Thermodynamics analysis, process modeling, simulation, and economics of direct and indirect route for methanol production

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Abstract

The concentration of greenhouse gases (CO2 and CH4) is increasing in the atmosphere which is a crucial subject that must be addressed. The emission of greenhouse gases must be reduced or captured and converted to useful chemicals. The synthesis of a valuable chemical like methanol from greenhouse gas is a very important due to its application as a building block in the synthesis of wide range of chemicals. So, present work emphasizes on the thermodynamics analysis, process modeling, simulation, and economics of the direct (CO hydrogenation) and indirect (CO2 hydrogenation) route for methanol production. A thermodynamic model has been developed to get a better insight into the effect of process parameters on conversion and selectivity. Based on thermodynamic, an optimum operating condition for maximizing the conversion of CO2 & H2 and methanol yield have been suggested with respect to commercial operation. Further, process modeling, and simulation of both direct and indirect route using Aspen plus simulator has been established based on literature and industrial data. This modeling & simulation study can be used for accurately predicting the process performance with respect to the real data. Moreover, a comparative economic analysis for methanol production via direct and indirect route has been calculated to envisage net present value (NPV). This study illustrated the optimum value of product based on the effects of reactions parameters, process conditions and economics of the processes.

**Keywords**: Carbon dioxide, Hydrogen, Methanol, process modeling, simulation, economics.

* 1. Introduction

Greenhouse gas emissions are incessantly increasing leading to the global climate change, affecting humans as well as environments. Most greenhouse gas emissions are associated with consumption of fossil fuels due to increasing industrial activities, deforestation etc. Excessive CO2 (major component of greenhouse gases) emission has been posing serious environmental issues in recent decades (Bisotti et al., 2022). To mitigate the environmental impact, valorization of the emitted CO2 into chemicals and fuels such as methanol, dimethyl ether etc. has been widely investigated. In this context, commercially, methanol is produced from a mixture of CO/CO2/H2 (synthesis gas containing ca. 3 vol% CO2) using a Cu/ZnO/Al2O3 catalyst at typical reaction conditions of 503–543 K and 50–120 bar pressure (Bisotti et al., 2022; Cui et al., 2019). Also, CO2 hydrogenation to methanol production route is explored by many researchers. Several experimental studies reveal that CO2 in the synthesis gas is an important carbon source for methanol synthesis (Kiss et al., 2016; Nyári et al., 2020; Nyári et al., 2022). Three main reactions involved during methanol production process are, namely CO2 hydrogenation Eq.(1), CO hydrogenation Eq.(2), and reverse water gas shift reaction Eq.(3).

So, in this work, direct (CO hydrogenation) and indirect route (CO2 hydrogenation) for methanol production is evaluated by study of thermodynamics, process modeling & simulation and economics of the processes. Thermodynamics study and process modeling & simulation is carried out using Aspen Plus V12 simulator. Economics for methanol production by direct & indirect route has derived based on assumptions and cost indexes.

* 1. Methodology
     1. Thermodynamic study

Thermodynamic analysis involves the determination of phase and equilibrium compositions of a particular system at specified operating conditions. Gibbs free energy minimization technique is used for the determination of equilibrium configuration of the system (Cui et al., 2019). Aspen Plus Simulator is used to predict equilibrium composition using Gibbs phase reactor. Peng-Robinson (PR) equation of state was applied for components involved in the system. Species CO2, H2, H2O, CO and CH3OH were considered for the thermodynamic study. Stoichiometric number (SN) ratio for direct and H2/CO2 feed ratio for indirect process was considered for methanol production.

The feed conversion, methanol yield and SN ratio are evaluated by Eq.(4) to Eq.(9).

* + 1. Process modeling and simulation

A comparative study of direct (CO hydrogenation) and indirect (CO2 hydrogenation) methanol production processes were performed using Aspen Plus based on industrial plants (Kiss et al., 2016; Nyári et al., 2020; Nyári et al., 2022).

