

# Solar Thermochemical Conversion of Carbon Dioxide into Fuel via $\text{MnFe}_2\text{O}_4$ based Two-Step Redox Cycle

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## Research Article

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2                               **based Two-Step Redox Cycle**

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## ABSTRACT

Thermodynamic efficiency analysis of  $MnFe_2O_4$  based  $CO_2$  splitting (CDS) cycle is reported. HSC Chemistry software is used for performing the calculations allied with the model developed. By maintaining the reduction nonstoichiometry equal to 0.1, variations in the thermal energy required to drive the cycle ( $\dot{Q}_{TC}$ ) and solar-to-fuel energy conversion efficiency ( $\eta_{solar-to-fuel}$ ) as a function of the ratio of the molar flow rate of inert sweep gas ( $\dot{n}_{inert}$ ) to the molar flow rate  $MnFe_2O_4$  ( $\dot{n}_{MnF}$ ), i.e.,  $\dot{n}_{inert}/\dot{n}_{MnF}$ , reduction temperature ( $T_{red}$ ), and gas-to-gas heat recovery effectiveness ( $\varepsilon_{gg}$ ) are studied. The rise in  $\dot{n}_{inert}/\dot{n}_{MnF}$  is responsible for the decrease in  $T_{red}$ . At  $\varepsilon_{gg} = 0.7$ ,  $\dot{Q}_{TC}$  increases from 176.0 kW to 271.7 kW when  $\dot{n}_{inert}/\dot{n}_{MnF}$  escalates from 10 to 100. Conversely,  $\eta_{solar-to-fuel}$  reduces from 14.9% to 9.9% due to the similar increment in  $\dot{n}_{inert}/\dot{n}_{MnF}$ . The difference between  $\dot{Q}_{TC}$  at  $\dot{n}_{inert}/\dot{n}_{MnF} = 10$  and 100 decreases from 363.3 kW to 19.2 kW as  $\varepsilon_{gg}$  rises from 0.0 to 0.9. As  $\dot{Q}_{TC}$  and subsequently  $\dot{Q}_{solar}$  reduces as a function of  $\varepsilon_{gg}$ ,  $\eta_{solar-to-fuel}$  increases noticeably. At  $\varepsilon_{gg}$  equal to 0.9 and  $\dot{n}_{inert}/\dot{n}_{MnF}$  equal to 10 as well as 20, the maximum  $\eta_{solar-to-fuel}$  equal to 17.5% is realized.

Keywords:  $MnFe_2O_4$ ,  $CO_2$  splitting, thermodynamic model, solar fuels, gas-to-gas heat recovery

## 1. Introduction

The hazardous effects associated with the incessant emissions of CO<sub>2</sub> can be resolved by using technologies such as the solar thermochemical CO<sub>2</sub> splitting (CDS) cycle(Bhosale et al. 2019). This cycle is capable of splitting CO<sub>2</sub> into CO by using solar thermal power. The solar thermochemical community's final aim is to produce solar syngas by combining CO produced from CDS and H<sub>2</sub> produced from H<sub>2</sub>O splitting (WS)(Agrafiotis et al. 2015). A variety of fuels can be manufactured using the solar syngas via the catalytic Fischer Tropsch process.

The redox chemistry associated with the metal oxides (MOs) is used for driving the solar thermochemical cycle. Several MOs redox systems were investigated until now for both CDS and WS. The list includes ZnO/Zn(Koepf et al. 2016), SnO<sub>2</sub>/SnO/Sn(Abanades et al. 2008), Fe<sub>3</sub>O<sub>4</sub>/FeO/Fe(Kodama et al. 2006), ferrites(Amar et al. 2015), ceria(Bulfin et al. 2015), doped ceria(Takalkar et al. 2019), and perovskites(Dey et al. 2015). Among all the above mentioned MOs, ferrites (which are doped iron oxides) were examined for WS application more than CDS. The ferrites investigated until now mainly includes NiFe<sub>2</sub>O<sub>4</sub>(Bhosale 2019a), CoFe<sub>2</sub>O<sub>4</sub>(Scheffe et al. 2010), ZnFe<sub>2</sub>O<sub>4</sub> (Tamaura et al. 2001), Sn-ferrite(Bhosale et al. 2011), Mg-ferrite(Randhir et al. 2018), Ni-Zn-ferrite(Fresno et al. 2009), and Ni-Mg-ferrite(Takalkar et al. 2020).

Mn-ferrite ( $MnFe_2O_4$ ) was also tested for H<sub>2</sub> generation via WS reactions. A redox system comprised of Mn-ferrite/ZnO/H<sub>2</sub>O was examined for WS application at 1273 K(Inoue et al. 2004). 70% of the theoretical H<sub>2</sub> production is reported by Mn-ferrite nanoparticles produced via ball milling(Padella et al. 2005). Solid-state synthesized Mn-ferrite showed five times lower H<sub>2</sub> production aptitude than the Mn-ferrite prepared using high energy ball milling(Alvani et al. 2005). The rate of H<sub>2</sub> production via WS reaction was higher in the case of Mn-ferrite as compared

to  $ZnFe_2O_4$  and  $Fe_2O_3$  (Go et al. 2008). A powdered mixture comprised of Mn-ferrite and CaO produced 0.4 to 0.9 ml of  $H_2$ /g in three WS cycles performed at 1273 K (Tamura et al. 1998). A study also reported that the Mn-ferrite got segregated during the WS reaction (Ehrensberger et al. 1996). Sol-gel-derived Mn-ferrite nanoparticles were also tested for  $H_2$  production via thermochemical WS reaction (Bhosale et al. 2012).

All the studies mentioned above are experimental investigations of Mn-ferrite based WS cycle. Besides experimentally determined fuel production capacity, estimation of solar-to-fuel energy conversion efficiency ( $\eta_{solar-to-fuel}$ ) is also an essential step towards the judgment of a MO's suitability for solar thermochemical cycles. Recently,  $\eta_{solar-to-fuel}$  of Mn-ferrite based WS cycle has been reported (Bhosale 2019b). However, this study estimates  $\eta_{solar-to-fuel}$  without considering the thermal energy requirements allied with the heating of inert sweeping gas and separation of gaseous components. Besides, the utilization of Mn-ferrite based redox reactions for CDS is not yet studied. Hence, in this investigation, a theoretical model for the  $MnFe_2O_4$  based CDS cycle is developed and a detailed thermodynamic efficiency analysis is carried out.  $\eta_{solar-to-fuel}$  is calculated by considering the energy penalties associated with the heating of inert sweep gas and separation of inert/ $O_2$  and  $CO_2/CO$  gas mixtures.

## 2. Thermodynamic Model and Equations

By considering the following assumptions, a thermodynamic model is developed for the determination of  $\eta_{solar-to-fuel}$  and other process parameters of  $MnFe_2O_4$  based CDS cycle. The developed thermodynamic model is presented in Fig. 1.

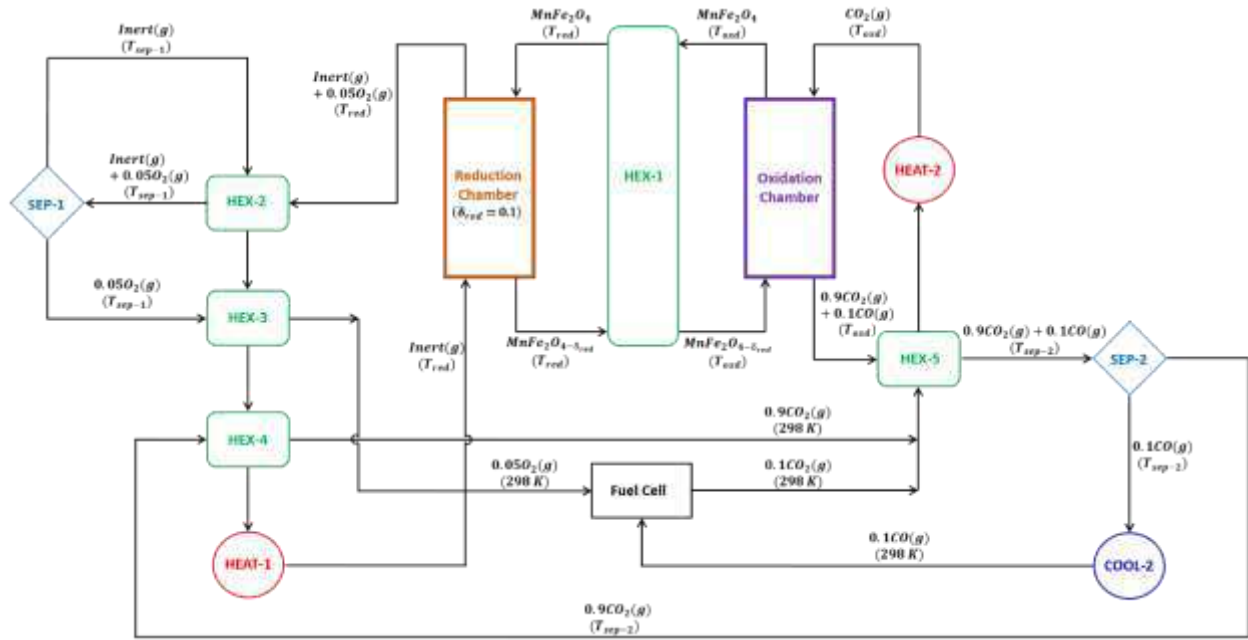
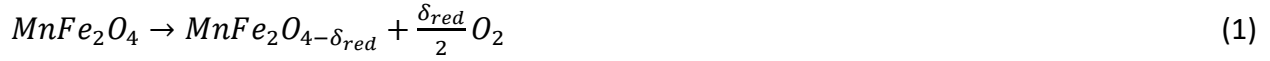


Fig. 1. Schematic of the process model of  $MnFe_2O_4$  based  $CO_2$  splitting cycle.

- 1) All processes operated at steady-state
- 2) Ideal gas behavior
- 3) Reduction, as well as oxidation chambers, are operated at isothermal conditions
- 4) Chemical equilibrium between the  $MnFe_2O_4$  and the gases
- 5) The efficiency of an Ideal  $CO_2/CO$  fuel cell equal to 100%
- 6) All reactions undergo complete conversion
- 7) Kinetic/potential energy and viscous losses are not considered
- 8) No side reactions
- 9) 20% of thermal energy losses from the reduction chamber
- 10) All the calculations are standardized to  $\dot{n}_{MnF} = 1 \text{ mol/s}$

As shown in Fig. 1, separate reaction chambers are installed to reduce and re-oxidize the Mn-ferrite, as per Eqs. (1) and (2). These two chambers are operated isothermally, i.e., the reduction

chamber at reduction temperature ( $T_{red}$ ) and the re-oxidation chamber at oxidation temperature ( $T_{oxd}$ ).



The equations listed above shows that the reduction and re-oxidation of  $MnFe_2O_4$  occurs in two separate steps. Step-1 deals with the release of  $O_2$  due to thermal reduction of  $MnFe_2O_4$ . On the other hand, re-oxidation of  $MnFe_2O_{4-\delta_{red}}$  is carried out in step-2, which results in the production of CO vi thermochemical CDS. All the calculations are performed by assuming  $\delta_{red} = 0.1$ .

The inert sweeping gas method is applied to maintain the partial pressure of  $O_2$  in the reduction chamber. The entrance of the inert sweep gas in the reduction chamber is located at the state  $red_1$ . Likewise, state  $red_2$  indicate the exit of the inert sweep gas from the reduction chamber.  $MnFe_2O_4$  is shuttled in the reduction chamber from state  $red_3$  to  $red_4$ . Estimation of the heat energy needed for the thermal reduction of  $MnFe_2O_4$  is carried out by using the following equation.

$$\dot{Q}_{MnF-red} = \dot{n}_{MnF} \Delta H |_{MnFe_2O_4 \rightarrow MnFe_2O_{4-\delta_{red}} + \frac{\delta_{red}}{2} O_2} \quad (3)$$

By using Eq.(4), the thermal energy needed for the heating of  $MnFe_2O_4$  from  $T_{oxd}$  to  $T_{red}$  is calculated.

$$\dot{Q}_{MnF-sens} = \dot{n}_{MnF} \Delta H |_{MnFe_2O_4 @ T_{oxd} \rightarrow MnFe_2O_4 @ T_{red}} \quad (4)$$

Thermal reduction of  $MnFe_2O_4$  results in the release of  $O_2$  from the ferrite crystal lattice. The released  $O_2$  is further conveyed away from the reduction chamber with the help of inert sweep gas. After exiting the reduction chamber, the gas mixture containing inert sweep gas and  $O_2$  is

cooled down from  $T_{red}$  to  $T_{sep-1}$  by using HEX-2 (gas-to-gas heat exchanger). After cooling, the gas mixture is further transported to separator-1 to separate  $O_2$  from the inert sweep gas. The separator-1 is operated with an assumed efficiency ( $\eta_{sep-1}$ ) equal to 15% and as per the process described in published literature (Ehrhart et al. 2016). The heat energy required for the separation of  $O_2$  from inert sweep gas is calculated as per the following set of equations:

$$\dot{Q}_{sep-1} = \dot{n}_{MnF} \left[ \frac{T_{sep-1}}{\eta_{sep-1}} (\Delta S_{mix,red_2} - \Delta S_{mix,red_1}) \right] \quad (5)$$

$$\Delta S_{mix,red_1} = -R \{ n_{inert} \ln(1 - y_{O_2,red_1}) + n_{O_2,red_1} \ln y_{O_2,red_1} \} \quad (6)$$

$$\Delta S_{mix,red_2} = -R \{ n_{inert} \ln(1 - y_{O_2,red_2}) + n_{O_2,red_2} \ln y_{O_2,red_2} \} \quad (7)$$

HEX-3 (gas-to-gas heat exchanger) is placed in the model to reduce the temperature of  $O_2$  separated from the inert sweep gas from  $T_{sep-1}$  to  $T_0 = 298$  K. After cooling,  $O_2$  is transferred to an ideal CO/ $O_2$  fuel cell. The inert sweep gas, separated from the  $O_2$ , is heated from  $T_{sep-1}$  to  $T_{red}$  by going through a series of three gas-to-gas heat exchangers, namely, HEX-1, HEX-2, and HEX-3. If required, supplementary heat is also provided with the help of an auxiliary heater-1. The energy required to heat the inert sweep gas is estimated as follows:

$$\dot{Q}_{inert-heat} = \varepsilon_{gg} [\dot{Q}_{(inert+O_2)-cool} + \dot{Q}_{O_2-cool} + \dot{Q}_{CO_2-cool}] + \dot{Q}_{heater-1} \quad (8)$$

Where,

$$\dot{Q}_{inert-heat} = \dot{n}_{inert} \Delta H|_{inert@T_{sep-1} \rightarrow inert@T_{red}} \quad (9)$$

$$\dot{Q}_{(inert+O_2)-cool} = \dot{n}_{inert} \Delta H|_{inert@T_{red} \rightarrow inert@T_{sep-1}} + \dot{n}_{O_2} \Delta H|_{O_2@T_{red} \rightarrow O_2@T_{sep-1}} \quad (10)$$

$$\dot{Q}_{O_2-cool} = \dot{n}_{O_2} \Delta H|_{O_2@T_{sep-1} \rightarrow O_2@T_0} \quad (11)$$



$$\dot{Q}_{CO_2-cool} = \dot{n}_{CO_2} \Delta H|_{CO_2@T_{sep-2} \rightarrow CO_2@T_0} \quad (12)$$

To carry out the thermochemical CDC, CO<sub>2</sub> (in an excess amount, 10 $\delta_{red}$ ) enters the oxidation chamber at the state  $oxd_3$ . After completion of the CDC reaction, a gas mixture comprised of unreacted CO<sub>2</sub> and produced CO leaves the oxidation chamber at the state  $oxd_4$ . Alternatively,  $MnFe_2O_{4-\delta_{red}}$  is shuttled from states  $oxd_3$  to  $oxd_4$  in a counter-current fashion relative to the gases encountered. As the CDC reaction is carried out at  $T_{oxd} = 1000$  K, the temperature of  $MnFe_2O_{4-\delta_{red}}$  is decreased from  $T_{red}$  to  $T_{oxd}$  with the help of HEX-1 (solid-to-solid heat exchanger). As the solid-to-solid heat recovery effectiveness ( $\epsilon_{ss}$ ) is assumed to be zero, the heat energy liberated during the cooling of  $MnFe_2O_{4-\delta_{red}}$  is not reused for the heating of  $MnFe_2O_4$ . The heat dissipated during CO production vis CDC is computed by using the following equation.

$$\dot{Q}_{MnF-oxd} = -\dot{n}_{MnF} \Delta H|_{MnFe_2O_{4-\delta_{red}} + (10\delta_{red})CO_2 \rightarrow MnFe_2O_4 + (10\delta_{red} - \delta_{red})CO_2 + (\delta_{red})CO} \quad (13)$$

$\dot{Q}_{MnF-oxd}$  is assumed to be rejected to the ambient.

