

Notation

$[P_i]$: Partial pressur of component i, atm

T : Temperature, °R

T_k : Temperature, °K

t : time, hr

k : reaction rate constant, $\text{hr}^{-1}\text{atm}^{-n}$

$-E_a$: activation energy, $\frac{\text{Btu}}{\text{lbmol}}$ of reactant

n : catalyst coeffiecient, dimensionless

K_e : Equilibrium constant, atm^{-2}

H_0 : enthalpy, J/(mol. K)

R : gas constant, $\frac{\text{J}}{\text{mol. K}}$

θ_i : characteristic vibration temperatures of molecule i, K

Q : Heat generated or released , kW

$H_{\text{in/out}}$: Enthalpy of input and output stream, kJ/mol

$F_{\text{in/out}}$: Molar flowrate of reactants and products, mol/sec

h_{wall} : Heat transfer coefficient from gas to wall, $\frac{\text{W}}{\text{m}^2 \times \text{K}}$

A : Surface area of element exposed to coolant, m^2

D : Diameter of the reactor, m

l : length of element which is exposed to coolant

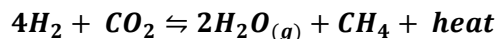
Introduction

Analysis shows that fossil fuel sources are under the threat of fast decrease. Although these sources are highly efficient and economically beneficial, they have high level of environmental risks and hazards as well. Considering these important facts, encourages different countries to change their energy policy and to focus more on non-fossil fuels. To have more energy security and less environmental problems, lead to finding as much renewable sources as possible.

One of the sustainable sources in the renewable category is biogas. Some authors define biogas as those gases which are produced through anaerobic digestion. But there is a wider definition that considers biogas as all combustible gases from biological sources (Taglia P.G 2010) and also includes gases from pyrolysis or thermal gasification. Biogas is mainly methane and carbon dioxide together with some other inert gases. (Violeta Bescós 2008) Methane is the main part of biogas which could be used as fuel and energy source, so companies are more interested in optimizing the biogas production process in the way to have as much methane as possible.

The reaction

In order to increase the biogas supply, different methods can be used. One of them is to use Sabatier reaction. It is called "Sabatier" reaction after its investigator who was a Belgian chemist. He discovered this reaction to hydrogenise carbon compounds in a catalytic bed at ~480-650 K which is called methanation. In this reaction the CO₂ which exists in biogas stream reacts with H₂ and produces CH₄ again. Therefore the product would have more CH₄ than the biogas process itself (Lunde 1974)



Hydrogen in this reaction could be prepared through different methods such as steam reforming and water electrolysis. In order to have a complete renewable pathway for methane production, water electrolysis using electricity provided by wind farms, would be a better choice.

Methanation is a highly exothermal reaction which produces -165 kJ/mol produced CH₄. This parameter should be considered in design of the reactor, so that the accumulation of the heat does not destroy the catalysts. The equilibrium is more favorable at low temperature, but the reaction rate is higher at high temperature so controlling the temperature in an applicable

range is important. In industry, using heat exchanger around the reactor wall is a method to control temperature fluctuation in bed.

Aim of the project

In this thesis, a lab-scale Sabatier reactor is simulated. Studying different parameters such as reactant temperature, coolant temperature and pressure in this project gives the optimum point to run the reaction. Kinetics of reaction through the bed and temperature profile are final results.

Methodology

The studied input gas contains 60 vol% CH₄ and 40 vol% CO₂ which is typical for the gas leaves an anaerobic digester. Hydrogen is added then at stoichiometric ratio (4 H₂ per CO₂)

In order to simulate the reaction, the methodology is to divide the bed in **20** hypothetical elements in which a conversion of **4.5%/element** is assumed. The final yield is thus assumed to be 90% (expressed as **reacted hydrogen/inlet hydrogen**). The temperature in each cross section is considered to be the same and so there is just temperature profile along the length of the bed. This simulation has been done all in excel, since the method was numerical based.

