Designing a new method to remove carbon dioxide as an environmental pollutant and produce methanol

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Abstract

Carbon dioxide is one of the flue gases emitted from fossil fuels that are harmful to the environment and humans. Producing valuable methanol from syngas is a proper method to recover CO₂ without requiring pretreatment. In this study, a new method is developed to produce methanol from flue gases emitted from fossil fuels. This process is simulated using Aspen Plus 8.0 software, and the results are compared with the data obtained by previous researches. Results confirmed the accuracy of the calculations and efficiency of the newly designed process. The purity of the produced methanol and the operational conditions are improved in this simulation.

Keywords Methanol · Carbon dioxide · Flue gas

1 Introduction

Nowadays, CO₂ removing and converting it into valuable products have become very important throughout the world. Removing it due to environmental requirements is not only for its hazardous impacts on global weather, but also for its unknown potential to produce some worthy materials [1, 2]. Separation of CO₂ from other waste products is a cost-benefit process and is not complicated [3–7]. The produce of methanol from syngas is a proper method to recover CO₂ without requiring pretreatment [8, 9]. In this process, methane gas is also injected as a hydrogen supplier. The CO₂ dry reforming and methane oxidation have been proposed by researchers for utilizing CO₂ with no pre-purification [3]. Attending the production of carbon (soot) in this method and deactivation of catalysts in reactor, subsequently, the carbon formation in the syngas production reactor should reduce to its minimum [10–12].

Injecting H₂O and O₂ into the process reduces the carbon formation on catalysts. In addition, the ratio of produced H₂ to CO in this reactor, which are the basic materials for producing methanol, should be designed

in a desirable range [13–15]. There are several studies that investigated the CO₂ removing using the described method [16, 17], but few studies focused on the methanol production potential of this method [8].

In this study, a novel process for producing methanol from the flue gas has been presented using the Aspen Plus 8.0 software. The purity percentage of the produced methanol and working conditions have been improved in this simulation. The results of simulation have been validated using data obtained in the earlier similar researches. The aim of this study is designing an economical process for industries producing high-purity methanol from the flue gas. For this purpose, industrial data of flue gas have been used.

2 Simulation of process

Simulation of methanol production from flue gasses has been performed using the Aspen Plus 8.0 software. The new design has been based on high purity, low capital and operational costs, and also reducing the cost of

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Fig. 1 Process flow sheet of methanol production from flue gas and methane as reactants

Table 1 The composition of flue gas stream (mol%)

Component	Molar percent
CO ₂	10
H ₂ O	20
O ₂	3
N ₂	67

conservation/storage of methanol at high temperatures and pressures.

Figure 1 shows the process flow diagram of high-quality methanol production from the flue gasses and natural gas. M1 is a mixer to mix flue and CH₄ gases that pass the heater h1, for increasing its temperature, and that enter a gasifier reactor to produce the syngas. The syngas temperature is decreased in C1, and this gas is mixed with a recycled and purged gas in M2, is compressed and also heated up in compressor–heater (H2), and finally is injected into the MEOHRTX to produce methanol. The produced methanol should be separated and purified in a suitable separator.

In this study, the defined flue gas properties have been extracted from the published data from an industrial unit [8]. Composition of the used stream is shown in Table 1. This table shows that the input stream consists of both CO₂ and H₂O, which reacted together and produced methanol. The molar flow rate and temperature of the stream are 1000 kmol/h and 150 °C, respectively. Moreover, a methane stream (natural gas at STP conditions) is fed into the system, as another feed.