HEX-5 (gas-to-gas heat exchanger) and an auxiliary heater-2 are installed in the model to pre-heat CO<sub>2</sub> from  $T_0$  to  $T_{oxd}$ . Eq. (14) is used to calculate the heating energy in the case of the CO<sub>2</sub>.

$$\dot{Q}_{CO_2-heat} = \epsilon_{gg} [\dot{Q}_{(CO_2+CO)-cool}] + \dot{Q}_{heater-2} \quad (14)$$

Where,

$$\dot{Q}_{CO_2-heat} = \dot{n}_{CO_2} \Delta H|_{CO_2@T_0 \rightarrow CO_2@T_{oxd}} \quad (15)$$

$$\dot{Q}_{(CO_2+CO)-cool} = \dot{n}_{CO_2} \Delta H|_{CO_2@T_{oxd} \rightarrow CO_2@T_{sep-2}} + \dot{n}_{CO} \Delta H|_{CO@T_{oxd} \rightarrow CO@T_{sep-2}} \quad (16)$$

The resue of CO<sub>2</sub> is possible only if it is separated from CO, for which a separator-2 is included.

Separator-2 is operated at  $T_{sep-2} = 400$  K and efficiency ( $\eta_{sep-2}$ ) equal to 15% (Carrillo and Scheffe 2019). As the CO<sub>2</sub>/CO separation is carried out at 400 K, the CO<sub>2</sub>/CO gas mixture temperature is reduced from  $T_{oxd}$  to  $T_{sep-2}$  by passing through HEX-5. Following three equations are used for determining  $\dot{Q}_{sep-2}$  (heat energy needed for the separation).

$$\dot{Q}_{sep-2} = \dot{n}_{MnF} \left[ \frac{T_{sep-2}}{\eta_{sep-2}} (\Delta S_{mix,oxd_4} - \Delta S_{mix,oxd_3}) \right] \quad (17)$$

$$\Delta S_{mix,oxd_3} = -R \{ n_{CO_2} \ln(1 - y_{CO,oxd_3}) + n_{CO,oxd_3} \ln y_{CO,oxd_3} \} \quad (18)$$

$$\Delta S_{mix,oxd_4} = -R \{ n_{CO_2} \ln(1 - y_{CO,oxd_4}) + n_{CO,oxd_4} \ln y_{CO,oxd_4} \} \quad (19)$$

CO separated from the CO<sub>2</sub>/CO gas mixture is further cooled down to  $T_0$  with the help of an auxiliary cooler-1 (heat rejected to the ambient). CO at 298 K is then transported to the fuel cell, which is installed in the model to complete the thermochemical  $MnFe_2O_{4-\delta_{red}}$  based CDC cycle. The fuel cell's outlet stream, which is CO<sub>2</sub> at 298 K, is first mixed with the unreacted CO<sub>2</sub> (separated from the CO) and then transferred to the oxidation chamber via passing through HEX-5 and heater-2.

The total amount of heat energy essential for the operation of  $MnFe_2O_4$  based CDS cycle is computed by using Eq.(20)

$$\dot{Q}_{TC} = \dot{Q}_{MnF-red} + \dot{Q}_{MnF-sens} + \dot{Q}_{heater-1} + \dot{Q}_{heater-2} + \dot{Q}_{sep-1} + \dot{Q}_{sep-2} + \dot{Q}_{surf} \quad (20)$$

Where,

$$\dot{Q}_{surf} = 0.2 \times \dot{Q}_{MnF-red} \quad (21)$$

For the estimation of solar-to-fuel energy conversion efficiency ( $\eta_{solar-to-fuel}$ ) it is important first to calculate the solar energy required to drive the cycle ( $\dot{Q}_{solar}$ ). Hence,  $\dot{Q}_{solar}$  is determined by using the following set of equations.

$$\dot{Q}_{solar} = \frac{\dot{Q}_{TC}}{\eta_{absorption}} \quad (22)$$

Here,

$$\eta_{absorption} = 1 - \left( \frac{\sigma T_{red}^4}{IC} \right) \quad (23)$$

For the estimation of  $\eta_{absorption}$ ,  $\sigma$ ,  $I$ , and  $C$  are taken as  $5.6705 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$ ,  $1000 \text{ W/m}^2$ , and 3000 suns, respectively.

Re-radiation losses from the model are also calculated by using Eq.(24)

$$\dot{Q}_{re-rad} = \eta_{absorption} \times \dot{Q}_{solar} \quad (24)$$

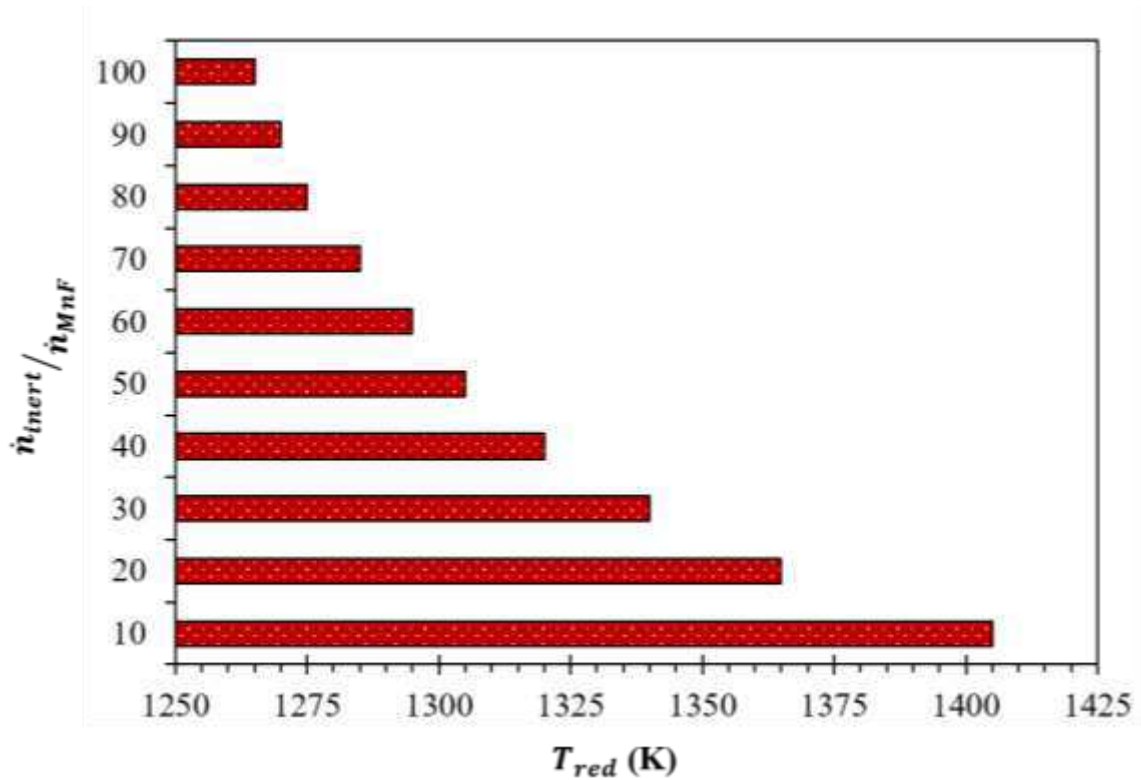
Finally,  $\eta_{solar-to-fuel}$  is estimated as follows:

$$\eta_{solar-to-fuel} = \frac{\dot{n}_{CO} \times HHV_{CO}}{\dot{Q}_{solar}} \quad (25)$$

### 3. Results and Discussion

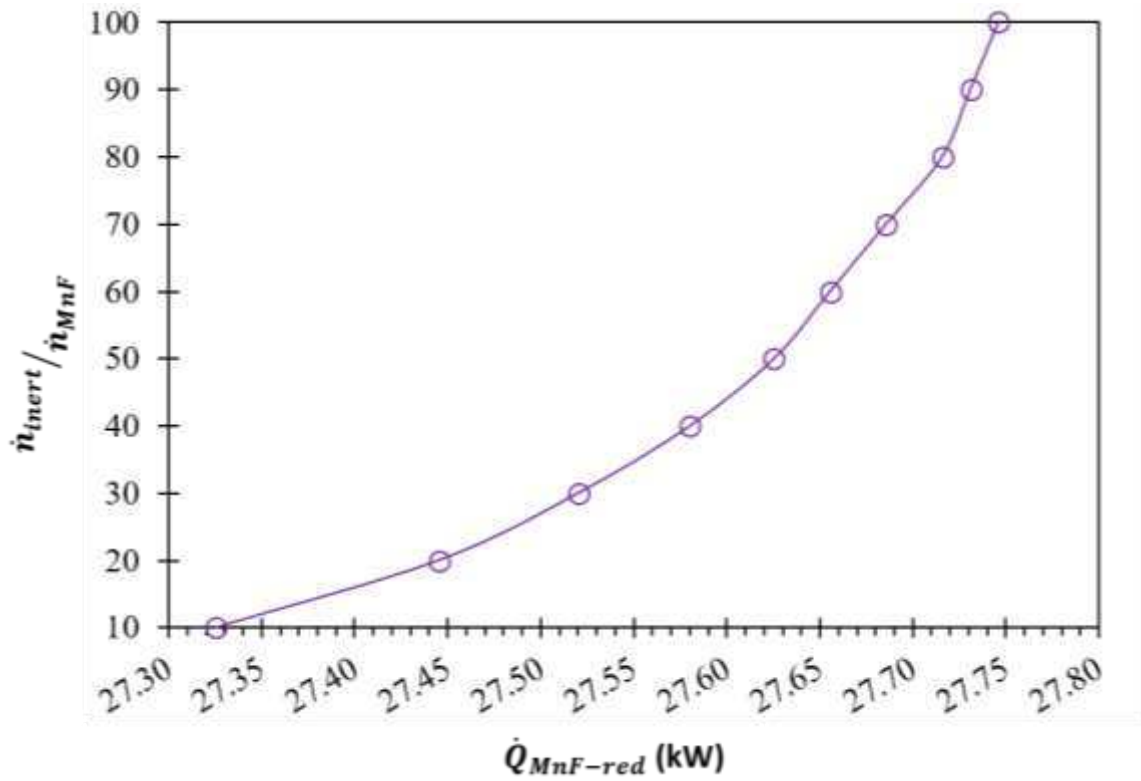
Reduction temperature ( $T_{red}$ ) required for attaining  $\delta_{red} = 0.1$  is estimated as a function of the ratio of the molar flow rates of inert sweep gas ( $\dot{n}_{inert}$ ) and  $MnFe_2O_4$  ( $\dot{n}_{MnF}$ ), i.e.,  $\dot{n}_{inert}/\dot{n}_{MnF}$ . As per the data presented in Fig. 2, the highest  $T_{red}$  equal to 1405 K is recorded for  $\dot{n}_{inert}/\dot{n}_{MnF}$  equal to 10. A further rise in  $\dot{n}_{inert}/\dot{n}_{MnF}$  from 10 to 100 reduces  $T_{red}$  from 1405 K

214 to 1265 K. Interestingly, the decrease in  $T_{red}$  is higher (100 K) when  $\dot{n}_{inert}/\dot{n}_{MnF}$  upturns from  
 215 10 to 50 as compared to a rise in  $\dot{n}_{inert}/\dot{n}_{MnF}$  from 50 to 100 ( $T_{red}$  reduces by 40 K). These  
 216 observations confirm that the effect of  $\dot{n}_{inert}/\dot{n}_{MnF}$  on  $T_{red}$  is less weighty during the increment  
 217 in  $\dot{n}_{inert}/\dot{n}_{MnF}$  from 50 to 100.



218  
 219 Fig. 2. Effect of  $\dot{n}_{inert}/\dot{n}_{MnF}$  on the temperature required for the reduction ( $T_{red}$ ) of  $MnFe_2O_4$   
 220 ( $\delta_{red} = 0.1$ ).  
 221  
 222  
 223

224 The effect of  $\dot{n}_{inert}/\dot{n}_{MnF}$  on the energy required for the reduction of  $MnFe_2O_4$  into  
 225  $MnFe_2O_{4-\delta_{red}}$  ( $\delta_{red} = 0.1$ ) is explored, and the obtained results are presented in Fig. 3. As the  
 226 pre-heating of both inert sweep gas and  $MnFe_2O_4$  are carried out separately (not in the  
 227 reduction chamber), the heat energy needed for both pre-heating operations are not included in  
 228 the computation of  $\dot{Q}_{MnF-red}$ . Presented results show that the rise in  $\dot{n}_{inert}/\dot{n}_{MnF}$  results in a  
 229 very minute change in  $\dot{Q}_{MnF-red}$ . As  $\dot{n}_{inert}/\dot{n}_{MnF}$  increases from 10 to 100, although  $T_{red}$   
 230 reduces by 140 K,  $\dot{Q}_{MnF-red}$  upsurges only by a factor of 1.02.



231  
 232 Fig. 3. Effect of  $\dot{n}_{inert}/\dot{n}_{MnF}$  on the thermal energy required ( $\dot{Q}_{MnF-red}$ ) for the reduction of  
 233  $MnFe_2O_4$  ( $\delta_{red} = 0.1$ ).

Eq.(4) is applied for the calculation of  $\dot{Q}_{MnF-sens}$ . As mentioned in section 2, heat energy dissipated during the cooling of  $MnFe_2O_{4-\delta_{red}}$  is not recuperated for the pre-heating of  $MnFe_2O_4$ . Variations recorded in  $\dot{Q}_{MnF-sens}$  due the rise in  $\dot{n}_{inert}/\dot{n}_{MnF}$  are presented in Fig. 4. The reported trends show that the change in  $T_{red}$  has a considerable effect on  $\dot{Q}_{MnF-sens}$ . As per the results,  $\dot{Q}_{MnF-sens}$  reduces below 77.9 kW by 16.0%, 24.6%, 29.6%, and 33.3% as the  $T_{red}$  decreases below 65 K, 100 K, 120 K, and 135 K due to the rise in  $\dot{n}_{inert}/\dot{n}_{MnF}$  from 10 to 30, 50, 70, and 90, respectively. Overall increase in  $\dot{n}_{inert}/\dot{n}_{ZnF}$  from 10 to 100 is responsible for the reduction in  $\dot{Q}_{MnF-sens}$  from 77.9 kW to 51.0 kW, respectively.

