Generalized thermodynamic analysis of methanol synthesis: Effect of feed composition

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ABSTRACT

Synthesis of methanol is one of the ways of conversion of the greenhouse gas CO$_2$ into an useful chemical. Methanol is synthesized from a feed mixture comprising of primarily CO, H$_2$, and CO$_2$. The objective of the present work is to study the effect of feed composition on synthesis of methanol. First, the conditions under which the kinetic approach and the thermodynamic approach are equivalent are established. The performance characteristics of the reactor under single phase and two phase conditions are then analyzed using the thermodynamic approach. The Gibbs free energy minimization approach is implemented using Aspen Plus for this purpose. The effect of feed composition on the overall conversion of CO + CO$_2$ to methanol and conversion of CO$_2$ is depicted as contour plots for isothermal and adiabatic operations. These can be viewed as performance characteristics of the reactor which aid in selection of suitable feed composition for maximum methanol productivity and CO$_2$ utilization.
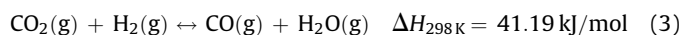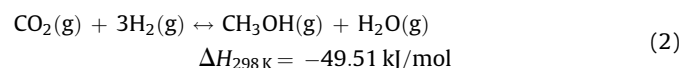
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1. Introduction

Fossil fuel burning is an important source of anthropogenic CO$_2$ production. The carbon dioxide (CO$_2$) from the flue gases of thermal plants can be captured in several ways (e.g. chemical absorption) which can effectively decrease the rate of accumulation of CO$_2$ in the atmosphere. One of the methods of capture is to convert the CO$_2$ to a useful chemical, one among them being methanol. Methanol is an industrially important chemical as it acts as a feedstock for the synthesis of various chemicals. It is also directly used as an antifreeze or a solvent [1]. It can be blended with gasoline and used as an automobile fuel [2]. Life cycle analysis of methanol synthesis from different routes has been performed in [3,4]. These studies have also considered mixing CO$_2$ recovered from flue gases of thermal power plants with syngas in the production of methanol. They show that adding CO$_2$ results in a reduced energy consumption as well as a lower environmental impact.

The first catalyst used for large scale production of methanol was developed by BASF in 1923. This was a Cr$_2$O$_3$/ZnO catalyst and the reaction was carried out at about 30 MPa and 573–673 K [5]. Later in 1960, the availability of technology to produce sulphur free synthesis gas made it possible to use the more selective Cu/ZnO/Al$_2$O$_3$ catalyst. This catalyst made it possible for synthesis gas hydrogenation to methanol to be carried out under milder conditions at lower pressures of 6–8 MPa and temperatures in the range of 523–553 K [6]. This is called the ICI low pressure process [7]. Currently, Cu/ZnO/Al$_2$O$_3$ based catalysts are used for syngas hydrogenation to methanol. This has a very high selectivity (99.9%) toward methanol [5]. However these cannot be used at temperatures above 573 K and are highly sensitive towards poisoning by sulphur [8].

The important reactions involved in the production of methanol from synthesis gas are [9]:

$$CO(g) + 2H_2(g) \leftrightarrow CH_3OH(g) \quad \Delta H_{298\,K} = -90.70\,kJ/mol \quad (1)$$

$$CO_2(g) + 3H_2(g) \leftrightarrow CH_3OH(g) + H_2O(g)$$
$$\Delta H_{298\,K} = -49.51\,kJ/mol \quad (2)$$

$$CO_2(g) + H_2(g) \leftrightarrow CO(g) + H_2O(g) \quad \Delta H_{298\,K} = 41.19\,kJ/mol \quad (3)$$

The first two reactions are hydrogenation of CO and CO$_2$ to methanol, i.e. methanol synthesis reactions while the third is the reverse water gas shift reaction (RWGS). The reactions are

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Nomenclature

CO_{in}	moles of carbon monoxide in the inlet feed
CO_{out}	moles of carbon monoxide in the outlet
$CO_{2\ in}$	moles of carbon dioxide in the inlet feed
$CO_{2\ out}$	moles of carbon dioxide in the outlet
CO/H_2	ratio of moles of carbon monoxide to hydrogen
CO_2/H_2	ratio of moles of carbon dioxide to hydrogen
S.N.	stoichiometric number
X_{CO+CO_2}	conversion of CO + CO2
X_{CO}	conversion of CO
X_{CO_2}	conversion of CO2
τ	residence time (s)

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reversible and are limited by thermodynamics. The methanol synthesis reactions are exothermic and proceed with decrease in number of moles. Hence lower temperatures and higher pressures drive the equilibrium of the methanol synthesis reactions forward in accordance with Le Chatelier's principle. The reverse water gas shift reaction is an endothermic reaction and proceeds with no change in the number of moles [9].

