

## Minimizing the Entropy Production of the Methanol Producing Reaction in a Methanol Reactor\*

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### Abstract

The entropy production of the reaction that produces methanol in a methanol reactor, has been minimized. The results show that the entropy production of the reaction can be reduced by more than 70%. The optimal path through the reactor is characterized by a driving force for the chemical reaction that is close to constant. The entropy production due to heat transfer across the reactor walls in this state is large, however. Variations of the reactor design show that it is possible to accomplish considerable reductions of the entropy production due to heat transfer in the reaction-optimal state.

*Key words: Reactor, minimum entropy production rate, irreversible thermodynamics*

### 1. Introduction

We have earlier shown that it is possible to minimize the entropy production in a chemical reactor (Kjelstrup et al. (1999), Kjelstrup and Island (1999), Sauro et al. (1999), Bedeaux et al. (1999)). The subsequent changes in the other parts of the process has, however, not been dealt with fully yet. In this work we study a reactor with two reactions occurring in parallel; the hydrogenation of carbon dioxide to form methanol and the water-gas shift reaction. The path of minimum entropy production for the methanol producing reaction (called the methanol reaction from now on) is found at a given, constant production of methanol. The entropy production due to heat exchange becomes large, when the methanol reaction has its minimum value, but we shall see that it is critically dependent on design variables like the reactor tube diameter, the distribution of catalyst over the reactor, and so on. This means that an improved second law efficiency for the total system seems feasible.

The methanol reactor is studied because of its industrial importance. Methanol is produced industrially in different reactor designs. We have chosen to study an ideal plug flow reactor. Several reactions take place in the methanol reactor, but two of them dominate, the methanol synthesis reaction and the reverse water gas shift reaction (called the shift reaction from now on). As a reference we have chosen a reactor that is specified by data in the literature (van den Bussche and Froment (1996)).

The purpose of the study is to find the path that gives minimum entropy production for the methanol reaction. This path is called the reaction-optimal path, and we call the reactor with such a path a reaction-optimal reactor. The degree of conversion, the temperature and the pressure in the reaction-optimal reactor are far from their corresponding values in the reference reactor. The amount of product is the same in the reference and optimized case.

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TABLE I. REACTOR SPECIFICATIONS

Quantity	
Inner diameter /m	0.016
Length /m	0.15
Overall heat transfer coefficient /Jm <sup>-2</sup> s <sup>-1</sup> K <sup>-1</sup>	60
Catalyst density / kg m <sup>-3</sup>	1775
Catalyst porosity	0.50
Pellet diameter / m	0.0005
Cooling water temperature / K	523

TABLE II. BOUNDARY CONDITIONS

Quantity	Reference	Optimal
Inlet temp. /K	493.2	636.4
Inlet press. /bar	85	85
Initial flow rate /mole s <sup>-1</sup>	0.0033	0.0033
<u>Mole fractions</u>		
CO <sub>2</sub>	0.03	0.018
H <sub>2</sub>	0.82	0.808
CO	0.04	0.052
H <sub>2</sub> O	0.005	0.017
CH <sub>3</sub> OH	0.005	0.005
N <sub>2</sub>	0.10	0.10

We have previously studied a tubular reactor containing the exothermal sulfur dioxide oxidation ( Kjelstrup and Island (1999) ), a reactor with one chemical reaction. We shall devise a better method for calculation of the optimal path than used previously.

## 2. Conservation Equations

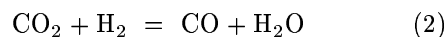
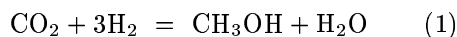
We consider a tubular reactor filled with a copper based catalyst containing ZnO and Al<sub>2</sub>O<sub>3</sub>. The catalyst density is  $\rho_c = 1775$  kg/m<sup>3</sup>, and the porosity is  $\varepsilon = 0.5$ . The tube is 15 cm long and has an inner diameter of  $a = 1.6$  cm. The cooling water in the reference reactor has a temperature of 523 K. Reactor specifications are given in TABLE I.

