

Thermodynamic Feasibility Studies of Dry Methane Reforming to Acetic Acid

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Abstract

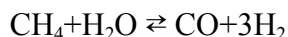
An analysis of the thermodynamic feasibility of acetic acid from dry reforming of methane(DRM) with the feedstock of biogas has been carried out in this project. The Gibbs free energy and equilibrium constants have been examined for steam reforming of methane(SRM), DRM, direct conversion of acetic acid from methane and carbon dioxide and conversion from syngas to acetic acid in both gas and liquid phases at different temperature and pressure. Furthermore, the extent of reactions of DRM and conversion from syngas to acetic acid in both phases were examined at different temperatures, pressures and feed ratios, either parallel or simultaneously. The study shows that DRM has no thermodynamically drawbacks compared to SRM and direct conversion is not possible. In addition, high feed ratios make the extent of the reaction for DRM reach a maximum at a low temperature but high pressure does the opposite. On the other hand, the extent of reactions for the conversions was kept at maximum for a higher temperature when the pressure and feed ratio are both high. Lastly, the extent of reactions for simultaneous reactions could not be calculated.

1. Introduction

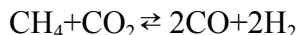
1.1 Motivation and background

Carbon dioxide(CO₂) emissions have been discussed again and again, as it is one of the major greenhouse gases which causes greenhouse effect and leads to other issues[1]. Different methods have been used to control it and one of them is the dry reforming of methane(DRM) which utilizes CO₂ and methane(CH₄) to produce synthesis gas, hydrogen(H₂) and carbon monoxide(CO). On the other hand, steam reforming of methane(SRM) uses water and the ratio of the product is different as shown below.

Steam reforming of methane:



Dry reforming of methane:



Then, the syngas can be used to manufacture end products and intermediate products in petrochemical industries. Dr. Nils Bottke, who works in the company BASF presented with his group about various possible products by synthesizing CO-rich syngas produced by DRM, for example, dimethyl ether, oxo-alcohols and other chemicals are shown in figure 1[2]. Looking through the possible products acetic acid was selected in this study which is a high-demand chemical[2, 3]. The market size of acetic acid was USD 9.30 billion in 2020 and it was estimated to be USD 13.41 billion in 2027 with a compound annual growth rate(CAGR) of 5.2%[4]. Also, the syngas produced by DRM can produce acetic acid in a 100% atom economy, meaning no side products. Lastly, the low C/H ratio of the product is not suitable for hydrocarbons with CH₂

groups. Other alternatives like diethyl ethers and oxo-alcohols do not have a 100% atom economy, then higher alcohols and lower olefins still require deeper research and development[2].

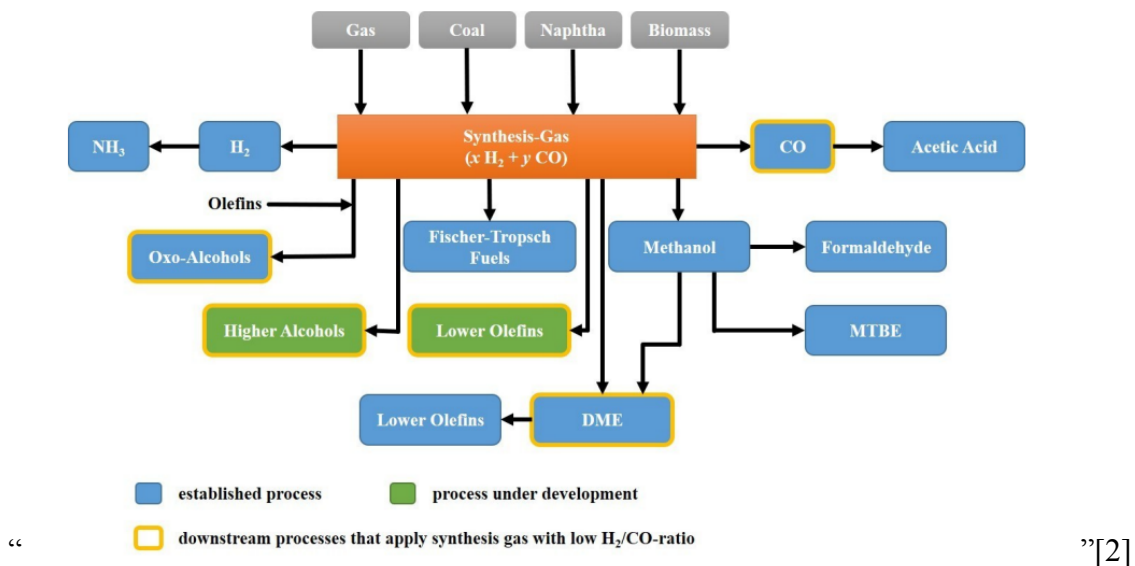
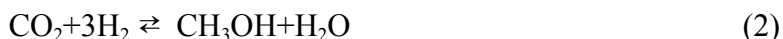


Figure 1- Possible products using synthesis gas

This project aimed to use biogas as a feedstock which has a composition of 60%CH₄ and 40%CO₂ or other varieties depending on the type of biogas with some uncertainties[5, 6]. As it is rich in CH₄ and CO₂ which are the reactants of DRM and the ratio is also close to 1:1, it can be a decent feedstock for DRM. It also prevents removal of CO₂ in biogas which is necessary for other biogas processes such as the production of biomethane[5, 6]. On the other hand, natural gas has roughly 81.3%CH₄ and only 0.89%CO₂ assuming Gronings gas would require extra CO₂ feedstock[7]. More importantly, biogas is a renewable feedstock produced by organic waste, so it is a sustainable process[5].

The traditional method to produce acetic acid starting from DRM needs to pass the production of methanol and uses a complicated catalytic system including homogeneous organometallic catalysts in the liquid phase with corrosive halide-based cocatalysts[8]. More specifically, three reactions occur in the methanol synthesis, water shift gas reaction(1), hydrogenation of carbon dioxide and carbon monoxide(2, 3) before utilizing acetic acid(4) as shown below[9].



1.2 Application

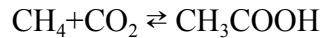
The produced acetic acid has various applications in different areas. The most common one is vinegar which is simply diluted acetic acid with some additives used in salad dressing and cooking. In chemical industries, it is better known as glacial(concentrated) acetic acid which is a

weak acid miscible with ethyl alcohol, diethyl ether and water. It is used as a solvent for organic compounds and mineral agents. The industrial manufacture of acetate esters and the production of pharmaceuticals such as aspirin also involve acetic acid. Other possible routes include use as a food preservative or acetylating agents, in areas of micropaleontology, electricity and production of H₂[10].

1.3 Approach

This will include the calculation of enthalpy, entropy of the process and more importantly the Gibbs free energy which defines the validity of the reaction. The dependent variables will be temperature and pressure. Both SRM and DRM will be examined to see if there is a big difference in reaction conditions. For the production of acetic acid, the direct conversion from CH₄ and CO₂ will be analyzed as well as synthesizing from syngas. As it is not certain which phase the product will be produced in, so both gas and liquid state product will be determined, the reactions are shown below.

Direct conversion



Synthesis from syngas



Several side reactions exist but they are not considered, so the selectivity of each reaction is assumed to be 100%. For example, dry reforming has the main reaction(5) which produces syngas and 3 side reactions namely, reverse water gas reaction(6), Boudouard reaction(7), and CH₄ decomposition(8)[9].



1.4 Hypothesis

Research shows that DRM and SRM are endothermic reactions and the synthesis of acetic acid from syngas is an exothermic reaction. Therefore it can be expected that DRM and SRM would require high temperature and the synthesizing acetic acid needs low temperature for the products to be favored. The direct conversion is an endothermic reaction, so a high temperature would be needed as well. The pressure should affect the equilibrium conversion and process temperature[1-3, 5-8].