* + 1. Economic analysis

Economic evaluation is conducted based on a variety of variables such as plant location, production capacity, project lifetime. Several assumptions have been made to perform the cost estimation of the project. Capital cost investment (CAPEX), operating cost (OPEX), and revenue of the plant (based on the projected methanol price) are three major parameters in the economic assessment of these processes (Zhang et al., 2017).

* 1. Results and discussion
     1. Thermodynamic analysis of direct and indirect process for methanol production
        1. Effect of temperature on feed conversion and product yield

(a)

Figure 1. conditions: P= 50 bar, (a) (direct) SN=2, (b) (indirect) H2/CO2=3 mol/mol

* + - 1. Effect of pressure on feed conversion and product yield

Table 1. reaction conditions: T= 523 K, direct: SN=2, indirect: H2/CO2=3 mol/mol

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | Direct Process | | | | Indirect Process | | |
| P (bar) | XCO2 | XH2 | XCO | YCH3OH | XCO2 | XH2 | YCH3OH |
| 10 | 2.6 | 7.3 | 8.2 | 7.6 | 16.89 | 6.71 | 1.62 |
| 20 | 2.7 | 21.6 | 24.9 | 22.6 | 18.69 | 9.91 | 5.53 |
| 30 | 2.8 | 34.6 | 40.3 | 36.3 | 21.10 | 13.82 | 10.17 |
| 40 | 3.1 | 44.8 | 52.2 | 47.0 | 23.79 | 17.75 | 14.73 |
| 50 | 3.3 | 52.5 | 61.2 | 55.1 | 26.55 | 21.50 | 18.98 |
| 60 | 3.7 | 58.5 | 68.2 | 61.4 | 29.30 | 25.02 | 22.88 |
| 70 | 4.0 | 63.3 | 73.7 | 66.4 | 31.99 | 28.32 | 26.49 |

* + - 1. Effect of feed composition on feed conversion and product yield

Table 2. reaction conditions: P=50 bar, T= 523 K

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Direct Process | | | | | Indirect Process | | | |
| SN | XCO2 | XH2 | XCO | YCH3OH | H2/CO2 | XCO2 | XH2 | YCH3OH |
| 1.85 | 3.29 | 51.88 | 60.16 | 51.63 | 1 | 12.52 | 25.07 | 6.28 |
| 2 | 3.33 | 52.53 | 61.21 | 55.12 | 2 | 20.36 | 23.51 | 13.33 |
| 2.17 | 3.38 | 53.20 | 62.29 | 59.02 | 3 | 26.55 | 21.50 | 18.98 |
|  |  |  |  |  | 4 | 31.60 | 19.68 | 23.57 |

The feed conversion and methanol yield are decreasing with rise in temperature at reaction conditions as shown in Figure 1. CO2 conversion is again increased from 503 K temperature for both processes. Hence, temperature has a minor effect on equilibrium on these reactions but kinetics play a major role at low temperture on copper based catalysts (Portha et al., 2017). The pressure has a positive effect on feed conversion and methanol yield as depicted in Table 1. It is showing an increasing trend with respect to preseure and hence pressure has a significant role for both processes. The effect of feed composition is shown in Table 2. There is an increment in methanol yield and minor rise in feed conversion with increasing SN ratio for direct process. For indirect route, H2/CO2 ratio has a positive effect on CO2 converion and methanol yield while H2 convesion is decreasing with increasing H2/CO2 ratio due to its excess amount in the feed. So, to optimize an industrial relevant conditions, one should use thermodynamic study for better insight on feed conversion and methanol yield.