We consider flow of mass and reaction along the tube, and conduction of heat through the tube walls. Gradients in temperature and concentration in the radial direction inside the tube, will be neglected. In other words, we have an ideal plug flow reactor. Feed composition and other boundary conditions are given in TABLE II. They were mostly taken from van den Bussche and Froment (1996).

The data of TABLES I and II, and the conservation equations below, defines our reference reactor.

Methanol is produced by hydrogenation of carbon dioxide at the same time that the shift

reaction takes place:



The rate equations were taken from van den Bussche and Froment (1996):

$$r_1 = \frac{p_{\text{CO}_2} p_{\text{H}_2}}{D^3} K_1'' \left( 1 - \frac{p_{\text{H}_2} O p_{\text{CH}_3\text{OH}}}{K_1^* p_{\text{CO}_2} p_{\text{H}_2}^3} \right) \quad (3)$$

$$r_2 = \frac{1}{D} k_1' p_{\text{CO}} \left( 1 - K_3^* \frac{p_{\text{H}_2} O p_{\text{CO}}}{p_{\text{CO}_2} p_{\text{H}_2}} \right) \quad (4)$$

In these expressions  $D$  is

$$D = 1 + \frac{K_{\text{H}_2\text{O}}}{K_8 K_9 K_{\text{H}_2}} \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} + \sqrt{K_{\text{H}_2} p_{\text{H}_2} + K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}} \quad (5)$$

and  $p_i$  are partial pressures. For details on the reaction rate constants ( $K_1''$ ,  $K_1^*$ ,  $k_1'$ ,  $K_3^*$ ,  $K_8$ ,  $K_9$ ,  $K_{\text{H}_2}$  and  $K_{\text{H}_2\text{O}}$ ), see van den Bussche and Froment (1996). The expressions were reported valid between 453 and 553 K, and between 15 and 51 bar. However here it is assumed that they can be used also at higher temperatures near the upper limit and at pressures up to 85 bar. The rates are given in moles per kg of catalyst and second.

The degree of conversion of CO<sub>2</sub> was taken as the common measure for the advancement of both reactions:

$$\xi_j = \frac{\Delta F_{\text{CO}_2, j}}{F_{\text{CO}_2}^0} \quad j = 1, 2 \quad (6)$$

Here  $F_{\text{CO}_2}^0$  is the initial molar flow rate of CO<sub>2</sub>, and  $\Delta F_{\text{CO}_2, j}(x)$  is the molar rate of CO<sub>2</sub>, consumed by reaction  $j$  up until a certain point in the reactor. All molar flows were related to the flow of carbon dioxide,  $F_{\text{CO}_2}^0$ , at the inlet. We assumed ideal gas in the calculations of partial pressures.

The reactor volume up to a position  $x$ , is proportional to the accumulated catalyst weight at that point,  $W(x)$ , in a uniformly filled tube:  $W(x) = (1 - \varepsilon) \rho_c V(x) = (1 - \varepsilon) \rho_c \pi a^2 x$ , and  $a$  is the radius of the tube. The accumulated amount of catalyst is therefore a measure of the distance from the inlet of the reactor. We have for the two reactions:

$$\frac{d\xi_j}{dW} = \frac{r_j}{F_{\text{CO}_2}^0} \quad j = 1, 2 \quad (7)$$

The energy balance is:

$$\frac{dT}{dW} = \frac{UT^2 \left( \frac{1}{T} - \frac{1}{T_a} \right) B - \sum_{1,2} r_j \Delta_r H_j}{C_p^*} \quad (8)$$

where  $B = 2/a(1-\varepsilon)\rho_c$  and  $C_p^* = \sum_i F_i^o C_{p,i} + F_{\text{CO}_2}^o [\xi_1 \Delta_{r,1} C_p + \xi_2 \Delta_{r,2} C_p]$ . The numerator is the net heat change per kg catalyst, and the denominator is the heat capacity for the same element. The reaction enthalpies are denoted  $\Delta_r H_j$ ,  $U$  is the modified heat transfer coefficient for heat transfer from the ambient (temperature  $T_a$ ) through the walls, and  $\Delta_{r,j} C_p$  is the heat capacities of the products minus the reactants of reaction  $j$ . The value of  $T_a$  is constant in the reference reactor (see TABLE II).

