AN EQUATION ORIENTED APPROACH TO STEADY
STATE FLOWSHEETING OF METHANOL SYNTHESIS
LOOP

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Abstract: An equation-oriented approach was developed for steady state
flowsheeting of a commercial methanol plant. The loop consists of fixed bed reactor,
flash separator, preheater, coolers, and compressor. For steady state flowsheeting
of the plant mathematical model of reactor and other units are needed. Reactor used in
loop is a Lurgi type and its configuration is rather complex. Previously reactor and
flash separator are modeled as two important units of plant. The model is based on
mass and energy balances in each equipment and utilizing some auxiliary equations
such as rate of reaction and thermodynamics model for activity coefficients of liquid.
In order to validate the mathematical model for the synthesis loop, some simulation
data were performed using operating conditions and characteristics of the
commercial plant. The good agreement between the steady state simulation results
and the plant data shows the validity of the model.

Keywords: Methanol synthesis loop, Simulation, Steady state flowsheeting

1. Introduction

Increasing competition in the process designs has
forced industries to develop and apply mathematical
simulation techniques to guarantee the quality of their
products. Main issues in this context are plant economy
and safety, purity of products, equipment costs,
minimum feedstock and utilities consumption and
environmental impacts. The pursuit of these goals leads
to a rapidly growing number of applications of
computer simulations both in the design phase and in
the operating phase of chemical plants such as
refineries, ethylene or gas processing plants, or air
separators. The traditional steady-state simulation is
important for the design or process synthesis of such
plants because they operate mostly in this mode.

Chemical flowsheeting as a means of performing
assessments of chemical process systems has a history
that is as old as the concepts of mass and energy
balances. At First, the calculations were carried out
using only pencil and paper, sometimes assisted by the
use of a slide-rule. It comes without saying that the
more detailed and complex the system under
observation is, the more time-consuming and tedious is
the solution of the equations and models necessary to
describe the chemical system. A major change in this
methodology was brought about by the introduction of
the computer. Now it became much easier and quicker
to carry out the calculations needed. At first, the
models that were already developed were transferred to
the computers as batch-models, where individual
models described every unit of a process system, with
no interaction between them. With the evolution of
more and more powerful computers, the idea of
connecting the different batch models with each other
emerged, thus, allowing model interaction within a
simulation [1]. The modeling tools in current
simulators may roughly be classified into two groups
[2]. An equation oriented (EO) chemical process
flowsheeting system, which may contain many
thousands of variables for a complex chemical process.
It is typically sparse, underspecified, and nonlinear [3].
Solution of such systems of nonlinear equation requires
extra powerful computer processors and efficient
numerical methods to converge. In addition to EO
method, there are the so-called SM (sequential
modular) simulators, where data are transferred
between the individual models, but they are solved one
at a time, in a predefined sequence. In comparison with
SM, EO are less robust but more flexible. The last
mentioned disadvantage of EO is negligible when the
number of equations is not so much and the resulted
equations set is not so nonlinear and spars as it is here.

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Methanol synthesis is among the industrial process that has most attraction for steady flowsheeting as methanol is being one of most resources for renewable energies. It has also started being used as a material for producing MTBE, for which demand is rising as an additive for automobile gasoline. The demand for methanol is steadily increasing. It is hoped that methanol can be used to generate power, because it is an environmentally sound fuel.

At present, methanol is produced from synthesis gas (a mixture of \( CO - CO_2 \) and \( H_2 \)) and the reaction is catalyzed by a catalyst composed of \( CuO-ZnO-Al_2O_3 \), in the low-pressure process at 50-100 atm and 200-300°C.

The mechanism of methanol synthesis is not fully understood. Although much work has been reported [4] and [5], there is still no agreement on the nature of the active sites and intermediates. Graaf have considered a mechanism in which \( CO \) and \( CO_2 \) are both adsorbed on the same active site [6]. On the other hand it have been suggested a mechanism in which \( CO \) and \( CO_2 \) undergo hydrogenation simultaneously on different catalyst sites through different pathways [7].

Fundamental aspects of the process and catalysts have been extensively studied and the results are summarized in recent reviews and books. However, there is still controversy over many important questions such as the role of catalyst components, kinetics and mechanism of the reaction and, in particular, whether \( CO \) or \( CO_2 \), is the main source of methanol. It is known that some quantity of \( CO_2 \), is necessary for the process to start and proceed.

