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# Exergy Analysis of Direct and Indirect Combustion of Methanol by Utilizing Solar Energy or Waste Heat

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The growing concern for energy, economy, and environment calls for an efficient utilization of natural energy resources for obtaining useful work. An important thermodynamic aspect in the assessment of the overall energy economy of any physical process is the combined energy and exergy analysis for the identification of process irreversibilities. This paper demonstrates the application of exergy analysis to gain a better understanding of methanol decomposition by using solar energy, based on a comprehensive kinetic model of methanol decomposition employing BASF K3−110 catalyst, then utilizing it in a power cycle and also an internal combustion engine. A comparison is presented between the direct and indirect combustion of methanol. The predictions in this study showed that combining solar thermal energy and methanol decomposition can upgrade the lower level of solar thermal energy to a higher one of chemical energy with syngas and decrease the chemical exergy loss associated in the indirect combustion of methanol. The exergetic efficiency could also be increased by about 6−7% compared with the conventional combustion of methanol.

## Introduction

The world energy consumption is largely dependent on fossil fuels, even today, where combustion plays a key role in the energy utilization process. The combustion of fuels is encountered in many industrial operations, such as heating, power production, transportation, and process industries.

More recently, methanol as an alternative fuel has received increased attention and has gained a potential application in both the transportation and the power generation sectors.[1] For the production of methanol, the most promising technologies are based on the intermediate production of synthetic gas that may be obtained from natural gas reforming or from coal gasification. Effective utilization of methanol as a fuel in conventional power systems will become an important issue in the future. Methanol decomposition has been studied since the 1960s, and correlative catalysts have been prepared. As shown in Figure 1, methanol can be decomposed easily by a catalyst at temperatures of about 200−300 °C via a middle-temperature endothermic process.[2]

An endothermic process that uses fossil fuels exclusively as chemical feeds and solar energy as the source of process heat qualifies as a hybrid solar/fossil fuel process. The products are fuels whose quality has been upgraded by solar energy, that is, the calorific value is increased above that of the fossil fuel by the solar energy input equal to the enthalpy change of reaction.

The concentrating solar collectors with parabolic troughs offer an attractive means of providing solar thermal energy at middle-temperatures (200−300 °C) that can provide the process heat required for driving methanol decomposition. This combination
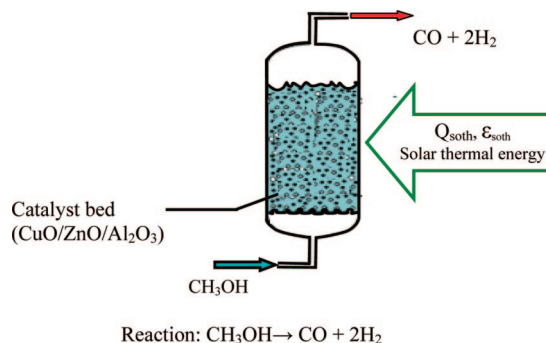


**Figure 1.** Fixed-bed catalytic reactor.

of solar thermal energy and methanol decomposition has two positive features: the heating value of methanol fuel can be upgraded and the middle-temperature solar thermal energy collected can be converted into chemical energy.

Recently, many papers about catalysts, reaction mechanism, thermodynamics, and kinetics of methanol decomposition have been published.[3−5] On the basis of the BASF K3−110 catalyst, comprised of a mixed oxide of copper and zinc supported on gamma-alumina, a comprehensive kinetic model of methanol decomposition was developed that was able to accurately predict the rates of production of both hydrogen and carbon monoxide for a wide range of operating conditions.[6,7] The BASF K3−110 catalyst composition and physical properties are summarized in Table 1.

**Exergy Analysis.** Exergy refers to the maximum theoretical work that can be obtained from a given form of energy using the environmental parameters as the reference state. One of

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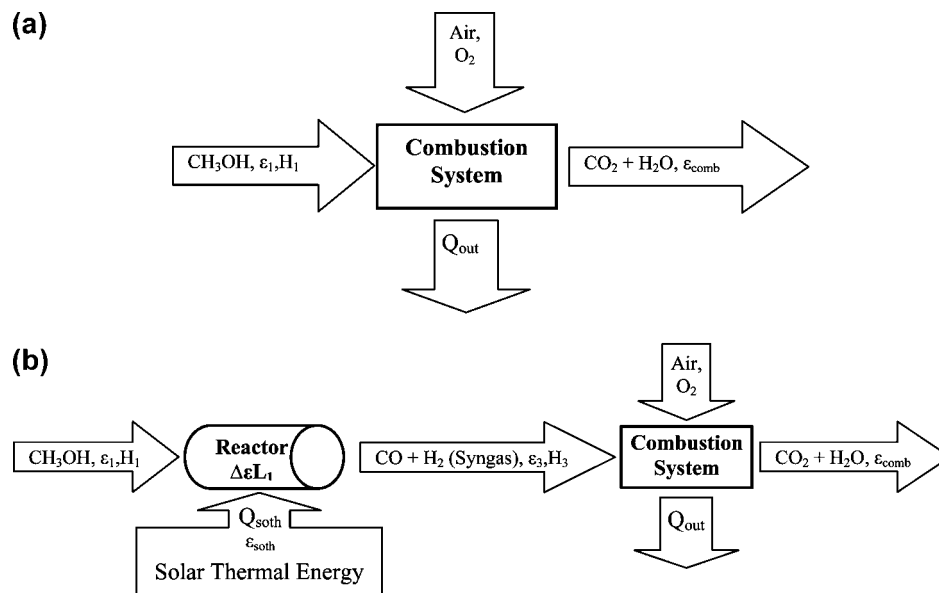‡ Department of Chemical and Petroleum Engineering.
(1) Jean, P. L. *Catal. Today* **2001**, *64*, 3–8.
(2) Nakagaki, T.; Ogawa, T.; Murata, K.; Nakata, Y. *ASME J. Eng. Gas Turbines Power* **2001**, *123*, 727–733.

(3) Brown, J. C.; Gulari, E. *Catal. Commun.* **2004**, *5*, 431–436.
(4) Fukuhara, C.; Igarashi, A. A. *J. Chem. Eng. Jpn.* **2002**, *35*, 1322–1329.
(5) Greeley, J.; Mavrikakis, M. *J. Catal.* **2002**, *208*, 291–300.

**(a)**



**(b)**



**Figure 2.** (a) Schematic of combustion system (direct combustion of methanol) showing the exergy transfer. (b) Schematic of reactor and combustion system (indirect combustion) showing the exergy transfer.

**Table 1. Catalyst Composition and Physical Properties (Troy et al.[13])**

| catalyst support (vender notation) | catalyst family | composition/ type/form | surface area ($m^2 g^{-1}$) | density ($g mL^{-1}$) |
|---|---|---|---|---|
| BASF K3−110 | non-zeolite | 1/8" pellets, 40% CuO, 40% ZnO, 20% $Al_2O_3$ | 113 | 1.5 |

the main uses of this concept is in the exergy balance, which may be considered as an account in the degradation of the given specific form energy. Exergy analysis is based on the second law of thermodynamics, according to which a complete transformation of heat into work is not possible.[8]

Almost one-third of the energy of a fossil fuel is wasted or "destroyed" during the combustion process in power generation. This has caused a renewed interest in exergy analysis, since effective management and optimization of thermal systems is emerging as a major modern technical challenge.[9] The exergy analysis enables a quantitative evaluation of the causes for a decrease in exergy due to thermodynamic imperfections of thermal and chemical processes. Poor thermodynamic performance is the result of exergy losses in combustion and heat-transfer processes.[10,11]

**Methanol as a Fuel.** The advantages of high energy density, easy availability, and safe handling/storage are now making methanol one of the most promising sources of hydrogen for fuel-cell systems and synthetic fuel in the future.[12,13] At present, methanol is an important industrial chemical and may play a significant role as a synthetic fuel for the future. The methanol production capacities installed throughout the world increased from $18 \times 10^6$ tons/year in 1985 to $25 \times 10^6$ tons/year in 1990, and these were expected to reach $35 \times 10^6$ tons/year by the year 2000.[14]

The world's resources of liquid hydrocarbons from crude oil are finite. Alternative fuels for the future should be considered, and the most promising candidates are liquid-based hydrocarbons, such as ethanol and methanol. If the economics of the two alcohols were equivalent, ethanol would be the alcohol of

choice for transportation use because the volumetric energy density is better, but the economics of methanol are more favorable, making it the better choice for replacement of petroleum-based fuels in the transportation and power sector.[15,16]

There is an abundance of coal in the world; this supply could support our energy needs for several hundreds of years. Coal could become a clean transportation fuel, with no sulfur content, by turning it into methanol through indirect liquefaction.

The important advantages of methanol as a fuel are a higher energy content per volume than other alternative fuels such as compressed natural gas or liquefied petroleum gas and the minimal changes needed in the existing fuel distribution network. Finally, methanol can considerably reduce automotive emissions and requires no antiknock additives because of its high octane number. It can be used directly as a replacement for gasoline in the gasoline and diesel blends. Methanol is also favored over conventional fuels because of its lower ozone-forming potential, lower emissions of pollutants—particularly benzene, polycyclic aromatic hydrocarbons, and sulfur compounds—and low evaporative emissions. On the other hand, compared to conventional fuels, its disadvantages include the possibility of higher formaldehyde emissions, higher acute toxicity and, at present, lower cost-effectiveness.[17]

**Methanol Production.** The potential resource base for methanol is huge, because it can be made from any organic material, such as natural gas, coal, and including biomass. It can also be made from waste, which becomes more important with every new landfill required.[16] As the demand for methanol is steadily increasing, its manufacture should also be considered. Presently, the majority of methanol is made from natural gas, but some methanol is also made from coal. In both cases, methanol is converted into synthesis gas, via catalytic steam reforming in the case of natural gas and through gasification in the case of coal. Further steps in a methanol plant are usually based on the ICI technology, which include syngas compression, methanol synthesis, and distillation of crude methanol. Natural-gas-based processes are very sensitive to the natural gas costs because about 0.63 ton of natural gas is needed to make 1 ton of methanol. For

(6) Peppley, B. A.; Amphlett, J. C.; Kearns, L. M.; Mann, R. F. *Appl. Catal. A: General* **1999**, *179*, 31–49.