Momentum conservation is expressed by Erguns equation:

$$\frac{dP}{dW} = -\frac{G}{\Omega} \left[ \frac{150(1-\varepsilon)\mu}{d} + 1.75G \right] \quad (9)$$

Here  $\Omega = d\rho_g \pi a^2 \rho_c \varepsilon^3$ ,  $G$  is the superficial mass velocity,  $\mu$  is the viscosity of the gas mixture,  $\rho_g$  the gas density, and  $d$  is the diameter of the catalyst pellets.

This set of conservation equations constitute the basis of the calculations. The profiles of the reference reactor were calculated with the above equations and the boundary conditions given in TABLES I and II. The profiles of the reaction-optimal reactor were calculated with the same equations and certain relations that reduce the need for specified boundary conditions. The aim of the present optimization was to replace some of the existing boundary conditions with new ones, compatible with minimum entropy production in the methanol reaction.

### 3. Minimizing the Entropy Production of the Methanol Reaction

At least one degree of freedom is necessary in order to change the profiles of the reference reactor. Degrees of freedom can be introduced in several ways. We shall here examine the (limited) case of one degree of freedom arising from changing the heat transfer along the reactor.

There is entropy production due to both reactions, due to heat transfer to the surroundings and due to the pressure drop in the reactor. The last contribution was found to be negligible. The local entropy production rate (in J/K s m<sup>3</sup>) for the two reactions and heat conduction is then, de Groot and Mazur (1985):

$$\sigma = \Gamma r_1 \left( -\frac{\Delta_r G_1}{T} \right) + \Gamma r_2 \left( -\frac{\Delta_r G_2}{T} \right) + J'_q \left[ \frac{1}{T} - \frac{1}{T_a} \right] \frac{2}{a} \quad (10)$$

where  $\Gamma = (1-\varepsilon)\rho_c$ . The reaction Gibbs ener-

gies are denoted  $\Delta_r G_j$ . There is one contribution from each of the two chemical reactions. The last term is the entropy production due to heat flux,  $J'_q$ , through the walls of the tube. The unconstrained minimum of  $\sigma$  is, of course, zero. All driving forces in Eq. (10) are then zero, a situation of no practical interest.

The total entropy production rate in the reactor is obtained by integrating Eq. (10) over the accumulated catalyst weight

$$\Sigma = \frac{1}{(1-\varepsilon)\rho_c} \int_0^{W_{\text{Tot}}} \sigma dW \quad (11)$$

The first, second, and third terms of the above equation will be referred to as  $\Sigma_{rx1}$ ,  $\Sigma_{rx2}$  and  $\Sigma_Q$ , respectively. The first two terms are the total entropy production in reaction 1 and 2, while the last term is the entropy production caused by the heat transfer between the reactor and the surroundings.

The constraint on the reactor optimization is that the production of (primary) product is constant. In the present reactor this means a constant production,  $J$ , of methanol:

$$J = \int_0^{W_{\text{Tot}}} r_1 dW \quad (12)$$

The conditional optimization can be formulated using the Lagrange function  $L$

$$L = \Sigma + \lambda_1 J \quad (13)$$

where  $\lambda_1$  is the Lagrange multiplier for the constraint. With only one variable (degree of freedom) to change the course of the reaction, namely the cooling temperature, we can only do one independent variation, or differentiation. The variable to choose is the force of the reaction of interest, namely  $-\Delta_r G_1/T$ . We have earlier shown (Kjelstrup et al (1999)) that the minimum of  $\Sigma$  with respect to the driving force of the methanol production, given no coupling between the reactions, is found from