At present, the prevailing view is that methanol is formed only from \( CO \) over X-containing catalysts [5]. Methanol synthesis, at a basic level, has practically always been expressed via the hydrogenation of \( CO \), i.e.

\[
CO + 2H_2 \leftrightarrow CH_3OH \tag{1}
\]

\[
CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \tag{2}
\]

Some investigators are of the opinion that \( CO \) hydrogenation is the principal chemical reaction. Others believe that methanol synthesis over Cu-based catalysts proceeds exclusively via hydrogenation of \( CO_2 \); i.e. Poland has also contributed to the development of methanol synthesis.

The reactions between \( CO_2 \) and \( H_2 \), as well as between \( CO \) and \( H_2 \), are both reversible and exothermic. They are also thermodynamically unfavorable, showing positive Gibbs free-energy changes due to reaction at temperatures higher than 150°C for \( CO \) hydrogenation and 180°C for \( CO_2 \) hydrogenation respectively. The fact that both reactions are exothermic and, in addition, proceed under volume contraction shows that highest conversions - and thus the highest methanol yield - are obtained at low temperatures and high pressures. Simultaneously with methanol synthesis, a reverse water-gas shift reaction or water-gas shift reaction takes place, depending on the reaction conditions. Therefore, three reactions can be assumed to occur in methanol synthesis:

\[
CO_2 + H_2 \leftrightarrow CO + H_2O \tag{3}
\]

Only (any) two of these are stoichiometrically independent and define the equilibrium composition of the gas mixture. The chemical equilibrium for methanol synthesis and the reverse water-gas shift reaction were determined experimentally by Graaf [6].

Frequently Research into the design and management of this process by conducting full-scale tests is costly and difficult. The proper simulation, control and optimization of processes involve an understanding of the complex interaction of many factors such as reactants fresh feed condition, recycle ratio and production conditions.

However, in most of the previous works the major goal is to simulate the synthesis reactor. But in this study the synthesis loop is considered and in addition of synthesis reactor, role of other equipments too is studied.

### 2. Experimental Procedure

Fig. 1 displays the Lurgi methanol production loop. The Makeup gas is mixed with recycle stream (Stream 2) and is brought to the desired pressure (5-10Mpa) in a multistage compressor. The effluent stream from recycle compressor is preheated by exchanging thermal energy with the product stream leaving the reactor and then passed over the catalyst packed in the tubes of the methanol synthesis reactor. The reactor is similar to a shell and tubes heat exchanger wherein there are 2692 tubes filled with copper/zinc oxide catalyst pellets. The reaction is exothermic and the reactor works isothermally, so cooling water is used to remove the excess heat. The exothermic formation of methanol occurs in the reactor at 200-300°C and heat of reaction is removed by boiling water injected into the shell of the reactor. The stream leaves the reactor after passing a heat exchanger, which produce steam, feed preheater, air cooler, and cooling water heat exchanger and then enters crude methanol separator (Stream 5). Methanol and water are separated from the reaction gas in separator at 313 K and 75 bar. Almost only methanol and water distribute between the phases. As the reactions for methanol production do not go to the completion, the unreacted components are recycled back to the reactor. A purge (Stream 8) from the recycle prevents accumulation of the light gases. Other components go into the recycle. The major amount of the exit gas from the separator is recycled to the suction side of the recycle compressor (Stream 7); however, a small amount is also purged to reformer.
burner and reformer reactor. The concentration and absolute value of inert substances and the stoicheiometry number govern the quantity of the purge gas.

![Fig 1. Flowsheet of commercial methanol synthesis loop](image)

The activation of copper/zinc oxide catalyst, which is used in the commercial reactor, shown in Fig. 1, is considered to be constant with time during the course of reactions and the methanol production in stream 4 is then also constant.

### 3. Mathematical Modeling

#### 3.1. Mathematical Model of Simplified Methanol Synthesis Loop

Basically, one always has to start from the idea that the target of the steady state flowsheeting is to predict the composition and flowrates of main internal and production streams. To be practical, however, in industrial scale many instruments and control devices are needed to keep the conditions at prescribed values. Here, it is considered that conditions of inlet streams including temperature and pressure are prefixed and the only aim is to study the performances of equipments on the compositions and flowrates of other streams. So, those parts of the process are calculated which influence appreciably the composition of these streams. Schematic presentation of such loop is shown in Fig. 2. Pressure of stream entering to reactor is 75bar and 500K. Temperature of inlet stream to separator is 313ºC and its pressure is 75bar. With these assumption and writing material balance duty of preheater, coolers, and energy that compressor required can be predicted.