(7) Peppley, B. A.; Amphlett, J. C.; Kearns, L. M.; Mann, R. F. *Appl. Catal. A: General* **1999**, *179*, 21–29.

(8) Durmayaz, A.; Yavuz, H. *Appl. Energy* **2001**, *69*, 39–57.

(9) Rakopoulos, C. D.; Kyritsis, D. C. *Energy* **2001**, *26*, 705–22.

the methanol plants in Western Europe, the natural gas cost is about 80% of the total methanol production cost.[13] Therefore, the utilization of other feedstocks, such as biomass or organic wastes, should also be considered.

Biomass can be converted to syngas by a process called partial oxidation and later converted to methanol. Biomass is organic material, such as urban wood wastes, primary mill residues, forest residues, agricultural residues, and dedicated energy crops (e.g., sugar cane and sugar beets) that can be made into fuel. The US Department of Energy estimates 2.45 billion metric tons a year of biomass are available for US fuel production. One ton can be converted to 186 gallons (721 L) of methanol. The total biomethanol production potential in Sweden is about 4 million tons/year, which could replace almost 30% of trans-portation fuel consumed in the country. In the U.S. and Canada the production potential is 28 million tons and 7 million tons of biomethanol, respectively.[18,19]

## Theoretical Considerations

Definitions of the partial molar enthalpy and entropy referring to the dead sate and the partial molar exergy (availability) are introduced in this section.

**Partial Molar Enthalpy.** It is assumed that, for a steady-state open (flow) system, the potential and kinetic energies associated with the flow of species are negligible. The application of the first law of thermodynamics gives the following relationship:[20,21]

$$\sum_k \bar{\beta}_{k,e} m_{k,e} - \sum_k \bar{\beta}_{k,i} m_{k,i} = Q - Q_0 - W_s \tag{1}$$

where $\bar{\beta}$ is the partial molar enthalpy at a reference state, which is defined as

$$\begin{aligned}\bar{\beta} &= \bar{h} - \bar{h}_0 \\ &= \bar{h} - \bar{h}^0 + \bar{h}^0 - \bar{h}_0 \\ &= (\bar{h}^0 - \bar{h}_0) + (\bar{h} - \bar{h}^0)\end{aligned} \tag{2a}$$

The following thermodynamic relationships are used for evaluating the enthalpy difference terms in eq 2a:

$$\bar{h} - \bar{h}^0 = \bar{h}(T, P)$$

$$d(\bar{h} - \bar{h}^0) = \left(\frac{\partial(\bar{h} - \bar{h}^0)}{\partial T}\right)_P dT + \left(\frac{\partial(\bar{h} - \bar{h}^0)}{\partial P}\right)_T dP \tag{2b}$$

$$\left(\frac{\partial(\bar{h} - \bar{h}^0)}{\partial T}\right)_P = \bar{c}_P \tag{2c}$$

$$\left(\frac{\partial(\bar{h} - \bar{h}^0)}{\partial P}\right)_T = \bar{v} - T\left(\frac{\partial \bar{v}}{\partial T}\right)_P \tag{2d}$$

(10) Szargut, J. *Appl. Energy* **1989**, *32*, 269–86.
(11) Rivero, R.; Garfias, M. *Energy* **2006**, *31*, 3310–26.
(12) Courty, P.; Chaumette, P. *Energy Prog.* **1987**, *7*, 23–30.
(13) Troy, A. S.; Kevin, C. O.; Rodney, L. B.; Howard, L. G. *Appl. Catal. B: Environmental* **2006**, *65*, 291–300.
(14) Hutcheson, R. C. Alternative Fuels in the Automotive Market: Report No. 2/95; CONCAWE Automotive Emissions Management, 1995; http://www.concawe.org;
(15) Ptasinski, K. J.; Hamelinck, C.; Kerkhof, P. J. A. M. *Energy Convers. Manage.* **2002**, *43*, 1445–1457.
(16) Nichols, R. J. *J. Sci. Ind. Res.* **2003**, *62*, 97–105.
(17) Macnaughton, N. J.; Pinto, A.; Rogerson, P. L. *Energy Prog* **1984**, *7*, 232–41.
(18) National Renewable Energy Laboratory. *Methanol from Biomass*; Prepared for the U.S. Department of Energy: **1995**.
(19) Borgwardt, R. H. *Ind. Eng. Chem* **1998**, *37*, 3760–3767.
(20) Denbigh, K. G. *Chem. Eng. Sci.* **1956**, *6*, 1–9.
(21) Keenan, J. H. *British J. Appl. Phys.* **1951**, *2*, 183–192.

Substituting eqs 2c and 2d into eq 2b yields eq 2e and its integrated from eq 2f

$$d(\bar{h} - \bar{h}^0) = \bar{c}_P \, dT + \left[\bar{v} - T\left(\frac{\partial \bar{v}}{\partial T}\right)_P\right] dP \tag{2e}$$

$$(\bar{h} - \bar{h}^0) = \int_r^s \bar{c}_P \, dT + \int_r^s \left[\bar{v} - T\left(\frac{\partial \bar{v}}{\partial T}\right)_P\right] dP \tag{2f}$$

where,
  $r$ = reference state ($T$ = 298.15 K, $P$ = 1 bar)
  $s$ = the system $T$ and $P$
By letting

$$\bar{\beta}^0 = \bar{h}^0 - \bar{h}_0 \tag{3}$$

and substituting eqs 2f and 3 into eq 2a, we obtain

$$\bar{\beta} = \bar{\beta}^0 + \int_{298.15}^T \bar{c}_P \, dT + \int_1^P \left[\bar{v} - T\left(\frac{\partial \bar{v}}{\partial T}\right)_P\right] dP \tag{4}$$

where $\bar{c}_P$ is the partial molar specific heat, and $\bar{v}$ is the partial molar volume. The first term on the right-hand side of eq 4, $\bar{\beta}^0$, is the partial molar chemical enthalpy. The second term in eq 4 is the partial molar thermal enthalpy, $\bar{\beta}_T$, that is,

$$\bar{\beta}_T = \int_{298.15}^T \bar{c}_P \, dT \tag{4a}$$

The third term in eq 4 is called the partial molar pressure enthalpy, $\bar{\beta}_P$, that is,

$$\bar{\beta}_P = \int_1^P \left[\bar{v} - T\left(\frac{\partial \bar{v}}{\partial T}\right)_P\right] dP \tag{4b}$$

The sum of the partial molar thermal enthalpy, $\bar{\beta}_T$, and the partial molar pressure enthalpy, $\bar{\beta}_P$, may be called the partial molar physical enthalpy, $\bar{\beta}_{Phy}$. Then, physical entropy is equal to the sum of thermal and pressure entropies, that is,

$$\bar{\beta}_{Phy} = \bar{\beta}_T + \bar{\beta}_P$$

$$\bar{\beta}_{Phy} = \int_{298.15}^T \bar{c}_P \, dT - \int_1^P \left[\bar{v} - T\left(\frac{\partial \bar{v}}{\partial T}\right)_P\right] dP \tag{4c}$$

**Partial Molar Entropy.** It is assumed that, for a steady-state open (flow) system, with the potential and kinetics energies associated with the flow of species through the system being negligible, the application of the second law of thermodynamics gives the following expression for the entropy generation of the process(note that the terms $\bar{\gamma}$ in the summations indicate the entropy of the species at the inlet and outlet):[20–22]

$$\sigma = \sum_k (\bar{\gamma}_{k,e} m_{k,e}) - \sum_k (\bar{\gamma}_{k,i} m_{k,i}) + \frac{Q_0}{T_0} - \frac{Q}{T_m} \tag{5}$$

where $\bar{\gamma}$ is the partial molar entropy, which is defined as

$$\begin{aligned}\bar{\gamma} &= \bar{s} - \bar{s}_0 \\ &= \bar{s} - \bar{s}^0 + \bar{s}^0 - \bar{s}_0 \\ &= \bar{s}^0 - \bar{s}_0 + \int_{298.5}^T \frac{\bar{c}_P}{T} dT - \int_1^P \left(\frac{\partial \bar{v}}{\partial T}\right)_P dP\end{aligned} \tag{6}$$

In addition, it is noted that:

$$\left(\frac{\partial \bar{\gamma}}{\partial T}\right)_P \equiv \left(\frac{\partial(\bar{s} - \bar{s}^0)}{\partial T}\right)_P = \frac{\bar{c}_P}{T} \tag{6a}$$

(22) Gaggioli, R. A. *Chem. Eng. Sci.* **1961**, *16*, 87–96.

$$\left(\frac{\partial \bar{\gamma}}{\partial P}\right)_T \equiv \left(\frac{\partial (\bar{s} - \bar{s}^0)}{\partial P}\right)_T = -\left(\frac{\partial \bar{v}}{\partial T}\right)_P \tag{6b}$$

By letting

$$\bar{\gamma}^0 = \bar{s}^0 - \bar{s}_0 \tag{7}$$

we obtain

$$\bar{\gamma}_0 = \bar{\gamma}^0 + \int_{298.5}^{T} \frac{\bar{c}_P}{T} dT - \int_1^P \left(\frac{\partial \bar{v}}{\partial T}\right)_P dP \tag{8}$$