$$\int_0^{W_{\text{Tot}}} \frac{\partial}{\partial \xi_1} \left[ \left( \frac{\Delta_r G_1}{T} - \lambda_1 \right) r_1 \right] dW = 0 \quad (14)$$

which simplifies to

$$\frac{\partial}{\partial \xi_1} \left[ \left( \frac{\Delta_r G_1}{T} - \lambda_1 \right) r_1 \right] = 0 \quad (15)$$

when we neglect that a variation in  $\xi_1$  at a given position in the reactor will affect the reaction rate and the force at other positions.

This equation gives minimum entropy production for the first reaction, under the constraint of a constant production of methanol.

With only one degree of freedom, we can replace a priori knowledge of  $T_a$  with Eq. (15).

#### 4. Calculations

The density of the gas mixture was estimated using the ideal gas equation. Standard enthalpies of formation at 298 K and heat capacities for the species were found in the literature, ( Aylward and Findlay (1994), Daubert and Danner (1992) ). The reaction Gibbs energies were found from the chemical potentials of the reactants and the products ( Graaf et al. (1986) ). The viscosity of the mixture was estimated from the viscosity of the pure species.

All calculations were done using Matlab 5.3 from MathWorks Inc. The Matlab function 'ode15s', that makes an equation discrete according to its degree of non-linearity ( Shampine and Reichelt (1997) ), was used to find the reference profiles and the reaction-optimal profiles.

The set of reference profiles were calculated from Eqs. (7), (8), and (9). As a control, we first reproduced the results of van den Bussche and Froment (1996) for their adiabatic reactor. The methanol produced by the reference reactor was  $1.3 \cdot 10^{-4}$  mole/s. This gives the constraint for the optimization.

The conversions, reactor temperature, ambient temperature, and pressure profiles in the reactor with minimum entropy production, were calculated by iteration, using Eq. (15) and the conservation equations. The boundary conditions were  $P = 85$  bar and  $\xi_1 = \xi_2 = 0$ . The inlet composition was chosen to assure  $\Delta_r G_2 = 0$  at the inlet. This choice is not the only possible choice.

The reference profiles were inputs for the calculations. The iteration started by finding the temperature profile that satisfied Eq. (15). A typical first guess of the Lagrange multiplier was -10 J/K mole. New conversion and pressure profiles were next calculated with the conservation equations for mass and momentum. The procedure was repeated until the Lagrange multiplier was found, that gave the correct production of methanol.

The convergence criterion for  $T$  was 0.1 K. For each converging solution, we obtained corresponding sets of entropy production,  $\lambda$ , and methanol production in the reactor.

#### 5. Results and Discussion

##### 5.1. The Reference Reactor

The results for the reference reactor are shown in *Figures 1-3* and in TABLE III. Most of the conversion of  $\text{CO}_2$  to methanol took

place in the first third of the reactor, see *Figure 1*. The shift reaction had a negative degree of conversion (not shown), in agreement with the literature van den Bussche and Froment (1996). The pressure gradient was small and negative (not shown).

The temperature profile had a maximum around 25% of the reactor length (see *Figure 2*). This can be explained by the exothermal nature of the methanol reaction. The rate of the methanol reaction had a maximum before the maximum in the temperature was reached. The production of heat up to the point with maximum rate and somewhat beyond was therefore larger than the rate of heat removal in this part of the reactor. In the last 75% of the reactor, removal of heat was larger than heat production. In *Figure 2* we have also plotted the temperature for which the given mixture would be in equilibrium. The difference between  $T$  and  $T_{eq}$ , is a measure of how far the methanol reaction is from equilibrium. The distance from equilibrium is largest in the beginning of the reactor, as expected, but it is still sizable beyond the peak of the maximum reaction rate. In the end of the reactor, the reactor temperature varied in the same manner as the equilibrium temperature.