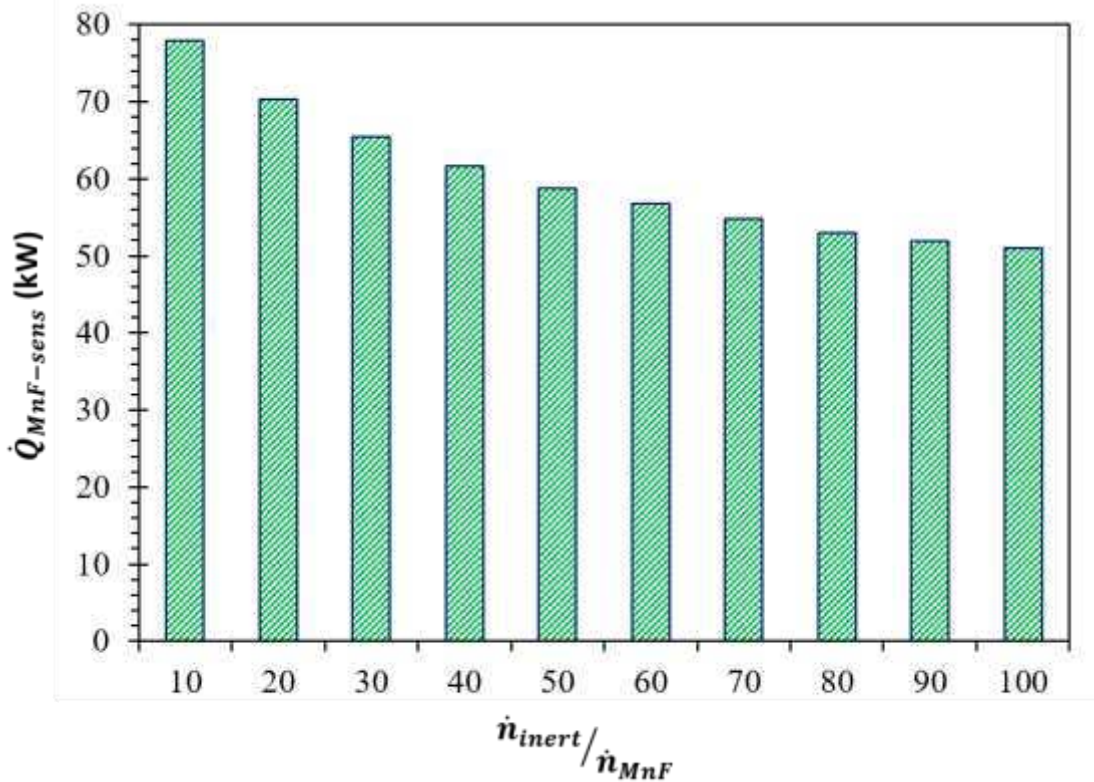


Fig. 4. Effect of  $\dot{n}_{inert}/\dot{n}_{MnF}$  on the thermal energy required ( $\dot{Q}_{MnF-sens}$ ) for the heating of  $MnFe_2O_4$  from oxidation temperature ( $T_{oxd}$ ) up to reduction temperature ( $T_{red}$ ).

As per the model presented in Fig. 1, after completion of the reduction step,  $MnFe_2O_{4-\delta_{red}}$  is transported to the oxidation chamber. In this chamber, the re-oxidation of  $MnFe_2O_{4-\delta_{red}}$  is conducted at steady  $T_{oxd} = 1000$  K. As the molar compositions and reaction temperature stay unchanged,  $\dot{Q}_{MnF-oxd}$  remains stable at 0.3 kW. This heat energy is not utilized for any purpose and is rejected to the ambient.

O<sub>2</sub> released during the reduction of  $MnFe_2O_4$  get mixed with the inert sweeping gas and moves out of the reduction chamber. For the reuse of inert sweeping gas, the O<sub>2</sub> has to be separated for this gas mixture. As this gas mixture has a temperature higher than 1000 K, ion transport membrane technology (operating temperature range: 1050 to 1200 K) is used for the separation (Anderson et al. 2016). The operating temperature of the separator-1 is assumed to be 1123 K. It is essential first to reduce the temperature of the gas mixture containing inert sweep gas and O<sub>2</sub> from  $T_{red}$  to  $T_{sep-1}$ . This is achieved by passing this gas mixture through HEX-2.

After attaining the separation temperature (1123 K), the gas mixture comprised of inert sweep gas and O<sub>2</sub> enters separator-1. Here, 99.9% of O<sub>2</sub> is separated from the inert sweeping gas. Eqs. (5) to (7) are applied for the determination of the heat energy required for the operation of separator-1 ( $\dot{Q}_{sep-1}$ ). All the calculations associated with the separator-1 are done based on the second law of thermodynamics ( $\Delta Q = T\Delta S$ ). Moreover, by estimating the entropy of mixing for each stream. As  $\dot{n}_{inert}/\dot{n}_{MnF}$  upsurges from 10 to 100,  $\dot{Q}_{sep-1}$  differs due to the variation in the mole fraction of O<sub>2</sub> at the states  $red_1$  and  $red_2$ . As shown in Fig. 5, the rise in  $\dot{n}_{inert}/\dot{n}_{MnF}$  from 10 to 30, 50, 70, and 90 results in an upturn in  $\dot{Q}_{sep-1}$  above 19.6 kW by 3.4 kW, 5.0 kW, 6.0 kW, and 6.8 kW, respectively.

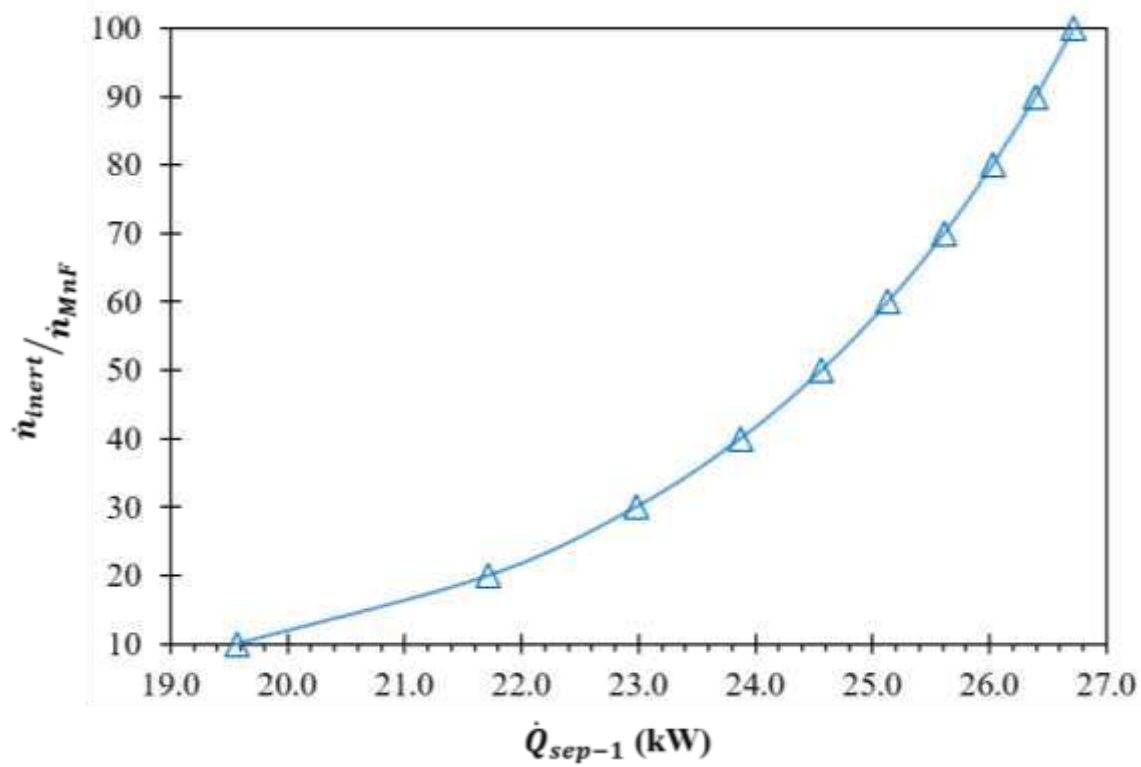


Fig. 5. Effect of  $\dot{n}_{inert}/\dot{n}_{MnF}$  on the thermal energy required for the operation of separator-1 ( $\dot{Q}_{sep-1}$ ).

The fuel cell is fed with the  $O_2$ , which is first separated from the inert sweep gas and then cooled to 298 K by passing through HEX-3. Alternatively, by going through HEX-2, HEX-3, HEX-4, and heater-1, the inert sweep gas is pre-heated from  $T_{sep-1}$  to  $T_{red}$ . Table 1 reports the influence of  $\dot{n}_{inert}/\dot{n}_{MnF}$  on  $\dot{Q}_{inert-heat}$ . Due to the increase in the  $\dot{n}_{inert}/\dot{n}_{MnF}$ , as per the expectations,  $\dot{Q}_{inert-heat}$  surges substantially. For instance, as  $\dot{n}_{inert}/\dot{n}_{ZnF}$  rises from 10 to 50 and then to 100,  $\dot{Q}_{inert-heat}$  increase from 95.8 kW to 307.4 kW and 478.4 kW, respectively.



Table 1. Effect of  $\dot{n}_{inert}/\dot{n}_{MnF}$  on thermal energy required after each gas-to-gas heat exchanger ( $\varepsilon_{gg} = 0.7$ ) for the pre-heating of inert sweep gas ( $\dot{Q}_{inert-heat}$ ).

$\dot{n}_{inert}/\dot{n}_{MnF}$	$T_{red}$ (K)	$\dot{Q}_{inert-heat}$ (kW)	$\dot{Q}_{inert-heat}$ Required		
			After HEX-2 (kW)	After HEX-3 (kW)	After HEX-4 (kW)
10	1405	95.8	28.4	27.5	24.9
20	1365	164.1	48.9	48.0	45.5
30	1340	220.4	65.8	64.9	62.4
40	1320	266.4	79.7	78.7	76.2
50	1305	307.4	92.0	91.0	88.5
60	1295	348.4	104.3	103.3	100.8
70	1285	382.6	114.6	113.6	111.1
80	1275	409.9	122.8	121.8	119.3
90	1270	445.9	133.6	132.6	130.1
100	1265	478.4	143.3	142.4	139.9

In HEX-2, heat energy released by inert/O<sub>2</sub> gas mixture during cooling from  $T_{red}$  to  $T_{sep-1}$  is utilized to pre-heat the inert sweep gas ( $\varepsilon_{gg} = 0.7$ ).  $\dot{Q}_{inert-heat}$  considerably decreased when the inert sweep gas passes through the HEX-2. As an example,  $\dot{Q}_{inert-heat}$  drops from 95.8 kW, 307.4 kW, and 478.4 kW to 28.4 kW, 92.0 kW, and 143.3 kW at  $\dot{n}_{inert}/\dot{n}_{MnF}$  equal to 10, 50, and 100, respectively.

After HEX-2, the inert sweep gas is then passed through HEX-3 ( $\varepsilon_{gg} = 0.7$ ) in which the cooling stream is  $O_2$ , which came out of separator-2. In this gas-to-gas heat exchanger,  $\dot{Q}_{inert-heat}$  decreases only by 0.9 kW for all  $\dot{n}_{inert}/\dot{n}_{MnF}$ . The reason for this lower drop in  $\dot{Q}_{inert-heat}$  is the lower molar flow rate of  $O_2$ .

In HEX-4 ( $\varepsilon_{gg} = 0.7$ ), heat energy dissipated during the cooling of unreacted  $CO_2$  is utilized to heat inert sweep gas. As the  $CO_2$  molar flow rate is much higher than  $O_2$ , as compared to HEX-3, the employment of HEX-4 is responsible for a more significant reduction in  $\dot{Q}_{inert-heat}$ . For all values of  $\dot{n}_{inert}/\dot{n}_{MnF}$ ,  $\dot{Q}_{inert-heat}$  decreases by 2.5 kW.

As shown in Table 1, even though a series of three gas-to-gas heat exchangers are installed, supplementary energy is still needed to heat inert sweep gas. Heater-1 provides the extra heat energy required. Due to the variation in  $\dot{n}_{inert}/\dot{n}_{MnF}$ ,  $\dot{Q}_{heater-1}$  also differs (Fig. 6). For example, as  $\dot{n}_{inert}/\dot{n}_{MnF}$  increases from 10 to 30, 50, 70, and 90,  $\dot{Q}_{heater-1}$  rises from 24.9 kW to 62.4 kW, 88.5 kW, 111.1 kW, and 130.1 kW, respectively.

The laboratory-scale thermochemical CDS experiments are carried out by using an excess amount of  $CO_2$ . Hence, in this thermodynamic study, the  $CO_2$  molar flow rate equal to 10 times  $\delta_{red}$  is used. After the completion of CDS, due to the excess supply of  $CO_2$ , the oxidation chamber's exit gas composition contains unreacted  $CO_2$  and CO produced. Unreacted  $CO_2$  can be reutilized for the re-oxidation of  $MnFe_2O_{4-\delta_{red}}$  (as shown in Fig. 1). To do this, the separation of  $CO_2$  from CO is necessary.

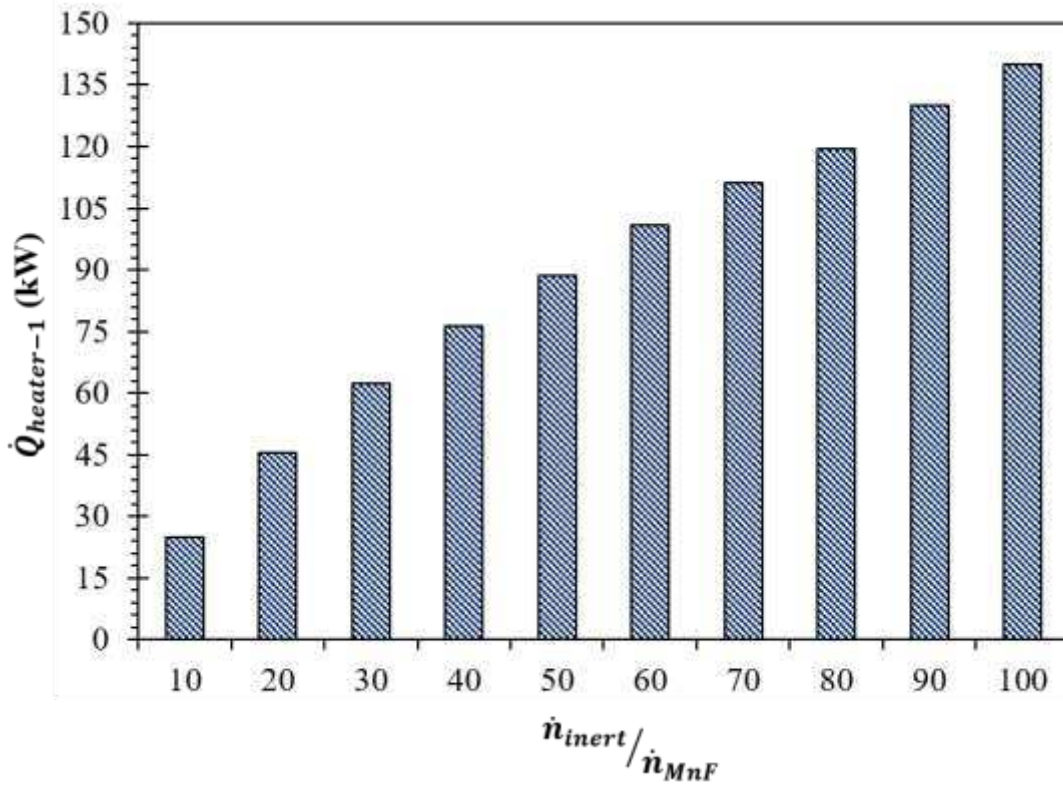


Fig. 6. Effect of  $\dot{n}_{inert} / \dot{n}_{MnF}$  on the thermal energy provided by heater-1 ( $\dot{Q}_{heater-1}$ ) for the pre-heating of inert sweep gas.

Separator-2 is installed in the process to separate CO<sub>2</sub> and CO gas mixture. It is operated at  $T_{sep-2} = 400$  K and hence the CO<sub>2</sub>/CO gas mixture, which exited the oxidation chamber at  $T_{oxd} = 1000$  K, is cooled by using HEX-5. After the reduction in the temperature, the CO<sub>2</sub>/CO gas mixture enters the separator-2 ( $\eta_{sep-2} = 15\%$ ). Similar to separator-1, 99.9% of CO is separated from the CO<sub>2</sub> stream. The heat energy required to achieve this separation ( $\dot{Q}_{sep-2}$ ) is calculated by solving Eqs. (17) to (19). The thermodynamic computations indicate that the mole fraction of CO remains stable at states  $oxd_3$  and  $oxd_4$ , even though  $\dot{n}_{inert} / \dot{n}_{MnF}$  increases from 10 to 100. Due to this, a stable value of 7.2 kW is recorded for  $\dot{Q}_{sep-2}$  (for all values of  $\dot{n}_{inert} / \dot{n}_{MnF}$ ).