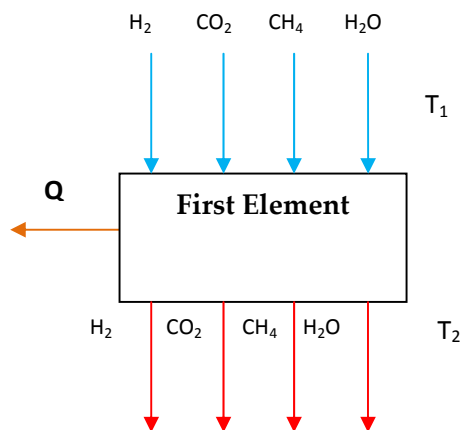


Fig 1. Schematic figure of one element in bed

In fig 1, there is a schematic view of one element of the 20 ones in the reactor tube. As it is clear, the streams with temperature T_1 and with different volumetric flows enter the element. The heat which is produced in the reaction can either increase the temperature of the effluent stream to T_2 or be released from the wall to the cooling media. In reality both of these mechanisms happen in parallel, but in our calculations we simulate them individually. The results of the isothermal and the adiabatic simulation then can be compared with one another.

As reactor tubes, the inner diameter of 35 mm was chosen since this is a standard diameter that is easily available and is used in laboratory reactor. Tube length up to 6 m is available and it seems logical to design the reactor for single pass. A load of 1.94 mmol/sec CO_2 and 90% conversion was assumed for tube and 10 bar pressure was chosen.

1 Discussion and results

1.1 Simulation and calculation data

1.1.1 Input data

There are some initial values used as the basis of calculations. These data were taken mainly from Lunde work as the major source of information in this task. Based on Lunde paper on modeling and simulation of Sabatier reactor, the estimated inlet flow in atmospheric pressure is 0.638 ft³/min (18.1 lit/min) (Lunde 1974). This value could be changed in 10 atm case easily, so the values for volumetric flow rate of each component in influent become as in table 1.

Input parameter	Unit	value
Reaction pressure	atm	10
Inlet temp	K	550
inlet flow of CO ₂ (20 °C, 10 atm)	lit/ min	0.28
inlet flow of CH ₄ (20 °C, 10 atm)	lit/ min	0.42
inlet flow of H ₂ (20 °C, 10 atm)	lit/ min	1.12
inlet flow of vapor	mol/ min	0
Reacted CO ₂ per stage	%	4.5
Inner diameter of reactor tube	mm	35

Table 1. Input data

The strategy is that hydrogen and carbon dioxide enter the reactor in stoichiometric ratio. In each hypothetical element 4.5% of the initial CO₂ should be converted. For instance, in the first element 4.5% of 0.28 lit/min converts and the rest flows to the second element. In the second element another 4.5% of 0.28 lit/min would convert and the rest gets to the third element and this process continues till the 20th element. This assumption then gives us a fixed conversion of 90% in all different cases under consideration

The described mechanism is the same for all other compounds in influent. The only thing which is necessary to mention is considering the existence of CH₄ from the beginning in the reactor. This stream is injected to the reactor separately just to simulate the real biogas stream which consists of both CH₄ and CO₂ together. The inlet concentration of methane does not change the equilibrium constant, but it is increasing the flow and the heat capacity.

We can think of the conversion as the fixed parameter and size of the bed reactor as the unknown parameter which should be calculated for different cases. Temperature profile along the reactor could be the other unknown parameter which depends on changes in size of the bed and other initial parameters.

In order to use the correlations in different articles for further calculation it is needed to change the flow rate unit from lit/min to mol/min. This is easily done by using the ideal gas equation. Pressure term in the correlation is equal to 10 atm which is the total pressure of the system and temperature is equal to 293 K.

1.1.2 Division of bed into 20 elements

In table 2, there are molar changes along the bed from top to bottom. The first row in this table is the input flow of the whole reactor and first element as well, but the other rows could be interpreted as the outflow of the element which is mentioned in the same row of the table. As it is shown, the total number of moles is reducing through the reaction. This is because of the non-equimolar characteristics of the reaction. Also the relation between molar flows of different components is based on stoichiometric ratio.