TABLE III. ENTROPY PRODUCTION RATES

Process	Reference reactor J/K s	Reaction-optimal reactor J/K s
Reaction 1	$1.62 \cdot 10^{-3}$	$3.80 \cdot 10^{-4}$
Reaction 2	$9.90 \cdot 10^{-5}$	$3.71 \cdot 10^{-5}$
Heat transfer	$7.26 \cdot 10^{-4}$	$4.94 \cdot 10^{-3}$
Total	$2.44 \cdot 10^{-3}$	$5.35 \cdot 10^{-3}$

The various contributions to the entropy production rate through the reactor are shown in TABLE III. Most of the entropy production in the reference reactor is due to the methanol reaction. The shift reaction has a much less significant contribution.

The entropy production due to heat transfer to the surroundings, had a minimum at the peak point of  $\sigma$ . Its major contribution to the total entropy production was in the end of the reactor. The total value of this contribution was second to the contribution from the methanol reaction, see TABLE III.

##### 5.2. The Reaction-Optimal Reactor

The results for the reaction-optimal reactor are shown in *Figures 1-3* and TABLE III. *Figure 1* shows the reaction-optimal normalized degree of conversion of the methanol reac

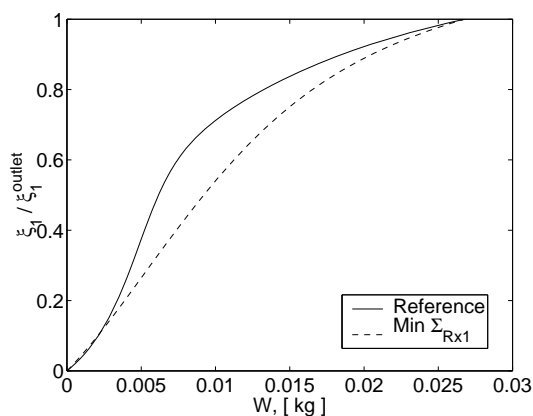


Figure 1. The normalized degree of conversion of  $\text{CO}_2$  in the hydrogenation of  $\text{CO}_2$  to methanol as a function of accumulated catalyst weight in the reference and the reaction-optimal reactor.

tion, compared to the corresponding degree of conversion in the reference reactor. The normalized conversions are obtained by dividing the calculated conversion profiles by their corresponding degree of conversion at the outlet. For both reactions, we found that the production was more uniformly distributed over the reactor in the reaction-optimal case than in the reference case.

The reaction-optimal temperature profile did not resemble the temperature profile of the reference reactor. It started high, and sank monotonously through the reactor. The reaction-optimal temperature profile (Figure 2) resembled the variation of the equilibrium temperature, which also is shown in the figure.

In Figure 3, we have plotted the driving force for the methanol reaction as a function of catalyst weight in the reference and the reaction-optimal reactor. We see here that, in the beginning of the reactor, the reaction-optimal driving force is much smaller

than the reference driving force. At a certain point, it becomes larger, however. The small variation of the driving force through the reaction-optimal reactor is striking. This behavior was also found for the ammonia reactor (Sauar (1998)). The optimal driving force reduced the entropy production of the methanol reaction considerably, see TABLE III. The entropy production of this reaction was reduced from  $1.6 \cdot 10^{-3}$  J/K s to  $3.8 \cdot 10^{-4}$  J/K s. This is a reduction of 76%. The value of the Lagrange multiplier was  $\lambda = -5.6$  J/K mole. The entropy production of the shift reaction was only 10% of that of the methanol reaction,  $3.7 \cdot 10^{-5}$  J/K s.