2. Methodology

2.1 Thermodynamic analysis

The first goal of this experiment is to determine the feasibility of reactions and their reaction conditions. For this purpose, the Gibbs free energy(ΔG) of each reaction has to be calculated. The simplest equation would be as follows:

$$\Delta G_{\text{products}} - \Delta G_{\text{reactants}} = \Delta G_{\text{reaction}} [11] \quad (\text{Equation 1})$$

Which can also be used for enthalpies and entropies. However, this can only be done for known ΔG values, such as the ΔG values at standard conditions(298K and 1 bar). To find the ΔG values of each compound at different conditions another equation is needed to combine with:

$$\Delta H_{\text{compound, Ref}} + C_p(T - T_{\text{Ref}}) - T(\Delta S_{\text{compound, Ref}} + C_p \ln(T/T_{\text{Ref}}) - R \ln(p/p_{\text{Ref}})) = \Delta G_{\text{compound}} [11] \quad (\text{Equation 2})$$

Where $\Delta H_{\text{compound, ref}}$ is the reference enthalpy change of the compound, $\Delta S_{\text{compound, ref}}$ is the reference entropy change of the reaction, C_p stands for the specific heat capacity at constant pressure, T stands for the temperature and p stands for the pressure. Ref at the subscript stands for reference condition, so $T_{\text{ref}} = 298\text{K}$ and $p_{\text{ref}} = 1\text{atm}$. In addition, R is the gas constant which equals $8.3145 \text{ J/K}\cdot\text{mol}$

The C_p is temperature dependent, but the calculation will become very complex, so the C_p at the reference temperature will be used. Another easier approach can use the following equation:

$$\Delta H_{\text{compound, ref}} - T\Delta S_{\text{compound, ref}} = \Delta G_{\text{compound, ref}} [11] \quad (\text{Equation 3})$$

However, it is less precise as in equation 3 the enthalpies and entropies are temperature independent. The corresponding graph can be found in appendix 1. In addition appendix 2 shows the graph for the results obtained from equation 2, but only ΔH was changing concerning temperature.

2.2 Equilibrium analysis

Furthermore, the results of the previous equations can be used to find the equilibrium constants of the reactions using the following equation:

$$K_{\text{reaction}} = \exp(-\Delta G_{\text{reaction}} / R \cdot T) [11] \quad (\text{Equation 4})$$

Where K is the equilibrium constant, $\Delta G_{\text{reaction}}$ is the Gibbs free energy at temperature T and specific pressure and R is the gas constant as stated before.

The program MATLAB was used to calculate and plot the above variables from a temperature of 298K to 1300K and pressure of 1 bar and 30bar, the code used is shown in the appendix.

The equilibrium constants can determine the conversion of the reaction using its relationship with the extent of reaction at the same pressure and temperature. The derived equations for DRM and conversion from syngas to acetic acid are shown below:

$$\frac{(2\xi)^4}{(n_{CH_4}-\xi)(n_{CO_2}-\xi)(n_{CH_4}+n_{CO_2}+2\xi)^2} = K_{DRM} \quad (\text{Equation 5})$$

$$\frac{\xi(2n_{CO}+2n_{H_2}-3\xi)^3}{(2n_{CO}-2\xi)^2(2n_{H_2}-2\xi)^2} = K_{Synthesis} \quad (\text{Equation 6})$$

Where n stands for the mole of the reactants in the feed and ξ stands for the extent of reaction which shows the changes in the amount of species over their corresponding coefficient. Equation 5 corresponds to DRM and equation 6 represents the synthesis of acetic acid from syngas. In this project, the feed ratio corresponding to the stoichiometric coefficients and higher feed ratio would be analyzed. Literature shows that some amount of CH_4 would be recycled during the industrial process, so most probably CH_4 has a higher feed. It also shows that more H_2 is produced via DRM leading to a higher feed for the second reaction. Increasing the feed of one of the reactants is enough for analysis since the reactants have the same reaction coefficient. Equations 5 and 6 represent stepwise reactions where the conversion happens after DRM. Another interesting research would be the extent of reactions for simultaneous reactions, so both reactions happen in the same reactor. Therefore other 2 equations are derived as shown below:

$$\frac{(2\xi_1-2\xi_2)^4}{(n_{CH_4}-\xi_1)(n_{CO_2}-\xi_1)(n_{CH_4}+n_{CO_2}+2\xi_1-3\xi_2)^2} = K_{DRM} \quad (\text{Equation 7})$$

$$\frac{\xi_2(2n_{CH_4}+2n_{CO_2}+2\xi_1-3\xi_2)^3}{(2\xi_1-2\xi_2)^4} = K_{Synthesis} \quad (\text{Equation 8})$$

Where ξ_1 is the extent of the reaction, DRM, and ξ_2 is for the synthesis of acetic acid from syngas. Equations 7 and 8 take both reactions simultaneously unlike equations 5 and 6 which take the reactions step by step.

3. Results and Discussion

3.1 Thermodynamic results

Using equation 1 the thermodynamic properties of the reactions at reference temperature can be calculated and the values are shown below.

$\text{CH}_4+\text{H}_2\text{O} \rightleftharpoons \text{CO}+3\text{H}_2$	$\Delta H = 206 \text{ kJ/mol}$	$\Delta S = 216 \text{ J/mol}$	$\Delta G = 141.632$
$\text{CH}_4+\text{CO}_2 \rightleftharpoons 2\text{CO}+2\text{H}_2$	$\Delta H = 247 \text{ kJ/mol}$	$\Delta S = 258 \text{ J/mol}$	$\Delta G = 170.116$
$\text{CH}_4+\text{CO}_2 \rightleftharpoons \text{CH}_3\text{COOH}_{(g)}$	$\Delta H = 37 \text{ kJ/mol}$	$\Delta S = -117 \text{ J/mol}$	$\Delta G = 71.866$
$2\text{CO}+2\text{H}_2 \rightleftharpoons \text{CH}_3\text{COOH}_{(g)}$	$\Delta H = -210 \text{ kJ/mol}$	$\Delta S = -375 \text{ J/mol}$	$\Delta G = -98.250$
$2\text{CO}+2\text{H}_2 \rightleftharpoons \text{CH}_3\text{COOH}_{(l)}$	$\Delta H = -263 \text{ kJ/mol}$	$\Delta S = -498 \text{ J/mol}$	$\Delta G = -114.596$

It can be seen from the enthalpy values that DRM, SRM and direct conversion are endothermic reactions and the conversion from syngas to acetic acid is exothermic for both gas and liquid phases. At 25K the entropies of DRM and SRM are positive showing an increase in disorder and the Gibbs free energy is positive meaning that the reaction is nonspontaneous. Then for the direct conversion, the entropy is negative and the Gibbs free energy is positive indicating that the reaction is nonspontaneous as well but the disorder decreases. Lastly, the conversion from syngas to acetic acid has negative entropies and Gibbs free energy indicating spontaneous reactions and a decrease in disorder[11].

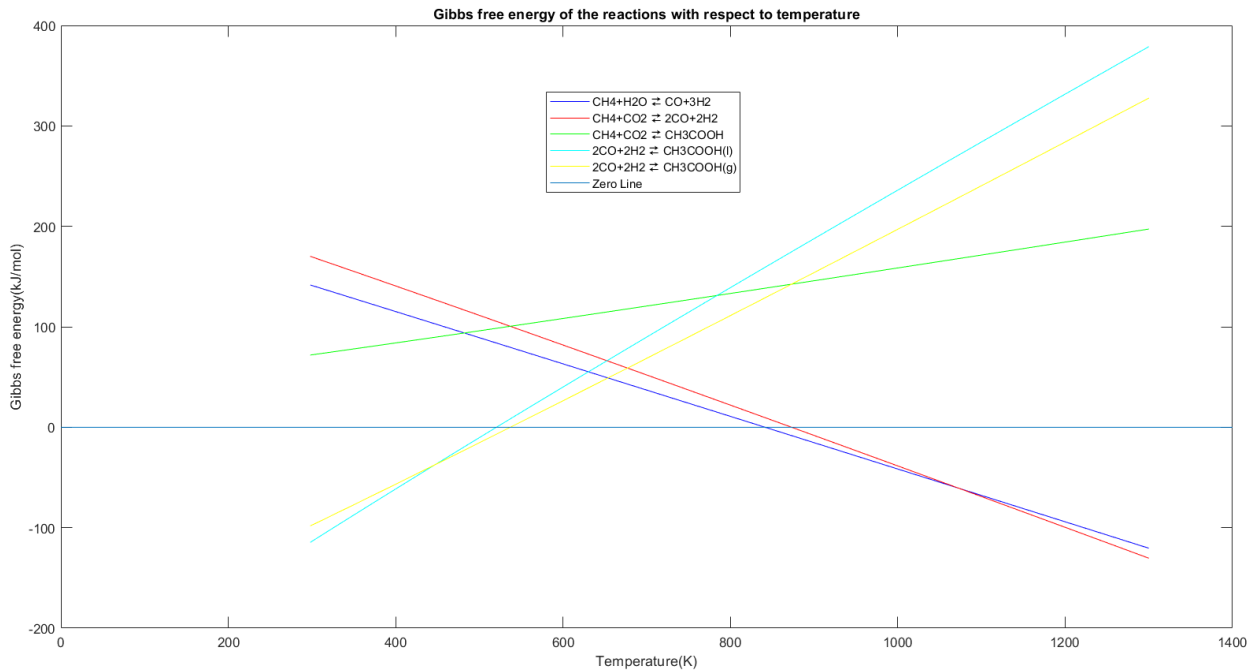


Figure 2. The Gibbs free energy of the reactions with respect to temperature.