No. of elements	n CO ₂ (mmol/min)	n H ₂ (mmol/min)	n CH ₄ (mmol/min)	delta CH ₄ (mmol/min)	nH ₂ O (mmol/min)	ntot (mmol/min)
0	116.45	465.8	174.7	0	0	756.95
1	111.21	444.84	179.92	5.25	10.5	746.50
2	106.00	424.00	185.16	10.50	21.00	736.16
3	100.73	403.00	190.40	15.72	31.44	725.60
4	95.50	382.00	195.64	21.00	41.92	715.06
5	90.25	361.00	201.00	26.20	52.40	704.65
6	85.00	340.00	206.12	31.44	63.00	694.12
7	80.00	319.10	211.36	36.7	73.40	683.90
8	74.53	298.11	216.60	41.92	83.85	673.10
9	69.30	277.15	221.84	47.16	94.32	662.61
10	64.05	256.20	227.10	52.40	104.80	652.15
11	58.81	235.23	232.32	57.64	115.30	641.70
12	53.56	214.30	237.56	62.88	125.80	631.122
13	48.32	193.30	242.80	68.12	136.25	620.70
14	43.08	172.35	248.04	73.36	146.73	610.20
15	37.85	151.40	253.30	78.60	157.21	599.76
16	32.60	130.42	258.50	84.00	167.70	589.22
17	27.36	109.50	263.8	89.08	178.17	578.83
18	22.12	88.50	269.00	94.32	188.67	568.30
19	17.00	67.54	274.25	99.56	199.13	557.92
20	11.65	46.60	279.50	104.80	209.61	547.40

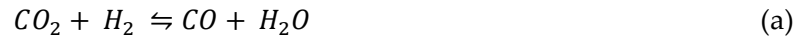
Table 2. Mole fractions in each element (4.5% conversion in each)

1.1.3 Cases for simulation

In this report there are two main cases considered. The first case is the **adiabatic** one in which all the generated heat is used to increase the temperature of the flows downward and nothing can be released to the surrounding. The second case then is known as the **real case** which happens in reality. The attempt in this case is to control temperature in the bed on the constant amount by cooling the bed in a heat exchanging mechanism with a coolant flows around the reactor.

1.1.4 Kinetic equation

Emmett did a complete research on carbon dioxide methanation which was published as a book named “catalysis”. He believed that the methanation process can be described as two consecutive reactions (Emmett 1951):



Since the first reaction is slow at the used reaction temperature (207-371°C) and the second one is more rapid than the (a), more in equilibrium form, then there is no carbon monoxide in the output stream. (Kester 1974)

Knowing the real reactions which are happening helps finding the catalytic mechanism and then formulating a model for the reaction. Since the reaction is in gas phase and reversible, reaction rate is dependent both on partial pressure of reactants and products. Lunde has found a correlation for calculating this parameter (Lunde 1974).

$$-\frac{d[P_{CO_2}]}{dt} = k \exp\left(\frac{-E_a}{RT}\right) \times \left\{ [P_{CO_2}]^n [P_{H_2}]^{4n} - \frac{[P_{CH_4}]^n [P_{H_2O}]^{2n}}{[K_e(T)]^n} \right\} \quad (1)$$

Lunde and Kester in the process of finding a well-suited correlation for rate of reaction did some experiments in laboratory reactors. Through these tests, they could estimate values for k, Ea and n with a rather good liability. In their investigation the following values were found:

$$k = 0.1769 \times 10^{10}$$

$$E_a = 16.84 \text{ kcal/gmol (30.320 btu/lbmol)}$$

$$n = 0.225$$

They derived these values from curves and lines of experimental results in different H₂/CO₂ ratios and also in different temperatures. (Lunde, Peter J., Kester, Frank L 1973)

