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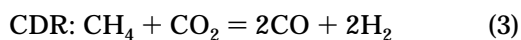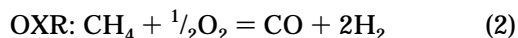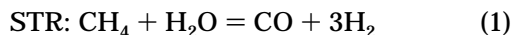
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The feasibility of ternary feed mixtures of CH_4 with O_2, H_2O, and CO_2 is analyzed in relation to the production of methanol syngas. Stoichiometric constraints are formulated in terms of three parameters characterizing the steam, partial oxidation, and carbon dioxide reforming reactions of methane. The equilibrium analysis is conducted using the methanol balance ratio μ and methane slip fraction χ as explicit design parameters. General results are derived for the feasibility of each ternary feed combination as a function of pressure and temperature in the range $1 < \mu < 3$ under carbon-free conditions. Numerical calculations indicate that $CH_4/O_2/CO_2$ feeds can be used in single-stage adiabatic reformers at low values of μ, but the produced syngas requires further treatment. Reforming based on $CH_4/O_2/H_2O$ feeds is endothermic at $\mu \geq 2$ under typical reaction conditions, thus requiring the application of a two-stage process involving primary and secondary reformers. Utilization of $CH_4/O_2/H_2O$ feeds in single-stage adiabatic reactors is feasible for $\mu = 1.7-1.9$, yielding syngas which can be upgraded by partial CO_2 removal. The endothermic $CH_4/CO_2/H_2O$ feed combination is always feasible for $1 < \mu < 3$.
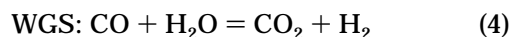
1. Introduction

Synthesis gas, a mixture of hydrogen and carbon oxides, plays a significant role in the chemical industry as a feedstock material. Examples of industrial processes utilizing various synthesis gas mixtures (syngas) include the manufacture of ammonia and methanol, hydroformylation and carbonylation reactions, and Fischer–Tropsch synthesis (Weissermel and Arpe, 1993). Each of these processes requires a different syngas composition, usually characterized in gross terms by the syngas ratio, i.e., the proportion of hydrogen to carbon monoxide, ranging from pure carbon monoxide, H_2:CO ratios of 1–3, to pure hydrogen.

Natural gas is the preferred feedstock for syngas production because of its wide availability and the relatively lower cost of the end product (e.g., methanol) as compared to residual oil and coal feedstocks (James et al., 1993). Three basic reactions may be used to convert natural gas to syngas: the steam reforming (STR), the partial oxidation or oxygen reforming (OXR), and the carbon dioxide reforming (CDR) of methane. These reactions are described by the following stoichiometric equations

$$\text{STR: } CH_4 + H_2O = CO + 3H_2 \tag{1}$$

$$\text{OXR: } CH_4 + \tfrac{1}{2}O_2 = CO + 2H_2 \tag{2}$$

$$\text{CDR: } CH_4 + CO_2 = 2CO + 2H_2 \tag{3}$$

coupled with the water–gas shift (WGS) reaction

$$\text{WGS: } CO + H_2O = CO_2 + H_2 \tag{4}$$

which is always active in methane reforming environments. The syngas ratio obtained with these reactions is >3 for steam, > or <2 for oxygen, and <1 for the carbon dioxide reforming of methane. Combinations of the basic reactions 1–4 or utilization of feeds comprising either ternary or quaternary mixtures of methane with steam, oxygen, and carbon dioxide can lead to the desired syngas composition.

The production of methanol makeup gas has attracted considerable research interest over the past few years because of the steady growth of methanol manufacture for meeting the increasing demands for methyl *tert*-butyl ether (MTBE), acetic acid, and formaldehyde (Farina and Supp, 1992). Several research groups are actively involved in the development of new catalysts and reactor designs for reforming methane to methanol makeup gas in a more energy-efficient manner (Tsang et al., 1995; Peña et al., 1996 and references therein). These research efforts are understood in view of the fact that about 60% of the total investment cost in modern methanol plants is accounted for by the synthesis gas generation section (Vannby and Winter Madsen, 1992).

The objective of the present work is to determine ranges of operating conditions for the production of methanol makeup gas starting from ternary feed mixtures of methane with steam, oxygen, and carbon dioxide, i.e., $CH_4/O_2/H_2O$, $CH_4/O_2/CO_2$, and $CH_4/CO_2/H_2O$. The syngas composition is parametrized in terms of the methanol balance ratio and the dry methane slip fraction which are introduced in section 2. Several formulas are derived in section 3 on the basis of atomic balance considerations, permitting direct calculation of the molar expansion coefficient, feed molar ratios, and

reactant conversions from the exit composition of a single-stage methane reformer. In section 4 it is shown that certain general conclusions regarding the feasibility of the above mixtures can be drawn by analysis of the atomic balance equations alone without explicit reference to thermodynamic equilibrium. The assumption of equilibrium is invoked in section 5, wherein numerical results are presented of the boundaries which define accessible regions in the parameter space for using the above mixtures under carbon-free conditions. The final results and certain general observations are summarized in the concluding sections.

2. Selection of Degrees of Freedom

The makeup gas from which methanol is produced consists mainly of hydrogen, carbon monoxide, and carbon dioxide. The influence of unconverted methane on the methanol synthesis reaction is considered negligible. Assuming that CO and CO_2 are ultimately converted into CH_3OH in the methanol reactor, while the excess oxygen atoms relative to carbon appear as water at the reactor outlet, the methanol reaction stoichiometry is given by the following equation

$$u\text{CO} + v\text{CO}_2 + (2u + 3v)\text{H}_2 = (u + v)\text{CH}_3\text{OH} + v\text{H}_2\text{O} \quad (5)$$
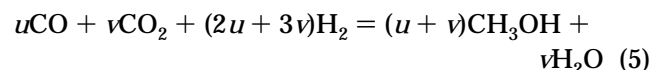
Here u and v denote respectively the mole numbers of carbon monoxide and carbon dioxide in the methanol reactor feed stream, which is derived from the exit stream of the synthesis gas generation section after water removal.

From eq 5 it is evident that the ideal syngas composition for methanol production must satisfy the stoichiometric constraint $[\text{H}_2] = 2[\text{CO}] + 3[\text{CO}_2]$ where [A] denotes the molar fraction of component A. This is equivalently expressed as $\mu = 2$ where the quantity μ is defined according to

$$\mu = \frac{[\text{H}_2] - [\text{CO}_2]}{[\text{CO}] + [\text{CO}_2]} \quad (6)$$

and is called the methanol stoichiometric number (SN) or the methanol balance ratio. Makeup gas with a stoichiometric number $\mu < 2$ leads to increased formation of byproducts in the methanol reactor, whereas when $\mu > 2$, the surplus hydrogen increases the recycle rate and has to be discharged with the purge gas stream, resulting in a less efficient and more expensive plant (Vannby and Winter Madsen, 1992).

Syngas mixtures with $\mu < 2$ contain an excess of carbon oxides relative to hydrogen, thus requiring removal of a certain fraction of CO_2, possibly after a partial CO shift step, to adjust the ratio close to the stoichiometric requirements. On the contrary, surplus of hydrogen, which is typical of steam reforming, implies a carbon deficiency. This, however, can be corrected by CO_2 addition downstream or upstream of the steam reformer, which is equivalent to using a ternary CH_4/CO_2/H_2O feed combination. Thus, even if the stoichiometric number of a syngas mixture deviates from the ideal value of $\mu = 2$, it can still be used in methanol synthesis once it is first subjected to the appropriate conditioning. This provides a larger degree of flexibility for the selection of the methanol balance parameter and permits the fulfillment of additional design specifica-

tions such as the adiabatic energy balance in autothermal reformers. For these reasons the feasibility analysis presented in subsequent sections was not limited to $\mu = 2$ but covered the wider range of $1 < \mu < 3$.

In addition to the methanol balance ratio, the methane content of the makeup gas must be kept sufficiently small in order to reduce slippage of methane in the purge stream of the methanol reactor and to improve the overall plant economics. For example, the methane exit concentration in the syngas generation section of the Lurgi methanol process typically amounts to about 5% on a dry basis (Farina and Supp, 1992). The dry methane content or slip fraction χ of a syngas mixture is defined as follows:

$$\chi = \frac{[\text{CH}_4]}{1 - [\text{H}_2\text{O}]} \quad (7)$$

In view of the importance of the methanol balance ratio μ and the dry methane content χ as key composition characteristics of methanol makeup gas, it is clearly desirable to consider those variables as explicit parameters, along with pressure and temperature, in the equilibrium thermodynamics analysis of methane reforming. In this way one can avoid the trial and error procedure which would be required for meeting the design specifications of μ and χ if the degrees of freedom were defined in terms of standard feed composition variables. Following the equilibrium computation based on the $\{P, T, \mu, \chi\}$ coordinates, the composition of all ternary feed combinations can be determined directly by atomic balance calculations.