In eq 8, the first term of the right-hand side, $\bar{\gamma}^0$, is the partial molar chemical entropy. The second term is the partial molar thermal entropy, $\bar{\gamma}_T$, that is,

$$\bar{\gamma}_T = \int_{298.5}^{T} \frac{\bar{c}_P}{T} dT \tag{8a}$$

The third term is the partial molar pressure entropy, $\bar{\gamma}_P$, that is,

$$\bar{\gamma}_P = -\int_1^P \left(\frac{\partial \bar{v}}{\partial T}\right)_P dP \tag{8b}$$

The sum of the partial molar thermal entropy, $\bar{\gamma}_T$, and the partial molar pressure entropy, $\bar{\gamma}_P$, is the partial molar physical entropy, $\bar{\gamma}_{Phy}$. That is, the physical entropy is the sum of the thermal and pressure entropies, that is,

$$\bar{\gamma}_{Phy} = \bar{\gamma}_T + \bar{\gamma}_P \tag{8c}$$

$$\bar{\gamma}_{Phy} = \int_{298.5}^{T} \frac{\bar{c}_P}{T} dT - \int_1^P \left(\frac{\partial \bar{v}}{\partial T}\right)_P dP \tag{8d}$$

**Partial Molar Exergy (Availability).** When the potential and kinetic energies associated with the flow of species through the system are negligible, combining eq 1 (the first law of thermodynamics) with eq 5 (the second law of thermodynamics) gives rise to:[21,22]

$$\sum_k (\bar{\beta} - T_0 \bar{\gamma})_{k,e} m_{k,e} - \sum_k (\bar{\beta} - T_0 \bar{\gamma})_{k,i} m_{k,i} +$$
$$T_0 \sigma = Q\left(1 - \frac{T_0}{T_m}\right) - W_s \tag{9}$$

By noting that

$$\bar{\beta} = \bar{h} - \bar{h}_0 \text{ and } \bar{\gamma} = \bar{s} - \bar{s}_0$$

we obtain:

$$\bar{\varepsilon} = (\bar{h} - \bar{h}_0) - T_0(\bar{s} - \bar{s}_0) = \bar{\beta} - T_0\bar{\gamma} \tag{10}$$

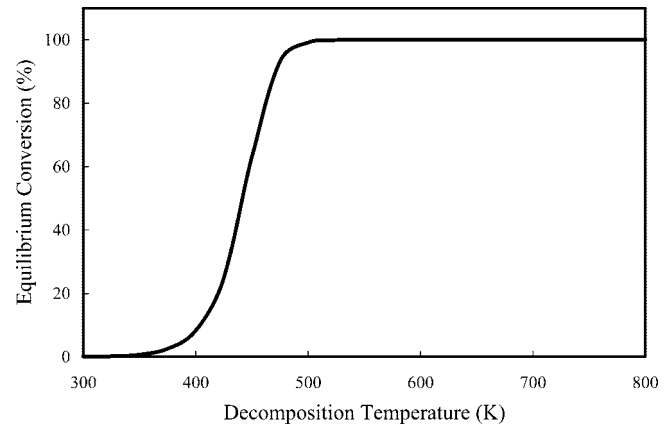Substitution of this expression into eq 9 gives rise to

$$\sum_k \bar{\varepsilon}_{k,e} m_{k,e} - \sum_k \bar{\varepsilon}_{k,i} m_{k,i} + T_0 \sigma = Q\left(1 - \frac{T_0}{T_m}\right) - W_s \tag{11}$$

where $\bar{\varepsilon}$ is the partial molar exergy. It can be evaluated by combining eq 4 with the expression obtained by multiplying eq 5 by $T_0$, as follows:

$$\bar{\varepsilon} = (\bar{\beta}^0 - T_0\bar{\gamma}^0) + \int_{298.5}^{T} \bar{c}_P\left(1 - \frac{T_0}{T}\right) dT +$$
$$\int_1^P \left[\bar{v} - (T - T_0)\left(\frac{\partial \bar{v}}{\partial T}\right)_P\right] dP \tag{12}$$

Next, by letting $\bar{\varepsilon}^0 = \bar{\beta}^0 - T_0\bar{\gamma}^0$, eq 12 is converted into the following expression.

$$\bar{\varepsilon} = \bar{\varepsilon}^0 + \int_{298.5}^{T} \bar{c}_P\left(1 - \frac{T_0}{T}\right) dT + \int_1^P \left[\bar{v} - (T - T_0)\left(\frac{\partial \bar{v}}{\partial T}\right)_P\right] dP \tag{13}$$



**Figure 3.** Equilibrium conversion of methanol with reaction (decomposition) temperature.

In eq 13, the first term of the right-hand side, $\bar{\varepsilon}^0$, is the partial molar chemical exergy (availability). The second term is the partial molar thermal exergy, $\bar{\varepsilon}_T$, that is,

$$\bar{\varepsilon}_T = \int_{298.15}^{T} \bar{c}_P\left(1 - \frac{T_0}{T}\right) dT \tag{13a}$$

The third term is the partial molar pressure exergy, $\bar{\varepsilon}_P$, that is,

$$\bar{\varepsilon}_P = \int_1^P \left[\bar{v} - (T - T_0)\left(\frac{\partial \bar{v}}{\partial T}\right)_P\right] dP \tag{13b}$$

It is noted that the partial molar physical exergy, $\bar{\varepsilon}_{Phy}$, refers to the sum of the partial molar thermal exergy, $\bar{\varepsilon}_T$, and the partial molar pressure exergy, $\bar{\varepsilon}_P$. That is, the physical exergy is the sum of the thermal and pressure exergies, that is,

$$\bar{\varepsilon}_{Phy} = \bar{\varepsilon}_T + \bar{\varepsilon}_P$$

$$\bar{\varepsilon}_{Phy} = \int_{298.15}^{T} \bar{c}_P\left(1 - \frac{T_0}{T}\right) dT + \int_1^P \left[\bar{v} - (T - T_0)\left(\frac{\partial \bar{v}}{\partial T}\right)_P\right] dP \tag{13c}$$

## Kinetics of Methanol Decomposition Reaction in the Absence of Water

As shown in Figure 2b, the chemical energy of methanol is released through two steps: an endothermic conversion reaction ($CH_3OH \rightarrow CO + 2H_2$) at lower temperatures and an exothermic combustion reaction ($CO + 2H_2 + 1.5O_2 \rightarrow CO_2 + 2H_2O$) at higher temperatures. In this study, the coupling of two processes is called the indirect combustion of methanol, which differs from the traditional direct (single-step) combustion of methanol ($CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O$), as shown in Figure 2a.

In the methanol decomposition process, liquid methanol feed is preheated in the preheater and evaporated in the evaporator. After that, the saturated methanol vapor is superheated to the inlet temperature of the catalyst bed of the reactor in the superheater. The solar thermal energy is absorbed as a form of sensible and latent heat of methanol in the receiver-heater. The methanol vapor then enters the receiver-reactor and undergoes an endothermic reaction driven by solar energy. The reaction is: $CH_3OH \leftrightarrow CO + 2H_2$, with $\Delta H_{298} = 90.64 \text{ kJ mol}^{-1}$ over a temperature range of 200–220 °C and at a pressure of 1 bar. In the reactor, the concentrated solar energy can be converted into the chemical energy associated with the syngas. After that, the upgraded syngas with CO and $H_2$ is fed into a combustor in the gas turbine and burned with the compressed air as shown in Figures 2a and 2b.

**Table 2. Parameters for Comprehensive Kinetic Model of Methanol Decomposition on BASF K3-110 Cu/ZnO/Al$_2$O$_3$ Catalyst (Peppley et al.[6,7])**

| rate constant or equilibrium constant | $\Delta S_i$ (J mol$^{-1}$ K$^{-1}$) or $k_i^\infty$ (m$^2$ s$^{-1}$ mol$^{-1}$) | $\Delta H_i$ or $E$ (kJ mol$^{-1}$) |
|---|---|---|
| $k_D^\infty$ (m$^2$ s$^{-1}$ mol$^{-1}$) | $3.8 \times 10^{20}$ | 170 |
| $K^*_{CH_3O}$ (bar$^{-0.5}$) | 30.0 | $-20.0$ |
| $K_H$ (bar$^{-0.5}$) | $-46.2$ | $-50.0$ |

The comprehensive kinetic model of methanol decomposition has been developed in the Langmuir−Hinshelwood rate expression based on the independent surface mechanisms. The final form of the rate expression for methanol decomposition reaction, eq 14, is given by eq 15.[6,7]

$$CH_3OH \leftrightarrow CO + 2H_2, \Delta H_{298} = 90.64 \text{ kJ mol}^{-1} \quad (14)$$

$$r_D = \frac{k_D K^*_{CH_3O(2)}\left(\dfrac{P_{CH_3OH}}{P_{H_2}^{0.5}}\right)\left(1 - \dfrac{P_{H_2}^2 P_{CO}}{k_D P_{CH_3OH}}\right) C_{S_2} C_{S_{2a}}}{\left[1 + K^*_{CH_3O(2)}\left(\dfrac{P_{CH_3OH}}{P_{H_2}^{0.5}}\right)\right](1 + K_{H(2a)}^{0.5} P_{H_2}^{0.5})} \quad (15)$$

In the above rate expression, the total site concentrations were set at 7.5 $\mu$mol m$^{-2}$ for type 2($C_{S_2}$) and 15 $\mu$mol m$^{-2}$ for type 2a($C_{S_{2a}}$).

