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MODELLING AND SIMULATION OF METHANOL PRODUCTION FROM COKE OVEN GAS

LETITIA PETRESCU[a]*, DUMITRITA-AURA CRISAN [a]

ABSTRACT. Coke Oven Gas (COG) is highly rated as a valuable by-product of coke production used in the steel industry. The production of methanol from COG-derived syngas has been investigated in the last period due to its practicality as well as to the recent interest in methanol over the past years. Two case studies, using COG and CO_2 as raw-materials, are simulated and compared in the present study. In the first case the intermediate step is the dry methane reforming (DMR) while in the second case the intermediate step is steam methane reforming (SMR). The syngas obtained is furthermore converted to methanol. Beside the transformation of COG into methanol, the present study deals also with the CO_2 emissions reduction, the CO_2 generated in the COG combustion is captured using amine based gas-liquid absorption technology (e.g. methyl diethanolamine - MDEA)). ChemCAD process flow-modelling software was used as a tool to produce 250 t/day of methanol with purities higher than 99%. The results showed that the most advantageous technological route of COG and CO_2 utilization is DMR, in which, a lower quantity of raw material (COG) and lower number of equipment is required to obtain the same amount of final product.

Keywords: *Coke Oven Gas, Process Modelling and Simulation, Methanol production, Technical evaluation.*

INTRODUCTION

Methanol is an important raw material synthetized in large quantities in the chemical industry. It is an important material in the production of various chemical solvents, antifreeze and fuels. One of the most common uses of methanol is in the formaldehyde production. Formaldehyde is further used in the production of plastics, including those for construction, car paints, explosives or as a preservative for organisms in biological laboratories. Other

[a] *Department of Chemical Engineering Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos str., RO-400028, Cluj-Napoca, Romania*
** Corresponding author letitiapetrescu@chem.ubbcluj.ro*

substances using methanol as a raw material / intermediate are: acetic acid, methyl tert-butyl ether (MTBE), dimethyl ether (DME), methylamine, dimethyl carbonate (DMC), chloromethane. Besides its applications in the chemical and power industry, methanol attracted attention through its potential for use in the automotive industry, where it can be used as a fuel or it can lead to other fuels generation (i.e. biodiesel). Storing energy in the form of methanol could put an end to fossil fuel dependence, transforming carbon dioxide into a raw material for an economy based on methanol. This status is expected to last in the near future or even to improve it in order to transform it in a central participant in the worldwide economic landscape [1]. For these reasons, every improvement to methanol production process, in terms of energy savings, optimization, and minimization of its environmental impact has potential to promote relevant economic progress.

Coke oven gas (COG), a by-product of the coking process, can be used in effectively reducing the CO_2 emissions caused by the steel industry. The production of methanol from COG-derived syngas has been investigated in the last period due to its practicality to obtain a liquid fuel instead of a gaseous product as well as to the recent interest in methanol over the past years [2]. The CO_2 emissions reduction in the steel industry can also be performed through transforming COG into valuable products such as synthesis gas, hydrogen or methanol [3]. The process to transform COG to methanol is quite complex. The COG has a complex composition at the exit of the coke oven. It suffers several transformations in order to be converted into synthesis gas and furthermore to methanol. Firstly, the COG is cooled to remove pitch, which may form deposits on the gas lines, and then the NH_3, H_2S, benzene, toluene and xylene are removed from the COG. Chemically speaking COG has the following composition: H_2 55 - 60%; CH_4 23 - 27%; CO 5 - 8%; N_2 3 - 6%; CO_2 2%. Traces of other hydrocarbons can also be present in the COG. The high calorific value of COG (e.g. 17 - 18 MJ/m^3) is due to the substances from its composition: H_2, CH_4, CO, C_2H_6.

Dry methane reforming (DMR) is a technology that converts two stable molecules, CH_4 and CO_2, into syngas. The process occurs at 700 – 900°C, at one atmosphere pressure or lower, using Ni, Rh and Ru catalysts. It is considered to be an effective method for methanol synthesis, due to the possibility of obtaining an optimal H_2/CO ratio in a single step, as long as the reaction takes place under stoichiometric conditions of CH_4 and CO_2. In addition, the process involves partial recycling of CO_2, half of the carbon dioxide produced by the system being recycled. COG–DMR is investigated as a first option in the present study [4].