In the newly designed process, two reactors have been applied. The first reactor is of RGIBBS type (based on minimization the Gibbs energy of system) and is used to

Table 2 The set of reactions

Reactor	Reaction	Number
RGIBBS	CO ₂ + CH ₄ → 2CO + 2H ₂	1
	H ₂ O + CH ₄ → CO + 3H ₂	2
	1/2O ₂ + CH ₄ → CO + 2H ₂	3
	2O ₂ + CH ₄ → CO ₂ + 2H ₂ O	4
	CH ₄ → C + 2H ₂	5
	2CO → C + CO ₂	6
	C + CO ₂ → 2CO	7
	C + H ₂ O → CO + H ₂	8
	C + O ₂ → CO ₂	9
REQUIL	2H ₂ + CO → CH ₃ OH	10
	CO ₂ + 3H ₄ → CH ₃ OH + H ₂ O	11
	CO + H ₂ O → CO ₂ + H ₂	12

generate syngas (1–9). The second one is of REQUIL type (based on thermodynamic calculations) and is used to generate methanol (10–12). Table 2 presents the set of the relevant reactions to these reactors. The presented reactions in the RGIBBS reactor produce the CO and H₂ gases, which are required to produce methanol. These components react together in the REQUIL reactor and produce methanol. The mixture gas produced in the first reactor is cooled down to 220 °C and is pressurized up to 50 bar, which are required at the methanol synthesis reactor. A three-stage compressor is used to create such pressure. Reactions (10 and 11) are the main reactions for methanol production that occurs inside this reactor, while the reaction (12) is a side reaction. N₂, as a flue stack part from

Table 3 Operating conditions for methanol production

Flow sheet element	Temperature (°C)	Pressure (bar)
Methanol reactor	220	50
Sep1 (adiabatic)	25	24
Sep2 (adiabatic)	25	1

Fig. 2 Effect of temperature on equilibrium product composition at CH₄/flue gas = 0.4 and pressure = 1 atm in GASIFIER [8]

the combustion of furnaces in power plants, inputs the designed system and reduces methanol production rate. Therefore, a gas cycle has been formed to make a higher percentage of methanol production and recover the reaction. In the recycle stream, the produced gas returned to the reactor. A separator has been placed here (Sep1) for the partial separation of impurities, which helps to remove waste gases. In the last step, another separator (Sep2) has been embedded that separates almost all N₂ from methanol. Operating conditions for the methanol production are listed in Table 3.

Based on the previous study [8], the temperature of the gas synthesis reactor, its pressure and the ratio of inlet molar flows were ranged from 400 to 1200 °C (Fig. 2), 1 to 5 atm (Fig. 3), and 0.4 to 1 (Fig. 4), respectively, and the most appropriate values for these variables were obtained. The mole fraction of carbon monoxide has been increased by increasing the temperature to its maximum value at 850 °C, but the fraction of CO₂ has been decreased to zero at this temperature. Therefore, CO₂ is the limiting reactant for the reaction.

Increasing the temperature increases the mole fraction of H₂ and decreases the mole fraction of CH₄. It shows a significant relationship between CH₄ consumption and H₂ production. Increasing CH₄/flue gas ratio increases the H₂ molar flow, but at the temperatures up to 850 °C, this relationship has been broken down. The CH₄/flue gas ratio also affects CO production, and CO flow rate starts to increase from zero at 400 °C. Increasing this ratio also increases the CO₂ production. Increasing the pressure from 1 to 5 atm decreases the hydrogen fraction and increases the methane fraction. At temperatures up to 100 °C, the pressure effect is negligible. According to these data, the best temperature and pressure for gasifier reactors are 850 °C and 1 atm, respectively. In addition, the best ratio of methane to flue gas is 0.4%.

3 Results and discussion

The properties of inlet and middle streams of this simulation are presented in Table 4. The archived data show the suitable separation of nitrogen in SEP2. It is also clear that the carbon dioxide is produced in the equilibrium reactor, which shows that the reaction 12 is more favored than the reaction 11 in this setup. The temperature and pressure of the gas synthesis reactor were set at 400 °C and 1 atm, respectively. In addition, the input streams (flow rate of methane and flue gas) were set at 400 and 1000 kmol/hr, respectively.