There are a rate constant and three equilibrium constants in the above equation. The temperature dependence of each of these constants can be expressed either using the Arrhenius equation or the van't Hoff equation.[6]

$$k_D = k_D^\infty \exp\left(\frac{-E_D}{RT}\right)$$

$$K^*_{CH_3O(2)} = \exp\left(\frac{\Delta S^*_{CH_3O(2)}}{R} - \frac{\Delta H^*_{CH_3O(2)}}{RT}\right)$$

$$K_{H(2a)} = \exp\left(\frac{\Delta S_{H(2a)}}{R} - \frac{\Delta H_{H(2a)}}{RT}\right) \quad (16)$$

**Reaction Equilibrium and Reaction Rate.** The values for all of the parameters are summarized in Table 2. The chemical equilibrium conversion of methanol is illustrated in Figure 3. The molar basis methanol conversion was predicted to be more than 90% over a temperature range of 473−500 K at a pressure of 1 bar. At temperatures below 400 K, the conversion rate increased slowly with the temperature, and it increased rapidly at temperatures above 400 K. These trends are consistent with recently reported results.[23] These predictions suggest that the solar collector temperature between 473 K (200 °C) and 500 K (227 °C) in the parabolic trough collectors would be suitable for the solar thermal decomposition of methanol, and the conversion of methanol can exceed 90%.

An indirect receiver-reactor[24] may be applied in this process. For a "real" solar receiver-reactor, the system may contain an internal preheater where a counter-flowing heat recovery fluid could extract heat from the catalyst bed of the reactor for maintaining isothermal conditions.

**Calculation Procedure for Decomposition Process and Direct and Indirect Combustion Process of Methanol.** Some of the assumptions made and the numerical values used in this analysis are listed below.

(1) Control volume operates at steady state with $W_S$ (work done) = 0;

(23) Yongtaek, C.; Stenger, H. G. *Appl. Catal. B: Environ.* **2002**, *38*, 259–269.
(24) Diver, R. B. *J. Solar Energy Eng.* **1987**, *109*, 199–203.

(2) No work done by the system or on the system;

(3) All reactants and products were modeled as an ideal gas with their $\bar{c}_P$ values listed in Table 3;

(4) The methanol decomposition temperature range, $T_D$, is 300−800 K;

(5) The combustion temperature range, $T_C$, is 1000−1400 K;

(6) The universal gas constant, $R$, is 8.314 kJ kmol$^{-1}$ K$^{-1}$;

(7) The ambient temperature, $T_0$, is 298.5 K.

**Energy Balance of the Methanol Decomposition Process.** Equation 1 was used to calculate the required heat quantity, $Q_u$, for the methanol decomposition process. That is, the useful solar energy input from solar collectors is:

$$2\bar{\beta}_{H_2} + \bar{\beta}_{CO} - \bar{\beta}_{CH_3OH} = Q = Q_u \quad (17)$$

Next, eq 4 was used for different species involved in the decomposition process. The pressure molar enthalpies for all species of process are equal to zero because of the ideal gas assumption.

$$\bar{\beta}_P = \int_1^P \left[\bar{v} - T\left(\frac{\partial \bar{v}}{\partial T}\right)_P\right] dP = 0 \quad (17a)$$

Therefore, the total partial molar enthalpy of H$_2$ from eq 4 is:

$$\bar{\beta}_{H_2} = \bar{\beta}_{H_2}^0 + \int_{298.15}^{T_D} \bar{c}_{P,H_2} \, dT \quad (17b)$$

Similarly,

$$\bar{\beta}_{CO} = \bar{\beta}_{CO}^0 + \int_{298.15}^{T_D} \bar{c}_{P,CO} \, dT \quad (17c)$$

$$\bar{\beta}_{CH_3OH} = \bar{\beta}_{CH_3OH}^0 + \int_{298.15}^{T_D} \bar{c}_{P,CH_3OH} \, dT \quad (17d)$$

Substituting eqs 17a−17d into eq 17 yields the following relationship for the useful heat quantity, $Q_u$:

$$Q_u = Q = 2\bar{\beta}_{H_2}^0 + \bar{\beta}_{CO}^0 - \bar{\beta}_{CH_3OH}^0 +$$
$$\int_{298.15}^{T_D} [2\bar{c}_{P,H_2} + \bar{c}_{P,CO} - \bar{c}_{P,CH_3OH}] \, dT \quad (18)$$

**Exergy Balance of the Methanol Decomposition Process.** Applying eq 11 to the methanol decomposition process yields the following exergy balance:

$$2\bar{\varepsilon}_{H_2} + \bar{\varepsilon}_{CO} - \bar{\varepsilon}_{CH_3OH} + T_0\sigma = Q\left(1 - \frac{T_0}{T}\right) \quad (19)$$

Next, eq 13b is used for the molar pressure exergy of species involved in the methanol decomposition process, as follows:

$$\bar{\varepsilon}_P = \int_1^P \left[\bar{v} - (T - T_0)\left(\frac{\partial \bar{v}}{\partial T}\right)_P\right] dP = \int_1^P \frac{T_0 R}{P} dP \quad (19a)$$

Thus, total molar pressure exergy of the methanol decomposition process is given by eq 19b.

$$\bar{\varepsilon}_{P,Total} = \bar{\varepsilon}_{P,CH_3OH} - 2\bar{\varepsilon}_{P,H_2} - \bar{\varepsilon}_{P,CO}$$

$$= T_0 R\left(\int_1^{P_{CH_3OH}} \frac{1}{P} dP - 2\int_1^{P_{H_2}} \frac{1}{P} dP - \int_1^{P_{CO}} \frac{1}{P} dP\right) \quad (19b)$$

Equation 19b is simplified as follows:

$$\bar{\varepsilon}_{P,Total} = T_0 R \ln\left(\frac{P_{CH_3OH}}{P_{H_2}^2 P_{CO}}\right) \quad (19c)$$

The partial molar exergies of H$_2$, CO, and CH$_3$OH from eq 13 are:

**Table 3. Materials and Their Specific Chemical Enthalpy, Entropy, Exergy and Specific Heat Capacity[28]**

| materials | $\bar{\beta}^0$ (kJ/kmol) | $\bar{\gamma}^0$ (kJ/kmol·K) | $\bar{\varepsilon}^0$ (kJ/kmol) | $\bar{c}_P$ (kJ/kmol·K) |
|---|---|---|---|---|
| $CH_3OH$ | $764.4762 \times 10^3$ | 32.8329 | $754.6920 \times 10^3$ | $8.374 + 0.12560 \times 10^{-3}T$ |
| $H_2(g)$ | $286.0422 \times 10^3$ | 169.7580 | $235.4238 \times 10^3$ | $27.842 + 2.93076 \times 10^{-3}T$ |
| $CO(g)$ | $283.1784 \times 10^3$ | 25.5633 | $275.5542 \times 10^3$ | $28.847 + 1.59098 \times 10^{-3}T$ |
| $CO_2(g)$ | 0 | $-67.4075$ | $20.0975 \times 10^3$ | $19.962 + 72.62279 \times 10^{-3}T$ |
| $H_2O(g)$ | $43.5008 \times 10^3$ | 119.1228 | $7.9842 \times 10^3$ | $33.838 + 9.21191 \times 10^{-3}T$ |
| $O_2(g)$ | 0 | $-13.0071$ | $3.8782 \times 10^3$ | $30.1466 - 15.6137 \times 10^{-3}T$ |

$$\bar{\varepsilon}_{H_2} = \bar{\varepsilon}^0_{H_2} + \int_{298.5}^{T_D} \bar{c}_{P,H_2}\left(1 - \frac{T_0}{T}\right)dT + \int_1^{P_{H_2}} \frac{T_0 R}{P}dP \quad (19d)$$

$$\bar{\varepsilon}_{CO} = \bar{\varepsilon}^0_{CO} + \int_{298.5}^{T_D} \bar{c}_{P,CO}\left(1 - \frac{T_0}{T}\right)dT + \int_1^{P_{CO}} \frac{T_0 R}{P}dP \quad (19e)$$

$$\bar{\varepsilon}_{CH_3OH} = \bar{\varepsilon}^0_{CH_3OH} + \int_{298.5}^{T_D} \bar{c}_{P,CH_3OH}\left(1 - \frac{T_0}{T}\right)dT + \int_1^{P_{CH_3OH}} \frac{T_0 R}{P}dP \quad (19f)$$

The final expression for the exergy loss, $T_0\sigma$, of the methanol decomposition process is obtained by combining eq 19 with eqs 19c−19f.

$$T_0\sigma = \bar{\varepsilon}^0_{CH_3OH} - 2\bar{\varepsilon}^0_{H_2} - \bar{\varepsilon}^0_{CO} + \int_{298.5}^{T_D}\left(\bar{c}_{P,CH_3OH} - 2\bar{c}_{P,H_2} - \bar{c}_{P,CO}\right)\left(1 - \frac{T_0}{T}\right)dT + T_0 R \ln\left(\frac{P_{CH_3OH}}{P_{H_2}^2 P_{CO}}\right) + Q\left(1 - \frac{T_0}{T}\right) \quad (20)$$

The values of $\bar{\beta}^0$, $\bar{\varepsilon}^0$, and $\bar{c}_P$ for all species in the methanol decomposition process are listed in Table 3.

The exergetic efficiency of the methanol decomposition process is defined as the ratio of exergy change of fluid across the reactor, $\varepsilon_{out} - \varepsilon_{in}$, to the total exergy input of the system, which consists of the exergy of the total heat input and the exergy of methanol feed. That is,

$$\eta = \frac{\varepsilon_{out} - \varepsilon_{in}}{Q\left(1 - \frac{T_0}{T}\right) + \varepsilon_{in}} \quad (21)$$

where $\varepsilon_{out}$ consists of the exergy of $H_2$, $\varepsilon_{H_2}$, and CO, $\varepsilon_{CO}$, and $\varepsilon_{in}$ is exergy of methanol ($CH_3OH$), $\varepsilon_{CH_3OH}$.