Using equations 1 and 2 figure 2 was obtained which shows the ΔG with respect to temperature. It shows that both DRM and SRM require a very high temperature to achieve a spontaneous reaction. It is due to the fact that the ΔH of the reactions decreases over the temperature and the ΔS of the reactions increases over the temperature. According to equations 2 and 3, it is obvious that the ΔG for DRM and SRM decreases concerning temperature. In addition, DRM shows more dependency on temperature as its slope is greater than the one for SRM, but SRM reaches spontaneity at a lower temperature, 850K compared to 900K for DRM. The results are in line with the literature, adding to that literature shows that the side reactions of DRM either have positive ΔG or more positive ΔG than the main reaction at higher temperatures as shown in the figure below[9]:

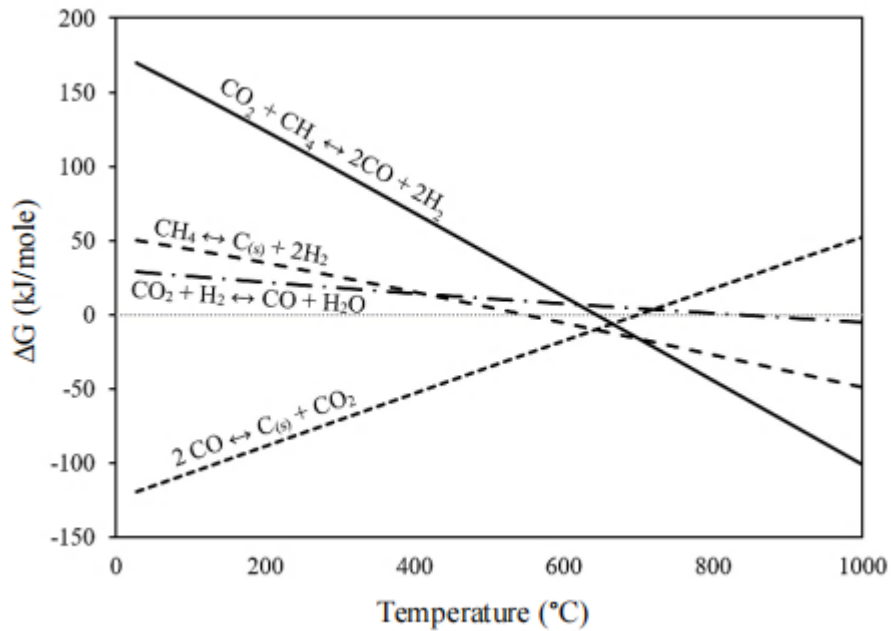


Figure 3. ΔG values for all possible reactions from DRM[8]

Since the production of syngas has the highest thermodynamic feasibility at high temperatures, the assumption that it has a very high selectivity can be valid at high temperatures. With the help of catalysts, this can be even more enhanced to ensure high selectivity[12, 13].

Furthermore, the ΔG of direct conversion shows an increasing trend over the temperature, so the reaction would be spontaneous at lower temperatures. However, according to Le Chatelier's principle, for endothermic reactions at a lower temperature the reactants are favored. Therefore it is expected that direct conversion is possible at very low temperatures, but the production would be minimal[13, 14].

Next, syngas conversions to acetic acid show a similar trend for the ΔG . They are spontaneous at low temperatures and it becomes nonspontaneous after around 550K. The difference between the two product phases is minimal, it shows that the conversion to liquid acetic acid is more sensitive to temperature as well as DRM.

Opposite to what was mentioned above, for exothermic reactions as the conversions at higher temperatures the reactants are favored. However, it is essential to know that the reaction rate at low temperatures is very small as the average kinetic energy of the reactant molecules is small. In order to make the reaction spontaneous at higher temperatures, another factor needs to be taken into account which is pressure[13].

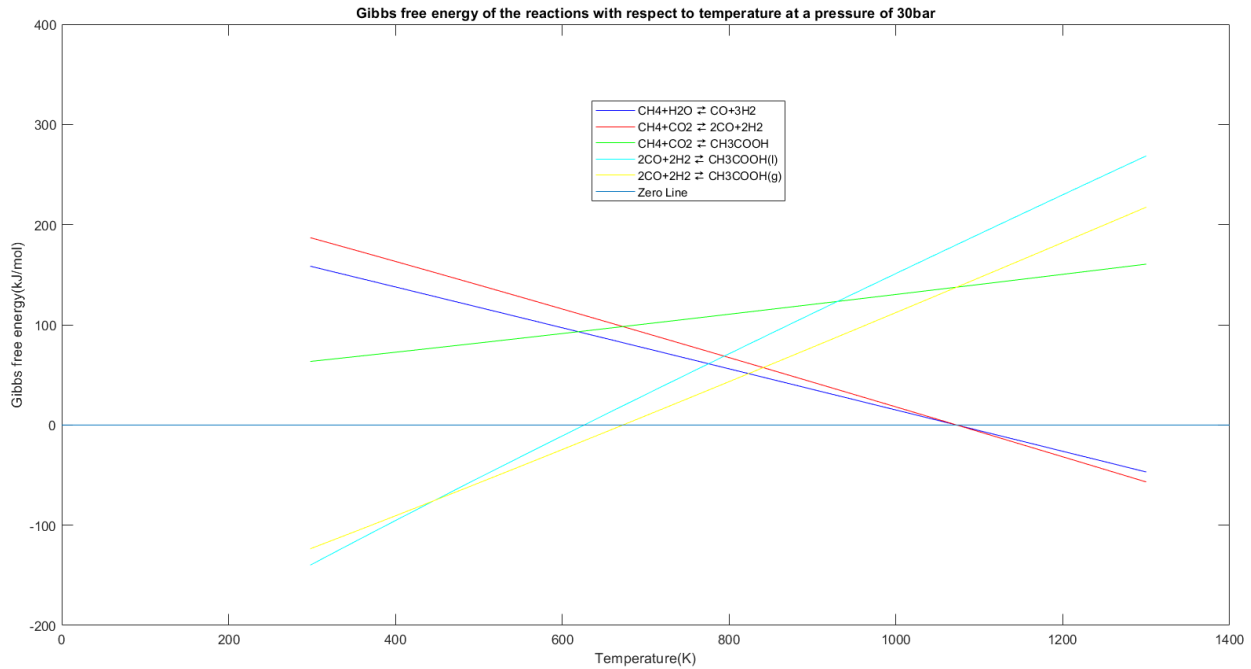


Figure 4. The Gibbs free energy of the reactions with respect to temperature at 30 bar.

Figure 4 shows the results obtained from equation 1 and 2 using 30 bar as pressure, the units of the pressure is not important as the equation uses the ratio of pressures. The results show that SRM and DRM require higher temperatures to achieve spontaneity which also means that higher energy is required to perform the reaction. Again DRM shows higher temperature dependency than SRM and both reactions become spontaneous at around 1080K.

In addition, the direct conversion is still not a favorable reaction, but it has become lower compared to the lower pressure. It can be estimated that the reaction is feasible at very high pressure and low temperature.

Next, the conversions of syngas to acetic acid show that they are spontaneous until roughly 600K which is an improvement compared to previous results. Again the conversion to liquid acetic acid is more sensitive to temperature and becomes nonspontaneous at a lower temperature than conversion to gas acetic acid. These results are in line with the fact that the entropies of the reactions are lower at higher temperatures.

After obtaining the ΔG of each reaction at different conditions it is needed to calculate the corresponding equilibrium constants as shown in equation 4 which can determine the exact conversion of each reaction.