The most common way of obtaining methanol is through methane steam reforming (SMR). In the present study, the methane used for methanol generation comes from COG produced in a steel plant, so COG-SMR is

considered as a second option. The conversion of COG into synthetic natural gas (SNG) is an efficient method to supply the high demand for natural gas on the market. The natural gas is a non-renewable energy source with a heat capacity between 20.1 and 38.26 MJ/m^3 and it is not accessible in the long term. The SNG can be used in the chemical, energetic and transportation industries. Compared to the equivalent coal mass, the natural gas use reduces carbon dioxide emissions by approximately 40%. COG is too rich in hydrogen to be used in the methanation reaction for producing SNG. The (H_2-CO_2)/(CO+CO_2) ratio in the COG is between 5 and 6, the optimum value for the methanation being approximately 3 a high quantity of hydrogen remaining unconverted. The various studies on the technologies where an additional carbon source is needed revealed that, the use of an internal carbon source, produced within the system, instead of using an external gas source, can be a convenient solution to solve this problem. A considerable amount of carbon dioxide results from the combustion of coke oven gas for heat generation. This carbon dioxide is separated and reintroduced into the process using the gas-liquid absorption (e.g. MDEA) [5]. The SNG obtained is further used in the methanol production process, using syngas as an intermediary product.

As already mentioned, two different methods of obtaining methanol are presented and compared in the present work (see Figure 1):

- DRM using COG and CO_2 as raw materials and
- SMR, with SNG as a raw material for SMR. SNG is obtained through COG methanation and CO_2 recycling.

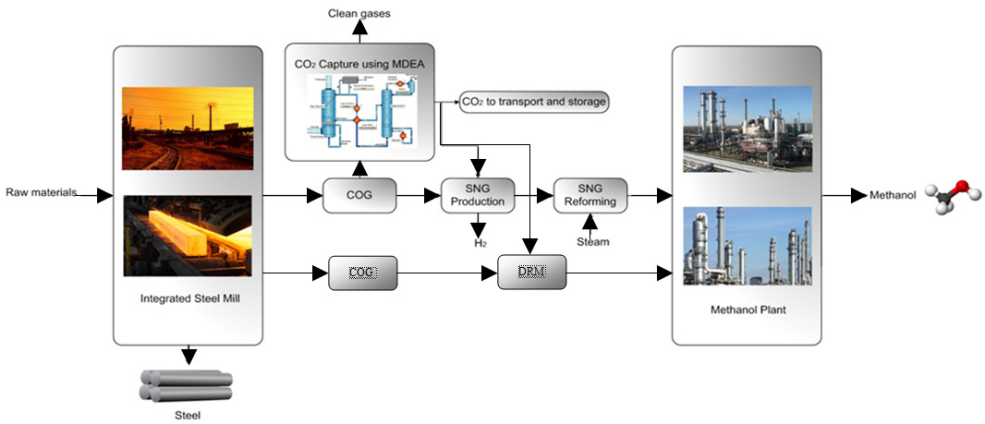

Figure 1. Methanol production from COG

The novelty of the present work consists on the technological comparison of the above mentioned technologies for methanol synthesis using COG and CO_2 as raw-materials.

RESULTS AND DISCUSSION

The cases investigated in the present work with their correspondent sub-processes are presented in Table 1.

Table 1. Cases investigated and their correspondent sub-processes

Case Name	Sub-process considered
Case A	COG combustion
	CO_2 capture using amine based gas-liquid absorption (i.e. MDEA)
	DMR for syngas generation
	Methanol synthesis from syngas
Case B	COG combustion
	CO_2 capture using amine based gas-liquid absorption (i.e. MDEA)
	SNG production
	SMR of SNG for syngas generation
	Methanol synthesis from syngas

A schematic representation of the two cases under study is illustrated in Figure 2 and Figure 3 under EXPERIMENTAL SECTION.
The main streams for *Case A* are reported in Table 2.

