising substitute of gasoline for fuelling cars. However, the current industrial production techniques of both zinc and syngas carry severe environmental consequences, especially CO_2 emissions. These emissions can be reduced substantially, by combining both the production of Zn and syngas and by replacing fossil fuels with concentrated solar energy as the source of high-temperature process heat. The proposed solar combined process, called "SynMet", can be represented by the overall reaction:

$$ZnO + CH_4 \rightarrow Zn + 2H_2 + CO \qquad (1)$$

The use of solar energy for supplying the enthalpy of the reaction upgrades the calorific value of the initial reactants by 39%. Thus, using the SynMet process, solar energy is converted into storable and transportable chemical fuels.

In recent articles [1-3] we described the process and the engineering design and testing of a solar chemical reactor for performing the SynMet process. The solar reactor concept features a gas-particle vortex flow confined to a windowed cavity-receiver that is exposed to concentrated solar irradiation. A continuous primary flow of methane was used to carry the particles of ZnO. A secondary flow of methane was also used as an aerodynamic curtain to protect the quartz window from deposition of particles and/or condensable gases. Because of the fluid mechanic characteristics of this kind of gas-solid vortex reactor, excess methane was used over the stoichiometric ratio [as given by Eq. (1)]. However, excess methane, or the use of any other carrier gas that is not participating in the reaction, results in a significant reduction of the energy conversion efficiency. Attempts to reduce the primary carrying flow to the stoichiometric amount resulted in plugging and sedimentation inside the cavity, while reducing the secondary protecting flow resulted in Zn condensation on the window.

In the present paper we examine the thermodynamic implications of non-stoichiometry on the solar energy conversion efficiency. We further describe an original and simple engineering solution to this problem and present experimental results that allowed nearly stoichiometric operation of the SynMet process.

2 THERMODYNAMIC IMPLICATIONS

The capability of a solar cavity-receiver to absorb the incoming solar power is expressed in terms of its absorption efficiency $\eta_{absorption}$, defined as the net energy absorbed $Q_{net,absorption}$ divided by the solar energy coming from the concentrator Q_{solar}. For a perfectly insulated blackbody cavity-receiver (no convection or conduction heat losses), it is given by [3,4]

$$\eta_{absorption} = \frac{Q_{net,absorption}}{Q_{solar}} = 1 - \frac{\sigma T^4}{IC} \qquad (2)$$

where T is the nominal reactor temperature, I is the normal beam insolation, C is the mean solar flux concentration ratio over the cavity's aperture (typically 500-10000 for large-scale solar concentrating facilities), and η is the Stefan-Boltzmann constant. $Q_{net,absorption}$ is used to heat the reactants ZnO and CH_4 to the reactor temperature and for supplying the heat of the reaction.

The solar energy stored at 298 K, ηH_{298K}, is 314.9 kJ/mol. Thus, assuming no heat recovery, the overall solar thermal energy conversion efficiency $\eta_{thermal}$ is given by [5]

$$\eta_{thermal} = \Delta H_{298K} \frac{1 - \left[\sigma T^4 / (CI)\right]}{\int_{298K}^{T} \left(c_{p,ZnO} + f \cdot c_{p,CH_4}\right) dT + \Delta H_{rxn}(T)} \qquad (3)$$

where c_p is the specific heat, ηH_{rxn} is the enthalpy change of the reaction at T, and f is the stoichiometric factor defined as the molar ratio of CH_4 to ZnO in the reactants. In Eq. (3) it is assumed that reactants are fed at 298 K and that $f \geq 1$. Figure 1 shows the variation of $\eta_{thermal}$ as a function of f, for various temperatures in the range 1300 - 1900 K, and for various solar flux concentration ratios in the range 3500-10000. As expected, the thermal efficiency is maximum for the stoichiometric molar ratio ($f=1$), and decreases monotonically with increasing stoichiometric factors because a larger portion of the solar energy input is lost in heating excess methane. For example, for a flux concentration of 5000 and a reactor temperature of 1300 K, $\eta_{thermal}$ reaches about 55% when f equals unity but decreases to about 27.5 % for $f>10$, and below 10% for $f>50$.
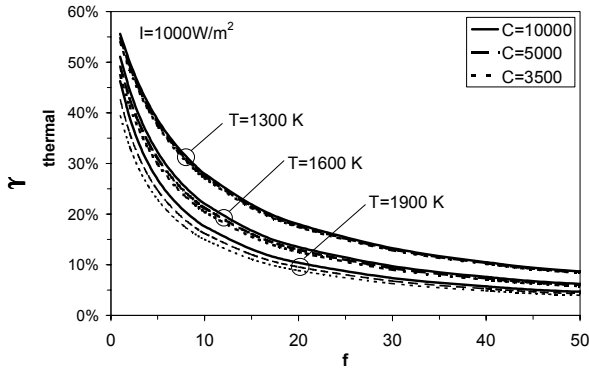
Fig. 1: Variation of the solar thermal conversion efficiency as a function of the stoichiometric factor for various temperatures and solar flux concentration ratios [5].

