

*Chapter 4*

**THERMODYNAMIC ANALYSIS OF SYNTHESIS GAS  
AND HIGHER HYDROCARBONS PRODUCTION FROM  
METHANE**

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**Abstract**

This chapter focused on thermodynamic chemical equilibrium analysis using method of direct minimization of Gibbs free energy for all possible methane reactions with oxygen (partial oxidation of methane), carbon dioxide (CO<sub>2</sub> reforming of methane), steam (steam reforming of methane), and autothermal reforming. Effects of feed ratios (methane to oxygen, carbon dioxide, and/or steam feed ratio), reaction temperature, and system pressure on equilibrium composition, conversion, and yield were studied. In addition, operating regions of carbon and no carbon formation were also considered at various reaction temperatures and feed ratios in the equilibrium system. It was found that the reaction temperature above 1100 K and CH<sub>4</sub>/CO<sub>2</sub> ratio unity were favorable for synthesis gas production for methane – carbon dioxide reaction. The Carbon Dioxide Oxidative Coupling of Methane reaction to produce ethane and ethylene is less favorable thermodynamically. In addition, steam reforming of methane is the most suitable for hydrogen production from methane with low coke formation from thermodynamic point of view.

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## Nomenclature

$\hat{\phi}$	fugacity coefficient of the species in solution	$J$	total number of different atoms that are present in the system
$\Delta C_p^\circ$	standard heat capacity at constant pressure, $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$K$	equilibrium constant
$\Delta G_T^\circ$	standard Gibbs free energy change at temperature $T$ , $\text{kJ}\cdot\text{mol}^{-1}$	$n$	number of atom in the molecule
$\Delta H$	heat of reaction change, $\text{kJ}\cdot\text{mol}^{-1}$	$n$	number of mol of species, mol
$\Delta H^\circ_0$	standard heat of reaction change, $\text{kJ}\cdot\text{mol}^{-1}$	$N$	number of moles in reaction mixture, mol
$\Delta H^\circ_{298}$	standard heat of reaction change at 298 K, $\text{kJ}\cdot\text{mol}^{-1}$	OCM	Oxidative Coupling Methane
$v$	stoichiometric number	$P$	total pressure (atm)
ATR	Auto Thermal Reforming	$R$	universal gas constant, $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$b$	total population of atom in the system	$T$	temperature, K
$C$	carbon coke	WGS	Water Gas Shift
$f$	fugacity of pure species, atm	$X$	conversion, %
$f'$	fugacity of species of solution, atm	$y$	mol fraction
$\bar{g}$	partial molar Gibbs free energy, $\text{kJ}\cdot\text{mol}^{-1}$	$Y$	yield, %
$g$	Gibbs free energy of the pure species, $\text{kJ}\cdot\text{mol}^{-1}$	<b>Superscripts and Subscripts</b>	
$G$	total Gibbs free energy, $\text{kJ}\cdot\text{mol}^{-1}$	$o$	standard condition
$I$	number of chemical species	$298$	standard temperature 298K
$j$	sequence number of atoms	$i$	species $i$ th
		$T$	at temperature $T$

## Introduction

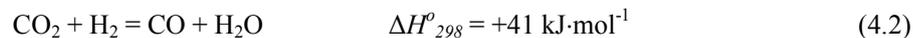
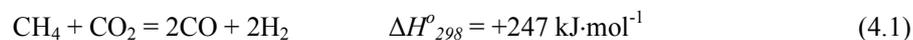
The utilization of CH<sub>4</sub> conversion to produce important chemicals, especially synthesis gas (H<sub>2</sub> and CO), provides several advantages from the environmental and energy perspectives. Natural gas is a fuel consisting of methane, ethane, carbon dioxide, H<sub>2</sub>S, and trace amounts of other compounds. It is highly desirable to utilize and to convert methane, typical component in natural gas, into higher value-added chemicals such as producing synthesis gas. Composition of natural gas varies widely from location to location, however, the largest component is methane.

Co-generation of synthesis gas and higher hydrocarbons from methane is important in utilization of the natural gas through reforming reactions. The reforming process yields synthesis gas with high H<sub>2</sub>/CO molar ratio and small amount of light hydrocarbons (C<sub>2</sub> hydrocarbons). The synthesis gas can be converted to liquid fuels by the Fischer-Tropsch process and also to various value-added chemicals, especially methanol and gasoline via the methanol-to-gasoline (MTG) process. The synthesis gas is also the main source of hydrogen for refinery processes and ammonia synthesis. Use of CO<sub>2</sub> as an oxidant for the selective oxidation of methane may also be beneficial, because it is expected that the replacement of O<sub>2</sub> with CO<sub>2</sub> inhibits the gas-phase non-selective oxidation and thus increases the selectivity to higher hydrocarbons. Previously, the thermodynamic calculation on equilibrium conversion of CH<sub>4</sub> to C<sub>2</sub> hydrocarbons (C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>) showed that the equilibrium conversion increased with rising temperature or CO<sub>2</sub>/CH<sub>4</sub> feed ratio (Istadi & Amin, 2005). However, thermodynamic equilibrium studies on the co-generation of synthesis gas and C<sub>2</sub> hydrocarbons from methane using various reforming processes have been conducted separately. Accordingly, the results of thermodynamic studies can identify the constraints placed in a reacting system and can provide the recommendation of suitable operating conditions for the catalytic reacting system theoretically.