![Fig 2. Simplified loop and boundaries, material balance is written around them](image)

To start mathematical modeling of methanol synthesis loop, it is noted that all streams at most contain $H_2$, $CO$, $CO_2$, $CH_4$, $H_2O$, $CH_3OH$, $N_2$ and $Ar$. Material balance equations are performed on three boundaries corresponding to Fig. 2.

In the case of no chemical reaction a material balances of the form:

$$\sum_{i=1}^n E_{yi} = \sum_{i=1}^n O_{yi}$$

is written. In above equation $E$ and $O$ are flowrates of incoming and outgoing streams from a boundary and $y_i$ and $y_0$ are their compositions. Material balance equations for the components that take apart in chemical reaction are as follows:

- $CO$:
  $$F_yCO_2(1-x_1) = E_{yCO_2}$$

- $CO_2$:
  $$F_yCO_2(1-x_2) = E_{yCO_2}$$

- $H_2$:
  $$F_yH_2(1-2x_1 - 3x_2) = E_{yH_2}$$

- $CH_3OH$:
  $$F(y_{CH_3OH} + y_{CO}x_1 + y_{CO_2}x_2) = E(y_{CH_3OH})$$

- $H_2O$:
  $$F_p(y_{H_2O} + y_{CO_2}x_2) = E(y_{H_2O})$$

In separator thermodynamic phase equilibrium of each component results in this equation:

$$y_i - k_i x_i = 0$$

In the last equation $k_i$ is phase equilibrium constant for component $i$. The loop can be forced to have specified amount of recycle ratio and so there will be another equation:

$$R - F(Recycle\ ratio) = 0$$

Finally, the auxiliary equation is that summation of mole fractions in each stream must be equal to unity:

$$\sum_{i=1}^n y_i = 1$$

#### 3.2 Mathematical Model of Methanol Synthesis Reactor

There is totally 2962 tube in this reactor. Since the performances of all tubes are the same it is needed only to model only one tube of the reactor. Length of each tube is 7.02m and their diameter is 3.8cm.

Material balance of components in gas phase is:

$$-F \frac{dy_i}{dz} + k_i a_i C_i (y_i - y_p) = 0;\ i = 1, 2, ..., 5$$
Fig 3. Catalyst bed of a single tube in reactor with cooling water

\( y_p \) is mole fraction of each component in gas phase while \( y_s \) is mole fraction of that component in catalyst or solid phase. In addition, \( F_i \) is total inlet molar flowrate, \( C_i \) is total inlet concentration, \( k_g \) is gas-solid mass transfer coefficient [8], and \( A_i \) is cross section area of tube.

By the aid of defining \( C' = C/C_{ref} \) and \( z' = z/L \) as nondimensional groups and rearrangements of equations one have:

\[
\frac{d y_p}{dz'} = \frac{k_g A_i L}{F_i} (y_s - y_p).
\]

This equation is subjected to the following boundary condition:

\[
y_p = y_{p,in}.
\]

Material balance for each component around catalyst phase can be written in this form:

\[
k_g A_i C_i y_p + (1-\varepsilon)\rho_s R_i = 0; \quad i = 1, 2, ..., 5
\]

\( \varepsilon \) is bed porosity and \( \rho_s \) is catalyst density. Reaction rate for different components are summarized in Table 1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Reaction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CH_3OH )</td>
<td>( R = r_1 )</td>
</tr>
<tr>
<td>( CO_2 )</td>
<td>( R = -r_1 + r_2 )</td>
</tr>
<tr>
<td>( CO )</td>
<td>( R = -r_2 )</td>
</tr>
<tr>
<td>( H_2 )</td>
<td>( R = -3r_1 + r_2 )</td>
</tr>
<tr>
<td>( H_2O )</td>
<td>( R = r_1 - r_2 )</td>
</tr>
</tbody>
</table>

\( r_1 \) and \( r_2 \) respectively are rate of \( CO_2 \) hydrogenation rate and water gas shift reaction.