Table 2. Main inputs and outputs for syngas production (*Case A*)

Parameters	Unit of measure	Streams			
		COG	CO_2 from CO_2 capture unit	Before DRM	After DRM
Pressure	atm	0.98	0.98	0.98	0.98
Temperature	°C	25	35	980	1000
Vapour fraction	-	1	1	1	1
Liquid fraction	-	0	0	0	0
Component mole flow-rate					
Carbon Monoxide	kmol/h	53.95	0.00	32.46	327.55
Hydrogen		535.94	0.00	324.60	613.00
Carbon dioxide		27.25	133.77	150.28	1.07
Water		0.00	0.06	0.06	3.41
Nitrogen		45.41	0.38	27.89	27.89
Methane		245.46	0.00	148.54	2.66
Methanol		0.00	0.00	0	0.00
Total flow-rate	kmol/h	907.82	134.23	683.83	975.58
Total flow-rate	kg/h	8997.99	5899.79	11343.09	11343.09

As noticed from Table 2, starting from 907.82 kmol/h of COG and 134.23 kmol/h of CO_2 captured a molar flow-rate of 975.58 kmol/h gaseous stream is obtained in the DRM. The DMR stream has a high content of hydrogen (e.g. 613.00 kmol/h) and CO (e.g. 327.55 kmol/h). Small traces of N_2, CO_2, CH_4 and CO_2 can be also found in the outlet of DMR. This stream is furthermore sent to methanol synthesis step. The main inputs and outputs streams for methanol production using DRM as intermediary step are presented in Table 3.

Table 3. Main inputs and outputs for methanol production (*Case A*)

Parameters	Unit of measure	Streams			
		After DRM	Before methanol synthesis	After methanol synthesis	Main product
Pressure	atm	0.98	107.08	106.1	0.98
Temperature	°C	1000	267	267	64.00
Vapour fraction	-	1	1	1	1
Liquid fraction	-	0	0	0	0
Component mole flow-rate					
Carbon Monoxide	kmol/h	327.55	499.35	179.77	0.01
Hydrogen		613.00	1392.61	736.25	0.03
Carbon dioxide		1.07	33.68	27.96	0.02
Water		3.41	0.19	5.92	0.34
Nitrogen		27.89	1338.08	1338.08	0.03
Methane		2.66	18.30	18.30	0.002
Methanol		0.00	4.44	329.76	325.09
Total flow-rate	kmol/h	975.58	3286.69	2636.05	325.58
Total flow-rate	kg/h	11343.09	56201.58	56201.58	10425.88

The gaseous stream obtained in the DMR (e.g. 975.58 kmol/h) is mixed with a recycled stream coming from methanol purification section. As noticed from Table 3, the inlet of the methanol reactor is about 3286.69 kmol/h. The ratio between H_2 and CO at the inlet of the reactor is around 3. CO and H_2 conversion in the methanol reactor is higher than 45%, more exactly 47.13%. A quantity of 325.58 kmol/h of methanol was produced in the above presented process.

The main inputs and outputs derived from process modeling and simulation in the second option investigated (*Case B*) are summarized in Table 4.

Table 4. Main inputs and outputs for SNG production (*Case B*)

Parameters	Unit of measure	Streams			
		COG	CO_2 from CO_2 capture unit	After methanation	SNG after purification
Pressure	atm	0.98	0.98	23.50	39.50
Temperature	°C	25	35	35	400
Vapour fraction	-	1	1	0.65	1
Liquid fraction	-	0	0	0.35	0
Component mole flow-rate					
Carbon Monoxide	kmol/h	60.94	0.00	0.00	0.00
Hydrogen		596.30	0,00	7.17	0.00
Carbon dioxide		30.32	59.88	0,00	0.00
Water		0.00	0.03	221.87	0.00
Methane		272.88	0.00	366.13	366.02
Nitrogen		50.53	0.19	42.72	19.22
Oxygen		0.00	0.005	0.00	0.00
Total flow-rate	kmol/h	1010.68	60.10	637.90	385.25
Total flow-rate	kg/h	10028.55	2641.26	11082.21	6410.86

As noticed from Table 4, starting from 1010.68 kmol/h of COG and 60.10 kmol/h of CO_2 a quantity of 385.25 kmol/h of SNG was obtained. A total conversion of COG to SNG was considered. This high conversion leads to a high purity SNG (e.g. 95% mole fraction). The SNG stream obtained from COG is furthermore used in methanol production. The main inputs and outputs streams for methanol production from SNG are presented in Table 5.