* + 1. Process modelling and simulation of direct and indirect process for methanol production



Figure 2. Process flow diagram for direct process to methanol production



Figure 3. Process flow diagram for indirect process to methanol production

The production capacity for methanol production is 3000 t/day for both routes are shown in Figure 2 and Figure 3 respectively. The feed consists of pure hydrogen, CO and CO2 are fed to the mixer. CO2 is pressurized to 69.7 bar in a 4-stage compressor with intercooling. The pressurized feedstock is sent to heater (HX1) and heated upto 509 K and fed to an isothermal multi-tubular reactor filled with catalyst. The products are separated after cooling (HX2) to 336 K in flash separator (Flash1) to liquids and non-reacted gases. The non-reacted gases are recycled to the reactor after purging (SPLITTER) and pressurized to 69.7 bar (COMP). On the liquid side, some of the remaining gases are further separated in another separator (Flash 2) and cooled down in HX3 before entering the first distillation column (DIST1), where water is separated from methanol as a bottom. Methanol enters the second distillation column (DIST2), where by-products and nonreacted gases are removed from methanol. The bottom of the DIST2 is recycled to the DIST1, due to containing a significant amount of methanol beside the water. Condensed product methanol leaves from the top of the DIST2 at 333 K and is further cooled down (HX4) to 303 K for storage. The off-gas streams are mixed (MIXER2) and burnt in a combustion reactor to flue gases generation as they contain H2 and methanol.

* + 1. Economic analysis of direct and indirect process for methanol production

|  |  |  |  |
| --- | --- | --- | --- |
| Item | Ratio factor | Direct Process Cost ($) | Indirect Process Cost ($) |
| 1. Direct cost |  |  |  |
| 1.1 Purchased equipment (delivered) | 1 | 138.50 | 192.50 |
| 1.2 Purchased equipment installation | 0.47 | 65.10 | 90.48 |
| 1.3 Instrumentation & Controls | 0.36 | 49.86 | 69.30 |
| 1.4 Piping | 0.68 | 94.18 | 130.90 |
| 1.5 Electrical systems | 0.11 | 15.24 | 21.18 |
| 1.6 Buildings (including services) | 0.18 | 24.93 | 34.65 |
| 1.7 Yard improvements | 0.1 | 13.85 | 19.25 |
| 1.8 Service facilities | 0.7 | 96.95 | 134.75 |
| Total direct costs |  | 498.60 | 693.00 |
| 2. Indirect cost |  |  |  |
| 2.1 Engineering and supervision | 0.33 | 45.71 | 63.53 |
| 2.2 Construction expenses | 0.41 | 56.79 | 78.93 |
| 2.3 Legal expenses | 0.04 | 5.54 | 7.70 |
| 2.4 Contractor’s fee | 0.22 | 30.47 | 42.35 |
| 2.5 Contingency | 0.44 | 60.94 | 84.70 |
| Total indirect costs |  | 199.44 | 277.20 |
| 3. Working capital (WC) | 0.89 | 123.27 | 171.33 |
| Fixed capital investment (FCI) |  | 698.04 | 970.20 |
| Total capital investment (TCI) |  | 821.31 | 1141.53 |

Table 3: Total capital investment estimation

The total product cost (TPC) was calculated by based on the economic assumptions on the costs of raw material, utility, operating and maintenance, patent, and royalty, depreciation, local tax and insurance, plant overhead, and general expenses. Total product cost based on direct and indirect processes were obtained 350 $/MT and 390 $/MT respectively. We assumed selling price of methanol should be 410 $/MT which is close to literature (Nyári et al., 2020). The net present value (NPV) is calculated by Eq.(10),

where CF is the cash flow, t is the year of the cash flow, i is the discount rate, and n is the total number of years.

* 1. Conclusions

This work investigated the effect of operating parameters (temperature, pressure, and flow composition) on feed conversion and methanol yield for direct and indirect routes for methanol production. Based on thermodynamic, pressure has a positive impact on the feed conversion and methanol yield. Furthermore, process modelling, and simulation of both direct and indirect routes using Aspen plus simulator has been established based on literature and industrial data. A comparative economic analysis for methanol production by direct and indirect route has been calculated based on assumptions and cost indexes to envisage net present value (NPV). The direct route is cheaper than indirect route for methanol production. Besides, indirect route has advantage over direct process, as it utilized captured CO2 in large quantity to mitigate the greenhouse gas effect which ultimately led to net-zero goal.

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