3.2 Equilibrium constant results

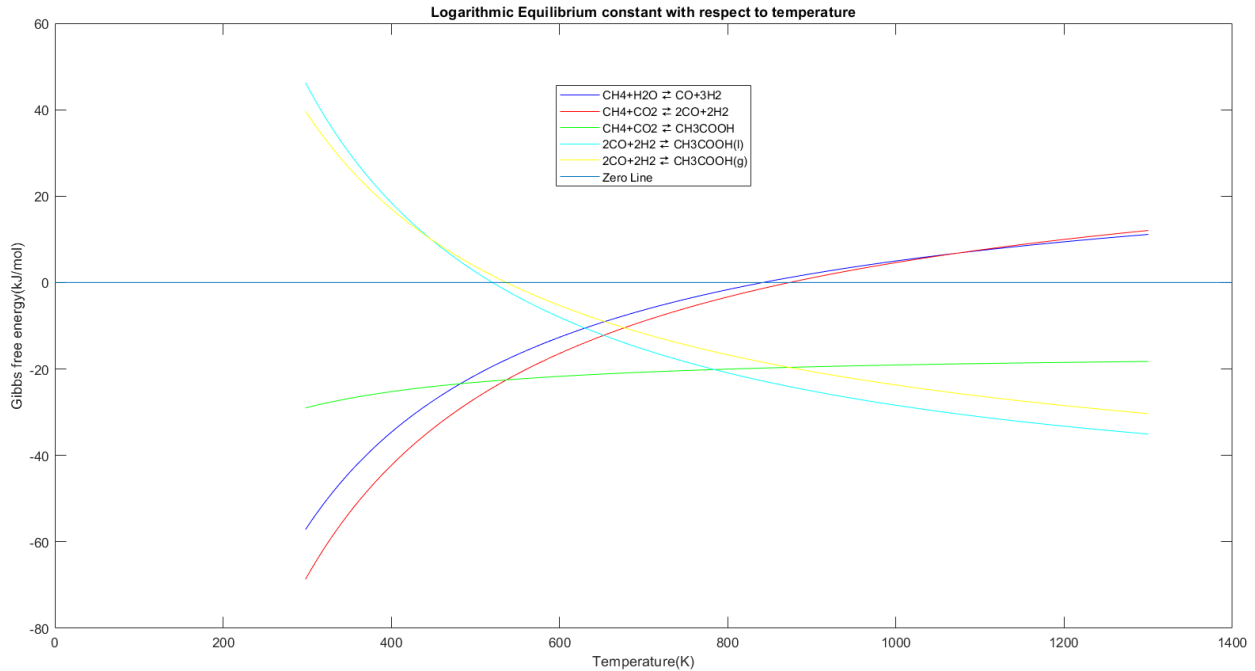


Figure 5. The logarithmic equilibrium constant with respect to temperature.

In figure 5 the equilibrium constants of each reaction are shown in logarithmic scale as the values of the equilibrium constants range from 10^{-20} to 10^{20} and the graphs become unreadable. The graph shows that the logarithmic equilibrium constants are positive after 900K for SRM and DRM meaning that there are products produced and this reflects the negative ΔG as shown in figure 2. Furthermore, higher temperatures lead to higher equilibrium constants which means that the conversions of reactants to products are higher. Again DRM shows higher temperature dependency and the conversion of DRM and SRM is similar. Therefore neither DRM nor SRM has an extreme advantage in producing syngas, the difference between them is just the ratio of the products and the reactants used. Since the produced CO: H₂ ratio is 2:2 for DRM, it is more suitable for producing acetic acid compared to SRM and it has a 100% atom economy.

An interesting finding is that the direct conversion shows that the equilibrium constant increases with increasing temperature which is opposite to the results shown in figure 2. This means that the reaction is only feasible at low temperatures, but the conversion would be incredibly low or even zero. More research is needed to explain the phenomena.

The conversion of syngas to acetic acid in both phases shows a positive logarithmic equilibrium constant until around 550K corresponding to the negative ΔG of the reactions 550K in a similar range. Again liquid phase conversion shows higher temperature dependency. The similar equilibrium constants show that converting to liquid or gas acetic acid does not make a

big difference. A similar graph is produced for the logarithmic equilibrium constants at higher pressure as shown below in figure 6:

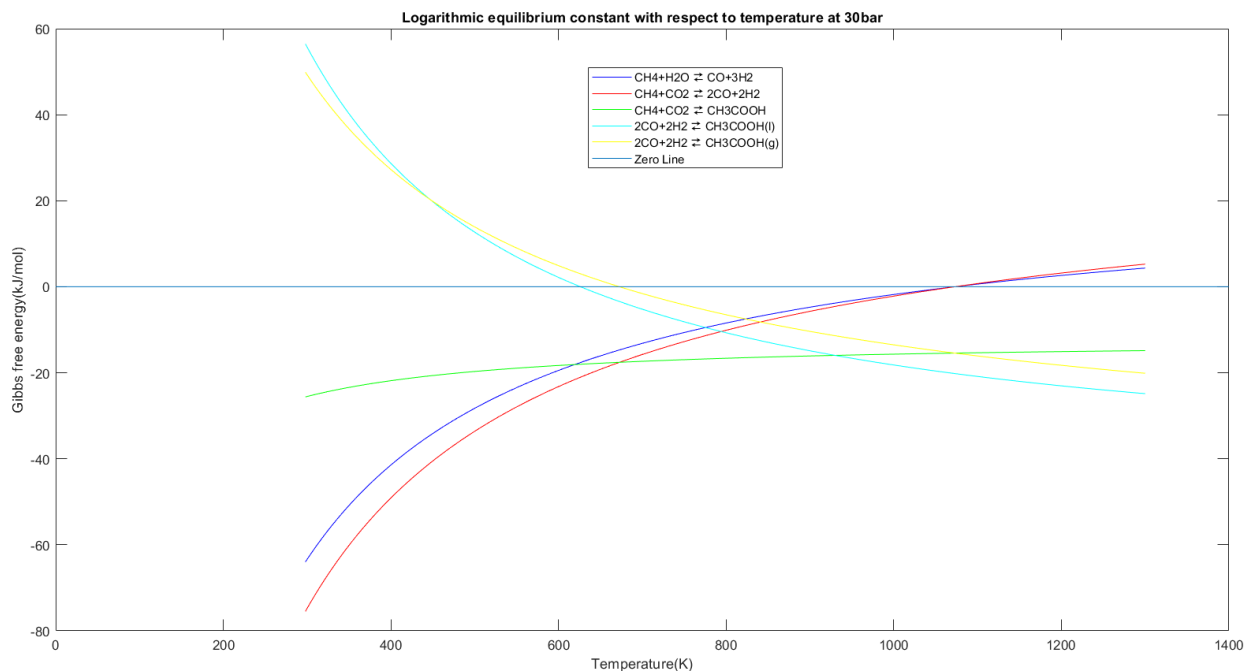


Figure 6. The logarithmic equilibrium constant with respect to temperature at 30 bar.

The logarithmic equilibrium constants of DRM and SRM are positive after around 1080K and the values are small indicating low conversion. This shows that higher pressure does not help DRM or SRM neither in feasibility nor amount of product and the temperature dependency remains the same. In addition, direct conversion does not show any change at a higher temperature. The conversion of syngas to acetic acid shows that the equilibrium constants remain positive until 600K. The results in figure 6 except for direct conversion are in line with the results in figure 4. Since the equilibrium constants cannot tell how much product is produced, the extent of reaction needs to be calculated. The main focus would be on DRM and conversion from syngas to acetic using equations 5 and 6.