As reported in Table 5, a flow-rate of 385.25 kmol/h of SNG is sent to the SMR for syngas production. SNG is converted into syngas using about 1004.10 kmol/h of steam. A flow-rate of 2072.86 kmol/h syngas is obtained. This stream is mixed with some recycled stream coming from methanol purification section. The flow-rate of the recycled stream is 348.44 kmol/h. The mixed stream is sent to methanol synthesis reactor. CO, CO_2 and H_2 are transformed into methanol, which is furthermore separated using a flash and a distillation column. The final flow-rate of methanol is 327.71 kmol/h, as noticed from Table 5.

Table 5. Main inputs and outputs for methanol production (*Case B*)

Parameters	Unit of measure	Streams			
		SNG	After reforming reactor	After methanol synthesis	Main product
Pressure	atm	39.50	38	107.5	0.98
Temperature	ºC	400	1000	267	64.49
Vapour fraction	-	1	1	1	1
Liquid fraction	-	0	0	0	0
Component mole flow-rate					
Carbon Monoxide	kmol/h	0.00	261.18	143.60	$2*10^{-3}$
Carbon dioxide		0.00	805.87	348.23	0.05
Hydrogen		0.00	1105.83	15570.88	0.10
Nitrogen		19.22	19.22	34.07	$2*10^{-4}$
Methane		366.02	24.27	1111.38	0.03
Water		0.00	581.77	80.72	2.44
Methanol		0.00	0.00	331.91	325.09
Total flow-rate	kmol/h	385.25	2072.86	17636.87	327.71
Total flow-rate	kg/h	6410.86	24499.58	81670.13	10463.54

The main technical key performance indicators obtained in the two investigated cases are reported in Table 6.

Table 6. Comparative results obtained in *Case A* and *Case B*

Parameter	Component	*Case A*	*Case B*
Raw-material (kmol/h)	COG	907.82	1010.68
	CO_2	134.23	60.10
Final product (t/day)	CH_3OH	250	250
MeOH (wt.%)		99.92	99.55
CO_2 capture rate (%)		84.53	84.77
No. of unit operations involved in the whole process		48	66
Energy consumption (MW)		13.50	14.20
CO_2 emissions (kg/h)		48.76	395.20

As presented in Table 6, different quantities of raw-materials (i.e. COG and CO_2) are used in the two investigated technologies in order to obtain the same quantity of methanol (e.g. 250 t/day). Higher quantities of COG are used in *Case B* compared to *Case A* (e.g. 1010.68 kmol/h vs. 907.82 kmol/h). The CO_2 flow-rate is two times lower in *Case B* compared to

Case A. High methanol purities are obtained in both cases. Almost pure methanol is obtained in *Case A*. The CO_2 capture rates are about 85% in both cases. The energy consumption in *Case A* is lower compared to the energy consumption used in *Case B* (e.g. 13.50 MW vs. 14.20 MW). The number of unit operations involved in *Case A* is lower compared to *Case B* (e.g. 48 units operations vs. 66 units operations). The CO_2 emissions in *Case A* are about eight times lower compared to the CO_2 emissions from *Case B*.

CONCLUSIONS

The aim of the present paper was to compare, from technological point of view, two processes for methanol production using COG and CO_2 as raw materials. In order to reach the proposed goal process flow-modeling tools (i.e. ChemCAD process simulator software) was used. The plant capacity in each case was set to 250 t / day. The simulations results are in accordance with the data from the scientific literature, fact which was demonstrated by models validation.

From a technological point of view, the most advantageous route, between the two investigated cases, is methanol production from COG through DMR – *Case A*, in which a lower quantity of COG is required to obtain the same amount of final product. The other solution investigated was methanol production from COG through SMR, denoted as *Case B*.

The two cases are compared using various key performance indicators. Less unit operations are involved in *Case A* compared to *Case B*. Considering the CO_2 emissions released in the two investigated cases it can be concluded that these emissions are eight times less in *Case A* compared to *Case B*. The technologies of methanol production from COG are in line with the current environmental problems, due to the following two aspects:1) they valorize a by-product of steel plants (i.e. COG), turning it into valuable products (SNG and methanol); 2) they reduce the CO_2 released into the atmosphere.

