

## Kinetic modeling and simulation of methanol synthesis model

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### Abstract

*Chemical process optimization is significant in the sense of predicting overall reaction scheme which may lead to better reactor design. Kinetic modeling is a behavior for designing and optimization of chemical process. A chemical process often consists of several equilibrium reactions. It's not an easy task to simulate equilibrium reactions in a conventional method. By considering reaction co-ordinate in a reaction scheme, it's easier to find out the effect of reactant and products in such reactions whether it's a reversible or irreversible. Here methanol synthesis model has taken into consideration for optimization by using reaction co-ordinate system. The main purpose of this research is to investigate methanol synthesis model which has done by simulation of gaseous equilibrium synthesis at ambient pressure.*

**Keywords:** Methanol Synthesis Model, Modeling and simulation, equilibrium reaction, reaction coordinate.

### Introduction

Imagine a fuel that can reduce harmful emissions and boost domestic economy around the globe. A fuel that commit our working demand which must clean, sustainable and made from abundant resources. Methanol is that type of fuel, a globally accessible fuel that already widely used by many countries around the world and it's making headline around the globe. Methanol is the simplest alcohol fuel and the source of energy for fuel cell. It's also a basic chemical building block, used in the production of wide range of commodities which touch our daily lives from plastics, solvents to windshield washer fluid. Methanol is producing from wide range of raw materials including biomass, natural gas, coal and even pollution emitted from factories and power plants. Countries around the world already using innovative sources to produce methanol fuel like using the waste from paper production called black liquor to create diesel fuel replacement, byproducts of bio-diesel production are made into bio-methanol, Carbon cycle international is using CO<sub>2</sub> emissions from Geo thermal power plant and renewable hydrogen for making methanol. As a basic alcohol, methanol is soluble, biodegradable, and readily absorbed in water. As compared to traditional gasoline, methanol produces less toxic and harmful emissions. At the same time it's a cheaper than gasoline. Due to all of reasons mentioned above, kinetics of methanol synthesis is growing dramatically among the researchers.

**Background:** The issue of sustainability is that which concerns many industries and given the option of moving from consumption of fossil fuels towards renewable/cleaner energy makes the synthesis of methanol very important. Methanol is the simplest alcohol (one carbon backbone). It is a clear, colorless liquid with a characteristics alcohol odor.

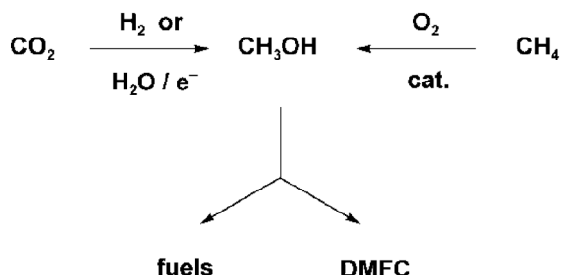
There are various means of producing methanol and these includes the anaerobic metabolism of many varieties of bacteria (natural), pyrolysis of wood, and most importantly from fossil fuel based synthesis gas, which is the main method of producing methanol industrially. According to the 1994 Nobel Prize in Chemistry winner, George Andrew Olah<sup>4</sup>, in terms of energy storage, methanol can replace fossil fuels, in what is now referred to as the methanol economy. Apart from the current use of methanol today as chemical feedstock for producing useful chemical products like, acetic acid.

**Available process routes:** From 1830 up until the mid-1920, the most abundant sources of methanol were wood derived and natural methanol. But destructive distillation wood was main carrier for the first mercantile production of methanol; hence methanol is sometimes called wood alcohol<sup>4</sup>. Apart from wood pyrolysis, there are various means of producing methanol and these includes the anaerobic metabolism of many varieties of bacteria (natural), and most importantly from fossil fuel based synthesis gas, which is the main method of producing methanol industrially<sup>4</sup>. The synthesis gas that was first used for the production of methanol was manufactured by coke gasification. In recent times, the synthesis gas is now almost invariably produced by steam reforming or partial oxidation of hydrocarbons, usually natural gas<sup>7</sup>.

Synthetic route for methanol production was first commercialized by BASF in Germany. Synthesis gas reaction which is a mixture of hydrogen and carbon dioxides. The reaction occurred over a zinc chromate catalyst at relatively high temperatures of 300 to 400°C and high pressures (250 to 350atm). Synthesis gas was derived from coal via the water gas reaction<sup>5</sup>. By 1965, a state-of-the-art, high pressure

methanol unit typically had the following characteristics: Capacity, 70 to 150 thousand tons per year; Operating pressure, 350atm; Consumption, 11-12 million kcal per ton of methanol (130-140 ft3 of natural gas per gallon).