\[
r_1 = k_1 K_1^2 K_{CO_2} \left[ \frac{\left(g_{P_{CO}}\right)^2}{(DEN)^2} \right]
\]

\[
r_2 = k_2 K_2^2 K_{CO_2} \left[ \frac{\left(p_{P_{CO}}P_{H_2O}ight)^2}{(DEN)^2} \right]
\]

\[
DEN = K_{H_2}P_{H_2} + K_{CO_2}P_{CO_2} + K_{CH_3OH}P_{CH_3OH} + K_{H_2O}P_{H_2O} + K_{CO}P_{CO}
\]

Ignoring longitudinal diffusion and considering a plug flow for gas phase, energy balance for gas phase is:

\[
-\rho_s u_i A_i C_i \frac{dT_g}{dz} + h_i A_i (T_g - T_s) + UP(T_s - T_g) = 0
\]

In this equation \( T_g \) is gas temperature, \( T_s \) is solid temperature, \( T_c \) is coolant temperature, \( h_g \) is heat transfer coefficient between gas and catalyst, \( p_i \) is tube perimeter, \( U \) is overall heat transfer coefficient, \( h_i \) is inside convective heat transfer coefficient, and \( h_o \) is outside (coolant side) convective heat transfer coefficient. Also \( k_u \) is conductive heat transfer coefficient and \( d_{in} \) and \( d_{out} \) are inside and outside tube diameters.

Energy balance for solid surface (catalyst) is written in the following form:

\[
-\rho_s A_i C_{in} \frac{dT_g}{dz} + h_i A_i (T_g - T_s) + UP A_i (T_s - T_g) = 0
\]

where \( \Delta H \) is heat of reaction and calculated by:

\[
(\Delta H)R = (\Delta H)r_1 + (\Delta H)r_2
\]

A definition of the form \( T^* = T/T_{ref} \) makes the energy balance equation dimensionless. Therefore, for energy balance of gas phase it is written:

\[
-\rho_s u_i A_i C_{in} \frac{dT_g}{dz} + h_i A_i (T_g - T_s) \frac{U P L}{\rho_s u_i C_{in}} (T_s - T_g) = 0
\]

Subjected to boundary condition:

\[
T_g^* = \frac{T_{g,in}}{T_{ref}} \quad \text{at} \quad z = 0.
\]

The algebraic equation that relates gas temperature and solid temperature is:

\[
(T_s - T_g) + \frac{U P}{h_i A_i} (T_s - T_g) + \frac{(1-\varepsilon)\rho_s A_i (\Delta H)R}{h_i A_i} = 0.
\]
3.3 Phase Equilibrium in Separator

For calculation of phase equilibrium constants in separator, equation of state of SRK is used. Details of this EOS can be easily found in every textbook. In first trial that there is no estimation about composition of feed to separator, three-parameter equation of Wilson can be used.

4. Model Solution

An equation-oriented method was applied to simulation of methanol synthesis loop. As it can be seen, for solution of mathematical model (4)-(12) must be solved simultaneously.

In ultimate case, it is assumed that all of components can exist in all streams. The temperature and pressure of inlet streams for all of equipments also are considered to be prefixed and only flowrate and composition of streams are unknown. Thus, number of unknown variables for each stream is 9. According to this, there are 45 unknowns. However, it is obvious that composition of purge and recycle streams are the same, therefore, only 37 unknowns remain. Numbers of equations that can be written in each boundary are detailed in Table 2.

<table>
<thead>
<tr>
<th>Tab. 2. Number of equations for each boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation</td>
</tr>
<tr>
<td>Boundary 1</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Boundary 2</td>
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<td></td>
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<tr>
<td></td>
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<tr>
<td>Boundary 3</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
</tr>
<tr>
<td>Recycle ratio</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

At this point, number of equations and unknowns are equal and systems of equations are solvable. When the first iteration is started, there all still 10 parameters that there is no complete information about them. They are two conversion degrees of CO, and CO in methanol reactor and also 8 phase equilibrium constant in separator. Phase equilibrium constant (as mentioned before) can be estimated by the aid of Wilson equation which does not need compositions of mixture, but conversion degrees of CO2 and CO have to be assumed. However, in next iterations, better estimations for these independent unknowns are calculated.

For numerical solution of nonlinear sets of equation, they are first become dimensionless and then a FORTRAN program solves them by the method of multidimensional convergence of Newton. Flow diagram of solution is brought at the end of paper (Fig. 4).

5. Results and Discussion

For this commercial methanol plant, gas is supplied without and with injection of additional CO2. Here these types of gases are named as: A, A′, respectively. Where A is gas without CO2 injection and A′ is the gas with CO2 injection. There is a good agreement between calculated and industrial data in all cases [9].