3. Atomic Balance Identities

The carbon, oxygen, and hydrogen atomic contents at the outlet of a single-stage methane reformer are given by the expressions

$$B_\text{C} = n\{[\text{CH}_4] + [\text{CO}] + [\text{CO}_2]\}$$

$$B_\text{O} = n\{[\text{CO}] + 2[\text{CO}_2] + [\text{H}_2\text{O}]\}$$

$$\frac{1}{2}B_\text{H} = n\{2[\text{CH}_4] + [\text{H}_2] + [\text{H}_2\text{O}]\} \quad (8)$$

where B_j denotes the total g-atom of the jth element (j = C, O, H) per mole of the feed mixture and n stands for the molar expansion coefficient defined as the ratio of the total number of moles produced divided by the total number of moles fed into the reactor.

When the feed stream consists of an arbitrary combination of methane with oxygen, water, and carbon dioxide, the atomic contents per mole of feed are equivalently given by

$$B_\text{C} = [\text{CH}_4]_0 + [\text{CO}_2]_0$$

$$B_\text{O} = 2[\text{O}_2]_0 + 2[\text{CO}_2]_0 + [\text{H}_2\text{O}]_0$$

$$\frac{1}{2}B_\text{H} = 2[\text{CH}_4]_0 + [\text{H}_2\text{O}]_0 \quad (9)$$

where the subscript 0 denotes feed conditions. Forming the sum $B_\text{O} + \frac{1}{2}B_\text{H}$ and invoking the mole fraction closure identities for the feed and exit streams, $[\text{CH}_4]_0$

+ $[O_2]_0$ + $[CO_2]_0$ + $[H_2O]_0$ = 1 and $[CH_4]$ + $[CO]$ + $[CO_2]$ + $[H_2]$ + $[H_2O]$ = 1, respectively, leads to the equation

$$B_O + \frac{1}{2}B_H = 2 = n\{2 - ([CO] + [H_2])\} \quad (10)$$

Hence, the relationship

$$n = \frac{2}{2 - ([CO] + [H_2])} \quad (11)$$

is derived, expressing the molar expansion coefficient as an explicit function of the mole fractions of the basic syngas components, carbon monoxide and hydrogen, at the reformer outlet.

It should be emphasized that eq 11 is a corollary of the atomic balance constraints of the system under consideration. Thus, eq 11 remains valid under both equilibrium and nonequilibrium reaction conditions, assuming negligible formation of higher hydrocarbons and oxygenates. It is easily verified that eq 11 is still valid at incomplete conversion of oxygen, implying that $B_O = n\{2[O_2] + [CO] + 2[CO_2] + [H_2O]\}$ in eq 8, as well as in the presence of an inert diluent. In the latter case eq 10 takes the form

$$B_O + \frac{1}{2}B_H + \frac{2}{\alpha_I}B_I = 2 = n\{2 - ([CO] + [H_2])\} \quad (12)$$

where α_I denotes the atomic number of inert molecules, e.g., $\alpha_I = 2$ for N_2 or $\alpha_I = 1$ for He, and B_I stands for the total g-atoms of inert species per mole of feed.

According to eq 11, the mole number of a methane-based feed undergoing reforming to synthesis gas can be doubled only in the theoretical limit of a complete conversion of all reactants into carbon monoxide and hydrogen, i.e., for any of the stoichiometric reactions 1−3. In all other cases, the thermodynamic equilibrium limitations (e.g., water−gas shift equilibration in parallel with reactions 1−3) will force the molar expansion coefficient to attain values in the range of $1 < n < 2$. For example, a syngas mixture derived from any arbitrary $CH_4/O_2/CO_2/H_2O/N_2$ feed combination and containing 50 mol % H_2 and 25 mol % CO will be characterized by an expansion coefficient of $n = 1.60$.

When carbon monoxide and hydrogen are also included in the feed (as in secondary reformers), eq 11 takes the more general form

$$n = \frac{2 - ([CO]_0 + [H_2]_0)}{2 - ([CO] + [H_2])} \quad (13)$$

Similar to the previous case, eq 13 remains valid in the presence of inert species and under operating conditions leading to incomplete conversion of oxygen but with negligible formation of higher hydrocarbons or oxygenates.

To proceed further, the analysis is restricted to feeds comprising ternary mixtures of methane with oxygen, water, and carbon dioxide, i.e., $CH_4/O_2/H_2O$, $CH_4/O_2/CO_2$, and $CH_4/CO_2/H_2O$. The former feed combination is essential to all industrial methane-reforming processes producing syngas with composition appropriate for the methanol synthesis reaction (Twigg, 1989; Christensen and Primdahl, 1994), while the latter is used for the production of oxo-synthesis gas (Rostrup-Nielsen, 1994). The composition of these feeds is

determined from the atomic balance identities discussed above, i.e., eq 9 in conjunction with eqs 8 and 11. The results are summarized below.

a. Feed CH₄/O₂/H₂O. The feed molar ratios are given by the general expressions

$$\frac{[O_2]_0}{[CH_4]_0} = \frac{3 - \mu}{2}X[CH_4] \quad (14a)$$

$$\frac{[H_2O]_0}{[CH_4]_0} = (\nu - 2)X[CH_4] \quad (14b)$$

where μ is given by eq 6 and the quantity ν is defined as

$$\nu = \frac{[H_2] + [H_2O]}{[CO] + [CO_2]} \quad (15)$$

$X[CH_4]$ denotes the conversion of methane, while it is implicitly assumed that $X[O_2] \approx 1$.

b. Feed CH₄/O₂/CO₂. The oxygen- and carbon dioxide-to-methane feed molar ratios are expressed as

$$\frac{[O_2]_0}{[CH_4]_0} = (1 - \xi)X[CH_4] \quad (16a)$$

$$\frac{[CO_2]_0}{[CH_4]_0} = \frac{2 - \nu}{\nu}X[CH_4] \quad (16b)$$

where $X[O_2] \approx 1$ and the quantity ξ is defined according to

$$\xi = \frac{[CO] - [H_2O]}{[H_2] + [H_2O]} \quad (17)$$

Combining eq 15 with eqs 6 and 17 leads to the identity

$$\nu = \frac{1 + \mu}{1 + \xi} \quad (18)$$

expressing ν as an explicit function of the parameters μ and ξ.

c. Feed CH₄/CO₂/H₂O. The feed molar ratios of carbon dioxide-to-methane and water-to-methane read

$$\frac{[CO_2]_0}{[CH_4]_0} = \frac{3 - \mu}{1 + \mu}X[CH_4] \quad (19a)$$

$$\frac{[H_2O]_0}{[CH_4]_0} = 2\frac{1 - \xi}{1 + \xi}X[CH_4] \quad (19b)$$

In all cases, therefore, the feed ratios of oxygen, water, and carbon dioxide relative to methane are directly proportional to the attained conversion of methane, with the proportionality factor being a simple function of the parameters μ, ν, and ξ. These characteristic quantities admit of the following physical meaning:

a. For the feeds under consideration the methanol balance ratio μ takes values in the range $\mu_{min} < \mu \leq \mu_{max}$ where $\mu_{min} = -1$ and $\mu_{max} = 3$. The lower bound ($\mu \rightarrow -1$) is attained when the reactor effluent contains negligible amounts of the partial oxidation products carbon monoxide and hydrogen, i.e., $[CO] + [H_2] \rightarrow 0_+$.

On the other hand, according to eq 14 or eq 19, the upper bound ($\mu = 3$) corresponds to CH_4/H_2O feeds with any finite composition. Consequently, the parameter μ constitutes a characteristic constant of the steam reforming reaction of methane, and as such it may be called the CH_4/H_2O reforming index.

b. The quantity ξ takes values in the range $\xi_{min} < \xi \leq \xi_{max}$ where $\xi_{min} = -1$ and $\xi_{max} = 1$. Similar to the steam reforming index, the lower limit ($\xi \rightarrow -1$) is approached when the reformer outlet contains negligible concentrations of carbon monoxide and hydrogen. Referring to eq 16 or eq 19, it is immediately deduced that the upper bound ($\xi = 1$) is attained in the case of CH_4/CO_2 feeds with any finite composition, suggesting that ξ is a characteristic constant of the dry carbon dioxide reforming reaction of methane, and thus it may be called the CH_4/CO_2 reforming index.

c. In general, the range of the quantity ν is $0 < \nu < \infty$, while according to eq 14 or eq 16, all CH_4/O_2 feed mixtures are characterized by the value $\nu = 2$. Hence, the parameter ν may be called the CH_4/O_2 reforming index or the methane partial oxidation ratio since it provides a characteristic constant of the oxygen reforming reaction of methane. Furthermore, it can be shown that when $\nu = 2$, then $(3 - \mu)/(1 + \mu) = (1 - \xi)/(1 + \xi)$, implying that this value is also compatible with a $CH_4/CO_2/H_2O$ feed mixture characterized by a steam-to-carbon dioxide ratio of 2 (eq 19a,b). It is interesting to observe that this particular $CH_4/CO_2/H_2O$ combination is stoichiometrically equivalent to a primary CH_4/O_2 feed in which a portion of methane is burned with all available oxygen to carbon dioxide and water, with the remaining portion being reformed to the corresponding equilibrium synthesis gas mixture via the steam and carbon dioxide reforming reactions. It may be recognized that these cases correspond to the direct and indirect routes of the partial oxidation reaction of methane (see Tsang et al., 1995 and references therein).