1.1.5 Equilibrium considerations

The rate of reaction is also depending on the equilibrium constant (K_e) and K_e itself is temperature dependent. The extended equation for equilibrium constant calculation is as following (Lunde, 1974):

$$K_e(T) = \exp\left[\left(\frac{1}{1.987}\right)\left(\frac{56000}{T_k^2} + \frac{34633}{T_k} - 16.4 \ln T_k + 0.00557 T_k\right) + 33.165\right] \quad (2)$$

In this equation, T_k stands for Temperature in Kelvin unit. This equation is derived based on thermodynamic data by Wagman and et al in 1945 according to methods described by Brewer and Pitzer in 1961. The heat capacities that were used in this equation derived from Bureau of Mines Bulletins in 1949, 1950 and 1960 (Lunde, Peter J., Kester, Frank L. 1974)

1.2 Simulation result for the adiabatic case with interstage cooling

In this case, it is assumed that the heat which is generated through the reaction in each element is not released from the reactor, but increases the temperature of the outflow instead.

First of all it is needed to have some strategy for bed sizing, so then it could be modified or completed with temperature and enthalpy considerations. The following steps are used to calculate the length of bed:

- I. Calculating the rate of reaction by equation (1)
- II. Changing the unit atm./hr to mol/m³.min by simple using of ideal gas correlation
- III. Calculating volume of bed by dividing produced CH₄ molar flow rate in each element with rate of reaction in that specific element.
- IV. Calculating length of each element by considering the fixed cross sectional area
- V. The strategy in simulating this case is based on enthalpy changes along the bed.

The enthalpy transformations occur because of temperature increase due to the exothermic nature of reaction. The total enthalpy is constant, but chemical enthalpy is converted to thermal enthalpy. In order to relate the enthalpy of components to temperature changes, there are some polynomial correlations in different articles. Constants in these correlations are experimentally determined for different gases. Frolov and et.al (2009) in an article derived different experimental correlations for enthalpy calculations of real gases.

The molar enthalpy for CO₂ with reference temperature of 0 K in ideal-gas case is given as follows in Frolov article:

$$\frac{H_0}{R} = 3.49663 T_k + 2.215 \times 10^{-15} T_k^2 + \sum_1^4 \theta_i / \left[\exp\left(\frac{\theta_i}{T_k}\right) - 1 \right] \quad (3)$$

In equation (3), θ_i for CO₂ has different values. $\theta_1 = 3380$ K, $\theta_2 = 1995$ K and $\theta_3 = \theta_4 = 960$ K.

In the same article, there is another correlation which would be applied for the thermal enthalpy of H₂ as an ideal gas. In this one the assumptions are the same as before and $\theta = 6323.26$ K.

$$\frac{H_0}{R} = 3.45905 T_k + 5.03107 \times 10^{-5} T_k^2 + \theta / \left[\exp\left(\frac{\theta}{T_k}\right) - 1 \right] \quad (4)$$

The given correlations are both for reactants, but in order to do the calculations for the adiabatic case it is needed to have functions for product enthalpies as well. For H₂O, there is a correlation in the same article as well; therefore the assumptions are nearly similar with two previous components.

$$\frac{H_0}{RT} = 4.021083 - 1.413913 \times 10^{-5} T_k + 1.714913 \times 10^{-8} T_k^2 + \sum_{i=1}^3 x_i / [\exp(x_i) - 1] \quad (5)$$

In equation 5, the new parameter x_i is just a simple θ_i to T ratio : ($x_i = \theta_i/T$). For H_2O the values for θ_i are as follows: $\theta_1 = 5260.73$ K, $\theta_2 = 2294.37$ K, $\theta_3 = 5403.36$ K.