**Energy Balance of Indirect and Direct Combustion of Methanol.** Equation 1 was used to calculate the heat release from the indirect and direct combustion process of methanol and yields the following expressions:

$$2\bar{\beta}_{H_2O} + \bar{\beta}_{CO_2} - 2\bar{\beta}_{H_2} - \bar{\beta}_{CO} - 1.5\bar{\beta}_{O_2} = Q_{C,indirect} \quad (22)$$

$$2\bar{\beta}_{H_2O} + \bar{\beta}_{CO_2} - \bar{\beta}_{CH_3OH} - 1.5\bar{\beta}_{O_2} = Q_{C,direct} \quad (23)$$

Next, eq 4 was used for different species involved in the combustion process, the pressure molar enthalpies for all species of combustion process are equal to zero because of the ideal gas assumption.

$$\bar{\beta}_P = \int_1^P\left[\bar{v} - T\left(\frac{\partial\bar{v}}{\partial T}\right)_P\right]dP = 0 \quad (23a)$$

Therefore, the total partial molar enthalpy of $H_2O$ from eq 4 is:

$$\bar{\beta}_{H_2O} = \bar{\beta}^0_{H_2O} + \int_{298.15}^{T_C} \bar{c}_{P,H_2O}\,dT \quad (23b)$$

Similarly,

$$\bar{\beta}_{CO_2} = \bar{\beta}^0_{CO_2} + \int_{298.15}^{T_C} \bar{c}_{P,CO_2}\,dT \quad (23c)$$

Because $O_2$ comes at ambient temperature,

$$\bar{\beta}_{O_2} = \bar{\beta}^0_{O_2} \quad (23d)$$

Substituting eqs 17b−17c and eqs 23b−23c into eq 22 yields the following relationship for the heat release from the indirect combustion process, $Q_{C,indirect}$:

$$Q_{C,indirect} = 2\bar{\beta}^0_{H_2O} + \bar{\beta}^0_{CO_2} - 1.5\bar{\beta}^0_{O_2} - 2\bar{\beta}^0_{H_2} - \bar{\beta}^0_{CO} + \int_{298.15}^{T_C}[2\bar{c}_{P,H_2O} + \bar{c}_{P,CO_2}]dT - \int_{298.15}^{T_D}[2\bar{c}_{P,H_2} + \bar{c}_{P,CO}]dT \quad (24)$$

Similarly, substituting eq 17d and eqs 23b−23c into eq 23 yields the following relationship for the heat release from the direct combustion process, $Q_{C,direct}$:

$$Q_{C,direct} = 2\bar{\beta}^0_{H_2O} + \bar{\beta}^0_{CO_2} - 1.5\bar{\beta}^0_{O_2} - 2\bar{\beta}^0_{CH_3OH} + \int_{298.15}^{T_C}[2\bar{c}_{P,H_2O} + \bar{c}_{P,CO_2}]dT - \int_{298.15}^{T_D}[\bar{c}_{P,CH_3OH}]dT \quad (25)$$

**Exergy Analysis of Indirect and Direct Combustion Process.** Applying eq 11 to the indirect and direct combustion process of methanol yields the exergy balance:

$$2\bar{\varepsilon}_{H_2O} + \bar{\varepsilon}_{CO_2} - 1.5\bar{\varepsilon}_{O_2} - 2\bar{\varepsilon}_{H_2} - \bar{\varepsilon}_{CO} + (T_0\sigma)_{indirect} = Q_{C,indirect}\left(1 - \frac{T_0}{T}\right) \quad (26)$$

$$2\bar{\varepsilon}_{H_2O} + \bar{\varepsilon}_{CO_2} - 1.5\bar{\varepsilon}_{O_2} - \bar{\varepsilon}_{CH_3OH} + (T_0\sigma)_{direct} = Q_{C,direct}\left(1 - \frac{T_0}{T}\right) \quad (27)$$

Next, eq 13b is used for the molar pressure exergy of species involved in the methanol combustion process, as follows:

$$\bar{\varepsilon}_P = \int_1^P\left[\bar{v} - (T - T_0)\left(\frac{\partial\bar{v}}{\partial T}\right)_P\right]dP = \int_1^P \frac{T_0 R}{P}dP \quad (28)$$

Thus, total molar pressure exergy of the indirect methanol combustion process is given by

$$(\bar{\varepsilon}_{P,Total})_{indirect} = 2\bar{\varepsilon}_{P,H_2} + \bar{\varepsilon}_{P,CO} + 1.5\bar{\varepsilon}_{P,O_2} - 2\bar{\varepsilon}_{P,H_2O} - \bar{\varepsilon}_{P,CO_2}$$
$$= T_0 R\left(2\int_1^{P_{H_2}}\frac{1}{P}dP + \int_1^{P_{CO}}\frac{1}{P}dP + 1.5\int_1^{P_{O_2}}\frac{1}{P}dP - 2\int_1^{P_{H_2O}}\frac{1}{P}dP - \int_1^{P_{CO_2}}\frac{1}{P}dP\right) \quad (28a)$$

Equation 28a is simplified as follows:

$$(\bar{\varepsilon}_{P,Total})_{indirect} = T_0 R \ln\left(\frac{P_{H_2}^2 P_{CO} P_{O_2}^{1.5}}{P_{H_2O}^2 P_{CO_2}}\right) \quad (28b)$$

Similarly, total molar pressure exergy of the direct methanol combustion process is given by

$$(\bar{\varepsilon}_{P,Total})_{direct} = T_0 R \ln\left(\frac{P_{CH_3OH}^2 P_{O_2}^{1.5}}{P_{H_2O}^2 P_{CO_2}}\right) \quad (28c)$$

The partial molar exergies of $H_2O$, $CO_2$, and $O_2$ from eq 13 are:

$$\bar{\varepsilon}_{H_2O} = \bar{\varepsilon}_{H_2O}^0 + \int_{298.5}^{T_C} \bar{c}_{P,H_2O}\left(1 - \frac{T_0}{T}\right)dT + \int_{1}^{P_{H_2O}} \frac{T_0 R}{P}dP \tag{28d}$$

$$\bar{\varepsilon}_{CO_2} = \bar{\varepsilon}_{CO_2}^0 + \int_{298.5}^{T_C} \bar{c}_{P,CO_2}\left(1 - \frac{T_0}{T}\right)dT + \int_{1}^{P_{CO_2}} \frac{T_0 R}{P}dP \tag{28e}$$

$$\bar{\varepsilon}_{O_2} = \bar{\varepsilon}_{O_2}^0 + \int_{298.5}^{T_C} \bar{c}_{P,O_2}\left(1 - \frac{T_0}{T}\right)dT + \int_{1}^{P_{O_2}} \frac{T_0 R}{P}dP \tag{28f}$$

The final expression for exergy loss of methanol indirect combustion process, $(T_0\sigma)_{indirect}$, is obtained by combining eq 26 with eqs 19d–19e, eq 28b, and eqs 28d–28f.

$$(T_0\sigma)_{indirect} = 2\bar{\varepsilon}_{H_2}^0 + \bar{\varepsilon}_{CO}^0 + 1.5\bar{\varepsilon}_{O_2}^0 - 2\bar{\varepsilon}_{H_2O}^0 - \bar{\varepsilon}_{CO_2}^0 +$$
$$\int_{298.5}^{T_D} (2\bar{c}_{P,H_2} + \bar{c}_{P,CO} + 1.5\bar{c}_{P,O_2})\left(1 - \frac{T_0}{T}\right)dT - \int_{298.5}^{T_C} (2\bar{c}_{P,H_2O} +$$
$$\bar{c}_{P,CO_2})\left(1 - \frac{T_0}{T}\right)dT + T_0 R \ln\left(\frac{P_{H_2}^2 P_{CO} P_{O_2}^{1.5}}{P_{H_2O}^2 P_{CO_2}}\right) + Q_{indirect}\left(1 - \frac{T_0}{T}\right) \tag{29}$$

Similarly, the final expression for exergy loss of methanol direct combustion process, $(T_0\sigma)_{direct}$, is obtained by combining eq 27 with eqs 19f, 28c, and 28d–28f.

$$(T_0\sigma)_{direct} = \bar{\varepsilon}_{CH_3OH}^0 + 1.5\bar{\varepsilon}_{O_2}^0 - 2\bar{\varepsilon}_{H_2O}^0 - \bar{\varepsilon}_{CO_2}^0 + \int_{298.5}^{T_D} (\bar{c}_{P,CH_3OH} +$$
$$1.5\bar{c}_{P,O_2})\left(1 - \frac{T_0}{T}\right)dT - \int_{298.5}^{T_C} (2\bar{c}_{P,H_2O} + \bar{c}_{P,CO_2})\left(1 - \frac{T_0}{T}\right)dT +$$
$$T_0 R \ln\left(\frac{P_{CH_3OH} P_{O_2}^{1.5}}{P_{H_2O}^2 P_{CO_2}}\right) + Q_{direct}\left(1 - \frac{T_0}{T}\right) \tag{30}$$

The overall exergetic efficiency of the indirect combustion of methanol is defined as the ratio of net exergy output of the system to the total exergy input of the system, which consists of exergy of the total heat input and the exergy of methanol feed. That is,

$$\eta_{indirect} = \frac{\varepsilon_{out} + Q_{indirect}\left(1 - \frac{T_0}{T}\right) - \varepsilon_{in}}{Q\left(1 - \frac{T_0}{T}\right) + \varepsilon_{in}} \times 100\% \tag{31}$$

The overall exergetic efficiency of the direct combustion of methanol is defined as the ratio of net exergy output of the system to the exergy of methanol feed. That is,

$$\eta_{direct} = \frac{\varepsilon_{out} + Q_{direct}\left(1 - \frac{T_0}{T}\right) - \varepsilon_{in}}{\varepsilon_{in}} \times 100\% \tag{32}$$

where $\varepsilon_{out}$ consists of the exergy of $H_2O$, $\varepsilon_{H_2O}$, and $CO_2$, $\varepsilon_{CO_2}$; and $\varepsilon_{in}$ is the exergy of methanol ($CH_3OH$), $\varepsilon_{CH_3OH}$.