The parameters μ, ν, and ξ are also involved in the conversion formulas of the reactants which are presented in the Appendix. These relationships can be used for calculating the conversions directly from the exit composition of methane reformers. Moreover, the following inequalities are easily established:

When $\mu \geq \rho$, then $\xi > 1/\rho$ when $-1 < \rho < 0$
$\qquad\qquad$ and $\xi < 1/\rho$ when $0 < \rho < 3$ (20)

When $\mu \geq \rho$ and $-1 < \rho < 3$, then $\nu > \max(0,\rho)$ (21)

It is remarked that eqs 14−21 remain unchanged in the presence of inert species.

4. Atomic Balance Constraints

Using the atomic balance identities derived above, certain useful conclusions can be drawn concerning the production of methanol syngas starting from the ternary feed combinations under consideration. Fixing the methanol balance ratio at the stoichiometric value of $\mu = 2$ and referring to the $CH_4/O_2/H_2O$ feed, it is immediately seen from eq 14a that the methane conversion is given by

$$X[CH_4] = 2\frac{[O_2]_0}{[CH_4]_0}; \qquad \mu = 2 \qquad (22)$$

Thus, the oxygen-to-methane feed ratio must be less than the stoichiometric ratio of the partial oxidation reaction 2, i.e., $[O_2]_0/[CH_4]_0 < 0.50$. Combining eq 14b with eq 22 leads to the relationship

$$\nu = 2 + \frac{1}{2}\frac{[H_2O]_0}{[O_2]_0}; \qquad \mu = 2 \qquad (23)$$

expressing the CH_4/O_2 reforming index as an explicit function of the steam-to-oxygen feed ratio. For example, in a specific application with $[O_2]_0/[CH_4]_0 = 0.425$ and $[H_2O]_0/[CH_4]_0 = 1$, which is typical of the syngas section of a stoichiometric methanol process, one finds $X[CH_4] = 0.85$ and $\nu = 3.18$ for a single-stage autothermal reformer. Note, however, that a slight increase of 5% in the specified methanol balance ratio, from the ideal value of $\mu = 2$ to $\mu = 2.1$, while retaining the same oxygen-to-methane molar feed ratio as used above, results in a notably larger increase of ca. 11% in the methane conversion, from 85% to 94.5%. Hence, as far as methane conversion is concerned at a fixed oxygen-to-methane feed ratio, it would be desirable to operate the reformer at an over-stoichiometric value of the methanol balance ratio.

The methane conversion attained when using a $CH_4/CO_2/H_2O$ feed with $\mu = 2$ follows from eq 19a as

$$X[CH_4] = 3\frac{[CO_2]_0}{[CH_4]_0}; \qquad \mu = 2 \qquad (24)$$

implying that $[CO_2]_0/[CH_4]_0 < 1/3$. Moreover, combining eq 19b with eq 24 gives the following expression for the CH_4/CO_2 reforming index:

$$\xi = \left[1 - \frac{1}{6}\frac{[H_2O]_0}{[CO_2]_0}\right]\bigg/\left[1 + \frac{1}{6}\frac{[H_2O]_0}{[CO_2]_0}\right]; \qquad \mu = 2 \qquad (25)$$

Since $\xi < 1/2$ by the inequality of eq 20, it follows that $[CO_2]_0/[H_2O]_0 < 1/2$. Hence, production of a syngas mixture with a methanol balance ratio $\mu = 2$ from the $CH_4/CO_2/H_2O$ feed combination will be stoichiometrically possible only when the molar feed ratios satisfy the inequalities $[CO_2]_0/[CH_4]_0 < 1/3$ and $[CO_2]_0/[H_2O]_0 < 1/2$. Similar to the $CH_4/O_2/H_2O$ case, operation of the reformer at an over-stoichiometric balance ratio will lead to a larger methane conversion at any given value of the carbon dioxide-to-methane feed ratio.

Obviously not all feed combinations are feasible for generating syngas mixtures with specific composition characteristics. For example, in the particular case of $\mu = 2$ considered above, the $CH_4/O_2/CO_2$ feed is not applicable since $\nu > 2$ through eq 21, thus leading to negative values of the carbon dioxide-to-methane feed ratio in view of eq 16b. The general constraints that must be satisfied for each of the ternary feeds $CH_4/O_2/H_2O$, $CH_4/O_2/CO_2$, and $CH_4/CO_2/H_2O$ are obtained from eqs 14, 16, and 19 by requiring that the corresponding molar feed ratios be positive definite numbers:

$$\text{Feed } CH_4/O_2/H_2O: \ \mu < 3, \quad \nu > 2 \qquad (26a)$$

$$\text{Feed } CH_4/O_2/CO_2: \ \xi < 1, \quad \nu < 2 \qquad (26b)$$

$$\text{Feed } CH_4/CO_2/H_2O: \ \mu < 3, \quad \xi < 1 \qquad (26c)$$

Confining the methanol balance parameter in the practical range $1 < \mu < 3$ and using eq 20, it follows that the CH_4/CO_2 reforming index is less than one ($\xi < 1$) irrespective of the other operating conditions. It is always possible, therefore, to generate syngas characterized by methanol balance ratios in the range $1 < \mu < 3$, starting from $CH_4/CO_2/H_2O$ feed combinations with composition dictated by the desired values of pressure, temperature, and dry methane content in the $\{P, T, \mu, \chi\}$ coordinate base. The only additional constraint that needs to be considered in this case is to operate the reformer inside the carbon-free region.

According to the relation of eq 21, the methane–oxygen reforming index is always greater than 2 when $\mu \geq 2$. Consequently, it will be possible to produce synthesis gas mixtures characterized by stoichiometric numbers in the range $2 \leq \mu < 3$ starting from an appropriate $CH_4/O_2/H_2O$ feed combination, assuming that the pressure is properly chosen in order to avoid carbon formation. In this case, however, application of the $CH_4/O_2/CO_2$ feed is not feasible since $\nu > 2$, thus violating the second condition of eq 26b.

When $\mu < 2$, the methane–oxygen reforming index may be either greater or less than 2 depending upon the specific values of the remaining parameters P, T, and χ. Thus, either the $CH_4/O_2/H_2O$ or the $CH_4/O_2/CO_2$ combination will have to be applied in order to produce synthesis gas with $1 < \mu < 2$. The choice of the feed type is dictated by the relative position of the carbon curve with respect to the $CH_4/O_2/H_2O$–$CH_4/O_2/CO_2$ stoichiometric boundary. The latter is defined by the limiting value $\nu = 2$ of the oxygen reforming index, which is compatible with the partial oxidation reaction of methane using a binary CH_4/O_2 feed.

The steam reforming and dry carbon dioxide reforming reactions, which are based on the binary CH_4/H_2O and CH_4/CO_2 combinations, yield the maximum values $\mu = 3$ and $\xi = 1$ of the parameters μ and ξ for the cases under consideration. Moreover, it should be pointed out that the condition $\xi < 1$ is not always fulfilled when $\mu < 1$. Additional conditions must be imposed in this case in order to ensure the applicability of $CH_4/O_2/CO_2$ and $CH_4/CO_2/H_2O$ feeds. This is not further elaborated since production of methanol makeup gas is not usually practiced using such low values of the CH_4/H_2O reforming index.

5. Results

The pressure $P_{\nu=2}$ defining the $CH_4/O_2/H_2O$–$CH_4/O_2/CO_2$ boundary when $\mu < 2$ can be calculated as a function of temperature T, methanol balance ratio μ, and dry methane content χ by invoking thermodynamic equilibrium at the reformer outlet. This assumption is justified in view of the fact that most catalytic methane reformers approach thermodynamic equilibrium to within $10-50$ K.

Following standard procedures (Smith and van Ness, 1975), the dry carbon dioxide reforming and water–gas shift reactions provide the following independent relations among the equilibrium mole fractions of the syngas components:

$$\frac{[CO]^2[H_2]^2}{[CH_4][CO_2]} = \frac{1}{P^2}K_{cdr}(T); \quad \frac{[CO_2][H_2]}{[CO][H_2O]} = K_{wgs}(T) \quad (27)$$

Ideal gas behavior is implicitly assumed in eq 27 which

is an acceptable approximation for the pressures and temperatures usually applied in methane reformers (Twigg, 1989). The equilibrium reaction constants and other thermodynamic parameters are calculated by using the NASA thermochemical polynomials (Burcat, 1984).