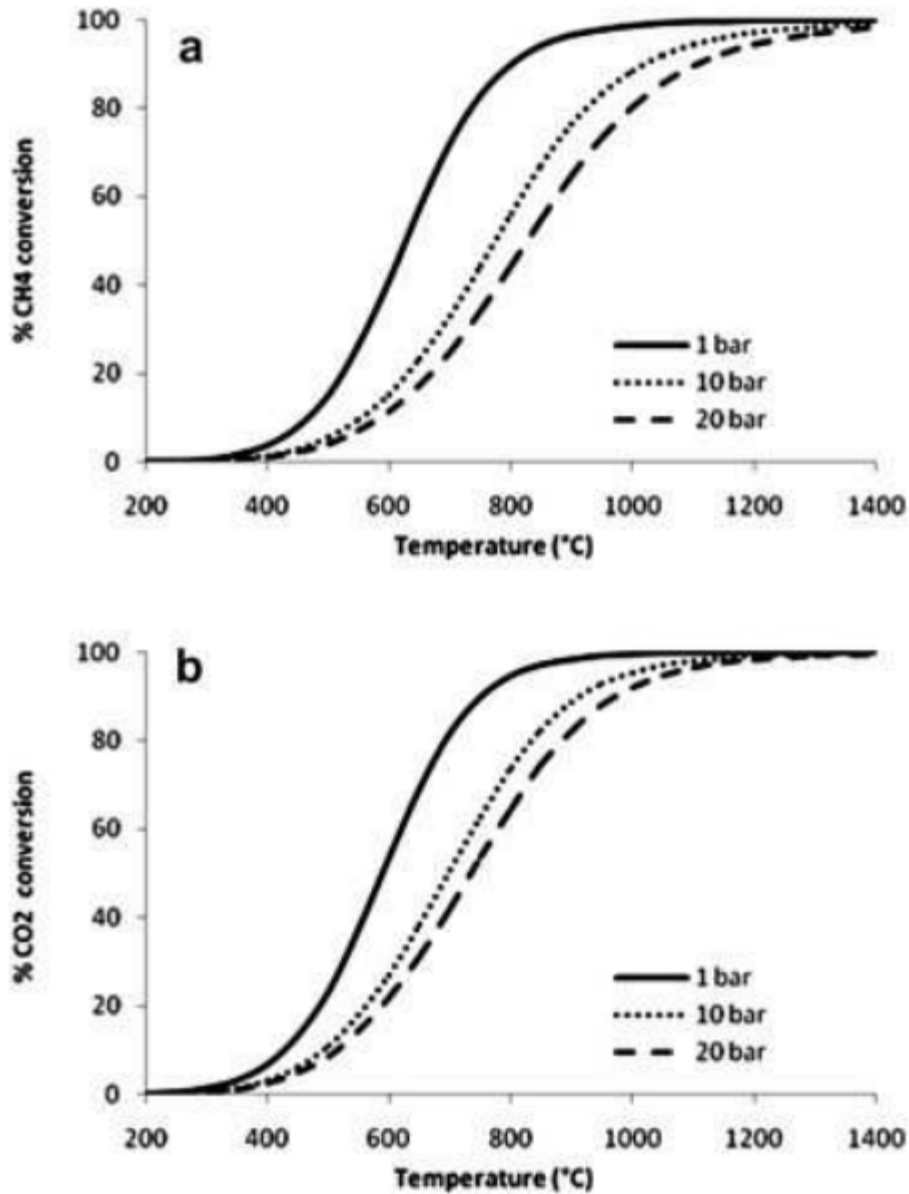
3.3 Extent of reaction results



Figure 7. The extent of reaction for DRM with respect to temperature

The extent of reaction for DRM is shown in figure 7 concerning temperature and using different conditions as shown in the legends. It shows that DRM using feed ratio of (CH4)1:1(CO2) and at a pressure of 1 bar reaches complete conversion, or the extent of reaction equals 1 at around 1150K. This is about 250K higher than the temperature where the reaction is feasible. On the other hand when the feed ratio becomes (CH4)1:5(CO2) the maximum is reached at a similar temperature where the product is favored. This tells that a higher feed ratio can enhance the reaction to have sufficient production using less energy.

The effect of pressure on the extent of reaction is negative, at a pressure of 30 bar the maximum production is reached at around 1100K for (CH4)1:5(CO2) feed ratio and higher than 1300K for (CH4)1:1(CO2) feed ratio. Research also shows similar results concerning the effect of pressure as shown below[2].



“ ”[2]

Figure 8. The DRM conversion with respect to temperature and pressure from literature

Therefore higher feed ratio is favorable at any conditions and higher pressure is not favorable. The conversion cannot be higher even if the temperature increases, so the temperature used should be right at the point where the maximum conversion is reached, but not higher to prevent waste of energy. Unless the rate of reaction is not pleasant at that temperature. Furthermore, the extents of reaction for syngas conversions to acetic acid in both phases are shown below.

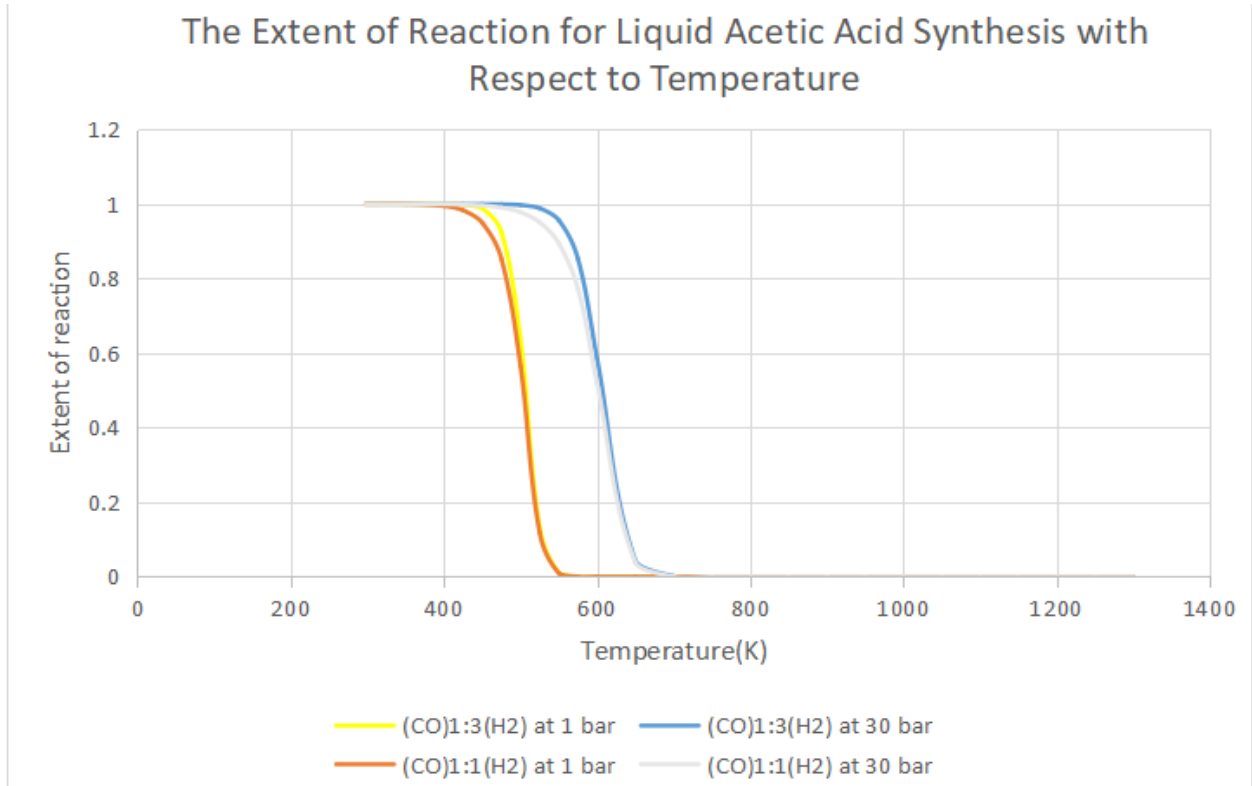


Figure 9. The extent of reaction for liquid acetic acid synthesis with respect to temperature

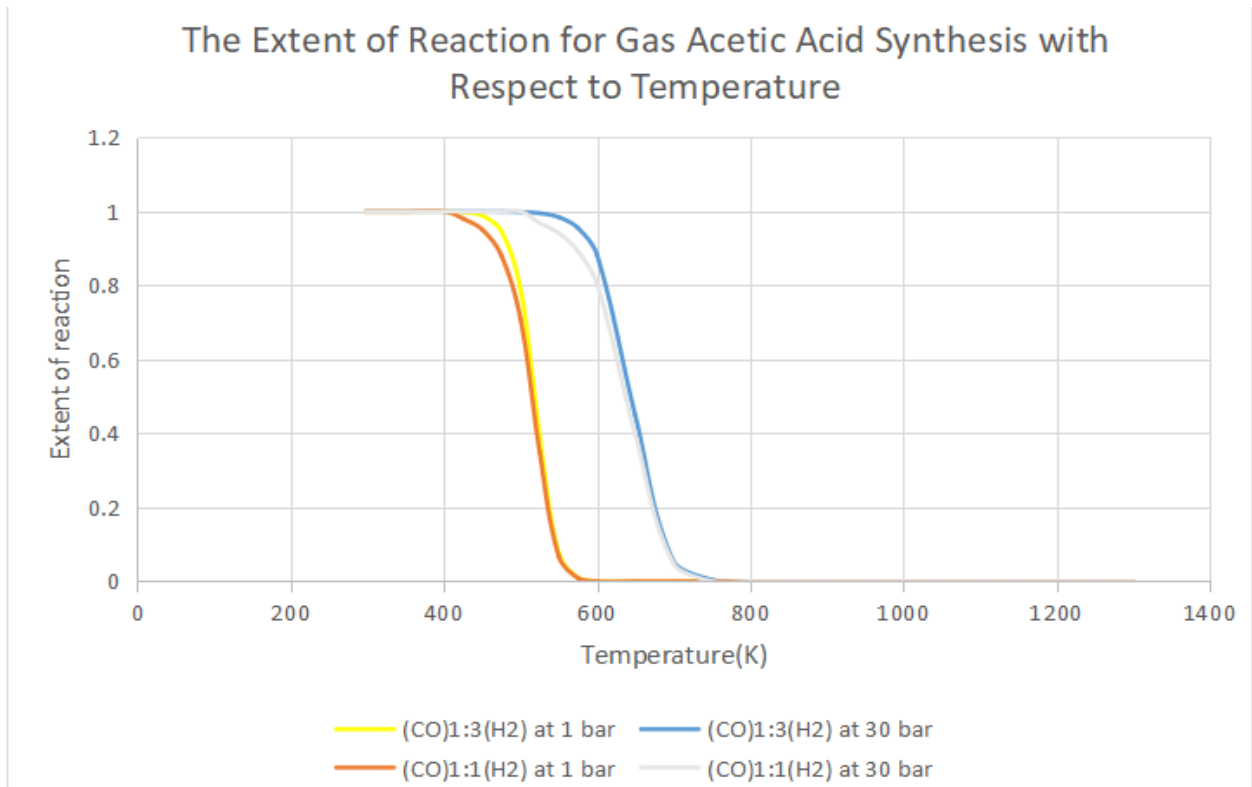


Figure 10. The extent of reaction for gas acetic acid synthesis with respect to temperature