**Modeling for Parabolic Trough Collector and Solar Exergy.** It is noted that the parabolic trough collectors employed in this process could be produced commercially. The thermal efficiency of the current parabolic trough collectors is higher than 50%, even when the direct solar radiation is at a level of 100 W m$^{-2}$ and the solar collector average temperature is lower than 200 °C.[25]

(25) Wyman, C.; Castle, J.; Kreith, F. *Solar Energy* **1980**, *24*, 517–540.
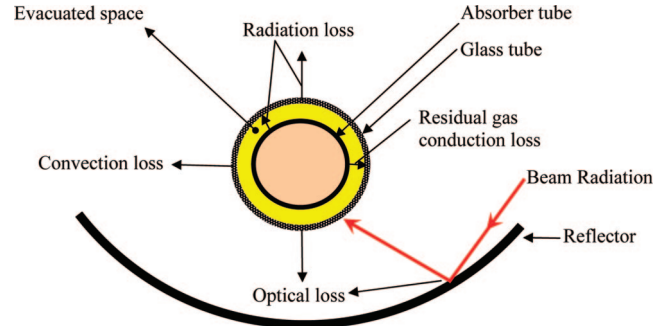


**Figure 4.** Modes of heat loss from an evacuated tubular absorber.

**Table 4. Typical Trough Collector Section Specifications[25]**

| item | parameters |
|---|---|
| collector area (m$^2$) | 547 |
| absorber length (m) | 99 |
| optical efficiency (%) | 73.3 |
| tube inner diameter of absorber (m) | 0.066 |
| tube outer diameter of absorber (m) | 0.07 |
| thermal conductivity of absorber (W m$^{-1}$ K$^{-1}$) | 54 |
| diameter of glass tube (m) | 0.115 |
| emissivity of glass tube | 0.9 |
| aperture width/tube diameter | 71 |

The well-documented thermal test results for an oil-based parabolic trough collector with characteristics given in Table 4 have been used to construct a general purpose efficiency model that can be applied to any working fluid.[26]

The energy balance equation for the quantity of thermal energy (the actual useful heat gain) produced by parabolic trough solar collector can be expressed as

$$Q_u = Q_{opt} - Q_L \tag{33}$$

The optical energy absorbed by the receiver is given by

$$Q_{opt} = \eta_{opt} A_a I_a(t) \tag{34}$$

where $A_a$ and $I_a(t)$ are aperture area of the collector (m$^2$) and irradiance (beam insolation) incident on parabolic collector aperture (W m$^{-2}$), respectively.

The optical efficiency of the concentrating collector is given by

$$\eta_{opt} = \rho_{sm}(\tau_g \alpha_r) I_f S_f \tag{35}$$

where $\rho_{sm}$, $\alpha_r$, $\tau_g$, $I_f$, and $S_f$ are specular reflectance of concentrating mirror, absorptance of the receiver, transmittance of any glass envelope covering the receiver, receiver intercept factor (fraction of reflected beam intercepted by receiver), and receiver shade factor (fraction of collector aperture not shadowed by receiver), respectively.

A model of thermal loss from the collector has been developed by[25] using a combination of the collector thermal loss from radiation, convection, and conduction as summarized in Figure 4.

(1) Thermal loss from the absorber tube outer wall to the evacuated glass tube (surrounding the absorber) occurs by radiation and residual gas conduction. Because of the high vacuum in the absorber element (0.1 Pa), convection is normally negligible.

(2) Heat loss from the absorber tube to the ambient air also occurs via the vacuum bellows and supports.

(3) Heat loss from the glass cover tube occurs by radiation to the sky and by convection to the surrounding air.

(26) Odeh, S. D.; Morrison, G. L.; Behnia, M. *Solar Energy* **1998**, *62*, 395–406.

A heat balance on the absorber tube and the evacuated glass tube has been considered to establish an expression for the overall heat loss from the collector. In short, the total heat loss can be computed in terms of $T_{ab}$ and ambient conditions, which are the dry bulb temperature $T_a$, the sky temperature $T_{sky}$, and the wind speed $v$, namely

$$Q_L = (a + cv)(T_{ab} - T_a) + \varepsilon_{ab}b(T_{ab}^4 - T_{sky}^4) \qquad (36)$$

where the coefficients $a$, $b$, and $c$ have been evaluated by curve-fitting eq 36 with heat loss for different absorber temperatures and ambient conditions. The coefficients $a$, $b$, and $c$ are $1.918 \times 10^{-2}$ W K$^{-1}$ m$^{-2}$, $2.02 \times 10^{-9}$ W K$^{-4}$ m$^{-2}$ and $6.608 \times 10^{-3}$ J K$^{-1}$ m$^{-3}$, respectively.

The absorber emissivity for cermet coating used on the solar thermal electric power generation plant can be related to the wall temperature of the absorber $T_w$ (K) at a range of 373–900 K:

$$\varepsilon_{ab} = 0.00042.T_w - 0.0995 \qquad (37)$$

The collector efficiency $\eta_{collector}$ can be expressed in terms of the thermal loss, as shown in eq 36, and the collector optical efficiency, $\eta_{opt}$, as

$$\eta_{collector} = \eta_{opt}K_\theta - (a + cv)\left(\frac{T_{ab} - T_a}{I}\right) - \varepsilon_{ab}b\left(\frac{T_{ab}^4 - T_{sky}^4}{I}\right) \qquad (38)$$

where $K_\theta$ is the incident angle modifier, and $I$ is the radiation intensity. In terms of the beam incidence angle to the collector normal, $h$, the angle modifier for the trough collector was determined by ref 27 as follows:

$$K_\theta = \cos(\theta) + 0.000\,994(\theta) - 0.000\,053\,69(\theta)^2 \qquad (39)$$

Eq 38 has a functional form to match the heat transfer processes and, most importantly, is independent of working fluid properties. This formulation allows the results of the oil-based collector tests to be converted to other working fluids or to direct boiling collectors.[26] So it is reasonable to model the collector used in solar reactors for methanol decomposition systems.

The output exergy ($E_o$) of the collector at temperature $T$ is:

$$E_o = Q_u\left(1 - \frac{T_a}{T}\right) \qquad (40)$$

The heat may be extracted from the receiver by the fluid flowing through the receiver tube; the heat rate extraction (the actual useful heat gain) by the working fluid is given by

$$Q_u = mC_P(T_o - T_i) \qquad (41)$$

The exergy delivering rate is given by:

$$E_o = mC_P\left[T_o - T_i - T_a \ln\left(\frac{T_o}{T_i}\right)\right] \qquad (42)$$

where $T_o$ and $T_i$ are the outlet and inlet temperatures of the collector fluid, respectively.

## Results and Discussion

**Upgrade of Energy Level from Solar Thermal Energy to Chemical Energy.** The middle-temperature solar thermal energy can be converted into chemical energy through methanol

(27) Dudley, V.; Kolb, G.; Mancini, T.; Matthews, C.; Sloan, M.; Kearney, D.; *Test Results SEGS LS-2 Solar Collector*. Sandia Report SAND94–1884; Sandia National Laboratories: Albuquerque, New Mexico, 1994.

(28) Jer-Hsiung, S. *Thermodynamically-based Analysis and Synthesis of Chemical Process Systems*; Ph.D Thesis, Kansas State University, 1980; 459 pages.
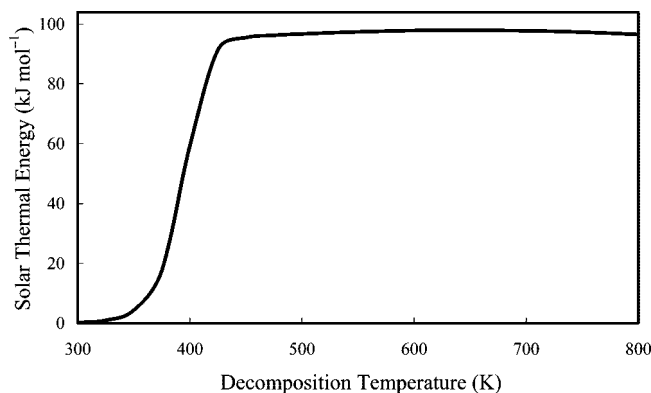


**Figure 5.** Required solar thermal energy with decomposition temperature.
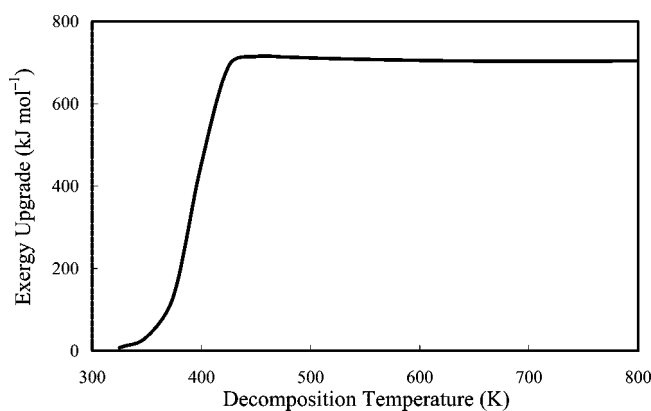


**Figure 6.** Upgraded exergy with decomposition temperature.

decomposition. From the viewpoint of energy level, this will be a breakthrough in the middle-temperature solar thermal energy.