Simultaneous solution of eqs 27 in conjunction with the specifications

$$\frac{[H_2] - [CO_2]}{[CO] + [CO_2]} = \mu; \quad \frac{[CH_4]}{1 - [H_2O]} = \chi \quad (28)$$

the mole fraction closure identity (noting that $[O_2] \cong 0$)
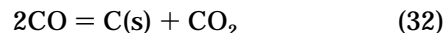
$$[CH_4] + [CO] + [CO_2] + [H_2] + [H_2O] = 1 \quad (29)$$

and the constraint equation

$$\frac{[H_2] + [H_2O]}{[CO] + [CO_2]} = \nu = 2 \quad (30)$$

determines the limiting pressure $P_{\nu=2} = P_{\nu=2}(T,\mu,\chi)$. The carbon pressure $P_c = P_c(T,\mu,\chi)$ is similarly obtained by replacing the constraint equation (30) with the relationship

$$\frac{[CO_2]}{[CO]^2} = PK_B(T) \quad (31)$$

where $K_B(T)$ denotes the equilibrium constant of the Boudouard coking reaction

$$2CO = C(s) + CO_2 \quad (32)$$

It is well-known that the value of K_B depends on the specific carbon modification, which is a function of the operating conditions and the catalyst formulation (Rostrup-Nielsen, 1984). A conservative estimate, however, of the carbon limit curve can be obtained by using free energy data of graphite, and this approximation was used in the present calculations.

Representative results are displayed in Figure 1 for four values of the methanol balance ratio ($\mu = 1.60(0.10)1.90$) and for two values of the dry methane slip fraction ($\chi = 0.5$, 5.0%). These graphs show that for fixed values of μ and χ both $P_{\nu=2}(T,\mu,\chi)$ and $P_c(T,\mu,\chi)$ curves are monotonically increasing functions of temperature. Moreover, at high temperatures the $CH_4/O_2/H_2O$–$CH_4/O_2/CO_2$ boundary pressure $P_{\nu=2}$ is larger than the corresponding carbon limit pressure P_c, while the trends are reversed at low temperatures. Consequently, the two curves intersect each other at some characteristic temperature $T_{c;\nu=2}$ which can be expressed as a function of the methanol balance ratio and methane slip fraction: $T_{c;\nu=2} = T_{c;\nu=2}(\mu,\chi)$. The associated characteristic pressure at the intersection point can also be expressed as a function of these parameters: $P_{c;\nu=2} = P_{c;\nu=2}(\mu,\chi)$.

It is evident that for fixed values of $\mu < 2$ and χ and for temperatures $T < T_{c;\nu=2}(\mu,\chi)$ the carbon limit curve defines the lowest permissible pressure for using the $CH_4/O_2/H_2O$ feed. On the other hand, when $T > T_{c;\nu=2}(\mu,\chi)$, the methane reformer can operate using either the $CH_4/O_2/H_2O$ or the $CH_4/O_2/CO_2$ feed combination depending upon the desired pressure level. Specifically, when $P > P_{\nu=2}(T > T_{c;\nu=2};\mu,\chi)$, the equilibrium synthesis gas mixture can be generated starting from
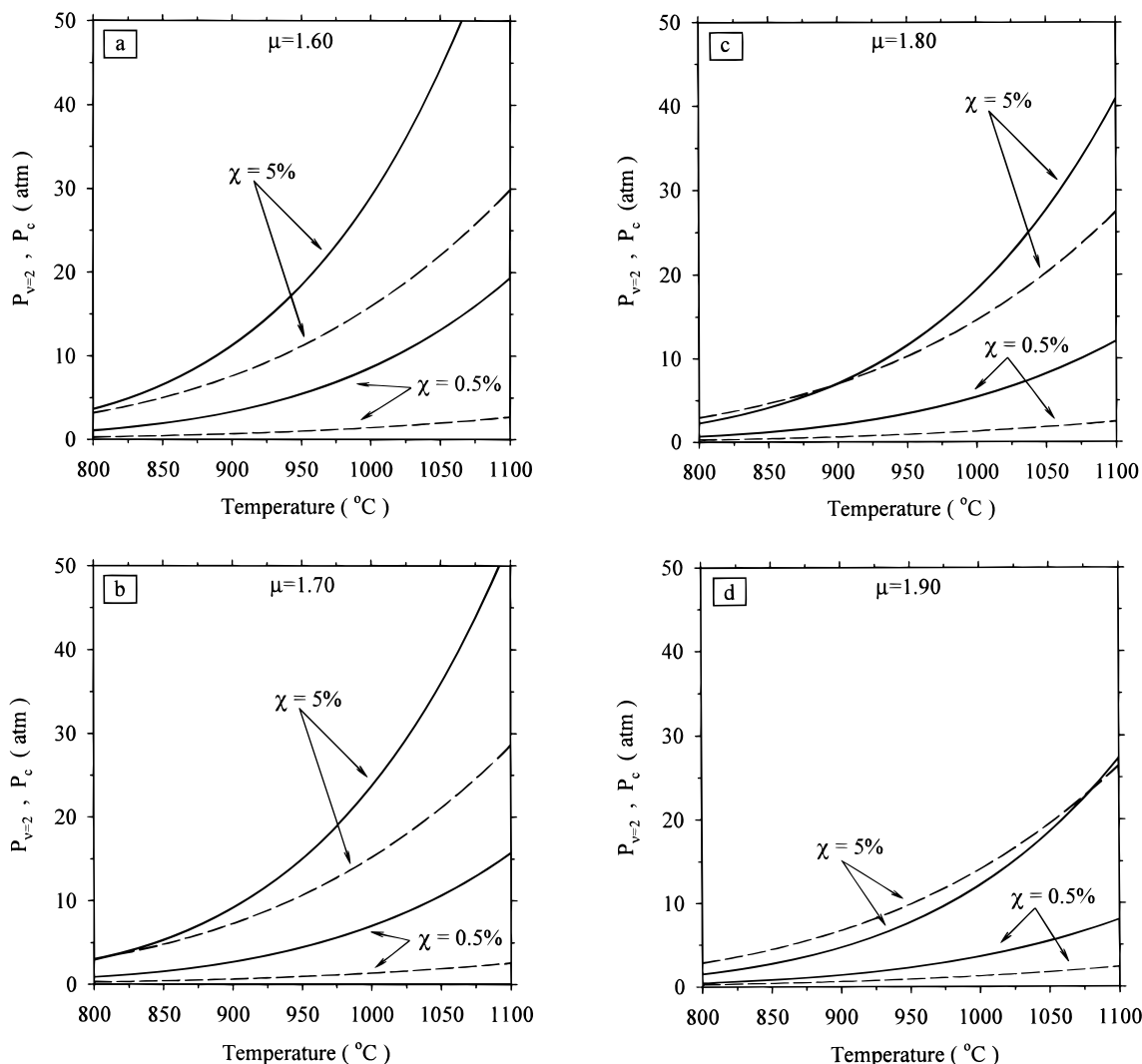
Figure 1. Equilibrium pressure (atm) along the $\nu = 2$ boundary (solid lines) and on the carbon limit curve (dash lines) as a function of temperature for various values of the methanol balance ratio μ and dry methane slip fraction χ: (a) $\mu = 1.6$, (b) $\mu = 1.7$, (c) $\mu = 1.8$, (d) $\mu = 1.9$. In each graph the upper two lines correspond to $\chi = 5\%$ while the lower two lines correspond to $\chi = 0.5\%$. The $CH_4/O_2/H_2O$ and $CH_4/O_2/CO_2$ feeds are feasible in the region above and below, respectively, the $\nu = 2$ boundary. The carbon limit curve defines the minimum permissible pressure or maximum temperature for carbon-free operation with any feed mixture in the $\{P, T, \mu, \chi\}$ coordinate system.

a $CH_4/O_2/H_2O$ feed, whereas a $CH_4/O_2/CO_2$ combination is required when $P_c(T > T_{c;\nu=2};\mu,\chi) < P < P_{\nu=2}(T > T_{c;\nu=2};\mu,\chi)$. Similarly, for any operating pressure $P < P_{c;\nu=2}(\mu,\chi)$ the carbon limit curve gives the maximum permissible temperature for using the $CH_4/O_2/H_2O$ feed mixture, while when $P > P_{c;\nu=2}(\mu,\chi)$, the equilibrium synthesis gas can be generated starting either from a $CH_4/O_2/H_2O$ feed when $T < T_{\nu=2}(P > P_{c;\nu=2};\mu,\chi)$ or from a $CH_4/O_2/CO_2$ feed combination when $T_{\nu=2}(P > P_{c;\nu=2};\mu,\chi) < T < T_c(P > P_{c;\nu=2};\mu,\chi)$.