There exist basic different behaviors for gases used with and without CO2 injection. Fig. 5 and 6 illustrate the variation of composition of reactants and product of synthesis reaction across the reactor length for gas A for gas and solid (catalyst) phases.

As Fig. 5 and 6 show, conversion of CO2 to methanol is practically stopped at certain length of reactor. This length is approximately 3.7m. However, concentration of some reactants like CH3OH, CO and H2 oscillate after this length.

When CO2 is injected to the feed gas, these oscillation omitted (Fig. 7 and 8). These results can be interpreted with accordance to the theory of Skrzypek regarding the mechanism of methanol synthesis reactions [5].

As it is was mentioned before, the prevailing theory which has received more support is that the methanol synthesis reaction progresses exclusively with CO2.
When sufficient amounts of $CO_2$ is available in the reactor, methanol is synthesized according to (2). At the same time $CO$ is converted to $CO_2$ in water-gas shift reaction (3). However, when $CO_2$ is not injected into the reactor, it consumed totally in the middle of reactor. In fact, $CO$ does not have sufficient to compensate the consumed $CO_2$. Since Methanol is synthesized exclusively from $CO_2$, it is not produced anymore. Instead, it decomposed to its reactants.

As a result, some amounts of $CO_2$ and $H_2$ produces in that length of reactor. Meanwhile $CO$ produces $CO_2$ according to the water-gas shift reaction. When sufficient amounts of $CO_2$ produced, the reverse action occurs and methanol synthesis reaction continues again.

Temperature variations are plotted in Fig. 9 and 10. Similar effects take place about temperature. Temperature oscillations are obvious after the same length where composition oscillations were occurred in the reactor (3.7m).

These effects are interpreted in a similar manner as explained about oscillations of composition along the reactor. When methanol synthesis and decomposition take place, one of them is exothermic while the other is endothermic. The exothermic and endothermic reactions increase and decrease the temperature both in solid and gas phases. It should be emphasized that heat transfer inside the reactor pipes is high and this does not let the solid and gas phases to have very different temperatures.

In Fig. 11 and 12 effect of recycle ratio is investigated. Recycle ratio varies in a wide range of 0.5 to 8. For each recycle ratio production of methanol is estimated by model. These indicate that an increase in recycle ratio result in an increase in methanol production as it causes the synthesis reactions to occur near the equilibrium states. However, the rate of increasing of methanol production (or the slope of the curve in Fig. 11 and 12) decreases while the recycle ratio is increased. When recycle ratio reaches to 4.5 in Fig. 11 and to 6 in Fig. 12 there is no more increasing in methanol production.
This effect is related to equilibrium nature of methanol synthesis reactions. Increasing of recycle ratio cannot overcome the thermodynamic restrictions of the reactions. In the other word, there are two limitations for methanol production in the reactor: Kinetic and Thermodynamic limitations. The first is limitation can be removed somehow by increasing the recycle ratio but the second limitation should be accepted. In addition, the figures show that maximum recycle ratio (after which there is no more production of methanol) is more for case A'. The reason is related to the effect of injection of $CO_2$ in case A'. In the case A, only the reaction $CO$ is going to reach to equilibrium while in the second case the reaction of both $CO$ and $CO_2$ should completed and this need more recycle ratio (in a continuous process) or more time (in a batch process).

It is interesting that currently the plant is working near optimal values of recycle ratios that the model calculates. It should be emphasized it is not practical to increase the recycle ratios even more than these values. The operation costs are the most important parameters in a plant and they increase with a high rate as the flowrates increased.

6. Conclusion

Equation oriented approach to steady state flowsheeting is a suitable and relatively simple method of simulation for process with the loop. The main advantage of this method is that the governing equations of all stages in processes are solved simultaneously and provides an easy way of optimization of complete industrial process.

In this study, an equation oriented approach is developed for mathematical modeling of methanol synthesis loop. The modeled loop consists of a reactor, a flash separator and a purge stream. This study emphasize on those theories which believe that methanol synthesis continues exclusively from $CO$ reaction. Nevertheless, it indicates sufficient amount of $CO_2$ should be present throughout the reactor in order to prevent the oscillation of composition and temperature profile along the reactor. This can be achieved by injection of additional $CO_2$ to synthesis gas; unless, about half of reactor remains useless. Recycle ratio play an important role in the methanol synthesis loop and increase the methanol production rate. However, when equilibriums of reactions are
reached there will be no significant increase in methanol production by an increase in the recycle ratio.