A solar-driven methanol decomposition process could consist of a dual process of energy transformation: the solar thermal energy as an energy donor releases the heat, and the methanol decomposition as an energy acceptor accepts the heat. For the combined process, energy and exergy balances are shown schematically in Figures 2a and 2b, respectively.

Figure 5 describes the predicted variation of the required solar thermal energy for the methanol decomposition process with the decomposition temperature. As shown, additional solar thermal energy needs to be supplied to the reactor system over the 425–500 K temperature range because the conversion of methanol into syngas is higher than 90%. The calculations indicated that about 90 kJ mol$^{-1}$ is needed to convert (decompose) methanol into syngas. This means that collecting this extent of solar thermal energy could bring about the higher conversion of solar thermal energy into chemical energy, while maintaining a good match between solar thermal energy and methanol decomposition.

The upgrade in the exergy from solar thermal energy, $\varepsilon_{soth}$, to chemical energy, $\varepsilon_3$, is the difference between them, that is,

$$\text{Upgraded Exergy} = \varepsilon_3 - \varepsilon_{soth}$$

The exergy difference between those of methanol, $\varepsilon_1$, and syngas, $\varepsilon_3$, acts as a driving force for raising the low level of solar thermal energy to the higher level of chemical energy.

Figure 6 illustrates the variations in the upgraded exergy in the exergy of solar thermal energy with the decomposition temperature. At the decomposition temperature of about 400–500 K, the exergy upgrade of solar thermal energy is relatively higher than at other process temperatures. Even though the exergy
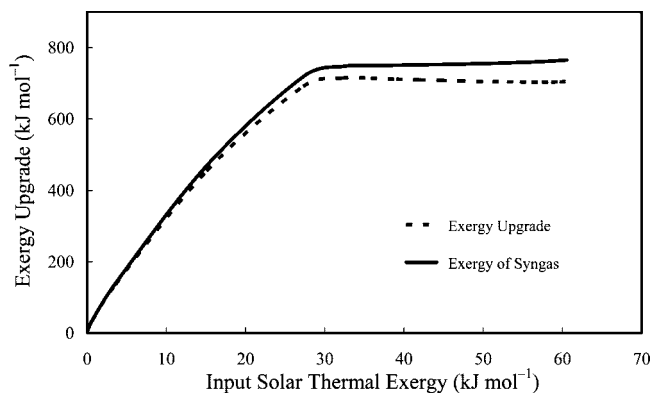
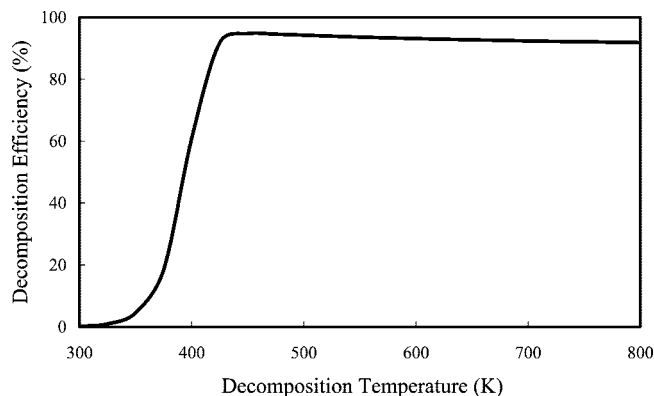**Figure 7.** Upgrade of exergy of methanol with solar thermal energy.



**Figure 8.** Exergetic efficiency of the methanol decomposition process.



**Figure 9.** Exergy loss of the methanol decomposition as a function of the decomposition temperature.

**Exergy Loss in Methanol Decomposition Process.** Figure 9 illustrates the exergy loss of the methanol decomposition process as a function of the decomposition temperature at a pressure of 1 bar. At collector temperatures of about 375−500 K, the exergy loss for decomposition process increases rapidly from 5.11 to 46.02 kJ mol$^{-1}$ at 500 K, which occurs due to more than 90% convertibility of methanol decomposition process over this temperature range. At decomposition temperatures above 500 K, and the exergy loss of the reaction gradually increases due to a high-temperature application, not because of the reaction process.

**Potential for Reducing Chemical Exergy Loss in Combustion.** In the direct combustion of methanol, the chemical energy of methanol is degraded directly to low-quality thermal energy. On the other hand, in the indirect combustion of methanol, the chemical energy of methanol could first be harvested in the solar decomposition of methanol; thus, the degradation in the energy level from chemical energy into thermal energy may be decreased in succession of the combustion of syngas. In other words, there is a cascade utilization of the chemical energy in the indirect combustion of methanol. An important point here is how this advantage of cascade utilization of chemical energy brings about the reduction of chemical exergy loss in the indirect combustion of methanol.

Fuel combustion can be considered as an exothermic reaction coupled with the heat sink. The combustion reaction plays the role of energy donor and releases the chemical energy to the heat sink as an energy acceptor.

For an effective comparison, it may be assumed that the direct and indirect combustions of methanol occur at the same temperature, and the combustion products are considered as part of the heat sink. In the indirect combustion of methanol, the exergy level from $\varepsilon_1$ to $\varepsilon_{comb}$ can be divided into two stages. The first stage is the use of the chemical energy level from $\varepsilon_1$ to $\varepsilon_3$, which involves the boosting of the lower level of solar thermal energy, $\varepsilon_{soth}$, to syngas. The second stage is the degradation of the syngas exergy, $\varepsilon_3$, to that of the combustion products, $\varepsilon_{comb}$, during the combustion of syngas.

Figures 10 and 11 indicate the chemical exergy losses in the direct and indirect methanol combustion processes over the applicable ranges of decomposition temperatures and combustion temperatures, respectively. As shown in these figures, the exergy loss of the direct combustion is much higher than that of the indirect combustion. This exergy loss of indirect combustion includes total exergy losses, namely, the exergy loss of methanol decomposition process and the exergy loss of combustion of syngas (partially combust products by methanol decomposition process, CO, and H$_2$). Whereas the exergy loss of the direct combustion process shows a nearly linear reduction

upgrade is decreased slightly beyond 500 K, there is no significant change in the upgraded exergy. In other words, at a temperature higher than 500 K, the exergy upgraded values remain constant with the decomposition temperature since almost all methanol quantity has reacted to become syngas. This means that collecting this temperature range of solar thermal energy could bring about the higher conversion of solar thermal energy into chemical energy and a good match between solar thermal energy and methanol decomposition. Thus, the driving force, ($\varepsilon_1 - \varepsilon_3$), may boost the energy level of solar thermal energy to the higher one of chemical energy to the greatest extent. Furthermore, a lower temperature, such as 400 K, is not sufficient for achieving a higher conversion of solar thermal energy into chemical energy.

Figure 7 illustrates the upgraded exergy of syngas and upgraded exergy as a function of input solar thermal exergy. As shown, the maximum upgraded value is slightly higher than 700 kJ mol$^{-1}$, which occurs at 27−40 kJ mol$^{-1}$ exergy of solar thermal energy. On the other hand, this solar thermal exergy range represents more than 90% conversion of methanol into syngas because the above solar thermal exergy range represents a 425−500 K range of decomposition temperature.

Figure 8 illustrates the efficiency of the decomposition process versus the decomposition temperature. At decomposition temperatures of about 425−500 K, the net efficiency is higher than 90%, and has the maximum value at about 473 K.

At collector temperatures above 500 K, the efficiency of the process gradually decreases due to the mismatch of energy levels between the solar thermal energy and the methanol decomposition. This shows that, in a region for a given solar radiation condition, collecting solar thermal energy at a temperature of about 500 K would be a preferable option for achieving a higher process efficiency.
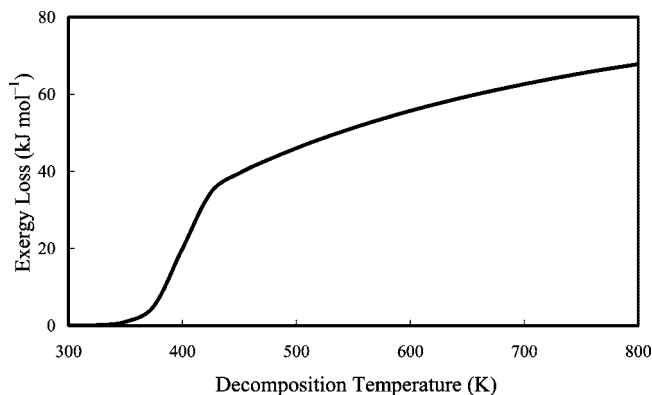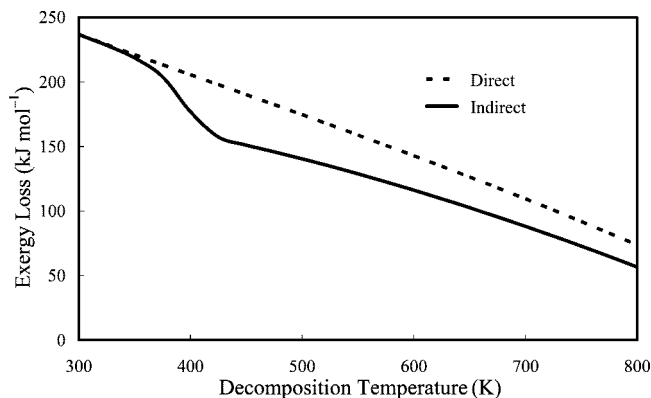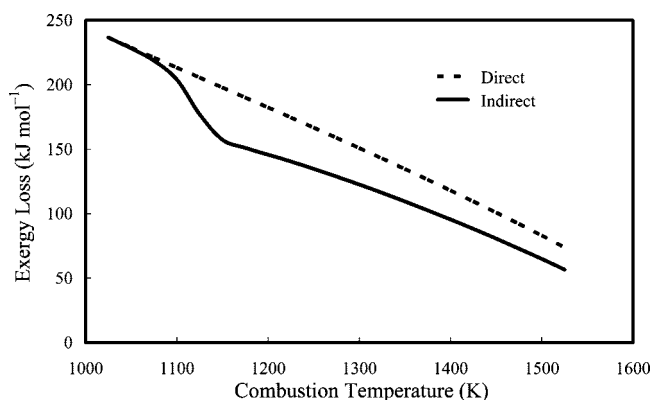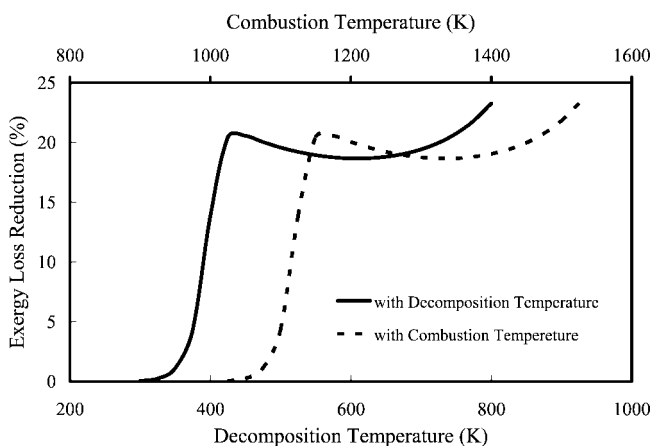
**Figure 10.** Exergy destruction of direct and indirect combustion with decomposition temperature.