Based on the methanol economy, methanol is produced in so many ways. Carbon dioxide is one the major causes of global warming. It occurs due to exhaust black emissions from vehicle and industries, also from power plants and burning of fossil fuels. It could be fruitful if carbon dioxide is converted into methanol which can be used as a carrier fuel. Such schematic of reaction is given below



**Figure-1:** Production of methanol from atmospheric carbon dioxide or from natural gas (methane), and its use as a fuel. DMFC Direct Methanol Fuel cell<sup>1</sup>.

## Materials and methods

Methanol production is carried out in two steps in a typical chemical plant. Firstly, methane is converted into synthesis gas which includes CO, CO<sub>2</sub>, H<sub>2</sub> and hydrogen. Catalytic synthesis of methanol from the synthesis gas is second step<sup>6</sup>. These steps can be conducted in various ways and technologies with respect to desired application. Three reactions are taking into consideration for further calculation and optimization of methanol synthesis model which are given below

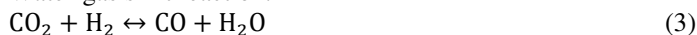
Hydrogenation of carbon monoxide:



Hydrogenation of carbon dioxide:



Water-gas shift reaction:



Three reactions which are used in methanol synthesis model are not independent. Equation 2 can easily be reproduced by algebraic manipulation of equations 1 and 3 and so forth. Therefore one of the equations can be dropped. The complete system for the methanol synthesis therefore only consists of two independent reactions.

Considering the reaction takes place at standard atmospheric pressure (1atm) and being it constant, we are going to investigate the temperature dependence of the equations and to calculate the reaction constants (K1 and K2) of both equations

by using Gibbs minimization involving temperature dependent Heat capacities and heat of formations.

Equations which are needed for calculation are given below,

$$\Delta \widetilde{h}_R = \sum_{i=1}^n \vartheta_i * \Delta \widetilde{h}_{f,i} \quad (4)$$

$$\frac{G}{RT} = \frac{\Delta h_{R,T}}{T} - \Delta S_{R,T} \quad (5)$$

$$C_{P,T} = A + BT + CT^2 + DT^{-2} \quad (6)$$

Equation-6 represents the temperature dependent heat capacities equation, where A, B, C and D different for different components. All of the values taken at gaseous state for calculation.

The equilibrium mole fractions have to be expressed in terms of reaction-progress variables. This way, more than two simultaneous reactions can be easily calculated. Reaction-progress Variables measure the extent to which a reaction has taken place. Equation (1) and (3) are considered for optimization, and the two needed variables are labeled as  $r_1$  and  $r_2$ .

**K<sub>1</sub> and K<sub>2</sub> Calculation:** To determine the equilibrium constants, we use the heat capacities and the heat of formation and the entropy of formation of the individual components at standard conditions. By using the calculated parameters, the equilibrium constants at different temperatures was determined and shown in the following Table-1.

**Table-1:** Calculated K values for different temperature.

Temperature (K)	K1	K2
300	16416.20377	91795.71789
350	86.08652622	8762.484951
400	1.557211925	1527.359083
450	0.065540479	397.8014543
500	0.005048206	137.0961567
550	0.000609229	57.85271427
600	0.000103688	28.38620255
650	2.311E-05	15.62673055
700	6.3916E-06	9.40956172

**Reaction coordinate:** Now that we have calculated the equilibrium constants for both the reactions at different temperatures in Kelvin, we have to establish the molar fractions

of the reaction components at equilibrium condition which done by using reaction co-ordinates ( $r_1$  and  $r_2$  for reactions 1 and 3 respectively). The reaction constants are represented by the ratio of the product of the molar fractions of the product to the product of the molar fraction of the reactants with the partial pressures at the reactant and product. In this case the pressure being constant, the partial pressures are the same in the reactants and the product hence can be neglected by mathematical cancelation. The relation can be seen below.

$$K_1 = \frac{Y_{CH_3OH}}{Y_{CO} * Y_{H_2}^2}$$

$$K_2 = \frac{Y_{CO_2} * Y_{H_2}}{Y_{CO} * Y_{H_2O}}$$

Since we have to determine the molar fractions of the components at equilibrium conditions, we have to develop a reaction co-ordinate system for the chemical reactions involved in the process, which can be seen the Table-2.

**Table-2:** Reaction coordinate system

Component	Molar Fraction	
	Initial	Final
CO	1	$1 - r_1 - r_2$
H <sub>2</sub>	1	$1 - 2r_1 + r_2$
CH <sub>3</sub> OH	0	$r_1$
CO <sub>2</sub>	0	$r_2$
H <sub>2</sub> O	1	$1 - r_2$
Total	3	$3 - 2r_1$