Unlike DRM, the synthesis of acetic acid requires as high a temperature as possible when keeping effective conversion to have a higher rate of reaction. Both figures 9 and 10 show that with higher pressure, the maximum conversion is kept for higher temperatures. Also, a higher feed ratio does the same work. The curves are very sharp for both reactions at different conditions meaning that the conversion rate is very sensitive to temperature, about 70-80K can change the rate from maximum to minimum. Again the liquid acetic acid synthesis is more temperature dependent[14, 15].

The research was planned to analyze the extent of reactions of DRM and synthesis of acetic acid through syngas simultaneously using equations 7 and 8. However, during the solving of equations, many errors came out and the values obtained were not reliable as shown in the table of the appendix. For the extremely small values, they were assumed to be 0 in the beginning and then the exact values were used, but still, the answers were not reliable. Either no solution popped up or values bigger than 1 as shown in the appendix. This could be caused by a lack of skills or the program wolfram could not do the job. Therefore it is left for future analysis.

Conclusion

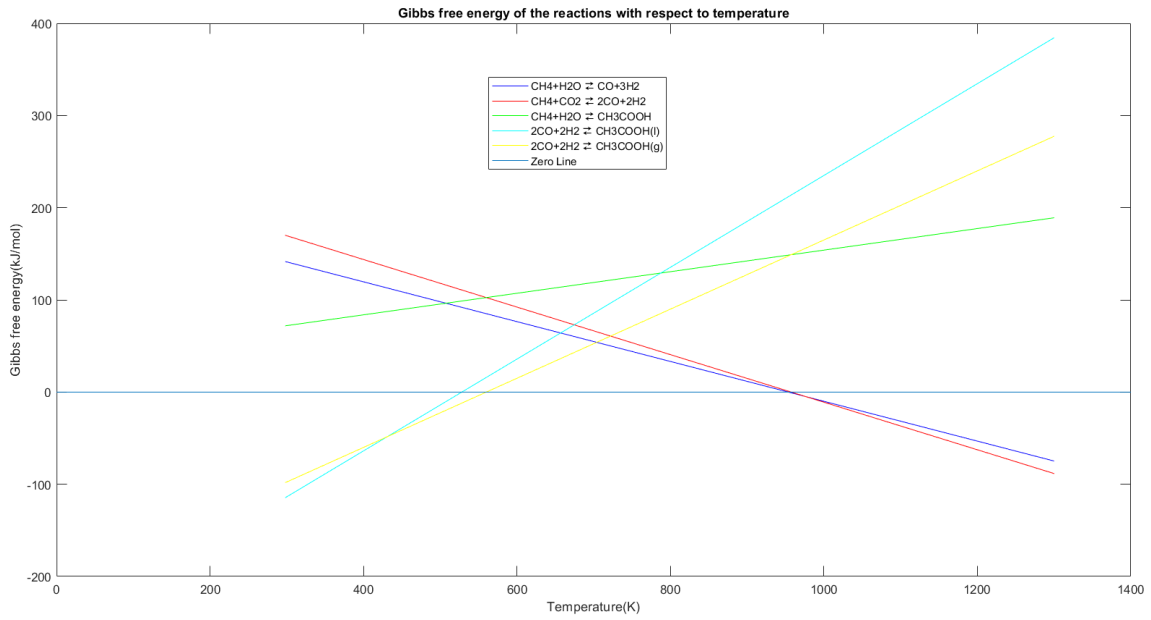
The calculation of thermodynamic properties shows that DRM and SRM are feasible at similar temperatures around 900K at a pressure of 1 bar and 1080K at a pressure of 30 bar. Direct conversion has a possibility to be sufficient at very low temperatures corresponding to thermodynamics, but equilibrium constants tell that high temperature is required. On the other hand conversion from syngas to acetic acid is possible from low temperatures until roughly 550K for either state at a pressure of 1 bar and around 600K at a pressure of 30 bar. The logarithmic equilibrium constants are positive in a similar range of temperature reflecting the thermodynamic results except for direct conversion,

Concluding, the syngas produced using DRM are more suitable for acetic acid production due to the 100% atom economy of the reaction. Also, a high feed ratio can effectively help the conversion rate for both reactions. On the other hand, high pressure lets the temperature range of maximum conversion be higher for DRM and extends the temperature range of maximum conversion for the synthesis. Overall, DRM requires a high feed ratio and low pressure, and acetic acid synthesis requires a high feed ratio and pressure. These summarize that the syngas produced by DRM can produce acetic acid. Unfortunately, the extent of reactions could not be calculated for simultaneous reactions. For future research, the rate of reaction can be taken into account since high conversion cannot tell how long it takes to produce such an amount of product. Also, methods can be found to investigate valid solutions for equations 7 and 8 to analyze simultaneous reactions.

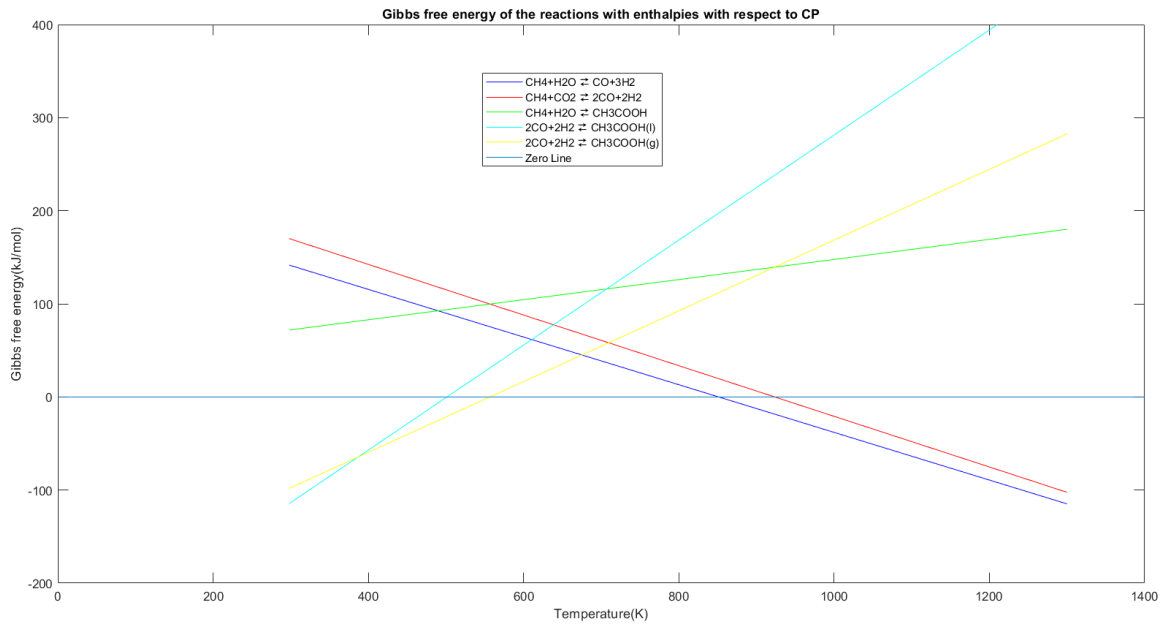
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Appendix



Appendix 1. Gibbs free energy of the reactions with respect to temperature only



Appendix 2. Gibbs free energy of the reactions with ΔH changing with respect to temperature