To calculate the thermal enthalpy for CH_4 there is another type of polynomial which is given by Passut and Danner (1972).

$$H = A + BT + CT^2 + DT^3 + ET^4 + FT^5 \quad (6)$$

A,B,C,D,E and F are coefficients regarding to enthalpy in Btu/lb and temperature in °R . For CH_4 the values for A to F are as following:

$$A = -5.58114, B = 0.564834, C = -0.282973 \times 10^{-3}, D = 0.417399 \times 10^{-6} \\ E = -1.525576 \times 10^{-10}, F = 1.958857 \times 10^{-14}$$

It is necessary to mention that since all the values in this report is in SI system, the enthalpy unit from equation (5) should be changed into SI

Now having the enthalpy function of all components in the reaction, the calculations could be done properly and knowing the fact that in Sabatier reaction there is -165 kJ/mol produced CH_4 heat production, the exit temperature of each element can be calculated by the following equations.

$$Q_{\text{generated}} = H_{\text{out}}F_{\text{out}} - H_{\text{in}}F_{\text{in}} \quad (7)$$

$$Q_{\text{generated}} = \left(165 \frac{\text{kJ}}{\text{mol}}\right) \times (4.5\%) \times (\text{entering flow of } CO_2 \text{ in the first element}) \quad (8)$$

Based on equation (8), the value for $Q_{\text{generated}}$ is a fixed amount for all elements which in this case is equal to 14.4 W per element. In equation (7) then, the left side is the same as equation (8), the F values are changing through the bed from top to bottom and enthalpies are changing due to the temperature changes, as well. H_{in} is a function of T_{in} and H_{out} is T_{out} dependent. The output temperature of each element is the input one for the next element. The other point which is necessary to mention is to assume the element temperature equal to input flow temperature. For example, in element number 1, the input flow temperature is 550K and it is assumed that the reaction in this element happens in 550 K as well.

In calculating the output temperature of each element, the temperature level increases to the point that the equilibrium conversion is reached in the middle of reactor and so the reaction could not go further and get to the assumed conversion of 90%. In table 3 there are results of adiabatic simulation on temperature and enthalpy aspects. As it is clearly shown the critical temperature happens somewhere around the 11th element. The equilibrium conversion (X_e) in this

case is 47% which is happening somewhere around the 11th element. The highest possible temperature which could be reached in adiabatic trial is 907.4469 K and in temperatures higher than that, equation (1) gets to zero or negative values and so it means that there could not be any reaction in temperatures higher than this. Therefore the 12th element and so forth ones do not play any role in this reaction!

Next step is to size each element and the whole bed respectively. The strategy has been already discussed, but there is some more to consider and it is about the steep increase of reaction rate by temperature rise. This fact then results in a very small volume for each element and so almost 50% conversion happens just in the first 1cm of the bed!

In table 3, there are calculation results of the 11 elements which reaction happens in them. It is clear enough that the volume of each element is decreasing sharply and also the rate of reaction is increasing in big steps even though the conversion is the fixed value of 4.5% in each element.

The graphical view of results in table 4 and 5 are given in following graphs. In figure 2, there are changes of yield and equilibrium conversion changes through the bed. It is clearly shown that in conversion around 50% the equilibrium and yield curve intercept one another. This means that the reaction gets to equilibrium at this point and so it cannot go further and increase the conversion of the reactants.

No. of elements	T _{gas} K	Yield	H(kW)	r _{CO2} (mol/lit.hr)	L (mm)
1	550	0.045	0.222	43.09	7.30
2	586.4	0.09	0.237	100.72	3.12
3	621.6	0.135	0.251	204.86	1.53
4	658.3	0.18	0.265	389.40	0.81
5	696	0.225	0.281	687.52	0.46
6	731.5	0.27	0.295	1077.38	0.29
7	767.1	0.315	0.310	1561.98	0.20
8	803.6	0.36	0.325	2095.01	0.15
9	838.6	0.405	0.340	2480.90	0.13
10	873.2	0.45	0.353	2497.60	0.126
11	907.4	0.495	0.368	1764.25	0.18
12	941.3	0.54	0.382	-266.58	-1.18

Table 3. Temperature changes along the bed and reactor sizing in the adiabatic case

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