In the similar study [8], an equilibrium distillation tower was used to increase the percentage of methanol purity. Manufacturing and maintenance of this tower have many expenses, as well as the supply of heat energy for re-boiling and condensing. One of the advantages of this study is the production of a high-purity methanol by optimizing the control parameters and without using a distillation tower.

Table 5 lists the characteristics of the main streams of the proposed process. Figure 5 shows a comparison between the molar stream flows in the new proposed process (1) and in the pervious similar one (2), which used a distillation tower instead of optimizing the parameters. The results show that the methanol purity for process (1) is 99.69% and greater than 99.57 in process (2). In addition, in Fig. 6, a similar comparison between the energy consumption of these two

Fig. 3 Effect of reaction pressure on equilibrium **a** hydrogen, **b** methane, **c** carbon monoxide, **d** carbon dioxide in GASIFIER [8]

processes has been shown. It is clear that a significant decrement (about 19%) in energy consumption has happened in this newly proposed process.

In this study, by making pressure changes in the pressure reducer valve and last separator, the pressure has been decreased to a standard value. These changes reduce the cost, by eliminating the distillation tower. Furthermore, conditions that are more comfortable have been determined for saving methanol in the reservoirs. Figure 7 shows a comparison between temperature and pressure of these systems, with distillation column and

without it. It is clear that the newly designed process has a lower temperature and pressure than the designed process in the previous study [8].

4 Conclusion

In the presented study, the production of methanol from flue gases was simulated using the Aspen Plus 8.0 software. The temperature and pressure of the gas production reactor and the molar ratio of CH₄/flue gas were optimized,

Fig. 4 Effect of $\text{CH}_4/\text{flue gas}$ ratio on equilibrium **a** hydrogen, **b** carbon monoxide, **c** carbon dioxide in GASIFIER [8]

Table 4 Inlet and middle streams specifications

	CH ₄	FLUEGAS	MIX-GAS	MIX-GAS	TO-REACT	SYN1
CH ₄	400	0	400	400	400	44.9918
CO ₂	0	100	100	100	100	1.5704
CO	0	0	0	0	0	453.438
H ₂	0	0	0	0	0	906.595
O ₂	0	30	30	30	30	1.5451×10^{-19}
H ₂ O	0	200	200	200	200	3.42141
C	0	0	0	0	0	5.4209×10^{-22}
N ₂	0	670	670	670	670	670
METHANOL	0	0	0	0	0	6.58933×10^{-7}
Total flow, kmol/h	400	1000	1400	1400	1400	2080.02
Total flow, kg/h	6417.1	27,733	34,150.1	34,150.1	34,150.1	34,150.1
Total flow, l/min	162,734	578,312	732,225	732,225	2.1794×10^6	3.19563×10^6
Temperature, °C	25	150	109.664	109.664	850	850
Pressure, bar	1.01325	1.01325	1.01325	1.01325	1	1.01325
Vapor frac	1	1	1	1	1	1
Liquid frac	0	0	0	0	0	0
Solid frac	0	0	0	0	0	0
Enthalpy, cal/mol	−17,803.2	−20,019.8	−19,386.5	−19,386.5	−11,987.5	−188.705
Enthalpy, cal/gml	−1109.73	−721.877	−794.758	−794.758	−491.434	−11.4937
Enthalpy, cal/s	$−1.9781 \times 10^6$	$−5.5611 \times 10^6$	$−7.5392 \times 10^6$	$−7.5392 \times 10^6$	$−4.6618 \times 10^6$	−109,030
Entropy, cal/mol K	−19.2605	2.39455	−2.50402	−2.50402	7.92369	16.2063
Entropy, cal/gm K	−1.20057	0.086343	−0.102654	−0.102654	0.324835	0.987094
Density, mol/cc	4.09666×10^{-5}	2.88195×10^{-5}	3.18663×10^{-5}	3.18663×10^{-5}	1.07063×10^{-5}	1.08482×10^{-5}
Density, gm/cc	0.000657218	0.000799252	0.000777314	0.000777314	0.000261158	0.000178108
Average, MW	16.0428	27.733	24.393	24.393	24.393	16.4182
Liq Vol 60F, l/min	357.052	774.271	1131.32	1131.32	1131.32	1856.66