Appendix 3. The extent of reactions using equations 7 and 8 based on the K_{DRM} and $K_{\text{Synthesis}}$ at pressure of 1 bar and feed ratio according to stoichiometric ratio

Temperature	K_{DRM}	$K_{\text{Synthesis}}$	ξ_1	ξ_2
298	1.51E-30	1.22342E+20	0	Error
350	6.99E-24	1.09707E+13	0	Error
400	4.29E-19	106581571.2	0	Error
450	2.32E-15	14329.61296	0	Error
500	2.30E-12	12.04559895	0	Error
550	6.61E-10	0.038227616	0	Error
600	7.49571E-08	0	0.0117	0
650	4.1491E-06	0	0.0318	0
700	0.000130698	0	0.0371	0
750	0.002620867	0	0.0771	0
800	0.036393866	0	0.144	0
850	0.373246368	0	0.247	0
900	2.972535465	0	0.393	0
950	19.12641988	0	0.587	0
1000	102.6354928	0	0.832	0
1050	471.287866	0	1.129	0
1100	1891.235207	0	1.480	0
1150	6748.975457	0	1.886	0
1200	21730.5732	0	2.347	0
1250	63907.12869	0	2.861	0
1300	173445.9949	0	3.429	0

Matlab code

Enthalpies

CO= (-111)

H2Og=(-242)

H2Ol=(-286)

CO2=(-394)

CH4=(-75)

AA=(-485)

AAg=(-432)

Entropies

SCO= (198)

SH2Og=(189)

SH2Ol=(70)

SCO2=(214)

SCH4=(186)

SAA=(160)

SAAg=283

SH2=131

Temperature

N=200

T(1)=298

T(2)=300

for n = 1:N

 T(n+2)=T(2)+n*5

end

R=8.314

Pressure

P(1)=0.1

P(2)=0.12

for n = 1:N

 P(n+2)=P(2)+n*0.02

end

Steam reforming

srdh=CO-H2Og-CH4

srds=3*SH2+SCO-SH2Og-SCH4

srdg=srdh-T*0.001*srds

Dry reforming

drdh=2*CO-CO2-CH4

drds=2*SH2+2*SCO-SCO2-SCH4

drdg=drdh-T*0.001*drds

Direct Conversion

$$dcdh = \text{AAg} - \text{CO}_2 - \text{CH}_4$$

$$dcds = \text{SAAg} - \text{SCO}_2 - \text{SCH}_4$$

$$dcdg = dcdh - T * 0.001 * dcds$$

Dry reforming conversion

$$drcdhg = \text{AAg} - 2 * \text{CO}$$

$$drcdsg = \text{SAAg} - 2 * \text{SH}_2 - 2 * \text{SCO}$$

$$drcdgg = drcdhg - T * 0.001 * drcdsg$$

$$drcdh = \text{AA} - 2 * \text{CO}$$

$$drcds = \text{SAA} - 2 * \text{SH}_2 - 2 * \text{SCO}$$

$$drcdg = drcdh - T * 0.001 * drcds$$

Enthalpies with respect to CP

$$\text{CO}_{cp} = (-111) + 29 * 0.001 * (T - 298)$$

$$\text{H}_2\text{O}_{gcp} = (-242) + 34 * 0.001 * (T - 298)$$

$$\text{H}_2\text{O}_{lcp} = (-286) + 75 * 0.001 * (T - 298)$$

$$\text{CO}_2_{cp} = (-394) + 37 * 0.001 * (T - 298)$$

$$\text{CH}_4_{cp} = (-75) + 35 * 0.001 * (T - 298)$$

$$\text{AA}_{cp} = (-485) + 124 * 0.001 * (T - 298)$$

$$\text{AAg}_{cp} = (-432) + 63 * 0.001 * (T - 298)$$

Entropies with respect to CP

$$\text{SCO}_{cp} = \text{SCO} + 29 * \log(T/298)$$

$$\text{SH}_2\text{O}_{gcp} = \text{SH}_2\text{Og} + 34 * \log(T/298)$$

$$\text{SH}_2\text{O}_{lcp} = \text{SH}_2\text{Ol} + 75 * \log(T/298)$$

$$\text{SCO}_2_{cp} = \text{SCO}_2 + 37 * \log(T/298)$$

$$\text{SCH}_4_{cp} = \text{SCH}_4 + 35 * \log(T/298)$$

$$\text{SAA}_{cp} = \text{SAA} + 124 * \log(T/298)$$

$$\text{SAAg}_{cp} = \text{SAAg} + 63 * \log(T/298)$$

$$\text{SH}_2_{cp} = \text{SH}_2 + 14.3 * \log(T/298)$$

Entropies with respect to CP at 30 bar

$$\text{SCO}_{cpp} = \text{SCO} + 29 * \log(T/298) - R * \log(3/0.1)$$

$$\text{SH}_2\text{O}_{gcpp} = \text{SH}_2\text{Og} + 34 * \log(T/298) - R * \log(3/0.1)$$

$$\text{SH}_2\text{O}_{lcpp} = \text{SH}_2\text{Ol} + 75 * \log(T/298) - R * \log(3/0.1)$$

$$\text{SCO}_2_{cpp} = \text{SCO}_2 + 37 * \log(T/298) - R * \log(3/0.1)$$

$$\text{SCH}_4_{cpp} = \text{SCH}_4 + 35 * \log(T/298) - R * \log(3/0.1)$$

$$\text{SAA}_{cpp} = \text{SAA} + 124 * \log(T/298) - R * \log(3/0.1)$$

$$\text{SAAg}_{cpp} = \text{SAAg} + 63 * \log(T/298) - R * \log(3/0.1)$$

$$\text{SH}_2_{cpp} = \text{SH}_2 + 14.3 * \log(T/298) - R * \log(3/0.1)$$

Giibbs free enrgy with enthalpies with respect to CP

Steam reforming

$\text{srdhcp} = \text{COcp} - \text{H2Ogcp} - \text{CH4cp}$
 $\text{srd s} = 3 * \text{SH2} + \text{SCO} - \text{SH2Og} - \text{SCH4}$
 $\text{srdgcp} = \text{srdhcp} - T * 0.001 * \text{srd s}$
 Dry reforming
 $\text{drdhcp} = 2 * \text{COcp} - \text{CO2cp} - \text{CH4cp}$
 $\text{drds} = 2 * \text{SH2} + 2 * \text{SCO} - \text{SCO2} - \text{SCH4}$
 $\text{drdgcp} = \text{drdhcp} - T * 0.001 * \text{drds}$
 Direct Conversion
 $\text{dcdhcp} = \text{AAgcp} - \text{CO2cp} - \text{CH4cp}$
 $\text{dcds} = \text{SAAg} - \text{SCO2} - \text{SCH4}$
 $\text{dcdgcp} = \text{dcdhcp} - T * 0.001 * \text{dcds}$
 Dry reforming conversion
 $\text{drcdhgcp} = \text{AAgcp} - 2 * \text{COcp}$
 $\text{drcdsg} = \text{SAAg} - 2 * \text{SH2} - 2 * \text{SCO}$
 $\text{drcdggcp} = \text{drcdhgcp} - T * 0.001 * \text{drcdsg}$

$\text{drcdhcp} = \text{AAcp} - 2 * \text{COcp}$
 $\text{drcds} = \text{SAA} - 2 * \text{SH2} - 2 * \text{SCO}$
 $\text{drcdggcp} = \text{drcdhcp} - T * 0.001 * \text{drcds}$
 Gibbs free energy with enthalpies and entropies with respect to CP

Steam reforming
 $\text{srdhcp} = \text{COcp} - \text{H2Ogcp} - \text{CH4cp}$
 $\text{srdscp} = 3 * \text{SH2cp} + \text{SCOcp} - \text{SH2Ogcp} - \text{SCH4cp}$
 $\text{srdgpcp} = \text{srdhcp} - T * 0.001 * \text{srdscp}$
 Dry reforming
 $\text{drdhcp} = 2 * \text{COcp} - \text{CO2cp} - \text{CH4cp}$
 $\text{drdscp} = 2 * \text{SH2cp} + 2 * \text{SCOcp} - \text{SCO2cp} - \text{SCH4cp}$
 $\text{drdgpcp} = \text{drdhcp} - T * 0.001 * \text{drdscp}$
 Direct Conversion
 $\text{dcdhcp} = \text{AAgcp} - \text{CO2cp} - \text{CH4cp}$
 $\text{dcdscp} = \text{SAAgcp} - \text{SCO2cp} - \text{SCH4cp}$
 $\text{dcdgpcp} = \text{dcdhcp} - T * 0.001 * \text{dcdscp}$
 Dry reforming conversion
 $\text{drcdhgcp} = \text{AAgcp} - 2 * \text{COcp}$
 $\text{drcdsgcp} = \text{SAAgcp} - 2 * \text{SH2cp} - 2 * \text{SCOcp}$
 $\text{drcdggpcp} = \text{drcdhgcp} - T * 0.001 * \text{drcdsgcp}$