It can be concluded that methanol production from COG and CO_2 capture through DMR offers several advantages.

EXPERIMENTAL SECTION
GENERAL PRESENTATION

Figure 2 illustrates the block flow diagram for *Case A*. The first intermediate step considered in this case is the DRM. The COG is mixed with a CO_2 stream which was previously generated during the total combustion of

some COG and captured using amine based gas-liquid absorption technology (using MDEA as a solvent). The methane-carbon dioxide mixture is introduced into the catalytic reforming reactor leading to syngas. The obtained syngas is cooled, compressed and sent to methanol synthesis step, where CO, CO_2 and H_2 are converted to methanol. The final step is the methanol separation. A methanol stream having a flow-rate of 250 t / day and a purity of 99.92% is obtained after the separation step.

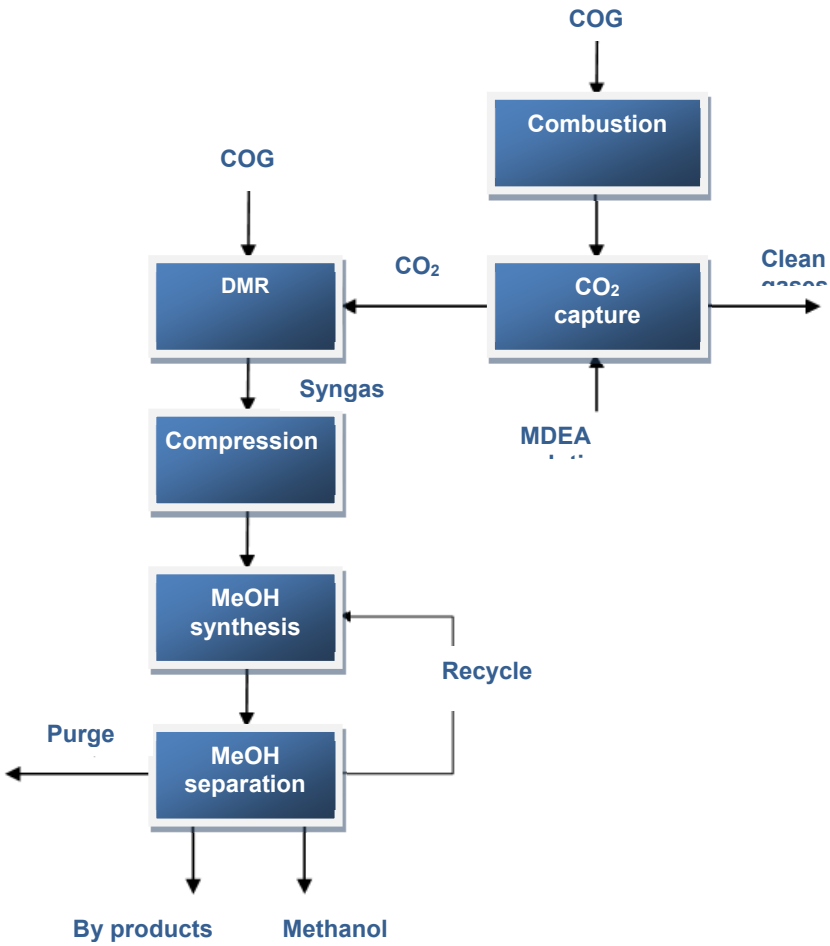

Figure 2. Simplified block flow diagram for *Case A*

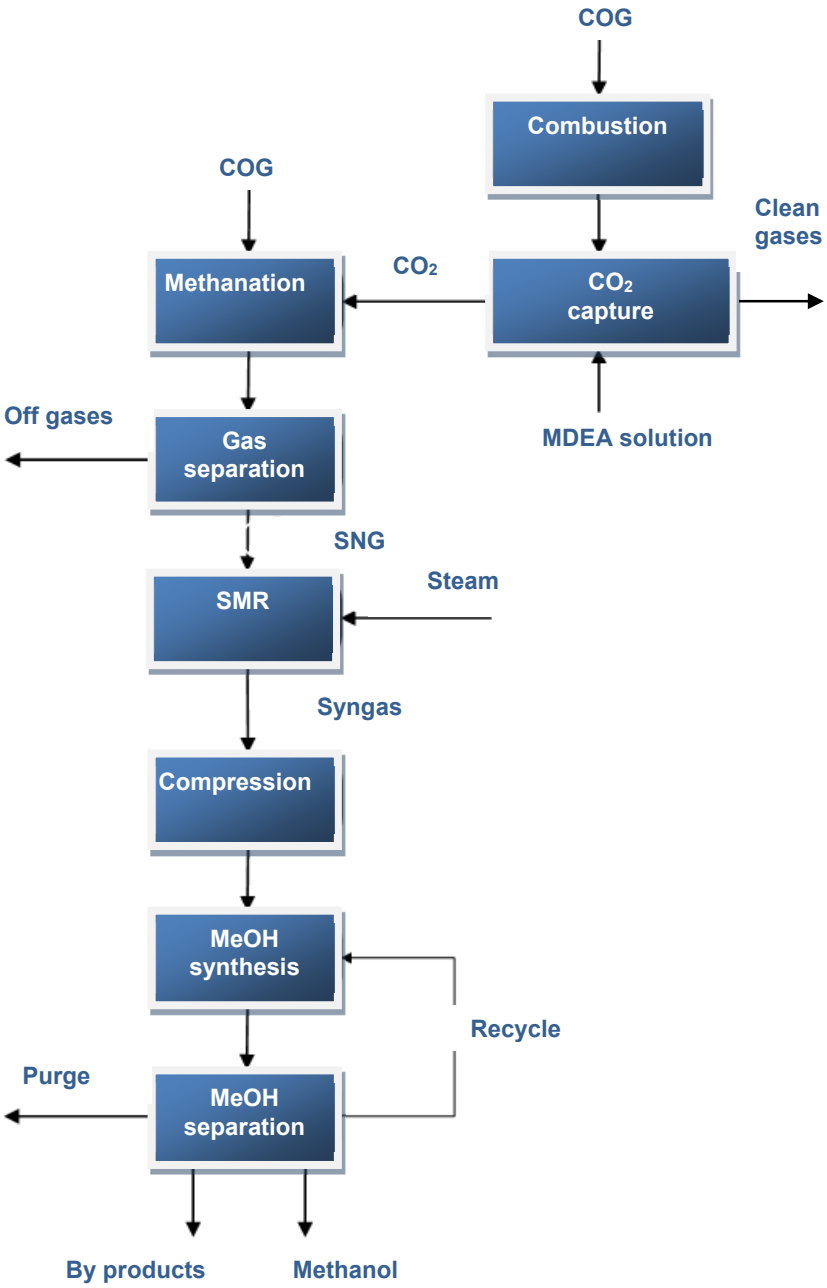

Figure 3. Simplified block flow diagram for *Case B*

Figure 3 shows the simplified block diagram for *Case B*. COG is the raw material also used in this case. It is divided into two streams, one part is sent to the combustion chamber and the rest to the methanation step. The combustion gases are sent to a CO_2 capture unit. As in the previous case, CO_2 capture is based on gas-liquid absorption. MDEA is the solvent used for CO_2 removal. After separation, pure CO_2 is reintroduced into the system together with the COG stream. The COG - CO_2 gas mixture obtained is sent to the methanation unit which leads to a rich CH_4 stream. This is furthermore separated in a stream containing 91.59% CH_4 called also SNG. Furthermore, SNG is fed to a SMR unit where, using steam, CH_4 is converted to syngas. The syngas is sent to the cooling unit, compressed and sent to the methanol synthesis step. The result of this step is a methanol rich product, which is purified in a separation system. The same productivity of methanol (e.g. 250 t / day) is obtained in *Case B*. Methanol purity in this case study is 99.55%.