Since the methanol synthesis reactions are restricted by equilibrium considerations, the conversion per pass through a packed bed reactor is low. Hence, there is a need to recycle the unconverted reactant gases to make the process economical [6]. Moreover, as the methanol producing reaction is strongly exothermic, it is essential to provide a suitable cooling mechanism to remove the excess heat produced. This is important to avoid catalyst deactivation from sintering at higher temperatures [10]. Recycling and cooling hence account for the major operating costs for conventional methanol synthesis [6]. There is hence a significant scope for optimizing the operation of the process.

Thomas and Portalski predicted the optimum conditions for methanol synthesis after studying the effect of temperature and pressure on the heat of reaction and the equilibrium constants [11]. Chemical equilibria in methanol synthesis were studied by Graaf et al. on the basis of thermo-chemical data and assuming ideal gas conditions [12]. Correction for non-ideality was performed using a Soave–Redlich–Kwong (SRK) equation of state. Chang et al. studied equilibrium compositions arising in the synthesis of methanol from CO [13]. The thermodynamics of methanol synthesis has also been studied in detail by Skrzypek et al. [14]. They examined the effect of temperature, pressure and various initial feed composition of reactants on the extent of equilibrium conversion of CO2 hydrogenation and reverse water gas shift reactions [14].

Methanol synthesis from CO and CO2 is favored thermodynamically at high pressures and low temperatures [9]. Under these conditions, the condensation of products such as methanol and water is also possible. The possibility of liquid phase formation was predicted and the equilibrium compositions for a chosen feed (H2/CO/CO2/CH4 = 74/15/8/3 vol.%) at 30 MPa and 473 K have been obtained by Chang et al., Castier et al., Gupta et al., Avami and Saboohi, Jalali and Seader [13,15–18]. These authors focused on developing methods and algorithms to obtain the equilibrium compositions at conditions which favor methanol condensation. Bennekom et al. used a thermodynamic model based on the modified SRK equation of state to predict the composition of vapour and liquid phases in phase and chemical equilibrium for methanol synthesis at high pressure and low temperature [19]. The algorithm developed by these authors involved integration of mole balance equations along the length of a long reactor and hence could predict the dew point as a function

of conversion of CO + CO2. The model results were also validated with their experimental data on high pressure methanol synthesis in a packed bed reactor [20].

The compositions and conversions obtained at equilibrium are strongly influenced by the initial composition of the feed as observed in Skrzypek et al. [14]. The reverse water gas shift reaction offers a mechanism for the interconversion between CO and CO2. It is hence important to study the effect of feed compositions on equilibrium conversion. The work of Skrzypek et al. which considers effect of feed gas composition does not consider formation of liquid phase [9,14]. Most of the other thermodynamic studies on methanol synthesis have been limited to feed gas of specific composition. Hence, the objective of the present work is to analyze the effect of all possible combinations of feed gas compositions on reactor performance encompassing both single and two phase regions.

First, a rate based approach is compared with an equilibrium approach for methanol synthesis using Aspen Plus. The conditions under which the predictions from both the approaches agree are established. Under these conditions, the thermodynamic model is then used to predict the influence of feed composition on the reactor performance viz. reactor outlet temperature, conversion of CO, conversion of CO2 and conversion of CO + CO2. This performance analysis is done first for single phase and then for two phase conditions.

2. Comparison of kinetic and thermodynamic approaches

2.1. Kinetic modeling of single phase methanol synthesis

Understanding the kinetics of the reaction is important to determine the conditions at which the reactions are kinetically limited and those when it is limited by equilibrium. Vanden Bussche and Froment proposed Langmuir–Hinshelwood–Hougen–Watson (LHHW) based kinetic model to predict the performance of methanol synthesis reactors [21]. This kinetic expression was implemented in Aspen Plus plug flow reactor block RPLUG. This implementation in Aspen Plus was done following the procedure detailed by Robinson [22]. A pseudo-homogeneous model is used to describe the packed bed reactor. The model assumes negligible axial mixing, uniform temperature and concentration in the radial direction. The temperature and concentration of the gas and catalyst are assumed to be the same, i.e. interphase transport resistances are neglected. Deactivation of catalyst is also not considered [23]. In the kinetic model, partial pressures instead of fugacities are used since both give almost identical results [21]. Hence, an ideal physical property model is used in the Aspen RPLUG block.

2.2. Thermodynamic modeling of single phase methanol synthesis

The methanol synthesis reactions are reversible exothermic reactions. Thermodynamics limits the conversion of the reactants CO, CO2 and H2 to methanol. The total Gibbs free energy minimization approach can be used for obtaining the equilibrium compositions. One of the advantages of this approach is that it requires the knowledge of only the participating species in the reaction. No particular knowledge of the stoichiometry of the reactions involved is required [24]. The total Gibbs energy minimization of the reaction mixture is performed using the RGIBBS block of Aspen Plus. The species assumed to be present in the reaction mixture, i.e. in the effluent stream are CO, CO2, H2, H2O and CH3OH. The Soave–Redlich–Kwong property model in Aspen Plus along with the binary interaction parameters from Bennekom et al. are used in the simulation [19]. Sensitivity analysis feature in Aspen Plus is used to study the effect of variation of temperature.