$\text{drcdhcp} = \text{AAcp} - 2 * \text{COcp}$
 $\text{drcdscp} = \text{SAAcp} - 2 * \text{SH2cp} - 2 * \text{SCOcp}$
 $\text{drcdggpcp} = \text{drcdhcp} - T * 0.001 * \text{drcdscp}$

Gibbs free energy with enthalpies respect to temperature and entropies with respect to temperature and pressure

Steam reforming

$$\text{srdhcp} = \text{COcp} - \text{H}_2\text{Ogcp} - \text{CH}_4\text{cp}$$

$$\text{srdscpp} = 3 * \text{SH}_2\text{cpp} + \text{SCOcpp} - \text{SH}_2\text{Ogcpp} - \text{SCH}_4\text{cpp}$$

$$\text{srdgpcscpp} = \text{srdhcp} - T * 0.001 * \text{srdscpp}$$

Dry reforming

$$\text{drdhcp} = 2 * \text{COcp} - \text{CO}_2\text{cp} - \text{CH}_4\text{cp}$$

$$\text{drdscpp} = 2 * \text{SH}_2\text{cpp} + 2 * \text{SCOcpp} - \text{SCO}_2\text{cpp} - \text{SCH}_4\text{cpp}$$

$$\text{drdgcpcpp} = \text{drdhcp} - T * 0.001 * \text{drdscpp}$$

Direct Conversion

$$\text{dcdhcp} = \text{AAgcp} - \text{CO}_2\text{cp} - \text{CH}_4\text{cp}$$

$$\text{dcdscpp} = \text{SAAgcpp} - \text{SCO}_2\text{cpp} - \text{SCH}_4\text{cpp}$$

$$\text{dcdgcpcpp} = \text{dcdhcp} - T * 0.001 * \text{dcdscpp}$$

Dry reforming conversion

$$\text{drcdhgcp} = \text{AAgcp} - 2 * \text{COcp}$$

$$\text{drcdscpp} = \text{SAAgcpp} - 2 * \text{SH}_2\text{cpp} - 2 * \text{SCOcpp}$$

$$\text{drcdgcpcpp} = \text{drcdhgcp} - T * 0.001 * \text{drcdscpp}$$

$$\text{drcdhcp} = \text{AAcp} - 2 * \text{COcp}$$

$$\text{drcdscpp} = \text{SAAcpp} - 2 * \text{SH}_2\text{cpp} - 2 * \text{SCOcpp}$$

$$\text{drcdgcpcpp} = \text{drcdhcp} - T * 0.001 * \text{drcdscpp}$$

Equilibrium constant with respect to temperature

$$\text{srkk} = \exp(-\text{srdgcpcscpp} / (0.001 * R * T))$$

$$\text{drkk} = \exp(-\text{drdgcpcscpp} / (0.001 * R * T))$$

$$\text{dckk} = \exp(-\text{dcdgcpcscpp} / (0.001 * R * T))$$

$$\text{drckk} = \exp(-\text{drcdgcpcscpp} / (0.001 * R * T))$$

$$\text{drckkg} = \exp(-\text{drcdggcpcscpp} / (0.001 * R * T))$$

Equilibrium constant with respect to temperature and pressure

$$\text{srkkp} = \exp(-\text{srdgcpcscpp} / (0.001 * R * T))$$

$$\text{drkkp} = \exp(-\text{drdgcpcscpp} / (0.001 * R * T))$$

$$\text{dckkp} = \exp(-\text{dcdgcpcscpp} / (0.001 * R * T))$$

$$\text{drckkp} = \exp(-\text{drcdgcpcscpp} / (0.001 * R * T))$$

$$\text{drckkqp} = \exp(-\text{drcdggcpcscpp} / (0.001 * R * T))$$

Plot

```
plot(T,srdg,'b',"DisplayName','Steam reforming')
```

```
title('Gibbs free energy of the reactions')
```

```
xlabel('Temperature(K)')
```

```
ylabel('Gibbs free energy(kJ/mol)')
```

```
legend()
```

```

xlim([0,1400])
ylim([-200,400])
hold on
plot(T,drdg,'r',"DisplayName",'Dry reforming')
plot(T,dcdg,'g',"DisplayName",'Direct conversion')
plot(T,drcdg,'c',"DisplayName",'Dry reforming conversion liquid')
plot(T,drcdgg,'y',"DisplayName",'Dry reforming conversion gas')
line([0,1400],[0,0])
hold off
Plot with enthalpies with respect to CP

```

```

plot(T,srdgcp,'b',"DisplayName",'Steam reforming')
title('Gibbs free energy of the reactions with enthalpies with respect to CP')
xlabel('Temperature(K)')
ylabel('Gibbs free energy(kJ/mol)')
legend()
xlim([0,1400])
ylim([-200,400])
hold on
plot(T,drdgcp,'r',"DisplayName",'Dry reforming')
plot(T,dcdgcp,'g',"DisplayName",'Direct conversion')
plot(T,drcdgcp,'c',"DisplayName",'Dry reforming conversion liquid')
plot(T,drcdggcp,'y',"DisplayName",'Dry reforming conversion gas')
line([0,1400],[0,0])
hold off
Plot with enthalpies and entropies with respect to CP

```

```

plot(T,srdgpcscp,'b',"DisplayName",'Steam reforming')
title('Gibbs free energy of the reactions with enthalpies and entropies with respect to CP')
xlabel('Temperature(K)')
ylabel('Gibbs free energy(kJ/mol)')
legend()
xlim([0,1400])
ylim([-200,400])
hold on
plot(T,drdgpcscp,'r',"DisplayName",'Dry reforming')
plot(T,dcdgpcscp,'g',"DisplayName",'Direct conversion')
plot(T,drcdgpcscp,'c',"DisplayName",'Dry reforming conversion liquid')
plot(T,drcdggpcscp,'y',"DisplayName",'Dry reforming conversion gas')
line([0,1400],[0,0])

```

hold off

Plot with enthalpies respect to temperature and entropies with respect to temperature and pressure

```
plot(T,srdgpcscpp,'b',"DisplayName",'Steam reforming')
title('Gibbs free energy of the reactions with enthalpies and entropies with respect to CP at a
pressure of 3Mpa')
xlabel('Temperature(K)')
ylabel('Gibbs free energy(kJ/mol)')
legend()
xlim([0,1400])
ylim([-200,400])
hold on
plot(T,drdgcpcscpp,'r',"DisplayName",'Dry reforming')
plot(T,dcdgcpcscpp,'g',"DisplayName",'Direct conversion')
plot(T,drcdgcpcscpp,'c',"DisplayName",'Dry reforming conversion liquid')
plot(T,drcdggcpcscpp,'y',"DisplayName",'Dry reforming conversion gas')
line([0,1400],[0,0])
hold off
```

Plot with Equilibrium constants with respect to temperature

```
plot(T,log(srkk),'b',"DisplayName",'Steam reforming')
title('Logarithmic Equilibrium constant with respect to temperature')
xlabel('Temperature(K)')
ylabel('Gibbs free energy(kJ/mol)')
legend()
```

hold on

```
plot(T,log(drkk),'r',"DisplayName",'Dry reforming')
plot(T,log(dckk),'g',"DisplayName",'Direct conversion')
plot(T,log(drckk),'c',"DisplayName",'Dry reforming conversion liquid')
plot(T,log(drckkg),'y',"DisplayName",'Dry reforming conversion gas')
line([0,1400],[0,0])
hold off
```

Plot with equilibrium constant with respect to temperature at 30bar

```
plot(T,log(srkkp),'b',"DisplayName",'Steam reforming')
title('Logarithmic equilibrium constant with respect to temperature at 3Mpa')
xlabel('Temperature(K)')
ylabel('Gibbs free energy(kJ/mol)')
```



```
legend()
```

```
hold on
```

```
plot(T,log(drkkp),'r',"DisplayName",'Dry reforming')
```

```
plot(T,log(dckkp),'g',"DisplayName",'Direct conversion')
```

```
plot(T,log(drckkp),'c',"DisplayName",'Dry reforming conversion liquid')
```

```
plot(T,log(drckkqp),'y',"DisplayName",'Dry reforming conversion gas')
```

```
line([0,1400],[0,0])
```

```
hold off
```