A supplementary cooler-1 is installed in the model to reduce the temperature of CO<sub>2</sub>/CO gas mixture) from  $T_{sep-2}$  to  $T_0$ . The heat energy dissipated during this cooling is assumed to be rejected to the ambient. As an essential step to close the cycle, CO<sub>2</sub> is then transported to the fuel cell and reacts with the O<sub>2</sub>, producing CO<sub>2</sub>.

CO<sub>2</sub> generated via the fuel cell reaction is then mixed with the unreacted CO<sub>2</sub>. Before entering into the oxidation chamber, the temperature of the CO<sub>2</sub> needs to be increased from 298 K up to  $T_{oxd} = 1000$  K. This is achieved by using HEX-5 and a supplementary heater-2. It is important to note that, even though  $\dot{n}_{inert}/\dot{n}_{MnF}$  increases from 10 to 100, the molar flow rate of CO<sub>2</sub> entering and exiting the HEX-5 and heater-2 is steady. Hence, after passing through HEX-5, the additional heat needed for the heating, i.e.,  $\dot{Q}_{heater-2}$  remains unchanged at 13.6 kW

As mentioned in section 2 and as per the previously published work (Lu et al. 2019), it is assumed that 20% of the heat energy associated with the reduction chamber is lost to the ambient due to the issues associated with the thermal insulation. By considering these surface heat losses and other necessary heat energy requirements,  $\dot{Q}_{TC}$  needed to drive the cycle is estimated as per Eq.(20). Fig. 7 shows the effect of change in  $\dot{n}_{inert}/\dot{n}_{MnF}$  on  $\dot{Q}_{TC}$ . It is visible from the plot that rise in  $\dot{n}_{inert}/\dot{n}_{MnF}$  yields into an increase in  $\dot{Q}_{TC}$ . For example,  $\dot{Q}_{TC}$  mounts above 176.0 kW by 28.6 kW, 49.7 kW, 69.5 kW, and 86.5 kW due to the increment in  $\dot{n}_{inert}/\dot{n}_{MnF}$  from 10 to 30, 50, 70, and 90, respectively. The reason for the enhancement in  $\dot{Q}_{TC}$  is the upsurge in  $\dot{Q}_{heater-1}$  and  $\dot{Q}_{sep-1}$  as a function of rise in  $\dot{n}_{inert}/\dot{n}_{MnF}$ .

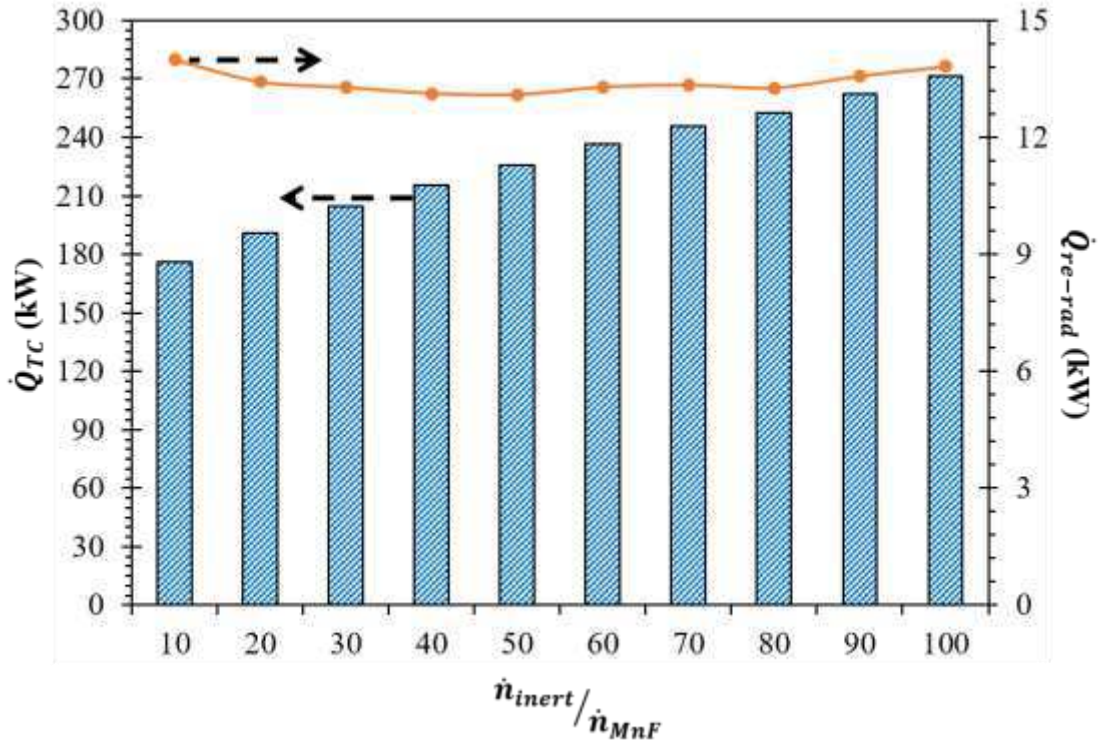


Fig. 7. Effect of  $\dot{n}_{inert}/\dot{n}_{MnF}$  on the thermal energy required to operate  $MnFe_2O_4$  based  $CO_2$  splitting cycle ( $\dot{Q}_{TC}$ ) and re-radiation losses ( $\dot{Q}_{re-rad}$ ).

After estimating  $\dot{Q}_{TC}$ ,  $\dot{Q}_{solar}$  and  $\dot{Q}_{re-rad}$  are calculated by employing Eqs. (22) and (24). Figs. 7 and 8 present the divergences allied with both  $\dot{Q}_{re-rad}$  and  $\dot{Q}_{solar}$ . Both  $\dot{Q}_{solar}$  and  $\dot{Q}_{re-rad}$  depends upon  $\eta_{absorption}$ , which in turn rely on  $T_{red}$ .  $\eta_{absorption}$  of this cycle increases from 92.6% to 95.2% due to the drop in  $T_{red}$  from 1405 K to 1265 K. This rise in  $\eta_{absorption}$  indicates that a higher percentage of solar energy is absorbed and hence  $\dot{Q}_{re-rad}$  losses are lower (Fig. 7). On the other hand, as  $\eta_{absorption}$  is less than 100%,  $\dot{Q}_{solar}$  is recorded to be higher than  $\dot{Q}_{TC}$  for all  $\dot{n}_{inert}/\dot{n}_{MnF}$  values. For example,  $\dot{Q}_{solar}$  is recorded to be higher than  $\dot{Q}_{TC}$  by 14.0 kW, 13.3 kW, 13.1 kW, 13.3 kW, and 13.6 kW at  $\dot{n}_{inert}/\dot{n}_{MnF}$  equal to 10, 30, 50, 70, and 90, respectively.

Fig. 8 shows the effect of  $\dot{n}_{inert}/\dot{n}_{MnF}$  on  $\eta_{solar-to-fuel}$ . For the estimation of  $\eta_{solar-to-fuel}$ , Eq.(25) is used. In this equation, the numerator is steady as  $\dot{n}_{CO}$  and  $HHV_{CO}$  are stable at 0.1 and 283.24 kW, respectively. Enhancement in  $\dot{n}_{inert}/\dot{n}_{MnF}$  is responsible for a rise in  $\dot{Q}_{solar}$  which in turn reduces  $\eta_{solar-to-fuel}$ . For example, as  $\dot{n}_{inert}/\dot{n}_{MnF}$  increases from 10 to 30, 50, 70, and 90,  $\dot{Q}_{solar}$  also rises from 190.0 kW up to 217.8 kW, 238.8 kW, 258.9 kW, and 276.1 kW, respectively. This increment in  $\dot{Q}_{solar}$  is responsible for the decrease in  $\eta_{solar-to-fuel}$  from 14.9% to 13.0%, 11.9%, 10.9%, and 10.3% when  $\dot{n}_{inert}/\dot{n}_{MnF}$  upsurges from 10 to 30, 50, 70, and 90, respectively. The obtained results confirm that the maximum  $\eta_{solar-to-fuel}$  (14.9%) is attainable at  $\dot{n}_{inert}/\dot{n}_{MnF}$  equal to 10 ( $T_{red} = 1405$  K,  $T_{oxd} = 1000$  K,  $\varepsilon_{gg} = 0.7$ , and  $\varepsilon_{ss} = 0$ ).

The results reported until now confirm that the prime reason for the increment in  $\dot{Q}_{solar}$  and reduction in  $\eta_{solar-to-fuel}$  is the rise in  $\dot{Q}_{MnF-sens}$ ,  $\dot{Q}_{heater-1}$ , and  $\dot{Q}_{CO_2-heat}$  as  $\dot{n}_{inert}/\dot{n}_{MnF}$  upturns from 10 to 100. All the calculations are conducted by assuming  $\varepsilon_{ss}$  and  $\varepsilon_{gg}$  constant at 0.0 and 0.7, respectively. It is a well-known fact that solids' heat recovery to solids is very difficult and not often used. On the other hand, gas to gas heat recovery is commonly used in the industry with gas-to-gas heat exchangers. To explore further, the effect of variation in  $\varepsilon_{gg}$  (from 0.0 to 0.9) on  $\dot{Q}_{solar}$  and  $\eta_{solar-to-fuel}$  is investigated here. 100% gas-to-gas heat recovery ( $\varepsilon_{gg} = 1$ ) is not practical and hence not considered.

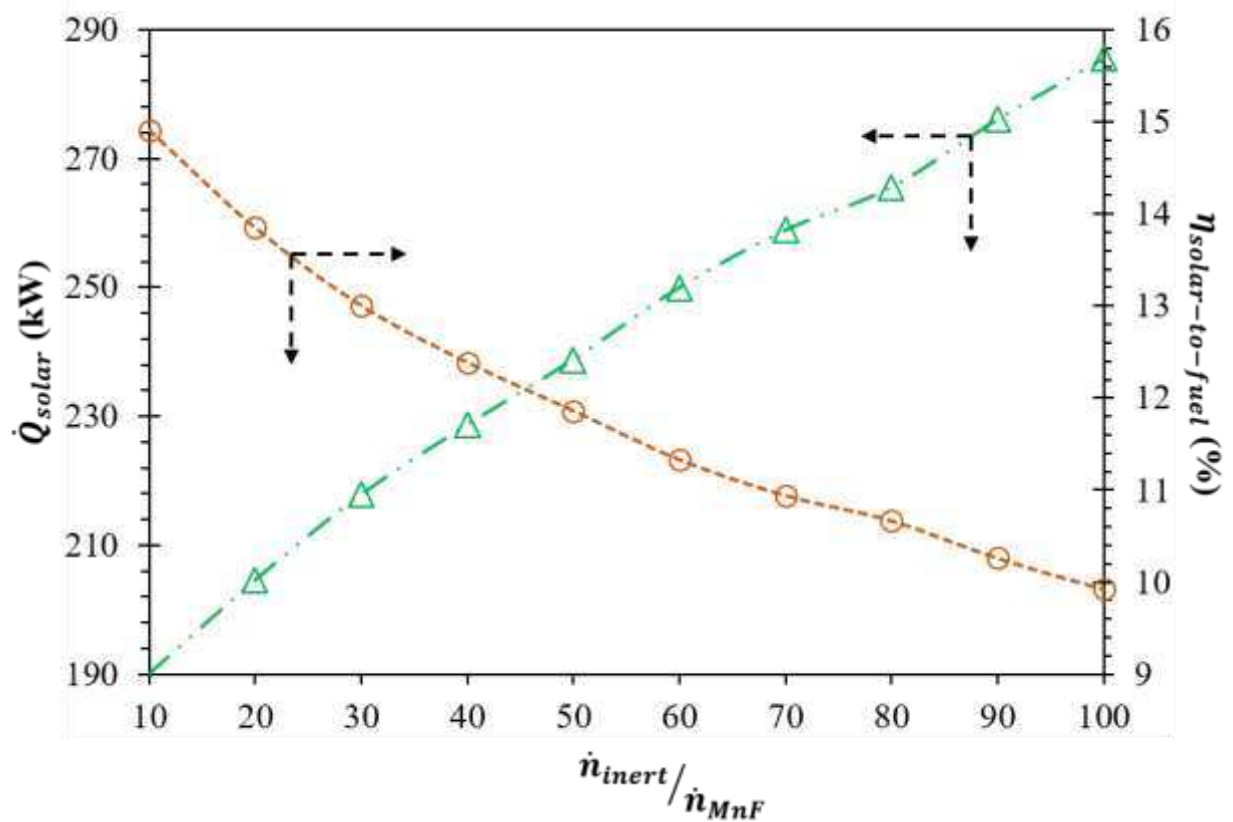


Fig. 8. Effect of  $\dot{n}_{inert}/\dot{n}_{MnF}$  on solar energy required to drive  $MnFe_2O_4$  based  $CO_2$  splitting cycle ( $\dot{Q}_{solar}$ ) and solar-to-fuel energy conversion efficiency ( $\eta_{solar-to-fuel}$ ).

Results indicate that  $\dot{Q}_{MnF-red}$  and  $\dot{Q}_{MnF-sens}$  remains unaltered due to the variation in  $\varepsilon_{gg}$ . Conversely,  $\dot{Q}_{heater-1}$  and  $\dot{Q}_{heater-2}$  are recorded to be varied considerably when  $\varepsilon_{gg}$  increases from 0.0 to 0.9. As per the trends reported in Fig. 9, at steady  $\dot{n}_{inert}/\dot{n}_{MnF}$ , a rise in  $\varepsilon_{gg}$  yields into a significant reduction in  $\dot{Q}_{heater-1}$ . For example, at  $\dot{n}_{inert}/\dot{n}_{MnF} = 10$ ,  $\dot{Q}_{heater-1}$  decreases by 91.2 kW when  $\varepsilon_{gg}$  surges from 0.0 to 0.9. Due to the similar upturn in  $\varepsilon_{gg}$ ,  $\dot{Q}_{heater-1}$  diminishes by 435.5 kW at  $\dot{n}_{inert}/\dot{n}_{MnF}$  equal to 100.

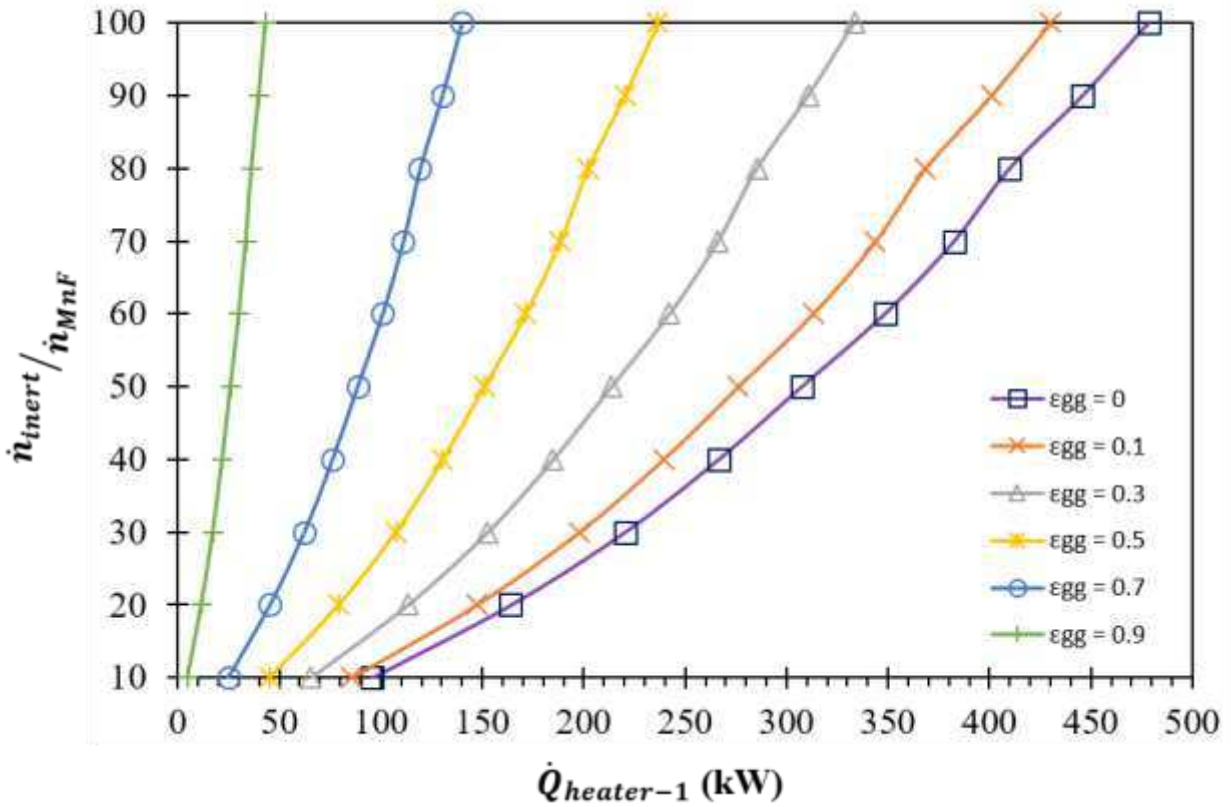


Fig. 9. Effect of  $\dot{n}_{inert}/\dot{n}_{MnF}$  and gas-to-gas heat recovery effectiveness ( $\epsilon_{gg}$ ) on the thermal energy provided by heater-1 ( $\dot{Q}_{heater-1}$ ) for the pre-heating of inert sweep gas.