**Figure 11.** Exergy destruction of direct and indirect combustion with combustion temperature.



**Figure 12.** Exergy loss reduction at different combustion and decomposition temperatures.

with temperature, the exergy loss of indirect combustion follows a different trend, although it also decreases with temperature. This is because, over the 375−500 K temperature range, methanol has 90% convertibility from methanol to syngas; that is, the exergy loss of methanol decomposition is much higher over this temperature range than at other temperatures. As indicated in Figures 9 and 10, the exergy loss decreases with an increase in temperature, because in the combustion process, the amount of thermal energy transferred to the heat sink (combustion product) increases with the combustion temperature.

Figure 12 presents the results for the percent exergy loss reduction for the indirect combustion process and the direct combustion process with different decomposition and combustion temperatures. Both curves show a similar trend. As discussed previously, for the methanol decomposition process
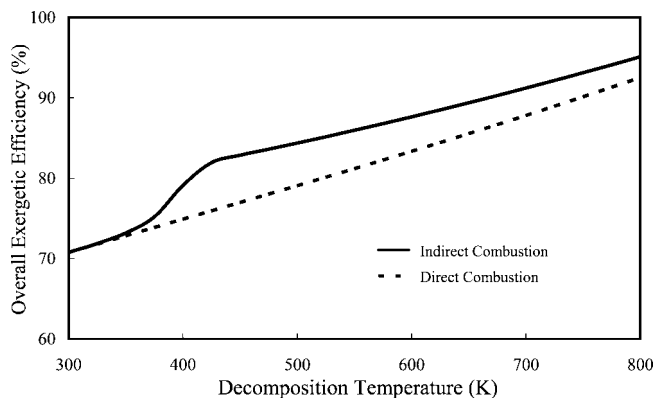


**Figure 13.** Overall exergetic efficiency with decomposition temperature.
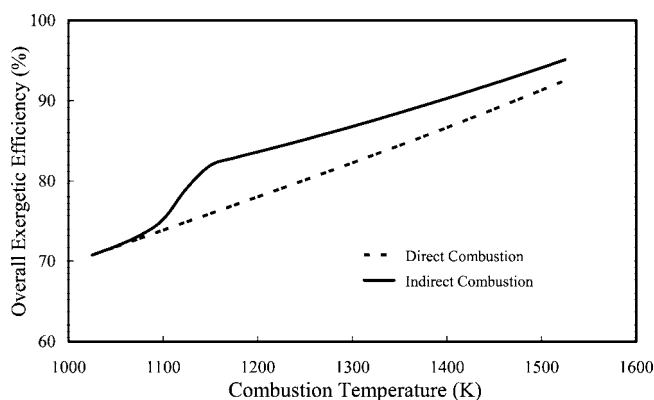


**Figure 14.** Overall exergetic efficiency with combustion temperature.

at 425−500 K, the conversion methanol into syngas is predicted to be more than 90%. As indicated in Figure 11, the exergy loss in the conversion of methanol could be decreased by more than 20% through the indirect decomposition−combustion process.

**Exergetic Efficiency.** Figures 13 and 14 illustrate the overall exergetic efficiency over the applicable ranges of decomposition and combustion temperatures, respectively, for the indirect (decomposition + combustion) and the direct combustion processes. It is noteworthy that the indirect combustion process has a higher efficiency than the direct combustion process. In Figure 13, the net efficiency of the indirect combustion process is higher than 80%, over the decomposition temperatures of 425−500 K, because methanol has a higher conversion (more than 90%) in the decomposition process. Below 350 K, however, there is no significant different between the direct and indirect processes because of a lower conversion of methanol in the decomposition process. The exergetic efficiency could also be increased by about 6−7% over with the conventional combustion of methanol.

As shown in Figure 14, the exergetic efficiency increases with the combustion temperature because more thermal energy is transferred into the combustion products, $CO_2$ and $H_2O$, at higher combustion temperatures. This significant improvement in the middle-temperature solar thermal energy for the generation of electricity can be attributed to the conversion of low-level solar thermal energy into high-level chemical energy, resulting in the generation of electricity in a higher efficiency performance.

## Conclusions

The predictions in this study showed that combining solar thermal energy and methanol decomposition can upgrade the

lower level of solar thermal energy to a higher one of chemical energy with syngas and decreased chemical exergy loss associated in the indirect combustion of methanol. The exergetic efficiency could also be increased by about 6−7% compared with the conventional combustion of methanol.

Methanol is a potential substitute for petroleum-based products. It can be directly used as a fuel to replace gasoline in internal combustion engine or conventional power plant efficiently and effectively, since it has a potential to increase its energy level. The decomposition temperature at 500 K can be attained easily by using solar energy, or even the waste heat from the exhaust gas of the internal combustion engine.

Furthermore, methanol is favorable over conventional fuels because of its lower ozone-forming potential, lower emissions of certain pollutants—benzene, polycyclic aromatic hydrocarbons, and sulfur compounds—and lower evaporative emissions. With these advantages in the use of methanol, the indirect combustion process could build a bridge connecting both high-efficiency use of middle-temperature solar thermal energy and effective utilization of chemical energy of methanol.

## Nomenclature

$\bar{c}_p$ = specific heat capacity (kJ mol$^{-1}$ K$^{-1}$).
$E$ = activation energy (kJ mol$^{-1}$).
$H_1$ = energy of methanol (kJ).
$H_3$ = energy of syngas (kJ).
$\bar{h}$ = specific enthalpy (kJ mol$^{-1}$).
$k$ = reaction rate constant (m$^2$s$^{-1}$mol$^{-1}$).
$k_D^{\infty}$ = pre-exponential term in the Arrhenius equation (m$^2$s$^{-1}$mol$^{-1}$).
$K^*$, $K$ = absorption coefficient for surface species (bar$^{-0.5}$).
$m$ = molar flow rate (mol s$^{-1}$).
$P$ = system pressure or partial pressure (kPa).
$Q$ = heat transfer (kJ).
$Q_0$ = heat loss to the environment (kJ).
$Q_{soth}$ = process heat provided by solar thermal energy (kJ).
$r$ = reaction rate (mol s$^{-1}$ m$^{-2}$).
$R$ = universal gas constant (= 8.314 J mol$^{-1}$ K$^{-1}$).
$\bar{s}$ = specific entropy (kJ mol$^{-1}$ K$^{-1}$).

$T$ = temperature (K).
$T_0$ = temperature at the dead state (K).
$T_m$ = temperature of the heat source (K).
$v$ = wind velocity (m s$^{-1}$).
$\bar{v}$ = specific volume (m$^3$/mol).
$W_s$ = shaft or other equivalent work (kJ).

*Subscripts*
a = ambient.
ab = absorber.
C = combustion.
CH$_3$O$^{(2)}$ = intermediate in mechanisms reaction.
CH$_3$OH = methanol.
D = methanol decomposition.
e = exit.
H$_2$ = hydrogen.
H$^{(2a)}$ = intermediate in reaction mechanism.
i = inlet.
k = material species.
L = loss.
o = output or outlet.
opt = optical.
Phy = Physical.
S$_2$,S$_{2a}$ = active site 2 and active site 2a.
u = useful.
w = wall.
0 = dead state.

*Superscripts*
0 = standard state.

*Greek Symbols*
$\bar{\beta}$ = partial molar enthalpy (kJ mol$^{-1}$).
$\bar{\gamma}$ = specific available entropy (kJ mol$^{-1}$ K$^{-1}$).
$\bar{\varepsilon}$ = partial molar exergy in the mixture (kJ mol$^{-1}$).
$\varepsilon_1$ = chemical exergy of methanol(kJ mol$^{-1}$).
$\varepsilon_3$ = chemical exergy of syngas (kJ mol$^{-1}$).
$\varepsilon_{comb}$ = chemical energy released by the combustion of syngas (kJ mol$^{-1}$).
$\varepsilon_{soth}$ = exergy of solar thermal energy (kJ mol$^{-1}$).
$\sigma$ = entropy production or generation (kJ mol$^{-1}$ K$^{-1}$).
$\eta$ = efficiency.