The reactions tacking place in the combustion step are (R_1 - R_3) presented below [5]:

(R_1): $H_2 + 0.5O_2 \rightarrow H_2O$ $\Delta H_{298K} = -285.83 kJ/mol$
(R_2): $CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$ $\Delta H_{298K} = -890.36\ kJ/mol$
(R_3): $2CO + O_2 \rightarrow 2\ CO_2$ $\Delta H_{298K} = -566\ kJ/mol$

All reactions are exothermic, generating heat for the process in which coal is turned into coke. The process temperature varies between 1250 - 1300˚C. In general, the excess air coefficient is between 1.2 - 1.3. For the simulation of the process, the air coefficient was set to 1.25. The reactions take place completely, all the components (H_2, CH_4, CO) being transformed into water and carbon dioxide.

The reactions occurring in the methanation step are (R_4 - R_6) [5]:

(R_4): $CO + 3\ H_2 \rightarrow CH_4 + H_2O$ $\Delta H_{298K} = -206\ kJ/mol$
(R_5): $CO_2 + 4\ H_2 \rightarrow CH_4 + 2H_2O$ $\Delta H_{298K} = -165\ kJ/mol$
(R_6): $CO + H_2O \rightarrow CO_2 + H_2$ $\Delta H_{298K} = -41\ kJ/mol$

The first two reactions are strongly exothermic, and the third reaction occurs only when the carbon monoxide concentration is low and the hydrogen is in excess. In the industry, the catalysts used for the methane process are nickel-based. They maintain high activity in a wide temperature range (200 - 700°C) and can convert almost 100% of CO and over 98% of the CO_2.

The reactions taking place in the CO_2 capture section are (R_7 – R_{10}) [5]:

(R_7): $MDEAH^+ + H_2O = MDEA + H_3O^+$
(R_8): $CO_2 + OH^- = HCO_3^-$
(R_9): $HCO_3^- + H_2O = H_3O^+ + CO_3^{2-}$
(R_{10}): $2H_2O = H_3O^+ + OH^-$

The reaction considered for DRM is R_{11} [2, 3]:

(R_{11}): $CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO$ $\Delta H_{298K} = 247.30$ kJ/mol

The interest for DRM technology is due to the low energy consumption, compared to the SMR, because it uses two greenhouse gases: CO_2 and CH_4 generating valuable products. CO_2 reforming allows the production of a synthesis gas with low H_2 / CO ratios, theoretically 1/1.

The reaction considered in SMR is R_{12} [2, 3]:

(R_{12}): $CH_4 + H_2O \rightarrow 3H_2 + CO$ $\Delta H_{298K} = 206.20$ kJ/mol

SMR is currently the main process for obtaining synthesis gas. This involves the catalyzed reaction between methane and steam to obtain the synthesis gas with an increased H_2 / CO ratio, the optimum value being 3/1.

The reactions taking place in the methanol synthesis are (R_{13} - R_{15}) [2, 3]:

(R_{13}): $CO + 2H_2 \leftrightarrow CH_3OH$ $\Delta H_{298K} = -90.79$ kJ/mol
(R_{14}): $CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$ $\Delta H_{298K} = -49.79$ kJ/mol
(R_{15}): $CO_2 + H_2 \leftrightarrow CO + H_2O$ $\Delta H_{298K} = 41.00$ kJ/mol

All of these reactions are reversible and depend on the reaction conditions. Methanol synthesis reactions are exothermic and maximum conversion is achieved under high pressure and low temperature.

DETAILS ON PROCESS MODELLING AND SIMULATION

The two cases have been modelled using ChemCAD process simulator developed by Chemstations [6]. *Case A* sub-processes have been listed in Table 1 and the assumptions used in process modelling and simulation are presented in Table 7.

Table 7. Process modelling assumptions for *Case A*

Case A	**Assumptions**
Input data specifications	COG molar composition: CO = 0.06 H_2 = 0.59 CO_2 = 0.03 CH_4 = 0.27 N_2 = 0.05 COG temperature: 25˚C COG pressure: 1 atm
COG combustion	Total combustion is considered. Combustion temperature: 1300˚C Excess air is used for combustion.
CO_2 capture	MDEA solution (50% wt.) is used for gas-liquid absorption. Absorption column: 30 trays. Desorption column: 10 trays.
DMR	The DMR catalytic reforming reactor is operated at 1000˚C and 0.98 atm. The flow obtained is cooled to 50˚C.
Syngas compression	After water removal and compression, the synthesis gas reaches 145˚C and 29.6 atm. The gas is furthermore compressed to 108.56 atm. The compressor efficiency is 75%.
Methanol synthesis	The methanol synthesis reactor is operated at 267˚C and 107 atm. The pressure drop in the reactor is 0.98 atm.
Methanol separation	The methanol purification unit consists of two separators whose resulting gaseous fluxes are compressed at 108.56 atm and returned to the process. The compressors are adiabatic and their efficiencies are 75%. The first separator is operated at 105 atm and 38°C. The second separator is operated at 1.97 atm and 38°C.The distillation column has 42 plates, the feed is made on plate 27. The pressure at the top of the column is 0.98 atm.