The influence of  $\epsilon_{gg}$  on  $\dot{Q}_{heater-2}$  is reported in Table 2. It is already understood that the rise in  $\dot{n}_{inert}/\dot{n}_{MnF}$  from 10 to 100 does not affect  $\dot{Q}_{heater-2}$ . Opposite to this, increment in  $\epsilon_{gg}$  decreases  $\dot{Q}_{heater-2}$ . The values reported in Table 2 shows that  $\dot{Q}_{heater-2}$  declines below 33.4 kW by 8.4%, 25.4%, 42.5%, 59.3%, and 76.3% due to the rise in  $\epsilon_{gg}$  from 0.1 to 0.3, 0.5, 0.7, and 0.9, respectively (for all  $\dot{n}_{inert}/\dot{n}_{MnF}$ ).



388 Table 2. Effect of gas-to-gas heat recovery effectiveness ( $\varepsilon_{gg}$ ) on the thermal energy provided  
 389 by heater-2 ( $\dot{Q}_{heater-2}$ ) for the pre-heating of CO<sub>2</sub> (for all  $\dot{n}_{inert}/\dot{n}_{MnF}$ ).

$\varepsilon_{gg}$	$\dot{Q}_{heater-2}$ (kW)
0.0	33.4
0.1	30.6
0.3	24.9
0.5	19.2
0.7	13.6
0.9	7.9

390

391 Fig. 10 shows that the rise in  $\varepsilon_{gg}$  reduces  $\dot{Q}_{TC}$  for all  $\dot{n}_{inert}/\dot{n}_{MnF}$ . As per the reported  
 392 trends,  $\dot{Q}_{TC}$  decreases by 116.7 kW, 228.7 kW, 306.9 kW, 374.5 kW, and 431.5 kW at  $\dot{n}_{inert}/\dot{n}_{ZnF}$   
 393 equal to 10, 30, 40, 50, and 90, respectively, due to the increment in  $\varepsilon_{gg}$  from 0.0 to 0.9. It is  
 394 also understood that the enhancement in  $\varepsilon_{gg}$  from 0.0 to 0.9 is responsible for the reduction  
 395 in the difference between  $\dot{Q}_{TC}$  at  $\dot{n}_{inert}/\dot{n}_{MnF}$  equal to 10 and 100. For example, the difference  
 396 between  $\dot{Q}_{TC}$  at  $\dot{n}_{inert}/\dot{n}_{MnF}$  equal to 10 and 100 decreases from 363.3 kW (at  $\varepsilon_{gg} = 0.0$ ) to  
 397 172.1 kW (at  $\varepsilon_{gg} = 0.5$ ) and 19.2 kW (at  $\varepsilon_{gg} = 0.9$ ).

398 Table 3 shows the effect of  $\varepsilon_{gg}$  on  $\dot{Q}_{solar}$  for all  $\dot{n}_{inert}/\dot{n}_{MnF}$  values. Similar to  $\dot{Q}_{TC}$ ,  $\dot{Q}_{solar}$   
 399 also decreases as a function of  $\varepsilon_{gg}$ . Even though there is no influence of  $\varepsilon_{gg}$  on  $\eta_{absorption}$ ,  
 400 the increment in  $\varepsilon_{gg}$  from 0.0 to 0.9 is responsible for lessening  $\dot{Q}_{solar}$  by 126.0 kW, 243.5 kW,

324.8 kW, 394.9 kW, and 453.8 kW at  $\dot{n}_{inert}/\dot{n}_{MnF}$  equal to 10, 30, 50, 70, and 90, respectively.

Alike  $\dot{Q}_{TC}$ , the increase in  $\varepsilon_{gg}$  also helps to decline the difference between  $\dot{Q}_{solar}$  at  $\dot{n}_{inert}/\dot{n}_{MnF}$  equal to 10 and 100. For example, the difference between  $\dot{Q}_{solar}$  at  $\dot{n}_{inert}/\dot{n}_{MnF}$  equal to 10 and 100 decreases from 374.1 kW to 334.3 kW, 254.7 kW, 175.1 kW, 95.5 kW, and 15.9 kW due to the upsurge in  $\varepsilon_{gg}$  from 0.0 to 0.1, 0.3, 0.5, 0.7, and 0.9, respectively. Similar to  $\dot{Q}_{solar}$ ,  $\dot{Q}_{re-rad}$  also drops considerably when  $\varepsilon_{gg}$  increases. In terms of numbers, the increment in  $\varepsilon_{gg}$  from 0.0 to 0.9 is responsible for a reduction in  $\dot{Q}_{re-rad}$  by 9.3 kW, 14.8 kW, 17.8 kW, 20.4 kW, and 22.3 kW at  $\dot{n}_{inert}/\dot{n}_{MnF}$  equal to 10, 30, 50, 70, and 90, respectively.

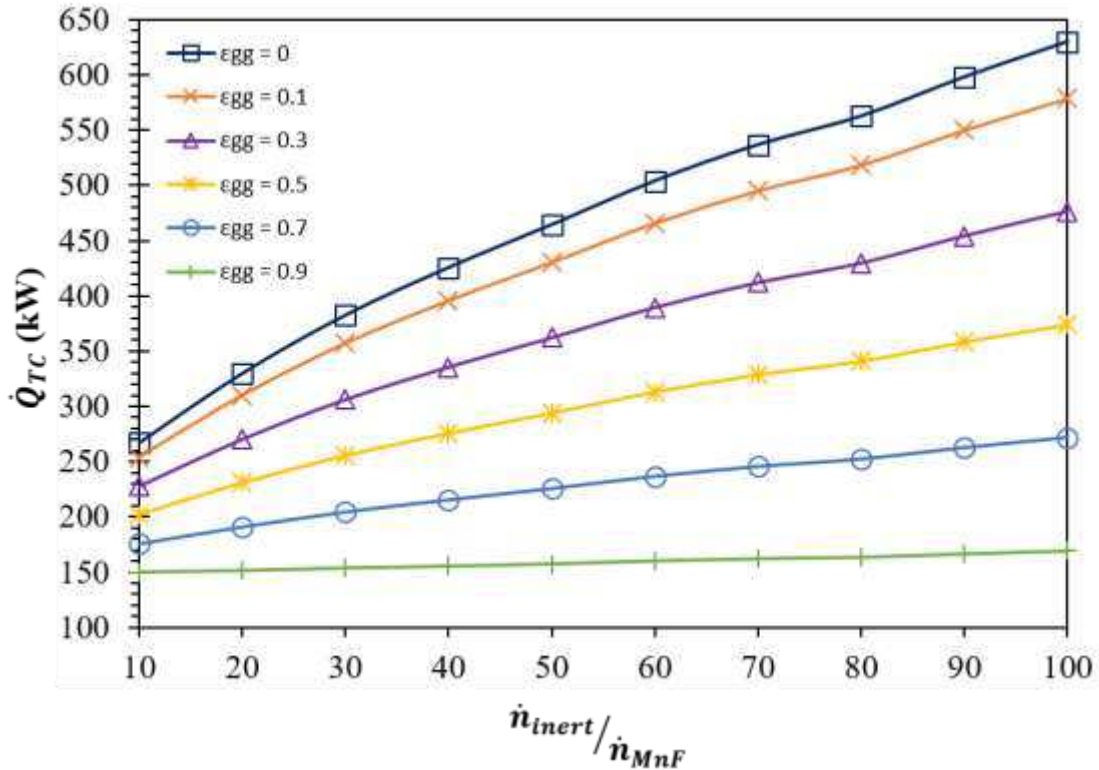


Fig. 10. Effect of  $\dot{n}_{inert}/\dot{n}_{MnF}$  and gas-to-gas heat recovery effectiveness ( $\varepsilon_{gg}$ ) on thermal energy required to drive  $MnFe_2O_4$  based  $CO_2$  splitting cycle ( $\dot{Q}_{TC}$ ).

Table 3. Effect of  $\dot{n}_{inert}/\dot{n}_{MnF}$  and gas-to-gas heat recovery effectiveness ( $\varepsilon_{gg}$ ) on the solar energy required to operate  $MnFe_2O_4$  based  $CO_2$  splitting cycle ( $\dot{Q}_{solar}$ ).

$\dot{n}_{inert}/\dot{n}_{MnF}$	$T_{red}$ (K)	$\dot{Q}_{solar}$ (kW)					
		$\varepsilon_{gg} =$ <b>0.0</b>	$\varepsilon_{gg} =$ <b>0.1</b>	$\varepsilon_{gg} =$ <b>0.3</b>	$\varepsilon_{gg} =$ <b>0.5</b>	$\varepsilon_{gg} =$ <b>0.7</b>	$\varepsilon_{gg} =$ <b>0.9</b>
10	1405	288.0	274.0	246.0	218.0	190.0	162.0
20	1365	352.7	331.6	289.2	246.9	204.5	162.2
30	1340	407.2	380.2	326.1	272.0	217.8	163.7
40	1320	451.5	419.7	356.0	292.3	228.7	165.0
50	1305	491.4	455.3	383.1	311.0	238.8	166.6
60	1295	532.4	492.0	411.3	330.6	250.0	169.3
70	1285	566.0	522.1	434.4	346.6	258.9	171.1
80	1275	592.3	545.6	452.3	358.9	265.6	172.2
90	1270	629.0	578.6	477.8	376.9	276.1	175.2
100	1265	662.1	608.3	500.7	393.1	285.5	177.9

Due to the significant decrease in  $\dot{Q}_{solar}$ ,  $\dot{Q}_{TC}$ , and  $\dot{Q}_{re-rad}$ ,  $\eta_{solar-to-fuel}$  of  $MnFe_2O_4$  based CDS cycle increases when  $\varepsilon_{gg}$  enhances from 0.0 to 0.9. The trends reported in Fig. 11 shows that as  $\varepsilon_{gg}$  increments from 0.0 to 0.9,  $\eta_{solar-to-fuel}$  improves from 9.8% to 17.5%, 5.8% to 17.0%, and 4.3% to 15.9% at  $\dot{n}_{inert}/\dot{n}_{MnF}$  equal to 10, 50, and 90, respectively. It is also understood that when the  $\dot{n}_{inert}/\dot{n}_{MnF}$  increases from 10 to 100, the drop in  $\eta_{solar-to-fuel}$  is in the range of 5% to 6% for  $\varepsilon_{gg}$  equal to 0.1 to 0.7. However, in the case of  $\varepsilon_{gg} = 0.9$ , as

$\dot{Q}_{solar}$  ranges from 162.0 kW to 177.9 kW,  $\eta_{solar-to-fuel}$  decreases by a lower amount (1.6%) when  $\dot{n}_{inert}/\dot{n}_{MnF}$  enhances from 10 to 100. In the end, by applying  $\varepsilon_{gg} = 0.9$ , maximum  $\eta_{solar-to-fuel}$  of 17.5% can be achieved by using  $\dot{n}_{inert}/\dot{n}_{MnF}$  equal to 10 as well as 20.

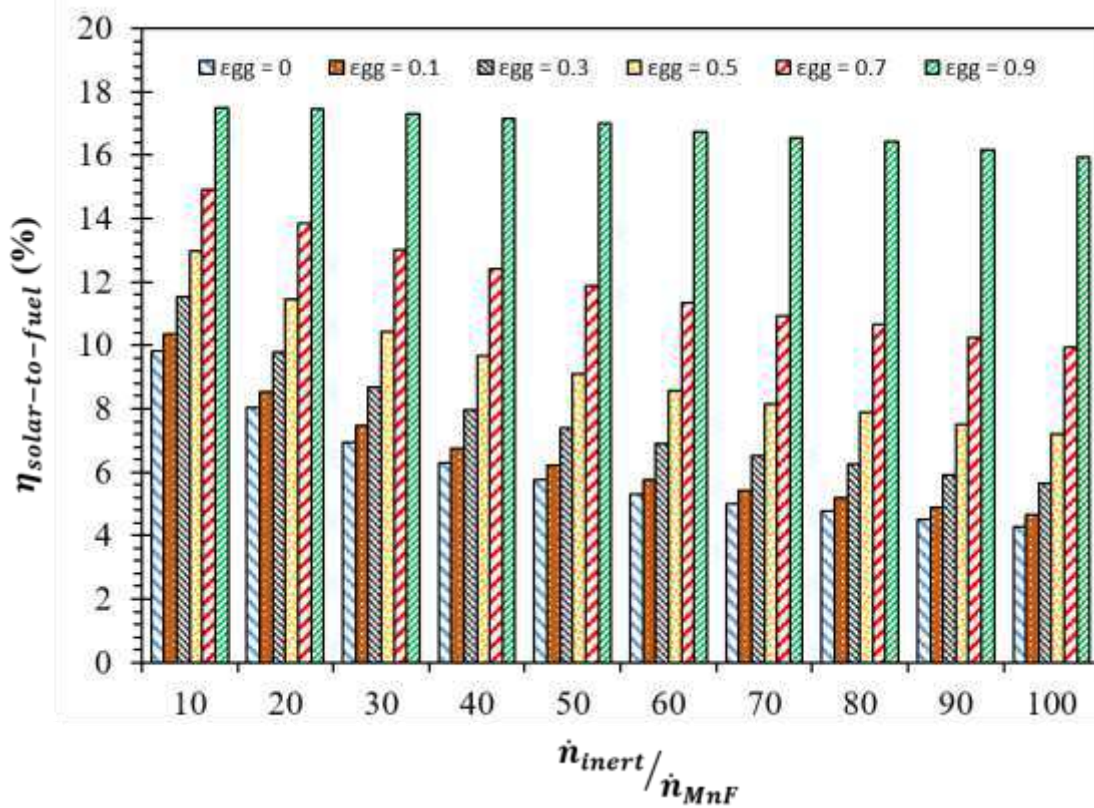


Fig. 11. Effect of  $\dot{n}_{inert}/\dot{n}_{ZnF}$  and gas-to-gas heat recovery effectiveness ( $\varepsilon_{gg}$ ) on solar-to-fuel energy conversion efficiency ( $\eta_{solar-to-fuel}$ ).