It must be emphasized that the carbon limit pressure or temperature discussed above refers to fixed values of the parameters μ and χ, which are treated as independent variables, and not to a fixed feed composition. Consequently, although the graphs of Figure 1 indicate that a higher pressure or a lower temperature is required in order to operate the reactor in the coke-free region, the results do not actually contradict the well-known trends and characteristics of carbon formation since the composition of the feeds change with pressure or temperature in the $\{P, T, \mu, \chi\}$ coordinate system. In fact, the steam concentration of the $CH_4/O_2/H_2O$ and $CH_4/CO_2/H_2O$ feed mixtures and also the oxygen concentration of the $CH_4/O_2/CO_2$ feed, calculated

at any temperature for fixed values of μ and χ, increase with increasing pressure, thus leading to the production of carbon-free syngas in agreement with the trends implied by Figure 1. Similarly, the steam or oxygen content of these feed combinations, calculated at any given pressure for fixed values of μ and χ, increases with a decreasing operating temperature as shown explicitly in the examples of Figures 3–6 discussed below.

The contour graphs of Figure 2 indicate that the characteristic temperature and pressure at the intersection point of the CH_4/O_2 and carbon limit curves increase with both the methanol balance ratio and the dry methane slip fraction. Moreover, for any operating temperature T or pressure P, the (μ, χ) parameter region in which application of the $CH_4/O_2/CO_2$ feed is feasible lies below the corresponding contour lines of parts a and b of Figure 2. For example, at $T = 900$ °C and with $\mu = 1.70$, the maximum slip fraction for application of the $CH_4/O_2/CO_2$ feed amounts to $\chi_{max} \cong 7.5\%$, whereas at $\mu = 1.90$ this value decreases to $\chi_{max} \cong 2.6\%$.

It is always possible to use an appropriate $CH_4/CO_2/H_2O$ feed combination for any point lying outside the carbon-forming region, i.e., $P > P_c(T,\mu,\chi)$ or $T < T_c(P,\mu,\chi)$. Clearly, this feed is stoichiometrically equiva-

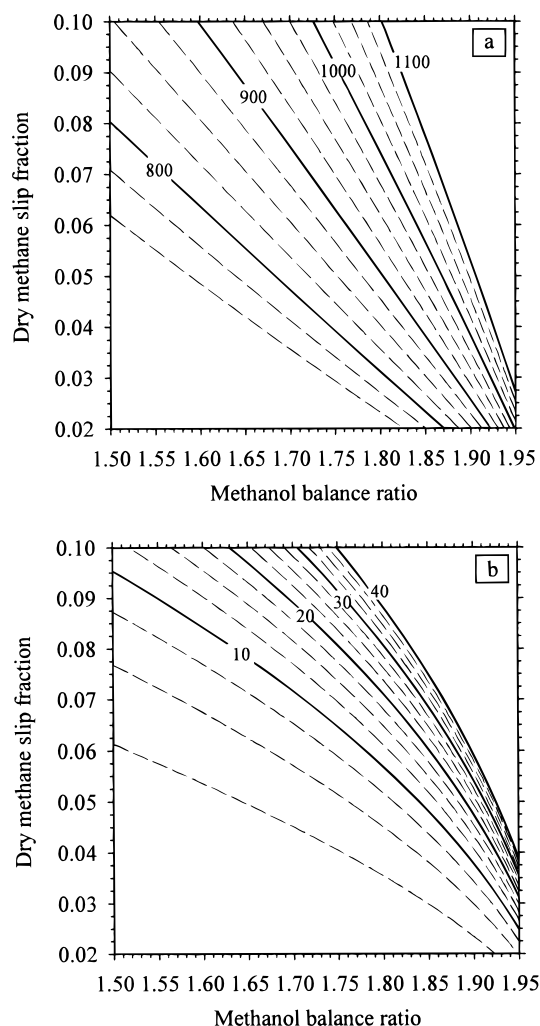**Figure 2.** Contour graphs of (a) the temperature $T_{c;\nu=2}$ (°C) and (b) the pressure $P_{c;\nu=2}$ (atm) at the characteristic intersection point of the carbon limit curve with the $\nu = 2$ boundary line as a function of the equilibrium dry methane slip fraction χ and methanol balance ratio μ.

lent to primary $CH_4/O_2/H_2O$ or $CH_4/O_2/CO_2$ feeds where a portion of methane is burned toward carbon dioxide and water. In the $CH_4/O_2/H_2O$ and $CH_4/O_2/CO_2$ cases, the role of the oxygen feed is 2-fold: first to supply a fraction of the oxygen atoms required for oxidation of methane and second to generate the necessary heat for transforming the feed molecules into synthesis gas with the composition dictated by the atomic balance and thermodynamic constraints. In autothermal reformers, these are supplemented by the adiabatic energy balance equation for specified temperatures of the inlet and outlet streams.

Detailed results of the equilibrium syngas composition, the feed molar ratios, methane conversion, and heat input requirements of a single-stage methane reformer are plotted in Figure 3 for the following operating conditions: $P = 20$ atm, $\mu = 1.70$, $\chi = 5.0\%$, feed temperature $T_0 = 500$ °C, and exit temperatures in the range of 800 °C $\leq T \leq 1040$ °C. Note that the carbon limit temperature in this case amounts to 1041.5 °C, while the binary CH_4/O_2 feed is obtained at 980 °C. Therefore, the $CH_4/O_2/H_2O$ and $CH_4/O_2/CO_2$ feed combinations are feasible over the temperature ranges $T \leq$ 980 °C and 980 °C $< T <$ 1041.5 °C, respectively. The results were obtained by numerical solution of eqs 27–30 using the atomic balance identities, eqs 14–19, while

the heat load per mole of feed was calculated through the adiabatic energy balance equation

$$Q = n\sum_i y_i H_i(T) - \sum_i y_{i,0} H_i(T_0) \qquad (33)$$

Here y_i and H_i denote respectively the mole fraction and molar enthalpy of the synthesis gas components ($i =$ CH_4, O_2, CO, CO_2, H_2, and H_2O). It must be emphasized that since three independent parameters (P, μ, χ) are fixed in this calculation, the equilibrium composition of the synthesis gas displayed in Figure 3a is a unique function of the operating temperature. Thus, at any given temperature T, the corresponding syngas composition will be identical for all possible feed combinations which are compatible with the specified values of P, μ, and χ.

In Figure 3d it can be observed that the $CH_4/O_2/H_2O$ feed, which is feasible up to 980 °C, is mildly exothermic, requiring the removal of 10–30 kJ/mol$_{feed}$, whereas the $CH_4/CO_2/H_2O$ feed combination requires the input of a considerable amount of heat (50–130 kJ/mol$_{feed}$). Under the selected conditions, adiabatic operation of the single-stage reformer will be possible with the $CH_4/O_2/CO_2$ feed at an exit temperature of about 1010 °C.

The methane conversion attained with both the $CH_4/$ O_2/H_2O and $CH_4/O_2/CO_2$ feeds is rather high (Figure 3c), reaching a maximum of 87.5% at the $\nu = 2$ boundary point ($T \cong 980$ °C). However, as shown in Figure 3a, the mole fractions of hydrogen and carbon dioxide obtained with the $CH_4/O_2/CO_2$ feed, i.e., for temperatures in the range 980 °C $< T <$ 1041.5 °C, are too low to allow upgrading to the required methanol stoichiometry ($\mu \approx 2$) by simple carbon dioxide removal. The H atom deficiency of the so-derived synthesis gas can be corrected either by direct hydrogen addition (if available) or by further downstream treatment in a CO shift reactor followed by partial CO_2 removal. An alternative to the latter option would be to use a quaternary mixture of CH_4 with all three reactants, O_2, H_2O, and CO_2, in a single-stage autothermal reformer.

It should be noted that the carbon dioxide content of the $CH_4/O_2/CO_2$ feed (Figure 3b) is quite low, less than about 6%, thus implying that the specified operating conditions are more relevant to the oxygen reforming of a natural gas feedstock containing an appreciable fraction of carbon dioxide. Higher CO_2 feed contents can be used when other process considerations allow utilization of the $CH_4/O_2/CO_2$ feed at lower values of the methanol balance ratio. An example is shown in Figure 4 where $\mu = 1.2$, with all other conditions being the same as above. In this case, adiabatic operation of a single-stage reformer can be realized at about 955 °C with a feed comprising 57% CH_4, 28% O_2, and 15% CO_2. Note that the $CH_4/O_2/H_2O$ combination at $\mu = 1.2$ is strongly exothermic, requiring the removal of 50–100 kJ/mol$_{feed}$, because of the larger oxygen feed concentration needed for satisfying the atomic constraints.