as well. The main advantage of the newly designed process was its ability to produce high-purity methanol with low costs, which is derived from conservation and storage of methanol at standard temperature and pressure. In order to facilitate the industrial use of this newly designed process, real data of a flue gas of an industrial unit were used as input stream for simulation. The newly designed method leads to significant reduction in costs and energy consumption (19% reduction) by eliminating the distillation tower, high-purity methanol (99.69%) and simpler storage conditions, by applying pressure corrections in

various parts of the process. The simulated data showed the profitability of the newly designed process and the introduced reactors and separators to produce methanol from the inlet gases. It was shown that the newly designed process works at lower temperature and pressure than the other designed processes in the similar previous studies. Finally, the results confirmed that the proposed process has the ability to produce this valuable material (methanol) from carbon dioxide, as an environmental pollutant, with low capital and operating costs.

Table 5 Stream results from methanol production via removing the distillation tower and pressure corrections

	SYN1	P4	PURGE1	PURGE2	P6
CH ₄	44.9918	0.333417	44.6554	0.305948	0.0274691
CO ₂	1.5704	0.292196	3.78457	0.148134	0.144062
CO	453.438	0.0845544	61.5636	0.0832253	0.00132917
H ₂	906.595	0.0626598	130.305	0.062326	0.000333837
O ₂	1.5451×10^{-19}	0	0	0	0
H ₂ O	3.42141	0.910275	0.00513507	0.000369681	0.909905
C	5.4209×10^{-22}	0	0	0	0
N ₂	670	2.31504	667.64	2.22489	0.0901467
METHANOL	6.58933×10^{-7}	381.158	8.13839	0.539519	380.618
Total flow, kmol/h	2080.02	385.156	916.092	3.36441	381.792
Total flow, kg/h	34,150.1	12,315.1	21,833.9	93.5054	12,221.6
Total flow, l/min	3.19563×10^6	259.74	15,667.1	1367.81	256.852
Temperature, °C	850	25	25	25	25
Pressure, bar	1.01325	24	24	1.01325	1.01325
Vapor frac	1	0	1	1	0
Liquid frac	0	1	0	0	1
Solid frac	0	0	0	0	0
Enthalpy, cal/mol	-188.705	-57,266.2	-3494.64	-14,118.5	-57,655.7
Enthalpy, cal/gm	-11.4937	-1791.01	-146.626	-507.997	-1801.12
Enthalpy, cal/s	-109,030	-6.1268×10^6	-889,280	-13,194.6	-6.1146×10^6
Entropy, cal/mol K	16.2063	-59.088	-4.38478	-4.00693	-59.4834
Entropy, cal/gm K	0.987094	-1.84799	-0.183974	-0.144173	-1.85821
Density, mol/cc	1.0848×10^{-5}	0.0247141	0.000974541	4.09951×10^{-5}	0.0247738
Density, gm/cc	0.000178108	0.790217	0.0232268	0.00113935	0.793037
Average, MW	16.4182	31.9743	23.8337	27.7925	32.0111
Liq Vol 60F, l/min	1854.66	259.261	815.935	2.88406	256.377

Fig. 5 Comparison between molar flow (kmol/h) of methanol (green color), output streams (red color) and the (1) suggested method, (2) with a similar process without pressure corrections and by using a distillation tower **Fig. 6** Comparison between consumed energy (kw) in two systems: without tower (green color) and with tower (red color)

Fig. 7 Comparison between outlet pressure (bar) (green color) and temperature (°C) (red color) in two systems: (1) without tower; (2) with tower

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Informed consent The research involved no human participants.

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