The principle of equipartition of forces, or

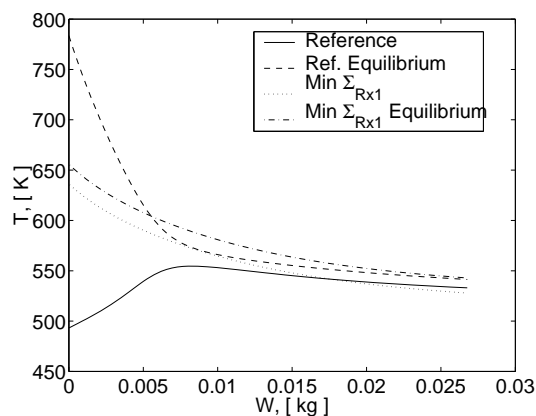


Figure 2. The temperature of the reaction mixture as a function of accumulated catalyst weight in the reference and reaction-optimal reactor compared to their respective equilibrium temperatures.

the isoforce principle, is a principle that gives boundary conditions compatible with minimum entropy production. It was first proven for linear flux-force relations (Sauar et al. (1996)), and has later been extended to certain classes of non-linear chemical reactions (Sauar (1998), Bedeaux et al. (1999)). The surprising finding is that, if the system has freedom to redistribute itself, the forces in the stationary state are often close to being equipartitioned (constant). The result that the force is almost constant for chemical reactions, can be explained by the distance from equilibrium not being too large in this reactor.

The new boundary conditions were significantly different from those given for the reference reactor. The new inlet temperature was  $T(0) = 636$  K, while that of the reference reactor was 493 K. The new and old mole fractions are given in TABLE II, and the new and old outlet temperatures were  $T(l) = 528$  K and 533 K, respectively. The total pressure at the inlet were equal for both the reference and the reaction-optimal case. The temperature of the cooling medium in the reaction-optimal reactor varied along the reactor. It started at 515 K, reached a maximum at around 540 K and decreased towards 515 K at the end of the reactor. The entropy production due to heat transfer was calculated from this temperature and the reactor temperature. It became enormous compared to the other terms in TABLE III,  $4.9 \cdot 10^{-3}$  J/Ks (the total heat transferred was -24.1 W). The entropy production due to heat transfer in the reference reactor, was for comparison  $7.3 \cdot 10^{-4}$  J/Ks. Because of the huge leap in  $\Sigma_Q$ , the total entropy production in the reaction-optimal reactor was twice the value in the reference reactor, see TABLE III.

Since the entropy production rate due to heat transfer dominated the total entropy production after the optimization of the methanol reaction, we did not obtain a better over-all situation. In order for the heat exchange process to be optimal, the difference in inverse temperature between the cooling medium and the reactor must be constant (Sauar et al. (1996), Nummedal and Kjelstrup (2000)). The driving force for heat transfer was far from constant in both reactors. It follows that there is probably a trade-off situation between the solution for a minimum in entropy production of the reaction, and a solution for a minimum in entropy production of heat exchange.

In order to investigate the potential for a reduction in the total entropy production rate, the effect of a variation in the catalyst weight distribution and the heat transfer coefficient were investigated. We found that a doubling of  $U$ , reduced  $\Sigma_Q$  by more than a factor of two. Already by this variation, the total entropy production rate will be less than that of the reference reactor. The entropy production rate of the reaction is independent of the heat transfer coefficient.

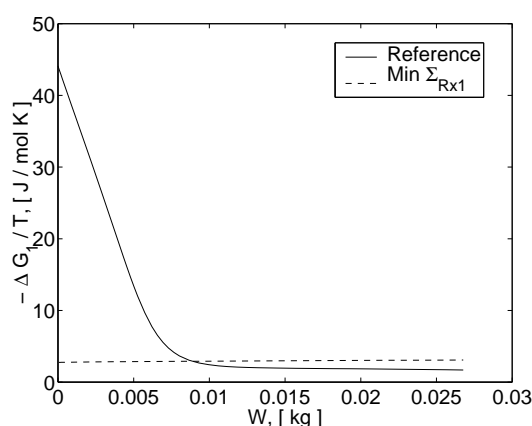


Figure 3. The driving force of reaction (1) through the reference reactor and the reaction-optimal reactor.