Small values of the methane slip fraction and high methanol balance ratios are possible only at low operating pressures with the $CH_4/O_2/CO_2$ feed. For example, Figure 1d shows that this feed is feasible only for pressures lying in the narrow range 2.5 atm $< P <$ 7.5 atm at a temperature of 1100 °C with $\mu = 1.90$ and $\chi =$ 0.5%. In general, therefore, the $CH_4/O_2/CO_2$ feed combination is more suitable for applications involving relatively low methanol balance ratios, e.g., $\mu < 1.50-$
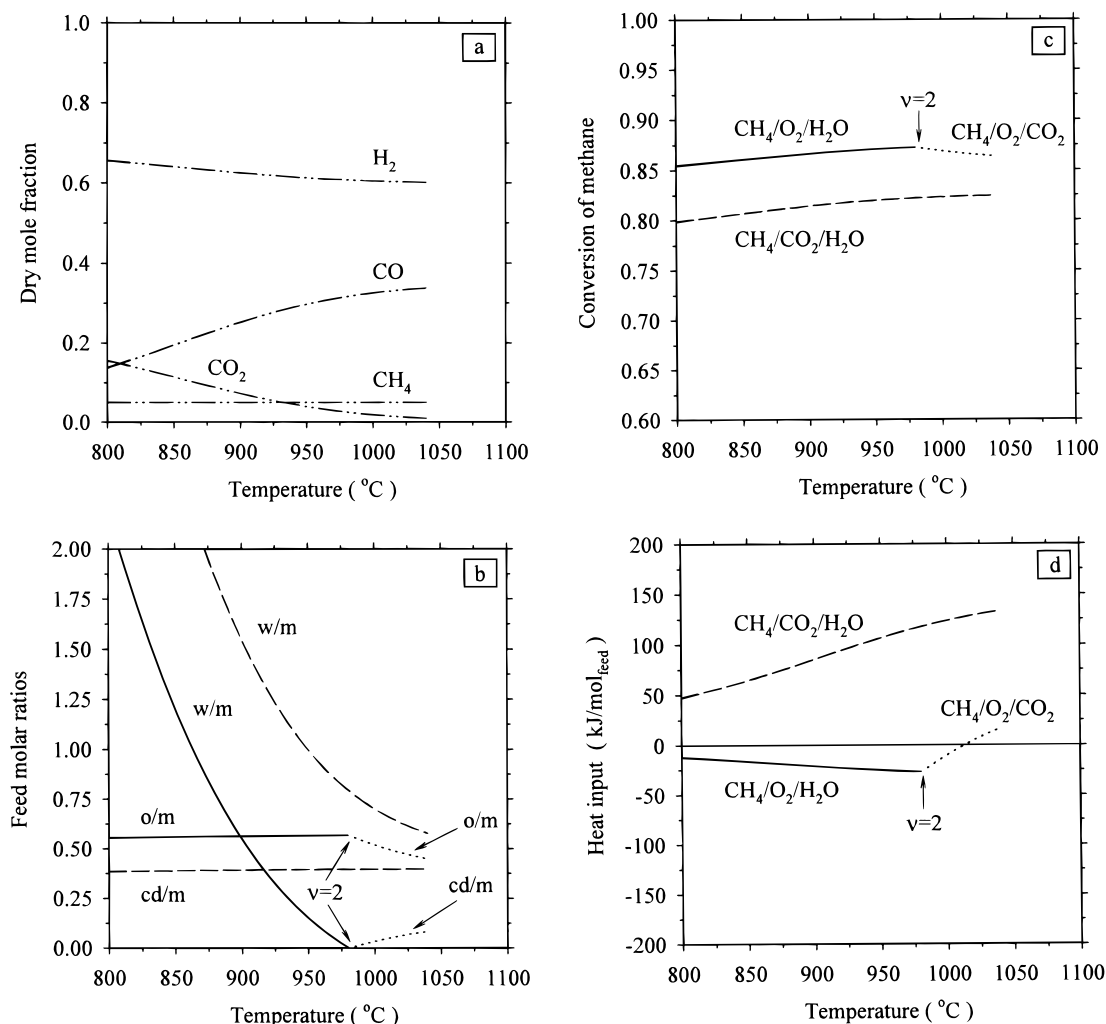
Figure 3. (a) Temperature variation of the equilibrium synthesis gas composition corresponding to the following specifications: pressure $P = 20$ atm, methanol balance ratio $\mu = 1.70$, dry methane slip fraction $\chi = 5\%$. Temperature variation of (b) the feed molar ratios (w/m $= [H_2O]/[CH_4]_0$, o/m $= [O_2]/[CH_4]_0$, cd/m $= [CO_2]/[CH_4]_0$), (c) the methane conversion, and (d) the heat input requirements (kJ/mol$_{feed}$) of the associated ternary feed mixtures: $CH_4/O_2/H_2O$ (solid lines), $CH_4/O_2/CO_2$ (dotted lines), and $CH_4/CO_2/H_2O$ (dashed lines). Operating conditions are as in part a with a preheat temperature of $T_0 = 500$ °C. The maximum allowable temperature for carbon-free operation is 1041.5 °C. The binary CH_4/O_2 feed (corresponding to $\nu = 2$ at the specified P, μ, and χ) is obtained at a temperature of 980 °C.

1.60, and high operating temperatures with not too small values of the dry methane slip fraction.

Numerical calculations indicate that application of the $CH_4/O_2/H_2O$ feed mixture in autothermal reformers is possible for stoichiometric numbers approaching but not exceeding the ideal value of the methanol synthesis reaction. An example is presented in Figure 5 for the following operating conditions: $P = 40$ atm, $\mu = 1.85$, $\chi = 5.0\%$, exit temperatures 800 °C $\leq T \leq 1100$ °C, and $T_0 = 500$ °C. In this case it is clearly observed that the heat load is rather small over the entire temperature range. Also note that under these specific operating conditions the energy balance equation $Q(T,P,\mu,\chi,T_0) = 0$ exhibits two positive roots, namely, $T_{adb,1} \cong 940$ °C and $T_{adb,2} \cong 1025$ °C, thus implying that multiple adiabatic points may be possible in certain parameter ranges. The dry composition of synthesis gas generated in a single-stage reformer operating at the lower adiabatic point of 940 °C amounts to about 22% CO, 8% CO_2, 65% H_2, and 5% CH_4. The corresponding conversion of methane and the molar expansion coefficient are about 86% and 1.77, respectively, while the composition of the $CH_4/O_2/H_2O$ feed is determined as 39% CH_4, 19% O_2, and 42% H_2O. This leads to molar feed ratios of $[O_2]_0/[CH_4]_0 = 0.49$ and $[H_2O]_0/[CH_4]_0 = 1.1$, which are very

close to the ideal stoichiometries of the steam and oxygen reforming reactions, eqs 1 and 2. In this particular case, removal of about 25% of the produced carbon dioxide is sufficient for upgrading the reformer effluent to methanol makeup gas.

At high values of the methanol balance ratio the $CH_4/O_2/H_2O$ combination appears to be endothermic over the temperature range 800 °C $\leq T \leq 1100$ °C. This is illustrated in Figure 6, which displays the heat load as a function of temperature in a single-stage methane reformer operating at $P = 40$ atm, $\mu = 2.1$, $\chi = 5.0\%$, and $T_0 = 500$ °C. For example, it can be observed that a net heat input of ca. 25 kJ/mol$_{feed}$ will be required to produce equilibrium synthesis gas with the above composition characteristics at a temperature of 985 °C. In this case the dry composition of the effluent stream amounts to ca. 24% CO, 5% CO_2, 66% H_2, and 5% CH_4, whereas the corresponding methane conversion and molar expansion coefficient are 85.3% and 1.59, respectively. The composition of the $CH_4/O_2/H_2O$ feed is calculated as 44% CH_4, 17% O_2, and 39% H_2O, indicating that smaller amounts of steam and oxygen will have to be used at $\mu = 2.1$, as compared to the sub-stoichiometric conditions of $\mu = 1.85$ discussed above, at nearly the same methane conversion.
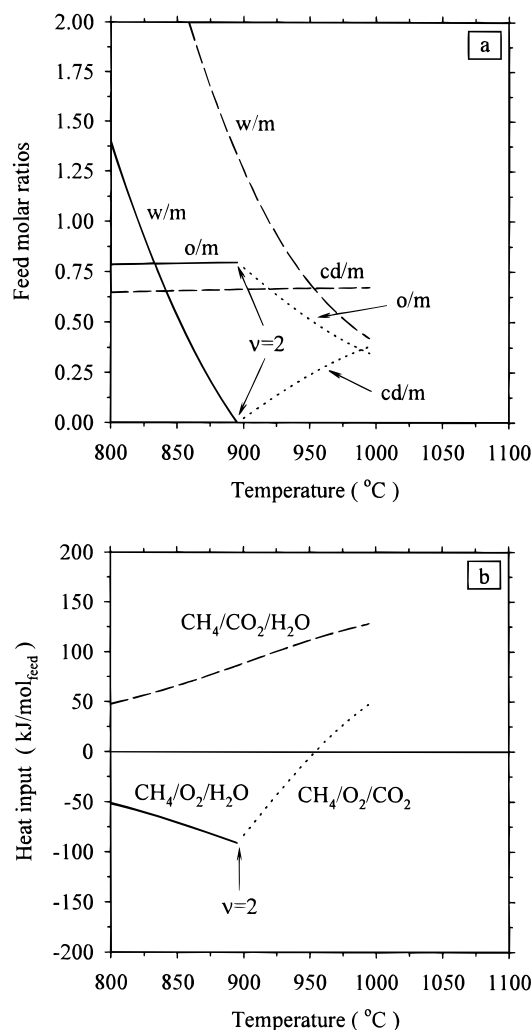
Figure 4. Temperature variation of (a) the feed molar ratios (w/m = $[H_2O]/[CH_4]_0$, o/m = $[O_2]/[CH_4]_0$, cd/m = $[CO_2]/[CH_4]_0$) and (b) the heat input requirements (kJ/mol$_{feed}$) of the $CH_4/O_2/H_2O$ (solid lines), $CH_4/O_2/CO_2$ (dotted lines), and $CH_4/CO_2/H_2O$ (dashed lines) ternary feeds. Operating conditions of the single-stage reformer: pressure P = 20 atm, methanol balance ratio μ = 1.2, dry methane slip fraction χ = 5%, and preheat temperature of T_0 = 500 °C. The maximum allowable temperature for carbon-free operation amounts to about 1000 °C. The binary CH_4/O_2 feed (corresponding to ν = 2 at the specified P, μ, and χ) is obtained at ca. 895 °C.