3   EXPERIMENTAL

The continuous injection of CH_4 in the primary vortex flow that carries the ZnO particles was substituted by a discontinuous pulsed feeding of CH_4 and an independent continuous feeding of ZnO. The secondary flow that protects the window remained unchanged (continuous flow). Figure 2 shows the experimental set-up. The ZnO powder is continuously fed by a spiral-type feeder located at the rear end of the reactor cavity. Short pulses of CH_4 are simultaneously injected through a tangential inlet nozzle at the site where the ZnO particles fall. The pulse duration and the time interval between consecutive pulses are controlled by a programmable logic module.
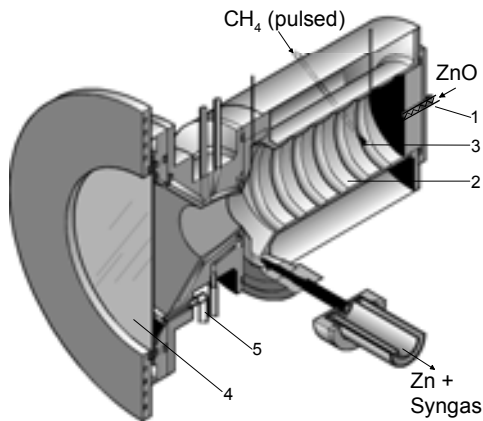

Fig. 2: Schematic of the reactor set-up. Legend: (1) spiral-type feeder; (2) reactor cavity; (3) primary CH_4 inlet; (4) quartz window; (5) secondary CH_4 flow for window protection.

The new system was first cold-tested. Qualitative flow pattern visualisation revealed the creation of a stable swirling particle cloud that would absorb the incoming high-flux solar irradiation efficiently and would further shield and protect the reactor walls. When compared to earlier experiments under similar conditions but using a continuous primary gas feeding, the particle cloud obtained for the pulsed gas feeding was much more dense and uniformly distributed over the cavity space. Experiments were also conducted at temperatures up to 1400 K with concentrated solar radiation at

the PSI solar furnace. Results are shown in Figure 3 for a set of representative experiments that lasted between 10 and 20 minutes. In each of these solar runs, a stable operation of the vortex flow was achieved while keeping the window clean from particles or condensable gases by means of the auxiliary flow.

The diagonal solid line indicates stoichiometric feeding of CH_4 and ZnO at the primary flow, i.e. $f_{primary}=1$. Below this line, CH_4 is deficient, i.e. $f_{primary}<1$. All data points lay in the region $f_{primary}<1$. Thus, a satisfactory operation was obtained without the need of working with excess methane at the primary flow. Operation under exact stoichiometric conditions will require an adjustment of the secondary continuous flow that is used for window protection. Experiments aimed at determining the fraction of ZnO reduced for various values of f are scheduled for the next measurement campaign.
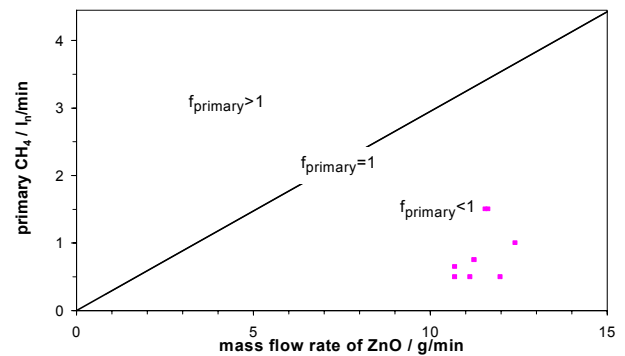
Fig. 3: Measured CH_4 mass flow rate as a function of the ZnO mass flow rate [5].

4   ACKNOWLEDGEMENT

5   REFERENCES

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