Case B sub-processes have been listed in Table 1 and the assumptions used in process modelling and simulation are presented in Table 8.

Table 8. Process modelling assumptions for *Case B*

Case B	Assumptions
Input data specifications	COG molar composition:CO = 0.06; H_2 = 0.59; CO_2 = 0.03; CH_4 = 0.27; N_2 = 0.05 COG temperature: 25˚C COG pressure: 1 atm
COG combustion	Total combustion is considered. Combustion temperature: 1300˚C Excess air is used for combustion.
CO_2 capture	MDEA solution (50% wt.) is used for gas-liquid absorption. Absorption column: 30 trays. Desorption column: 10 trays.
Methanation section	Three reactors are used for this section. The first reactor is operated at 620°C, the mixture obtained being furthermore cooled to 300°C. The second reactor is operated at 300˚C, the mixture obtained being subsequently cooled to 240˚C. The third reactor is operated at 240°C, the mixture obtained then cooled to 168°C. The gaseous product obtained by separation is rich in hydrogen and methane gas.
Gas separation	SNG with composition 95% CH_4 and 5% N_2 is obtained in this section.
SMR	High pressure steam (p = 118.4 atm, T = 360°C) is used in the SMR. The methane-steam mixture is preheated to 870°C before being introduced into the reforming reactor. The reforming reactor is a Gibbs type reactor, operating at 1000°C and 37.5 atm.
Syngas compression	The gas mixture leaving the reforming reactor is cooled and compressed in two steps to the desired pressure of 107 atm. Compressors efficiencies are 75%.
Methanol synthesis	The methanol synthesis reactor is operated at 267˚C and 107 atm. The pressure drop in the reactor is 0.98 atm.
Methanol separation	The methanol purification unit consists of two separators whose resulting gaseous fluxes are compressed at 108.56 atm and returned to the process. The compressors are adiabatic and their efficiencies are 75%. The first separator is operated at 105 atm and 38°C.The second separator is operated at 1.97 atm and 38°C. The distillation column has 42 plates, the feed is made on plate 27. The pressure at the top of the column is 0.98 atm.

The developed models were validated using literature date, the error between the proposed models and those found in the literature being less than 5%.

A comparative simulation-literature study was performed for the main flows obtained in Case B in order to validate the SNG production model developed in ChemCAD. The data obtained for the SNG production is in accordance with those from the literature (see Table 9).

Table 9. Model validation for SNG production process

Parameter	Unit of measure	SNG production	
		Present work	Literature [5]
Pressure	atm	19.70	19.73
Temperature	ºC	25	25
Vapour fraction	-	1	1
Liquid fraction	-	0	0
Composition			
Carbon Monoxide	Mole fractions	0	0
Hydrogen		0	0
Carbon dioxide		0	0
Water		0	0
Methane		0.95	0.95
Nitrogen		0.05	0.05
Oxygen		0	0

For methanol synthesis, the data obtained from process modelling and simulation was validated in comparison with scientific literature data (see Table 10).

Table 10. Model validation for methanol production process (*Case B*)

Parameter	Unit of measure	MeOH production	
		Simulation	Literature [7]
Carbon Monoxide	Mole fractions	0.00	0.00
Hydrogen		$3 \cdot 10^{-5}$	0.00
Carbon dioxide		$1.45 \cdot 10^{-5}$	0.009
Water		0.007	0.001
Methane		$9.07 \cdot 10^{-5}$	198 ppm
Nitrogen		$7.58 \cdot 10^{-5}$	727 ppm
Methanol		0.99	0.98

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