Acknowledgments

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Nomenclature

- \( A_c \): Cross section area of pipes of reactor \( (m^2) \)
- \( a_c \): Specific area of catalyst \( (m^{-1}) \)
- \( C_i \): Total input concentration \( (mol / m^3) \)
- \( C_{ref} \): Reference concentration \( (mol / m^3) \)
- \( C^* \): Dimensionless concentration
- \( C_{pe} \): Heat capacity of gas \( (kJ / kmol.K) \)
- \( d_m \): Inside diameter of reactor \( (m) \)
- \( d_{ow} \): Outside diameter of reactor \( (m) \)
- \( F \): Fresh feed flowrate \( (kmol/hr) \)
- \( F_t \): Total flowrate \( (kmol/hr) \)
- \( E \): Output flowrate \( (kmol/hr) \)
- \( h_g \): Heat transfer coefficient between gas and catalyst \( (W / m^2 K) \)
- \( K_i \): Phase equilibrium constant of component \( i \)
- \( K_{CN} \): Absorption constant of \( CH \) \( (atm^{-1}) \)
- \( K_{CO_2} \): Absorption constant of \( CO_2 \) \( (atm^{-1}) \)
- \( k_{f_1} \): Rate constant of hydrogenation of carbon monoxide \( (kmol/hr\,(kg\,cat.)) \)
- \( k_{f_2} \): Rate constant of hydrogenation of carbon dioxide \( (kmol/hr\,(kg\,cat.)) \)
- \( k_s \): Mass transfer coefficient between gas and catalyst \( (mol/m^3) \)
- \( K_{pH_2} \): Absorption constant of \( H \) \( (atm^{-1}) \)
- \( K_{HO_2} \): Absorption constant of \( HCO_2 \) \( (atm^{-1}) \)
- \( L \): Reactor length \( (m) \)
- \( n \): Number of components
- \( P \): Perimeter of a pipe inside the reactor \( (m) \)
- \( P \): Pressure \( (atm) \)
- \( P_t \): Critical pressure of component \( i \) \( (atm) \)
- \( \rho \): Partial pressure \( (atm) \)
- \( R \): Universal gas constant \( (8.314kJ / kmole \cdot K) \)
- \( R \): Recycle flowrate \( (kmol/hr) \)
- \( R_t \): Reaction rate of component \( I \) \( (kmol/hr\,(kg\,cat.)) \)
- \( (r_1)_{h_0} \): Reaction rate of hydrogenation of carbon monoxide \( (kmol/hr\,(kg\,cat.)) \)
- \( (r_2)_{h_0} \): Reaction rate of hydrogenation of carbon dioxide \( (kmol/hr\,(kg\,cat.)) \)
- \( (R_{th})_0 \): Overall production rate \( (kmol/hr\,(kg\,cat.)) \)
- \( T \): Temperature \( (K) \)
- \( T_c \): Critical temperature \( (K) \)
- \( T_e \): Ambient temperature \( (K) \)
- \( T_{ref} \): Critical temperature of component \( i \) \( (K) \)
- \( T_r \): Reference temperature \( (K) \)
- \( T_s \): Catalyst phase temperature \( (K) \)
- \( T_{v^*} \): Dimensionless temperature
- \( U \): Overall heat transfer coefficient \( (W / m^2 K) \)
- \( u_x \): Gas velocity \( (m / Sec) \)
- \( x_i \): Mole fraction of component \( i \)
- \( x_i \): Conversion of carbon monoxide
- \( x_2 \): Conversion of carbon dioxide
- \( z \): Length \( (m) \)
- \( z^* \): Dimensionless length
- \( \Delta z \): Length increment \( (m) \)
- \( \Delta H \): Heat of reaction \( (kCal / kmol) \)
- \( \varepsilon \): Porosity coefficient of bed
- \( \Phi^{v^*} \): Fugacity coefficient of liquid phase
- \( \Phi^{v^*} \): Fugacity coefficient of vapour
- \( \rho_s \): Bed density \( (kg / m^3) \)
- \( \omega_i \): Acentric factor

References


[5] Skrzypek, J., Lachowska, M., Grzesik, M., Sloczynski, J., Nowak, P., "Thermodynamic and