#### 4. Summary and Conclusions

A thermodynamic model for a high-temperature solar thermochemical CDS cycle driven by  $MnFe_2O_4$  is developed and used for the estimation of thermodynamics process parameters. An increase in  $\dot{n}_{inert}/\dot{n}_{MnF}$  from 10 to 100 is responsible for the decrease in  $T_{red}$  from 1405 K to 1265 K. The initial calculations which are performed at  $\varepsilon_{gg} = 0.7$  confirms a slight enhancement in  $\dot{Q}_{MnF-red}$  (0.4 kW) even though the  $T_{red}$  reduces by 140 K. Conversely,  $\dot{Q}_{MnF-sens}$  decreases by 26.9 kW due to the drop in  $T_{red}$  from 1405 K to 1265 K. The amount of heat energy required for the separation of inert from the inert/O<sub>2</sub> gas mixture increases by 7.2 kW as  $\dot{n}_{inert}/\dot{n}_{MnF}$  enhances from 10 to 100. Opposite to this, due to the unchanged molar flow rates of CO<sub>2</sub> and CO, the heat energy needed to separate CO from CO<sub>2</sub>/CO gas mixture remains steady. The rise in  $\dot{n}_{inert}/\dot{n}_{MnF}$  from 10 to 100 is also responsible for the increase in  $\dot{Q}_{heater-1}$  from 24.9 kW to 139.9 kW, respectively. This rise in the thermal energy required for the heating of inert sweep gas results in an enhancement in  $\dot{Q}_{solar}$  from 190.0 kW to 285.5 kW, which further decreases  $\eta_{solar-to-fuel}$  by ~5%. To improve the  $\eta_{solar-to-fuel}$ ,  $\varepsilon_{gg}$  is enhanced from 0.7 to 0.9, which significantly reduces  $\dot{Q}_{TC}$  and  $\dot{Q}_{solar}$ . At  $\varepsilon_{gg}$  equal to 0.9,  $\dot{Q}_{TC}$  and  $\dot{Q}_{solar}$  attains lowest values, i.e., 150.1 kW and 162.0 kW (at  $\dot{n}_{inert}/\dot{n}_{MnF} = 10$ ). The reduction in both  $\dot{Q}_{TC}$  and  $\dot{Q}_{solar}$  helps  $MnFe_2O_4$  based CDC cycle to accomplish  $\eta_{solar-to-fuel}$  equal to 17.5%.

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451    **Declarations**

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453    **Conflicts of interest/Competing interests:** No conflicts of interest/competing interests

454    **Availability of data and material:** Not applicable

455    **Code availability :** Not applicable

456    **Authors' contributions :** A single author paper

457    **Ethics approval :** Not applicable

458    **Consent to participate:** Not applicable

459    **Consent for publication:** Not applicable

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## 469 Nomenclature

470	$C$	Solar flux concentration ratio, suns
471	$HHV_{CO}$	Higher heating value of CO, kW
472	HEX-1	Heat exchanger-1
473	HEX-2	Heat exchanger-2
474	HEX-3	Heat exchanger-3
475	HEX-4	Heat exchanger-4
476	HEX-5	Heat exchanger-5
477	$I$	Normal beam solar insolation, W/m <sup>2</sup>
478	$MO$	Metal oxide
479	$n$	Molar amount, mol
480	$n_{CO,oxd_3}$	Molar amount of CO at state $oxd_3$ , mol
481	$n_{CO,oxd_4}$	Molar amount of CO at state $oxd_4$ , mol
482	$n_{O_2,red_1}$	Molar amount of O <sub>2</sub> at state $red_1$ , mol
483	$n_{O_2,red_2}$	Molar amount of O <sub>2</sub> at state $red_2$ , mol
484	$\dot{n}$	Molar flow rate, mol/s
485	$\dot{n}_{inert}$	Molar flow rate of inert, mol/s
486	$\dot{n}_{MnF}$	Molar flow rate of $MnFe_2O_4$ , mol/s
487	$\dot{n}_{inert}/\dot{n}_{MnF}$	Ratio of molar flow rates of inert to $MnFe_2O_4$
488	$\dot{n}_{CO_2}$	Molar flow rate of CO <sub>2</sub> , mol/s
489	$\dot{n}_{CO}$	Molar flow rate of CO, mol/s

490	$\dot{n}_{O_2}$	Molar flow rate of O <sub>2</sub> , mol/s
491	$\dot{Q}_{inert-heat}$	Thermal energy required to heat inert sweep gas, kW
492	$\dot{Q}_{(inert+O_2)-cool}$	Thermal energy released during cooling of inert + O <sub>2</sub> gas mixture, kW
493	$\dot{Q}_{(CO_2+CO)-cool}$	Thermal energy released during cooling of CO <sub>2</sub> + CO gas mixture, kW
494	$\dot{Q}_{CO_2-cool}$	Thermal energy released during cooling of CO <sub>2</sub> , kW
495	$\dot{Q}_{CO_2-heat}$	Thermal energy required to heat CO <sub>2</sub> , kW
496	$\dot{Q}_{heater-1}$	Auxiliary thermal energy required to heat inert sweep gas, kW
497	$\dot{Q}_{heater-2}$	Auxiliary thermal energy required to heat CO <sub>2</sub> , kW
498	$\dot{Q}_{O_2-cool}$	Thermal energy released during cooling of O <sub>2</sub> , kW
499	$\dot{Q}_{solar}$	Solar energy required to run the cycle, kW
500	$\dot{Q}_{sep-1}$	Thermal energy required for the operation of separator-1, kW
501	$\dot{Q}_{sep-2}$	Thermal energy required for the operation of separator-2, kW
502	$\dot{Q}_{surf}$	Thermal energy losses over the reduction chamber walls, kW
503	$\dot{Q}_{TC}$	Thermal energy required to run the cycle, Kw
504	$\dot{Q}_{MnF-red}$	Thermal energy required for thermal reduction of $MnFe_2O_4$ , kW
505	$\dot{Q}_{MnF-sens}$	Thermal energy required to heat the $MnFe_2O_4$ , kW
506	$\dot{Q}_{MnF-oxd}$	Thermal energy released during re-oxidation of $MnFe_2O_4$ , kW
507	$\dot{Q}_{re-rad}$	Re-radiation losses from the cycle, kW



508	$R$	Ideal gas constant (8.314 J/mol·K)
509	$T_0$	Ambient temperature, K
510	$T_{oxd}$	Oxidation (splitting) temperature, K
511	$T_{red}$	Reduction temperature, K
512	$T_{sep-1}$	Operating temperature of separator-1, K
513	$T_{sep-2}$	Operating temperature of separator-2, K
514	$y_{CO,oxd_3}$	Mol fraction of CO at state $oxd_3$ , mol
515	$y_{CO,oxd_4}$	Mol fraction of CO at state $oxd_4$ , mol
516	$y_{O_2,red_1}$	Mol fraction of O <sub>2</sub> at state $red_1$ , mol
517	$y_{O_2,red_2}$	Mol fraction of O <sub>2</sub> at state $red_2$ , mol
518	$\eta_{absorption}$	Solar energy absorption efficiency, %
519	$\eta_{sep-1}$	Efficiency of separator-1, %
520	$\eta_{sep-2}$	Efficiency of separator-2, %
521	$\eta_{solar-to-fuel}$	Solar-to-fuel energy conversion efficiency, %
522	$\delta_{red}$	Reduction nonstiochiometry
523	$\varepsilon_{gg}$	Gas-to-gas heat recovery effectiveness

524	$\varepsilon_{ss}$	Solid-to-solid heat recovery effectiveness
525	$\sigma$	Stefan – Boltzmann constant, $5.670 \times 10^{-8}$ (W/m <sup>2</sup> ·K <sup>4</sup> )
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# Figures

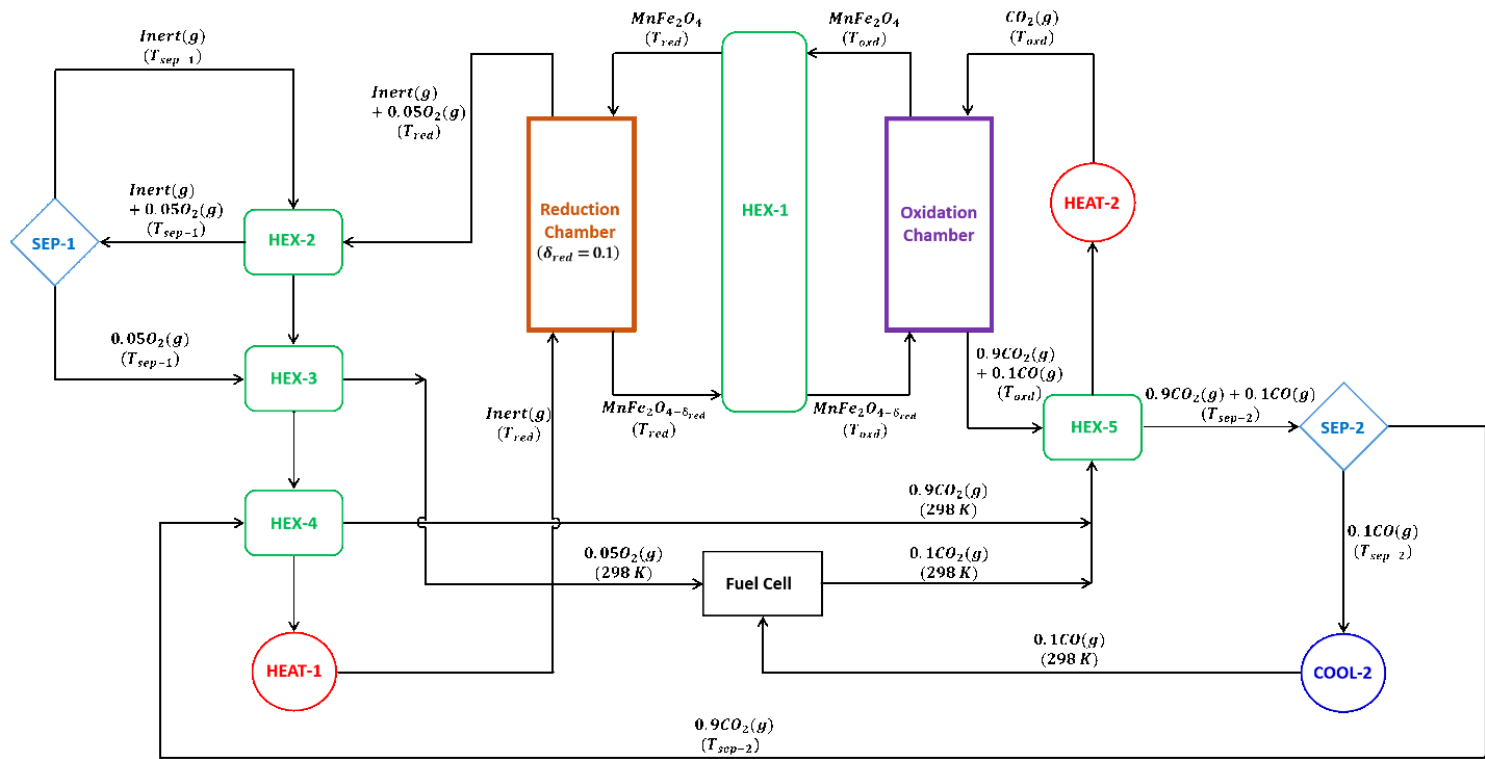
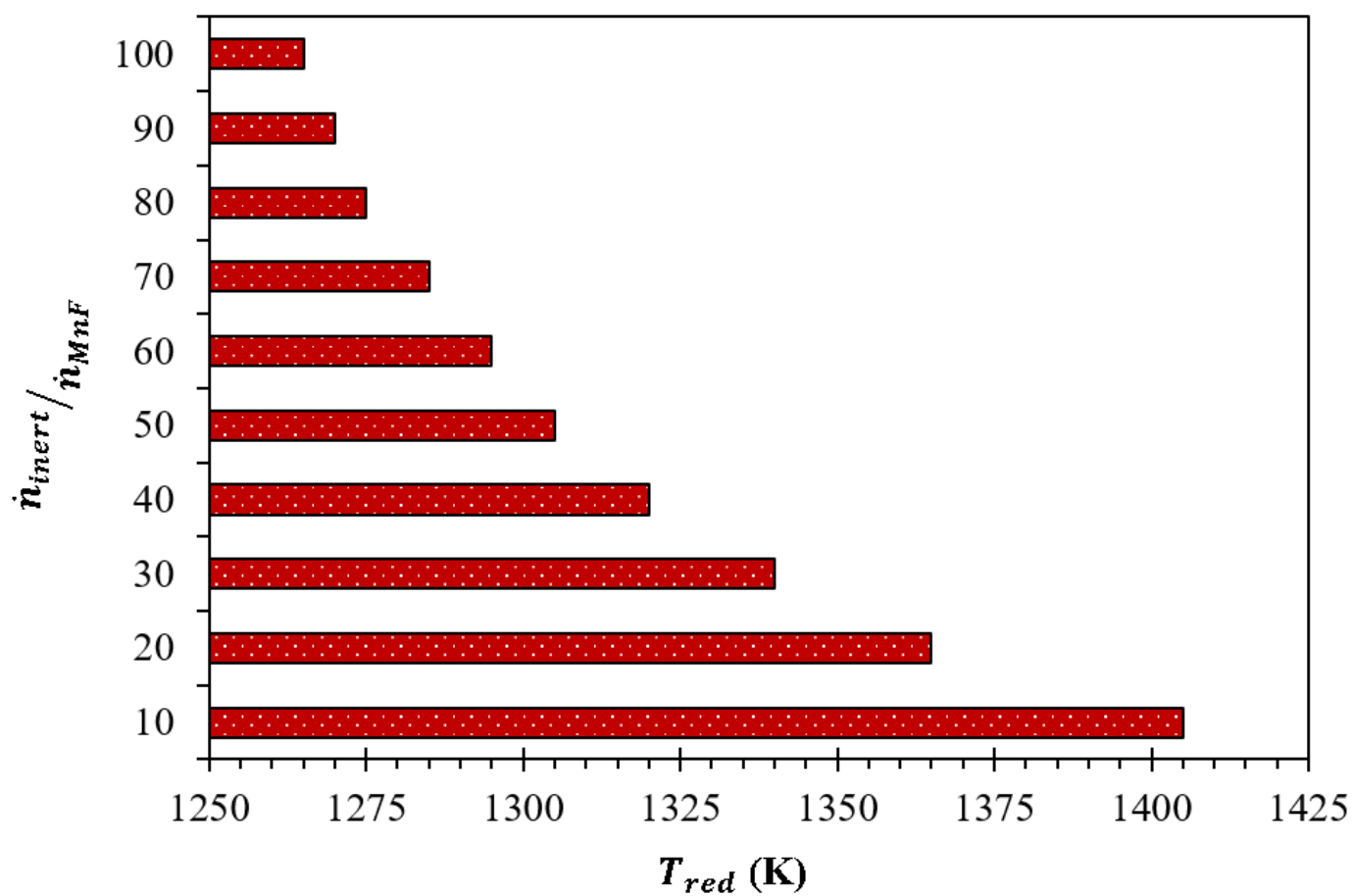


Figure 1

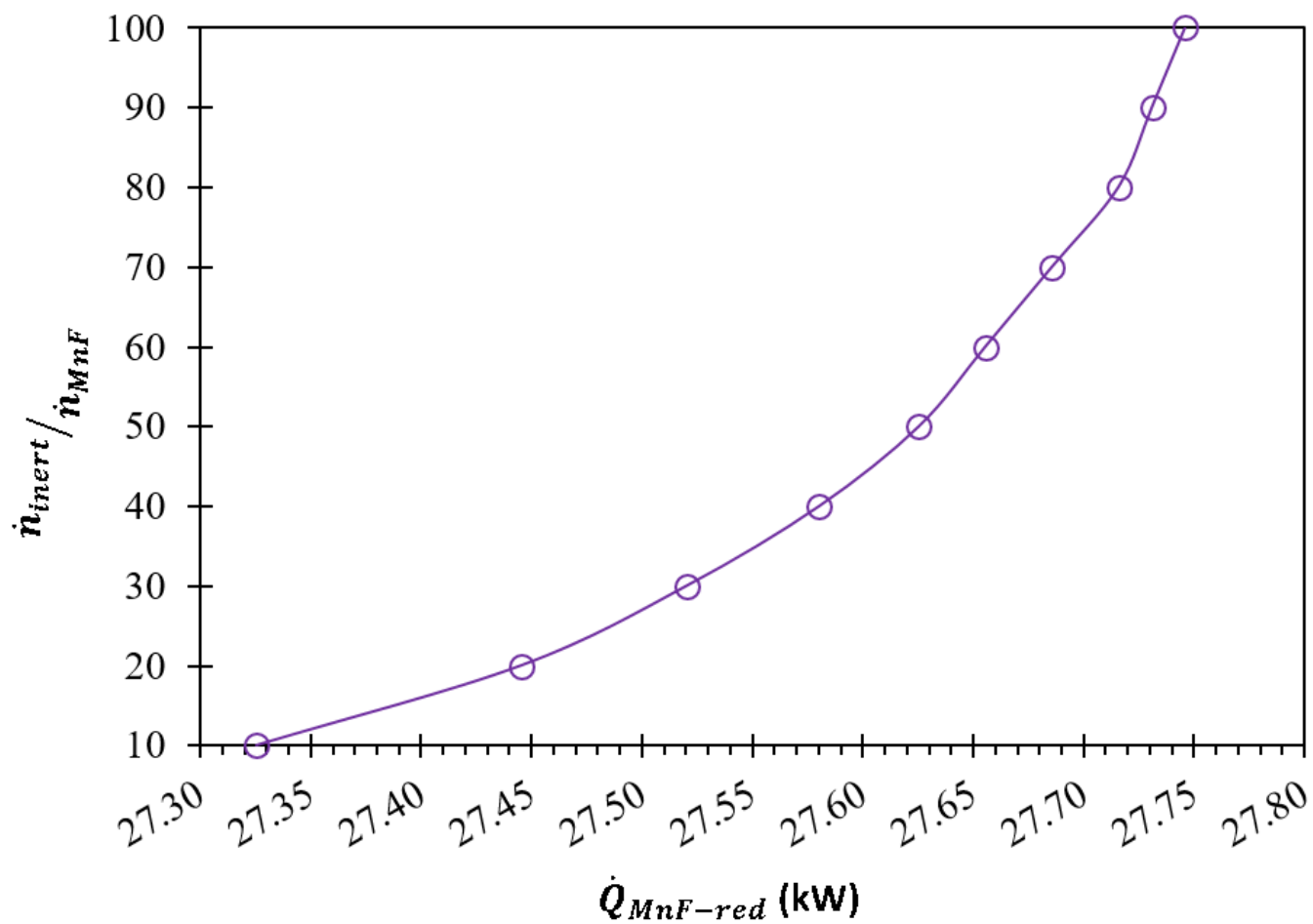
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**Figure 2**