One method of supplying the heat required at near- or over-stoichiometric values of the methanol balance ratio is to use two separate reformers instead of a single reactor. In this two-stage process, which is named combined reforming and is exemplified by the syngas section of a Lurgi methanol plant (Farina and Supp, 1992), the overall heat load of the process is supplied to a furnace-heated conventional steam reformer, leading to partial conversion of methane, while the primary gas effluent stream is further processed with additional natural gas in an oxygen-fed secondary reformer to reach the final equilibrium conversion. Alternatively, the heat requirements of the primary reformer can be met by direct heat exchange with the hot effluent gas of the secondary reformer. Various designs of this gas-heated reforming (GHR) process are possible, involving fixed or fluidized-bed catalytic reactors (Peña et al., 1996 and references therein).

It should be pointed out that the stoichiometric oxygen-to-methane feed ratio in the $CH_4/O_2/H_2O$ combination and the carbon dioxide-to-methane feed ratio
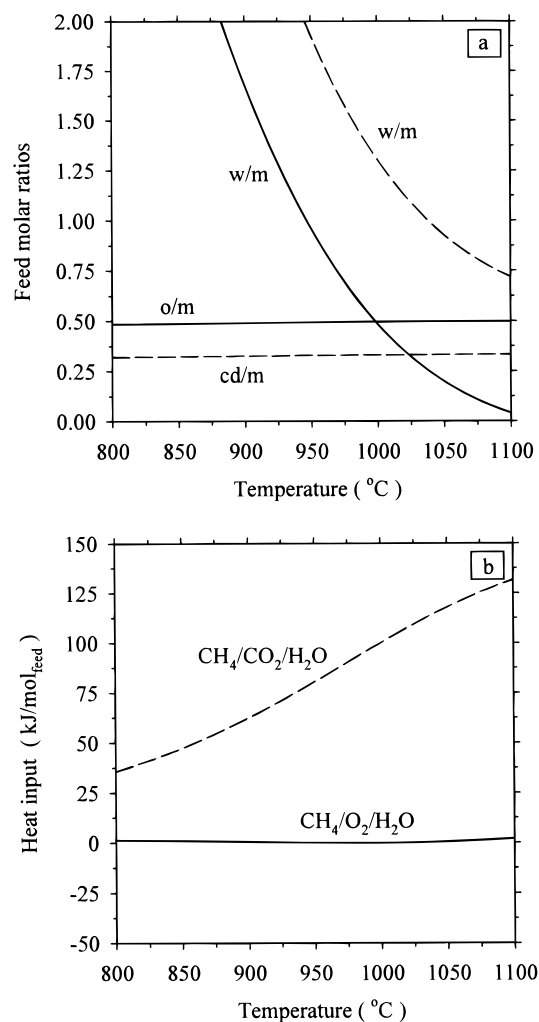

Figure 5. Temperature variation of (a) the feed molar ratios (w/m = $[H_2O]/[CH_4]_0$, o/m = $[O_2]/[CH_4]_0$, cd/m = $[CO_2]/[CH_4]_0$) and (b) the heat input requirements (kJ/mol$_{feed}$) of the $CH_4/O_2/H_2O$ (solid lines) and $CH_4/CO_2/H_2O$ (dashed lines) ternary feeds. Operating conditions of the single-stage reformer: pressure P = 40 atm, methanol balance ratio μ = 1.85, dry methane slip fraction χ = 5%, and preheat temperature T_0 = 500 °C. The maximum allowable temperature for carbon-free operation amounts to 1171 °C. The $CH_4/O_2/CO_2$ feed combination is not feasible under the specified reaction conditions.

in the $CH_4/CO_2/H_2O$ combination do not increase appreciably with temperature for fixed values of P, μ, and χ. On the contrary, in both cases the steam-to-methane feed ratio decreases rapidly with increasing values of temperature (see Figures 3b, 4a, 5a, and 6a).

6. Discussion

Based on atomic balance considerations, general expressions were derived relating the composition of $CH_4/O_2/H_2O$, $CH_4/O_2/CO_2$, and $CH_4/CO_2/H_2O$ ternary feeds to the methane conversion attained in each case. The expressions involve three parameters, namely, the methane−steam reforming index or methanol balance ratio μ, the methane−oxygen reaction index or partial oxidation ratio ν, and the methane−carbon dioxide reforming index ξ.

These parameters emerge from the atomic balance analysis of synthesis gas mixtures derived from methane-based feeds, and as such, they should be considered as natural reaction coordinates of methane reforming. In
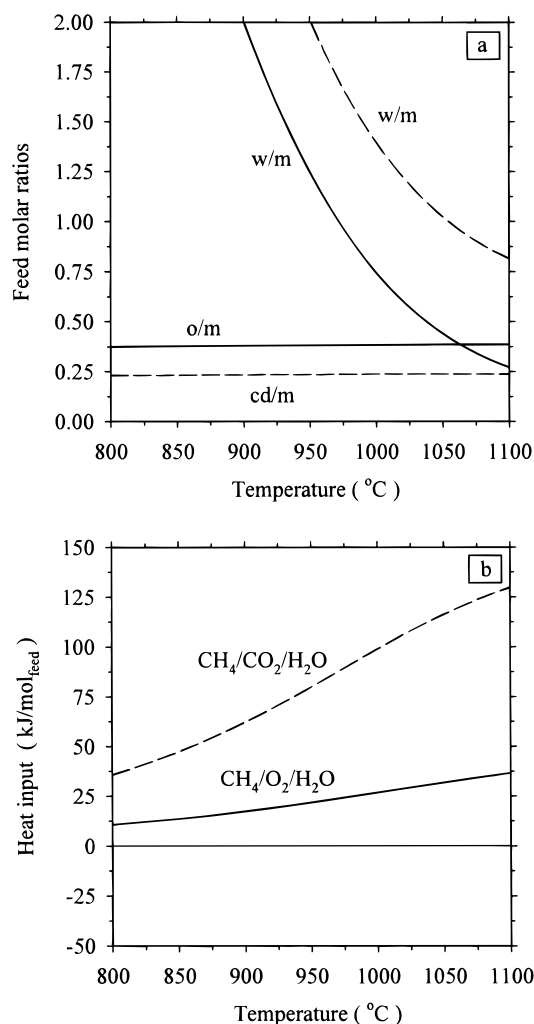
It is interesting to point out that the CH_4-CO_2 reforming index admits of a physical meaning similar to that of the CH_4-H_2O reforming index but with the roles of carbon and hydrogen atoms reversed: ξ is a direct measure of the relative difference between the concentrations of carbon monoxide (the C-atom-containing partial oxidation product) and water (the H atom deep oxidation product), scaled with the sum of the concentrations of hydrogen and water, being the H-atom-containing partial + deep oxidation products. This "reverse C—H" similarity between the parameters μ and ξ can be taken one step further. To produce methanol from a syngas mixture characterized by the ideal value of $\mu = 2$, water is first removed, and then the remaining components are fed into the methanol reactor where methanol synthesis takes place according to eq 5. It is easily verified that the chemical reaction obtained when reversing the roles of carbon and hydrogen atoms corresponds to the synthesis of formaldehyde according to the stoichiometry:

$$uH_2 + vH_2O + (u + 2v)CO = (u + v)HCHO + vCO_2$$

$$(35)$$
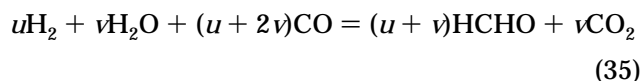
From eq 35 it is evident that the ideal syngas composition for formaldehyde production should satisfy the linear constraint $[CO] = [H_2] + 2[H_2O]$, which is equivalent to requiring that $\xi = 1$. In this theoretical case, carbon dioxide must be removed first from the syngas mixture (corresponding to the water removal step of methanol synthesis) before admitting the remaining components to a hypothetical formaldehyde synthesis reactor. Hence, by analogy to methanol, ξ may be called the formaldehyde balance ratio.