From the above mentioned Table-2, the equations can be rewritten as

$$K_1 = \frac{r_1 * (3 - 2r_1)^2}{(1 - r_1 - r_2) * (1 + r_2 - 2r_1)^2}$$

$$K_2 = \frac{r_2 * (1 + r_2 - 2r_1)}{(1 - r_1 - r_2) * (1 - r_2)}$$

**Solver Application:** The use of the solver to specify the progress-rate variables  $r_1$  and  $r_2$  by reduction of the sum of all errors of the equilibrium constants turned out to be problematic. The solver won't reduce both (or all three) errors, but rather only reduce one to a minimum. That's why the resulting calculations involved a repeated use of the solver routines, by first minimizing one error, then the other, and so forth. In order to satisfy both equations simultaneously we need to assume  $r_1$  and  $r_2$  values, so that it will give same  $K_1$  and  $K_2$  values

which we calculated by using temperature dependence heat capacity equation. Used the constraints  $t$ ,  $0 < r_1, r_2 < 1$ ,  $r_1$  and  $r_2$  cannot be higher than 1 and lower than 0.

**Molar fraction calculation:** By using  $r_1$  and  $r_2$  values obtained by solver application, we can now calculate the molar fractions of the individual components of the reactions at different temperatures.

**Table-3:** Molar fraction calculation

Component	Molar Fraction
CO	$1 - r_1 - r_2 / (3 - 2r_1)$
H <sub>2</sub>	$1 - 2r_1 + r_2 / (3 - 2r_1)$
CH <sub>3</sub> OH	$r_1 / (3 - 2r_1)$
CO <sub>2</sub>	$r_2 / (3 - 2r_1)$
H <sub>2</sub> O	$1 - r_2 / (3 - 2r_1)$

It is important to note that total molar concentration is always one during the calculation of molar fraction. Which makes the assumption correct.

## Results and discussion

The plots displayed above in the results section represent the molar fractions of the reaction components at different temperatures. By examining the plots, it can be seen that the plots have a similar trend with minor mole fraction differences. The temperature dependence of the equilibrium constants can be seen in the Table-1, suggesting that the temperature of the reaction process is a very important parameter that has to be considered. The similar trend of the curves as seen in the Figure-1 and Figure-2, suggest that the iterative solver setup in excel is a good option to determine the equilibrium of the gaseous reactions, provided having a logical assumptions at the initial step of the approximation.

## Conclusion

The predicted molar fractions are just estimations and in reality the estimations can change due to many factors. Some factors being the assumptions and the multiple solutions available while using the solver, because the solution being a mathematical.

**Notations:**  $\Delta \widetilde{h}_R$  = Enthaphy of reaction (KJ/mol),  $\vartheta_i$  = Stoichiometric Coefficient,  $\Delta \widetilde{h}_{f,i}$  = Enthaphy of formation (KJ/mol),  $\frac{G}{RT}$  = Gibbs Energy (KJ),  $\Delta S_{R,T}$  = Entropy of reaction (J/molK).

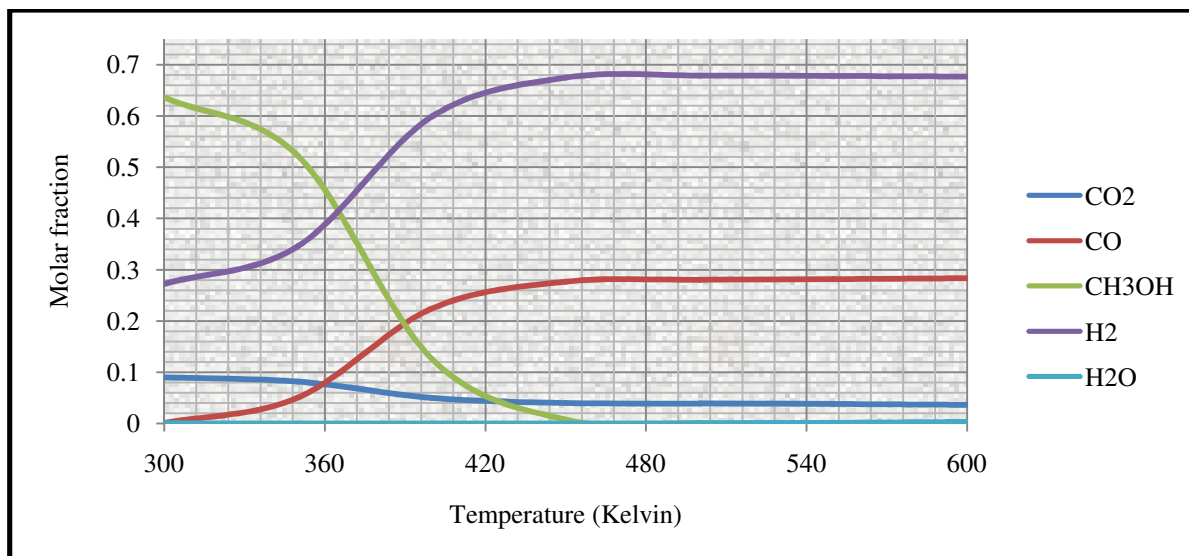


Figure-2: Plot of excel spreadsheets calculations

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