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**Figure 3**

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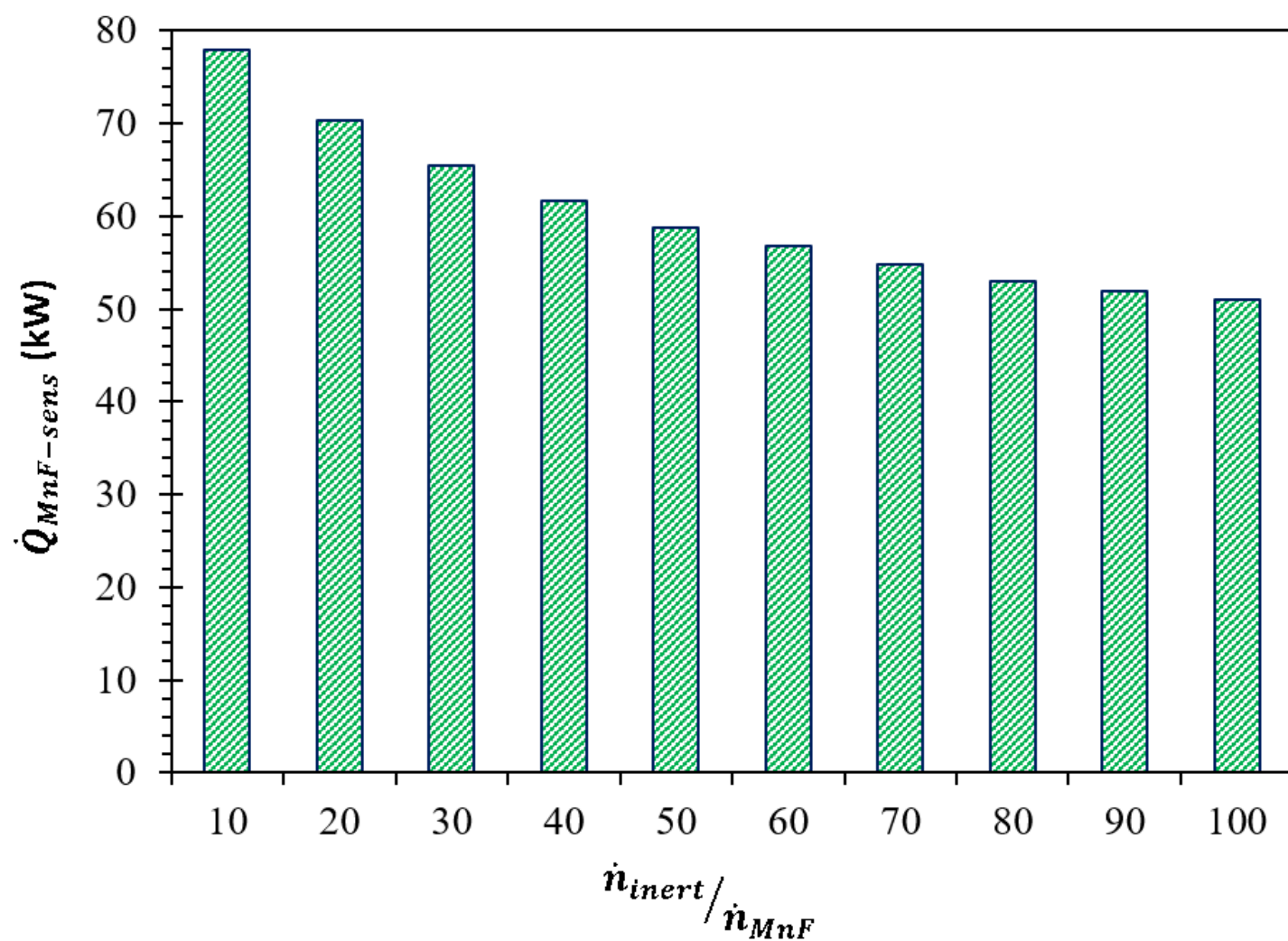
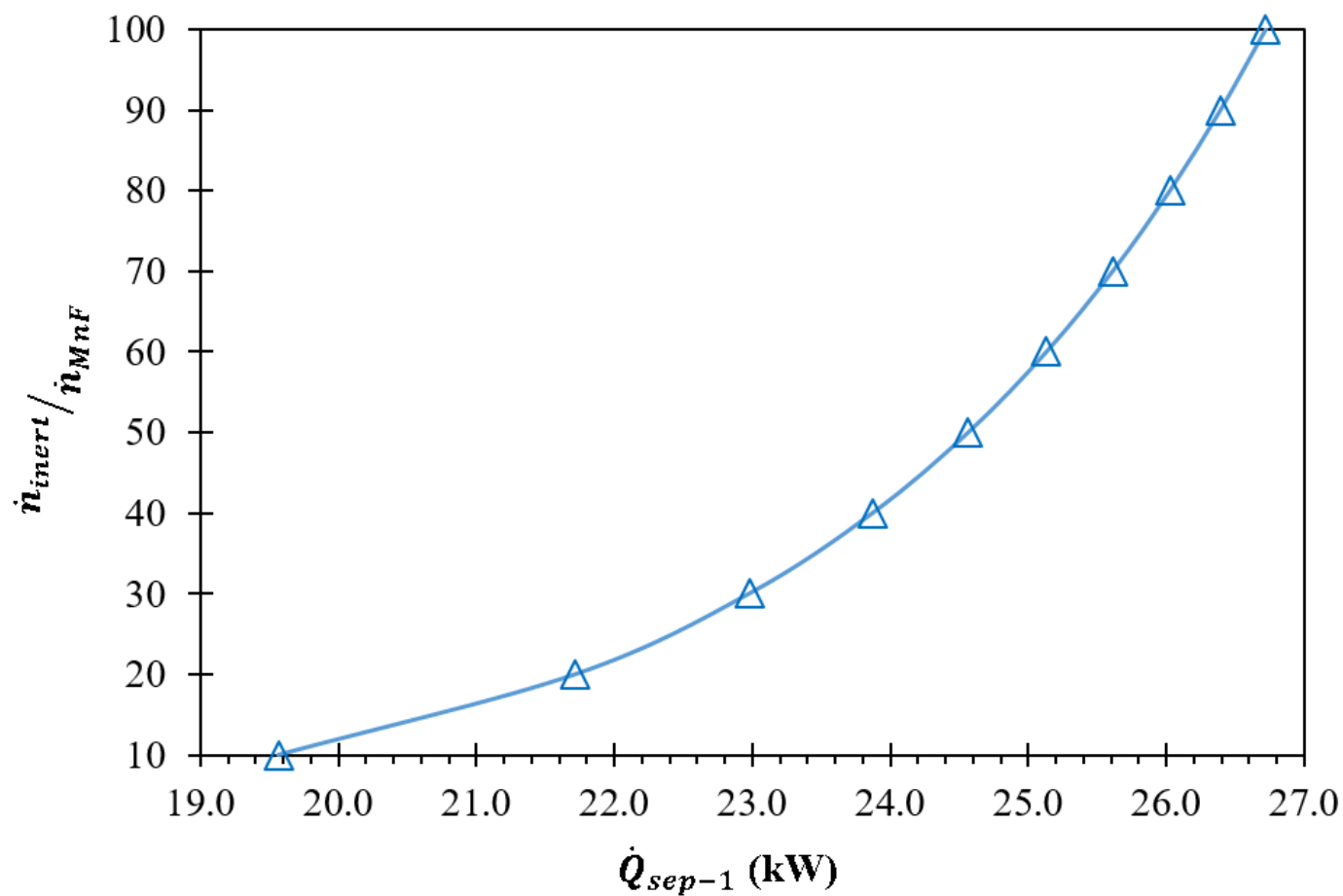


Figure 4

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**Figure 5**

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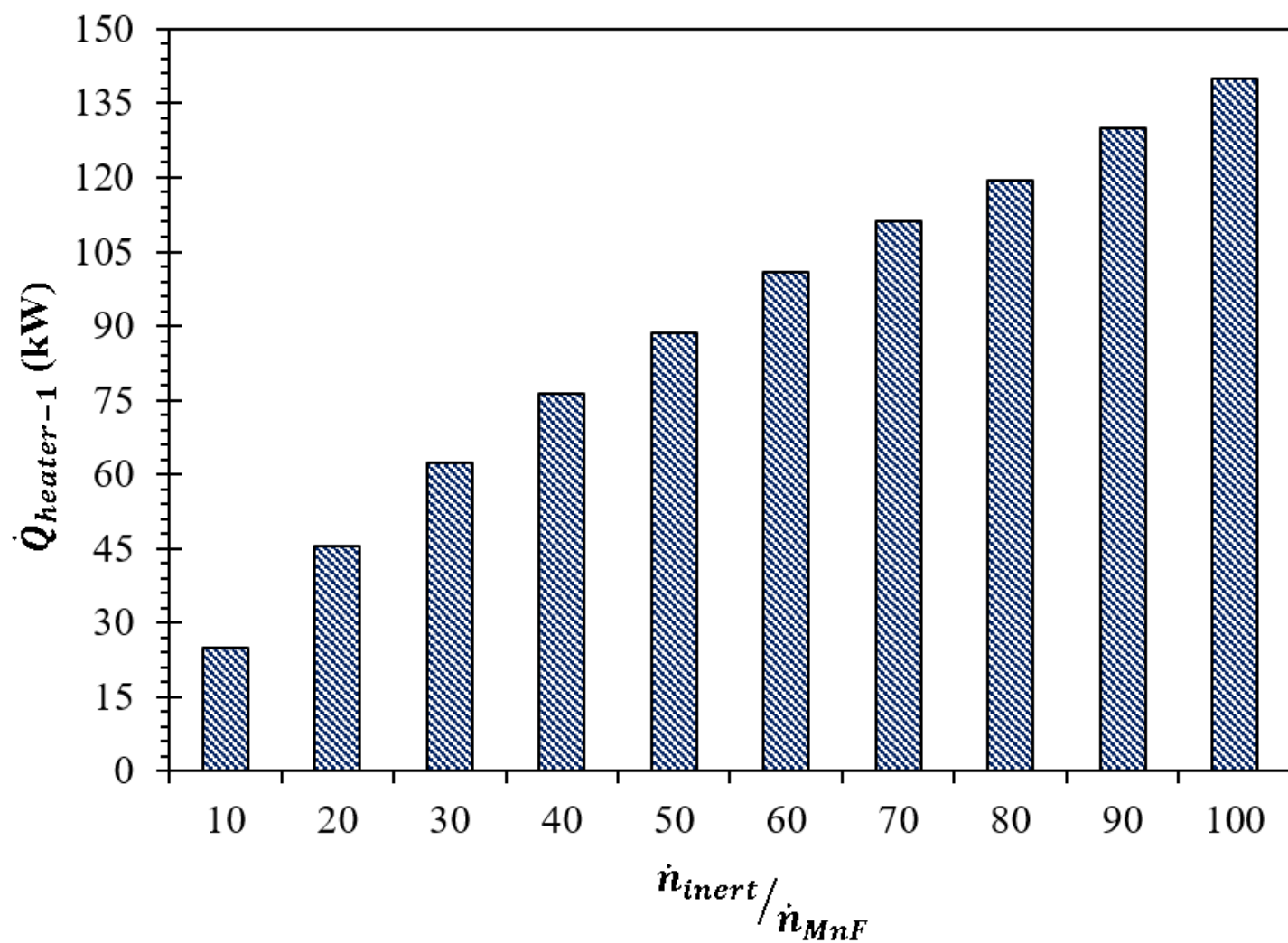
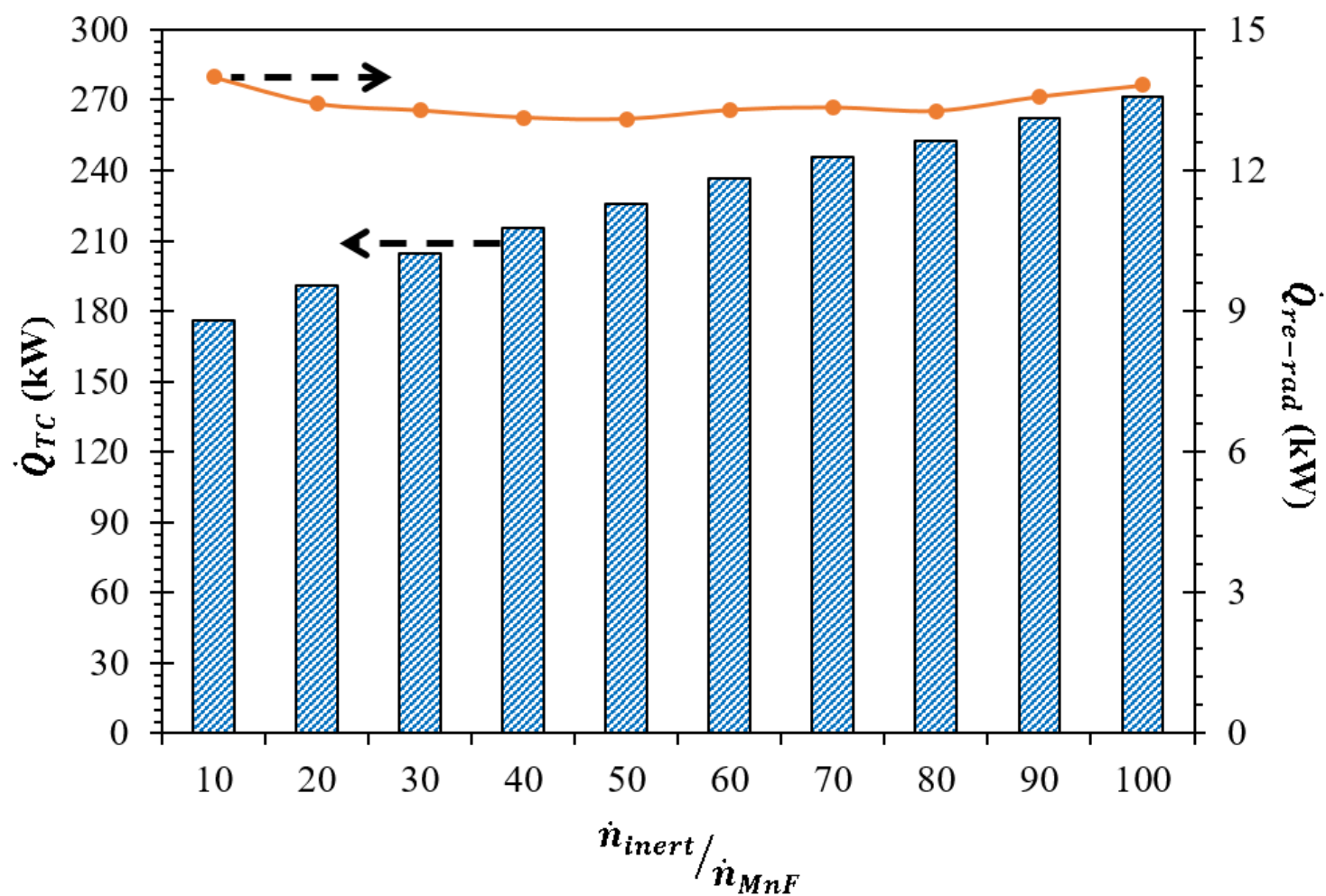