## 6. Conclusions

An increase in the total catalyst weight gave a significant reduction of the entropy production of the methanol reaction. A redistribution of a given weight was also investigated. According to the results above, we should strive for a distribution that gives a driving force for heat transfer that is close to constant. We shall not do this here, but present the results of a calculation that shows the potential of such a distribution. The reactor that has been calculated so far has an even distribution of catalyst. We repeated the same calculations for a reactor with catalyst

bed porosity decreasing linearly from 0.6 to 0.1. The lower value is probably not realistic, but serves the purpose of illustration. The catalyst density was similarly increased in a linear way from 1088 to 1775 kg/m<sup>3</sup>. By these changes the entropy production due to heat transfer was reduced by 18%, while the entropy production of the methanol reaction did not change significantly, giving a total reduction of the same.

The temperature profile in the reactor, the variation in the degrees of conversion, and the pressure profile were obtained by an iteration procedure. All variables constitute a consistent set. The procedure represents an improvement over the procedure used by Kjelstrup and Island (1999), who used the conversion profile of the reference reactor to define the equilibrium temperature and the optimum temperature profile.

We have devised a scheme to find the minimum entropy production for one of several chemical reactions in a chemical reactor at a given production. The scheme uses irreversible thermodynamics to calculate the local entropy production. An ideal methanol reactor was used as an example, and a reduction of 76% was obtained for the methanol synthesis. The total entropy production of the new reactor increased, but a new design could be suggested. Many trade-off situations exist and deserve to be further investigated.

## Nomenclature

$a$	Reactor diameter (m)
$d$	Catalyst pellet diameter (m)
$k_1'$	Reaction rate constants (see van den Bussche and Froment (1996))
$C_{p,i}$	Heat capacity (J/K mole)
$\Delta_{r,j}C_p$	Reaction heat capacity (J/Kmole)
$F_i^o$	Inlet feed (mole/s)
$G$	Superf. mass velocity (kg/m <sup>2</sup> s)
$\Delta_r G_j$	Gibbs free energy (J/mole)
$\Delta_r H_j$	Reaction enthalpy (J/mole)
$J$	Methanol production (mole/s)
$J_q'$	Heat flux (J/m <sup>2</sup> s)
$K_i$	( $i = 8, 9, H_2$ , or $H_2O$ ) Reaction rate constants (see van den Bussche and Froment (1996))
$K_i^*$	( $i = 1$ , or $3$ ) Reaction rate constants (see van den Bussche and Froment (1996))
$K_1''$	Reaction rate constants (see van den Bussche and Froment (1996))
$L$	Lagrange function (J/K s)
$P$	Total pressure (bar)
$p_i$	Partial pressure (bar)
$T$	Reaction temperature (K)

$r_j$	Reaction rate (mole/kg cat.)
$T_a$	Ambient temperature (K)
$U$	Heat transfer coeff. (J/K m <sup>2</sup> s)
$W$	Catalyst weight (kg)
$\epsilon$	Porosity
$\lambda_1$	Lagrange multiplier (J/K mole)
$\mu$	Gas mixt. viscosity (kg/m s)
$\rho_c$	Catalyst density (kg/m <sup>3</sup> )
$\rho_g$	Gas density (kg/m <sup>3</sup> )
$\sigma$	Local entropy prod. (J/K m <sup>3</sup> s)
$\Sigma$	Total entropy prod. (J/K s)
$\Sigma_{rxj}$	As above; for rx. $j$ (J/K s)
$\Sigma_Q$	As above; for cooling prod. (J/K s)
$\xi_j$	Degree of conversion of CO <sub>2</sub>
$\xi_1^{Outlet}$	The conversion of CO <sub>2</sub> at the reactor outlet

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