Synthesis gas production through reforming of methane can be carried out in four different ways, i.e.:

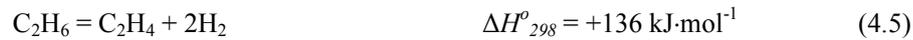
### 1. Methane – carbon dioxide reactions, contains:

#### a. Carbon dioxide Reforming of Methane (CORM)

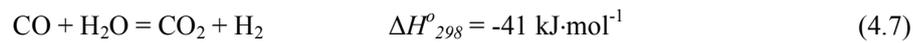
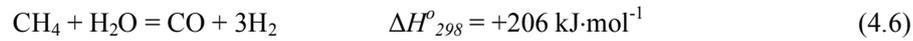


#### b. Carbon dioxide Oxidative Coupling of Methane (CO<sub>2</sub> OCM)



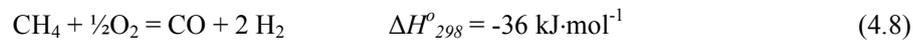


## 2. Methane – steam reactions (Steam Reforming of Methane – SRM)

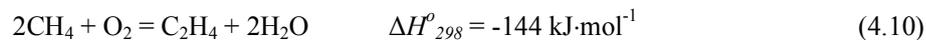
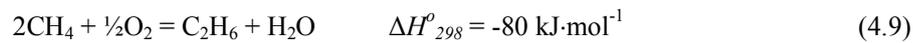


## 3. Methane – oxygen reactions, contains:

### a. Partial Oxidation of Methane (POM)



### b. Oxidative Coupling of Methane (OCM)



## 4. Auto Thermal Reforming (ATR)

Autothermal reforming (ATR) uses oxygen and carbon dioxide or steam in a reaction with methane to form syngas. The reaction takes place in a single chamber where the methane is partially oxidized. The reaction is exothermic due to the oxidation. The reactions can be described in the following equations,

using  $\text{CO}_2$ :



and using steam:



Research studies on synthesis gas production process were mainly focused on catalyst performance studies and the output of these studies cannot be easily compared due to the big differences among the basic process variables (feed composition, pressure, and temperature). However, the effects of temperature, pressure, or feed ratio on equilibrium conversions, yields,

and compositions can be analyzed via a thermodynamic analysis. The study on thermodynamic equilibrium composition has been used in investigating the feasibility of many types of reaction. Vasudeva et al. (1996) computed equilibrium compositions for steam reforming of ethanol to examine the viability of the process. Similarly, Chan and Wang (2000) examined the thermodynamic equilibrium compositions for simultaneous partial oxidation and steam reforming of natural gas. Global reaction balances and chemical equilibrium of steam reforming and partial oxidation to produce hydrogen were studied by Lutz et al. (2003; 2004) for the same objective. Thermodynamic chemical equilibrium on methane pyrolysis process were also reported by Guéret et al. (1997) using the direct Gibbs free energy minimization. Similar method was also performed by Lwin et al. (2000) on the hydrogen production from steam-methanol reforming. The method of the direct minimization of Gibbs free energy of a system was used by Chan and Wang (2000), Tang and Kitagawa (2005) and Guéret et al. (1997) for solving equilibrium thermodynamic analysis of supercritical water gasification of biomass, steam reforming of ethanol for hydrogen production, and methane pyrolysis, respectively. Meanwhile, the minimization of Gibbs free energy using Lagrange's multiplier was implemented by Douvartzides et al. (2003), and Chan and Wang (2000; 2004) for solving thermodynamic equilibrium analysis of solid oxide fuel cells, natural-gas fuel processing for fuel cell applications, autothermal methanol reformer, and catalytic combustion of methane, respectively.

This chapter focuses on thermodynamic chemical equilibrium analysis of all possible  $\text{CH}_4$  reactions in the co-generation of synthesis gas and/or  $\text{C}_2$  hydrocarbons through carbon dioxide reforming of methane, steam reforming of methane, partial oxidation of methane, and autothermal reforming. In this analysis, effect of various conditions, i.e. temperature, reactants feed ratio and system pressure, on chemical equilibrium (conversion, yield, and composition) are discussed. In addition, effects of reactant feed ratio and temperature on carbon formation in the reaction system at equilibrium are also investigated. Through the thermodynamic equilibrium analysis, the feasibility of methane reactions in producing synthesis gas could be addressed theoretically.

## Technique for Thermodynamic Chemical Equilibrium Calculation

There are two common ways to express the chemical equilibrium. One is based on equilibrium constants ( $K$ ), while the other is based on the minimization of Gibbs free energy (Smith et al., 2001). In recent years, thermodynamic equilibrium results utilizing Gibbs free minimization technique have been reported for methane reforming to syngas via various routes. There are two alternative methods for solving the minimization of Gibbs free energy:

1. Direct minimization, and
2. The use of Lagrangian multiplier

The direct minimization of Gibbs free energy was reported to be effective for complicated chemical equilibrium problems. The method, which is a default method in *Chemkin*, was used to solve the chemical equilibrium system at various temperatures, feed ratios, or system pressures without requiring detailed information about the homogeneous or heterogeneous