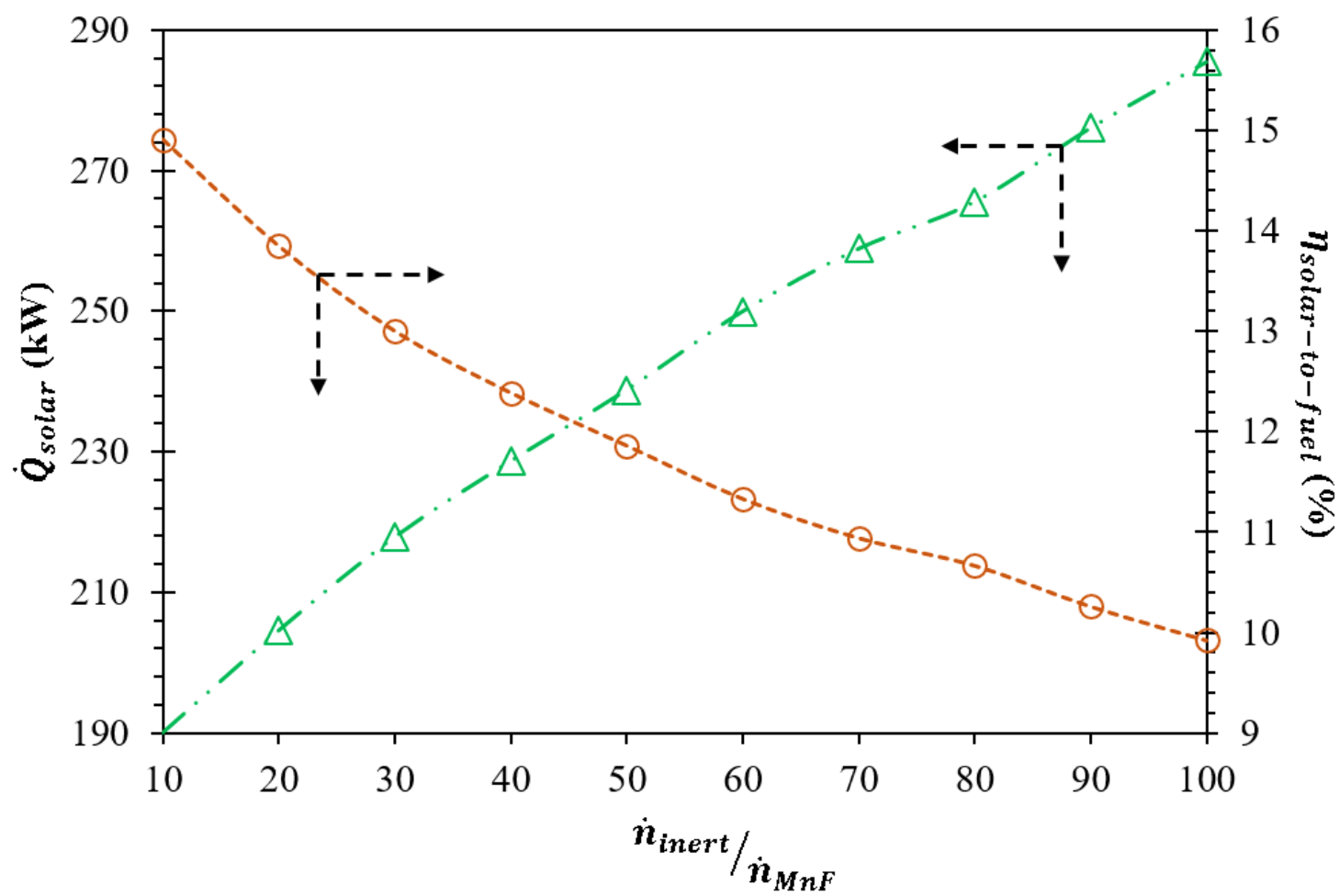
Figure 6

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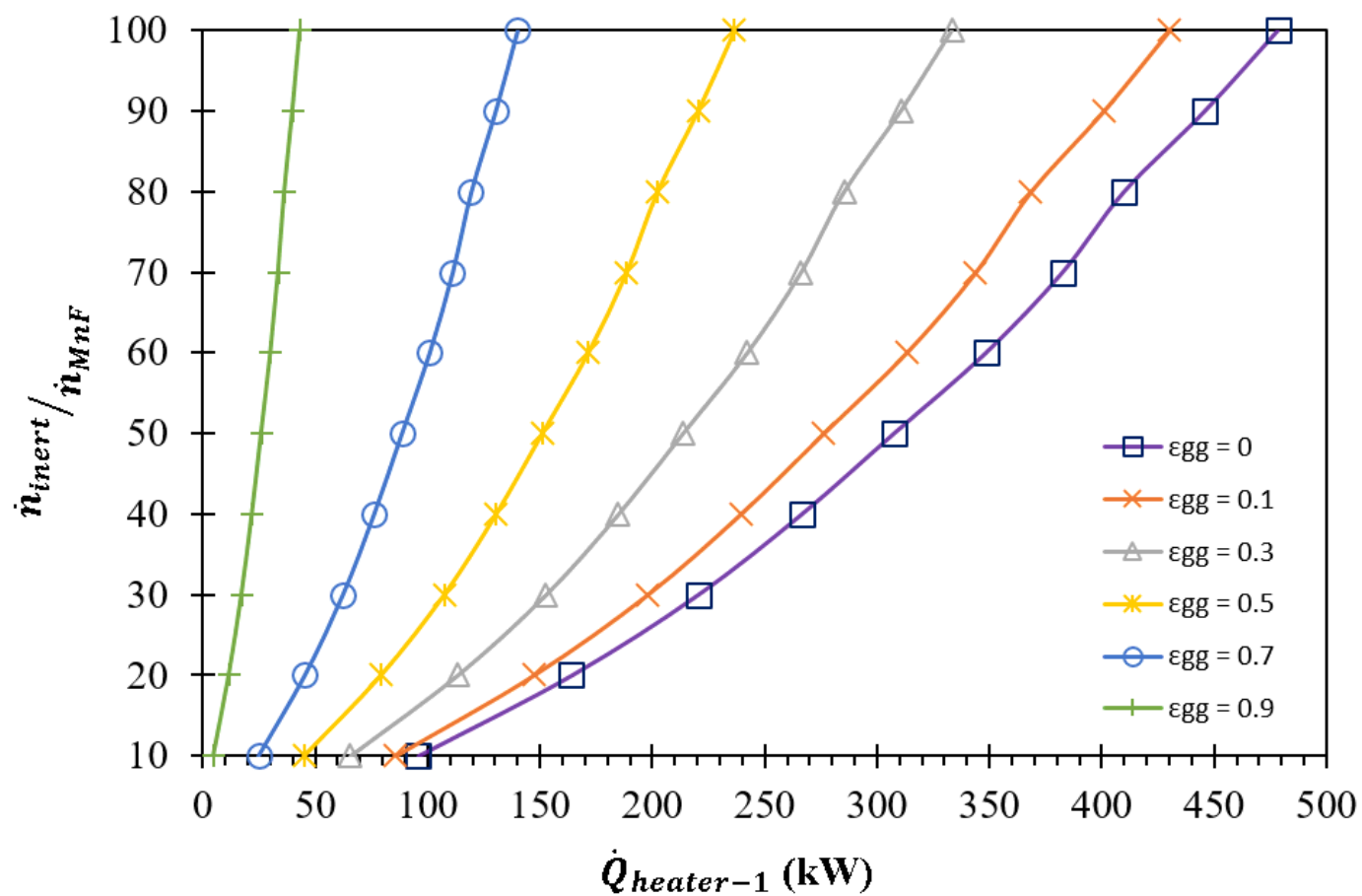


Figure 9

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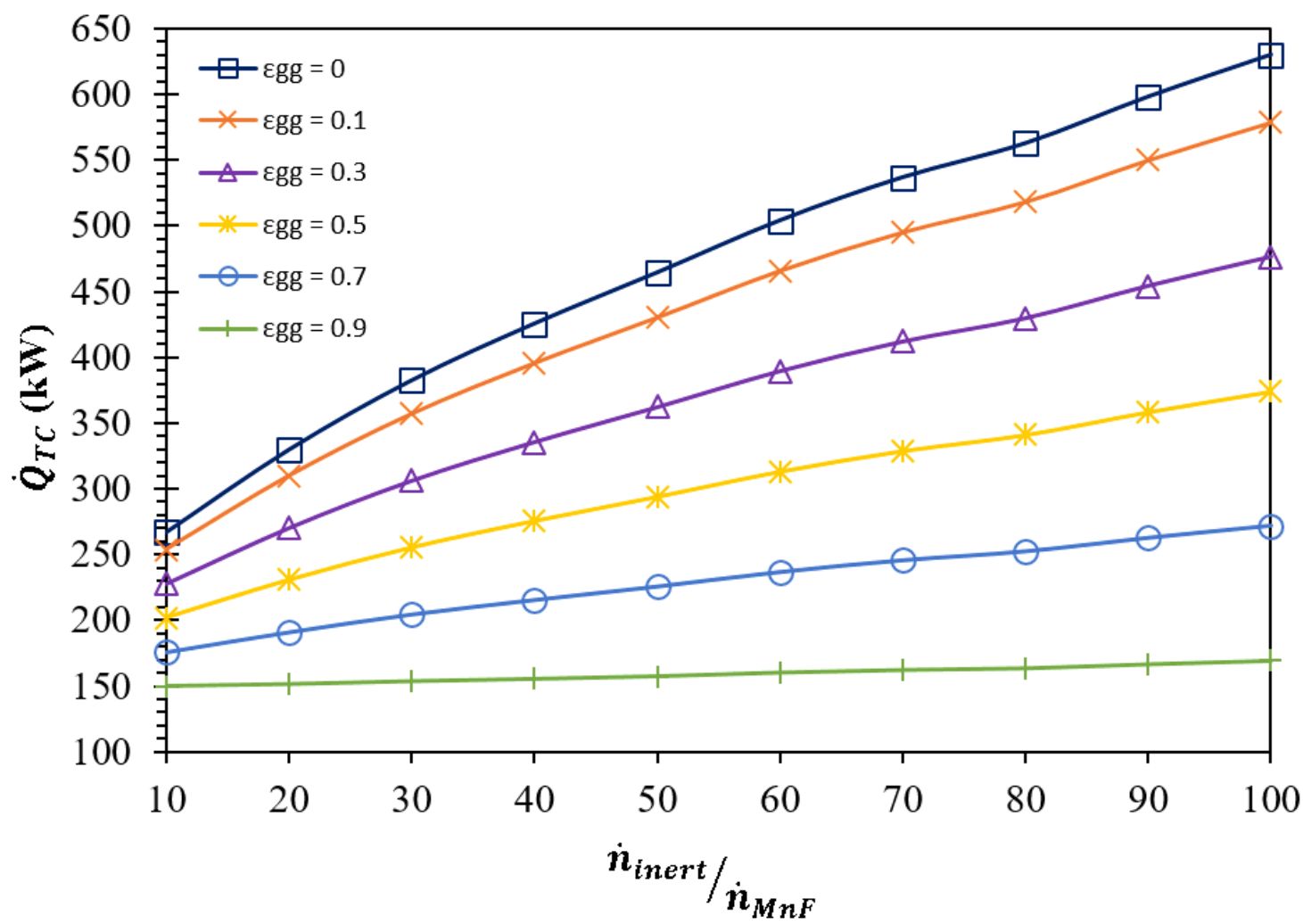


Figure 10

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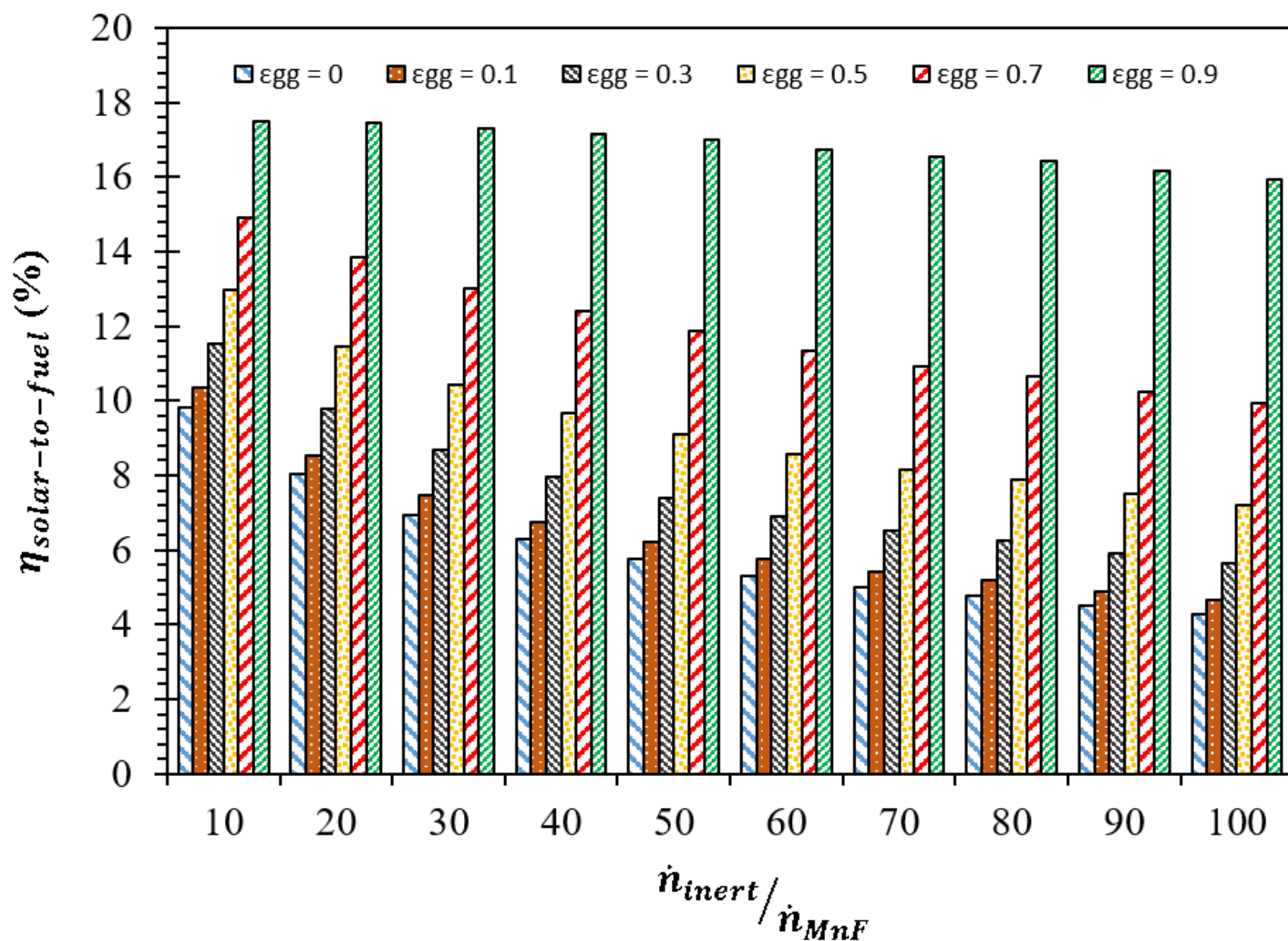


Figure 11

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