The CH_4-O_2 reforming index v provides a comparative measure of the total amount of the H-atom-containing partial + deep oxidation products ($H_2 + H_2O$) relative to the total amount of the C-atom-containing partial + deep oxidation products ($CO + CO_2$). As discussed above, this index can be expressed as an explicit function of μ and ξ using eq 20 and is identically equal to 2 for either a binary methane/oxygen feed or a ternary methane—carbon dioxide—water feed with a molar ratio $[H_2O]_0/[CO_2]_0 = 2$.

7. Conclusions

Application of the $CH_4/O_2/H_2O$ feed is always possible above the carbon limit curve when the methanol balance ratio is assigned values greater than or equal to 2, i.e., $2 \leq \mu < 3$, while in this case the $CH_4/O_2/CO_2$ combination is not feasible. On the other hand, utilization of the $CH_4/O_2/H_2O$ or $CH_4/O_2/CO_2$ feeds for syngas production with a methanol balance ratio in the range $1 < \mu < 2$ depends on the value of the operating temperature as compared to the temperature $T_{c;v=2}(\mu,\chi)$ defining the intersection point of the $v = 2$ boundary with the carbon limit curve. Specifically, when $T < T_{c;v=2}(\mu,\chi)$, the carbon boundary provides the minimum permissible pressure $P_c(T,\mu,\chi)$ above which application of a $CH_4/O_2/H_2O$ feed is possible. At higher temperatures, $T > T_{c;v=2}(\mu,\chi)$, utilization of the $CH_4/O_2/H_2O$ feed will be possible only for operating pressures exceeding the $P_{v=2}(T,\mu,\chi)$ limit value, while the feed combination $CH_4/O_2/CO_2$ is feasible only in the relatively narrow domain enclosed between the $P_c(T,\mu,\chi)$ and $P_{v=2}(T,\mu,\chi)$ pressure boundaries.

Figure 6. Temperature variation of (a) the feed molar ratios (w/m = $[H_2O]/[CH_4]_0$, o/m = $[O_2]/[CH_4]_0$, cd/m = $[CO_2]/[CH_4]_0$) and (b) the heat input requirements (kJ/mol$_{feed}$) of the $CH_4/O_2/H_2O$ (solid lines) and $CH_4/CO_2/H_2O$ (dashed lines) ternary feeds. Operating conditions of the single-stage reformer: pressure $P = 40$ atm, methanol balance ratio $\mu = 2.1$, dry methane slip fraction $\chi = 5\%$, and preheat temperature $T_0 = 500$ °C. The maximum allowable temperature for carbon-free operation amounts to 1187.5 °C. The $CH_4/O_2/CO_2$ feed combination is not feasible under the specified reaction conditions.

applications involving binary feeds of CH_4 with either one of H_2O, O_2, or CO_2, the parameters μ, v, and ξ define respectively intrinsic constants of the steam ($\mu = 3$), oxygen ($v = 2$), and carbon dioxide ($\xi = 1$) reforming reactions of methane.

The CH_4-H_2O reforming index provides a direct measure of the relative difference between the concentrations of the H-atom-containing partial oxidation product (H_2) and the C atom total oxidation product (CO_2), scaled with the sum of the concentrations of the C-atom-containing partial + deep oxidation products ($CO + CO_2$). It must be pointed out that although eq 6 is invariably used in the context of methanol production, the definition of μ and its meaning are independent of the methanol synthesis reaction. The stoichiometric requirements of the latter can also be described in terms of an alternative form of the methanol balance ratio

$$\hat{\mu} \equiv \frac{[H_2]}{2[CO]+3[CO_2]} = 1 \qquad (34)$$

For all values of the methanol balance ratio in the range $1 < \mu < 3$, equilibrium syngas mixtures can be generated starting from a $CH_4/CO_2/H_2O$ combination for pressures exceeding the carbon limit pressure $P_c(T,\mu,\chi)$. The composition of this feed can be deduced from the composition of the corresponding $CH_4/O_2/H_2O$ and $CH_4/O_2/CO_2$ mixtures after complete oxidation of a portion of methane with all oxygen to carbon dioxide and water.

Numerical calculations show that the $CH_4/O_2/CO_2$ feed combination is of practical interest only at low values of the methanol balance ratio, e.g., $\mu < 1.5$. Further conditioning of the syngas mixture by partial CO shift and carbon dioxide removal is needed in order to obtain a composition appropriate for methanol synthesis. On the other hand, the $CH_4/O_2/H_2O$ feed is endothermic for near- or over-stoichiometric values of the methanol balance ratio and under typical reaction conditions ($P = 20-40$ atm, methane slip < 5%, 800 °C $\leq T \leq 1100$ °C, $T_0 = 500$ °C), thus requiring the application of a two-stage process with primary and secondary reformers. Utilization of the $CH_4/O_2/H_2O$ feed in a single-stage adiabatic reactor is possible at intermediate values of the balance ratio, e.g., $\mu = 1.7-1.9$, leading to synthesis gas mixtures which can be upgraded to methanol makeup gas by partial carbon dioxide removal.

Acknowledgment

Nomenclature

B_j: total g-atom of the jth element per mole of feed

H_i: molar enthalpy of the ith component, kJ/mol_i

K_{rxn}: reaction equilibrium constant (rxn = str for steam reforming, cdr for carbon dioxide reforming, wgs for water–gas shift, and B for Boudouard)

n: molar expansion coefficient, mol_{prod}/mol_{feed}

P: pressure, atm (1 atm = 101.325 kPa)

Q: heat load per mole of feed, kJ/mol_{feed}

T: absolute temperature, K

$X[A]$: fractional conversion of reactant A (A = CH_4, O_2, CO_2, H_2O)

y_i: mole fraction of the ith component

Greek Symbols

μ: CH_4/H_2O reforming index or methanol balance ratio, defined in eq 6

ν: CH_4/O_2 reforming index or partial oxidation ratio, defined in eq 15

ξ: CH_4/CO_2 reforming index or formaldehyde balance ratio, defined in eq 18

χ: dry methane slip fraction, defined in eq 7

Subscripts

i: CH_4, O_2, CO, CO_2, H_2, H_2O

j: C, H, O

0: feed conditions

c: carbon limit boundary

$\nu = 2$: binary CH_4/O_2 feed mixture ($CH_4/O_2/H_2O-CH_4/O_2/CO_2$ boundary)

Appendix

Formulas expressing the fractional conversion of the reactants for each ternary feed in terms of the synthesis gas composition are presented below.

1. Feed $CH_4/O_2/H_2O$

$$X[CH_4] = \left[1 + \frac{[CH_4]}{[CO] + [CO_2]}\right]^{-1} \tag{1a}$$

$$X[H_2O] = \frac{1}{\nu - 2}\left[\nu\frac{[H_2]}{[H_2] + [H_2O]} - 2\right] \tag{1b}$$

2. Feed $CH_4/O_2/CO_2$

$$X[CH_4] = \left[1 + \frac{2[CH_4]}{[H_2] + [H_2O]}\right]^{-1} \tag{2a}$$

$$X[CO_2] = \frac{1}{2 - \nu}\left[2\frac{[CO]}{[CO] + [CO_2]} - \nu\right] \tag{2b}$$

3. Feed $CH_4/CO_2/H_2O$

$$X[CH_4] = \frac{1 + \mu}{4}\left[\frac{1 + \mu}{4} + \frac{[CH_4]}{[CO] + [CO_2]}\right]^{-1}$$

$$= \frac{1 + \xi}{2}\left[\frac{1 + \xi}{2} + \frac{2[CH_4]}{[H_2] + [H_2O]}\right]^{-1} \tag{3a}$$

$$X[CO_2] = \frac{1}{3 - \mu}\left[4\frac{CO}{[CO] + [CO_2]} - (1 + \mu)\right] \tag{3b}$$

$$X[H_2O] = \frac{1}{1 - \xi}\left[2\frac{[H_2]}{[H_2] + [H_2O]} - (1 + \xi)\right] \tag{3c}$$

Complete conversion of oxygen and negligible formation of higher hydrocarbons (C_{2+}) and oxygenates are assumed.

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