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Comparison between two methods of methanol production from carbon dioxide

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ABSTRACT

Over recent years there has been a significant increase in the amount of technology contributing to lower emissions of carbon dioxide. The aim of this paper is to provide a comparison between two technologies for methanol production, both of which use carbon dioxide and hydrogen as initial raw materials. The first methanol production technology includes direct synthesis of methanol from CO_2, and the second has two steps. During the first step CO_2 is converted into CO via RWGS (reverse water gas shift) reaction, and methanol is produced during the second step. A comparison between these two methods was achieved in terms of economical and energy-efficiency bases. The price of electricity had the greatest impact from the economical point of view as hydrogen is produced via the electrolysis of water. Furthermore, both the cost of CO_2 capture and the amounts of carbon taxes were taken into consideration. Energy-efficiency comparison is based on cold gas efficiency, while economic feasibility is compared using net present value. Even though the mentioned processes are similar, it was shown that direct methanol synthesis has higher energy and economic efficiency.

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1. Introduction

A few decades ago mankind started to become consciously aware of fossil fuel usage. In parallel the price of fuel increased excessively during the same period. These two facts encouraged research into the development of alternative fuels. Significant progress has been achieved within the field of renewable energy sources over the last few years but a lot of work still needs to be done in order to increase the usages of such energy [1]. The main goal of this paper was to compare two different syntheses routes for one such fuel. The basic problem associated with fossil fuel usages are the emissions of greenhouse gases, with CO_2 as a key culprit of this group. Therefore, it has become desirable to develop methods that would effectively decrease the level of CO_2 within the atmosphere. One such method includes methanol synthesis starting from carbon dioxide and hydrogen. This technology can be very useful for two reasons, firstly it reduces the level of CO_2 in the air and secondly it provides a substance that can be used as an alternative fuel or as a starting material during organic synthesis. Furthermore, methanol can be used for other purposes too, as it is one of the more frequently used components throughout the chemical industry.

In regard to the method of producing reactants, this methanol synthesis can also be considered as a 'green' process. This would be the case if the main reactants, CO_2 and hydrogen, were to be produced from green and renewable sources. This is very easily achievable as CO_2 can be provided from different sources using CCS (carbon capture and storage) technology, and hydrogen can be produced via water electrolysis with the needed electricity provided from renewable sources. Usage of renewable energy sources is highly desirable, as it is well-known that non-renewable energy sources are diminishing [2]. The process of methanol synthesis from carbon dioxide is a new technology and so far there have only been a few pilot-scale plants. This paper presents two processes for the conversion of CO_2 into methanol. The first process includes the direct synthesis of methanol from CO_2 and hydrogen, whilst the second covers two steps. During the first step the CO_2 is partially (to the equilibrium) converted into CO via a reverse water-gas shift reaction and during the second step the mixture is further conveyed to a reactor where it is converted into methanol. This process is also known as the CAMERE (carbon dioxide hydrogenation to methanol via reverse water gas shift) process. The reason why a two-step process has to be taken into consideration is the very low conversion of carbon dioxide during the direct synthesis process.

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The main aim of this paper was a comparison between the two stated methods. Process simulations were done using the ASPENPLUS program. Both process schemes were modelled using a Lurgi methanol synthesis process as the role model [3]. This model had to be modified however because the Lurgi process uses syngas (a mixture of carbon monoxide and hydrogen) as the starting raw material, whereas here the starting materials were carbon dioxide and hydrogen.

2. Two-step synthesis of methanol

As stated above, the simulation of this process scheme is modelled using ASPENPLUS, and the detailed schemes are given in the Appendix. Simplified process scheme of two-step process is presented in Fig. 1.

During the first step of the process the carbon dioxide is converted into carbon monoxide via RWGS (reverse water gas shift) reaction:

$$CO_2 + H_2 \rightarrow CO + H_2O \quad (1)$$

This reaction is an equilibrium endothermic reaction. Therefore the conversion of CO_2 increases at higher temperatures. The application of a catalyst is essential during this process because it ensures very selective conversion that is close to the equilibrium. It is reasonable to expect that the same catalyst, as for the WGS (water gas shift) reaction, would be suitable; that is a ZnO/Al_2O_3 catalyst [4].The dependence of the carbon dioxide conversion on temperature is presented in Fig. 2.

The activity of ZnO/Al_2O_3 is high and it can be seen that at temperatures above 650 °C the conversion approaches equilibrium (as represented by the dashed line). In regard to the activity of ZnO, it can be observed that it approaches equilibrium at lower temperatures. The reason why the ZnO catalyst is was not chosen for simulation is the wider and more commercial usage of the ZnO/Al_2O_3 catalyst. In order to ensure optimal conversion of CO_2 the RWGS reaction occurs at 800 °C and at that temperature the fractional conversion of CO_2 is approximately 60%. The pressure within the reactor is 16 bar [5].

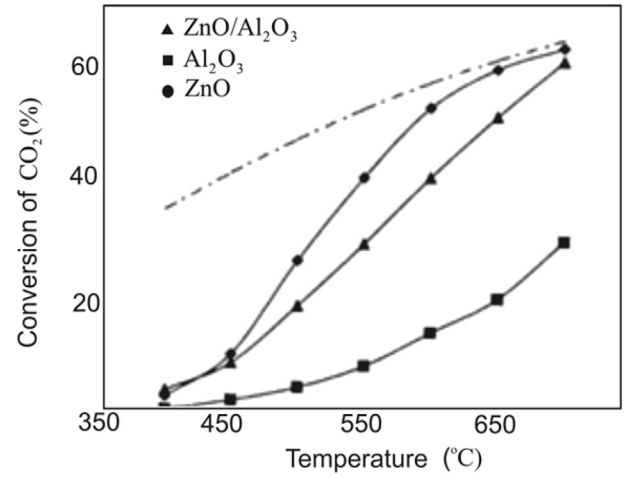

Fig. 2. Temperature dependence on CO_2 conversion for different catalysts.

The products from the first reactor are cooled down and the water is separated using a flash-separator. The reaction mixture then contains CO, CO_2, and H_2. Before it enters the second reactor, it is mixed with an additional amount of hydrogen in order to ensure the proper stoichiometric ratio of the reactants, which is dependent on the catalyst used and, in our case, the molar ratio of $CO:CO_2:H_2$ was equal to 1:1:4 [6].

The methanol synthesis occurs within the second reactor. A highly selective Cu/ZnO catalyst is used for this purpose. This catalyst is usually used for methanol synthesis, where the starting component is CO_2 rich syngas that is, in practice, usually derived from biomass. The catalyst is enriched with ZrO_2 in order to achieve higher conversions of CO_2 to methanol [6]. Fig. 3 represents the temperature dependences of both CO_2 and CO conversions to methanol.

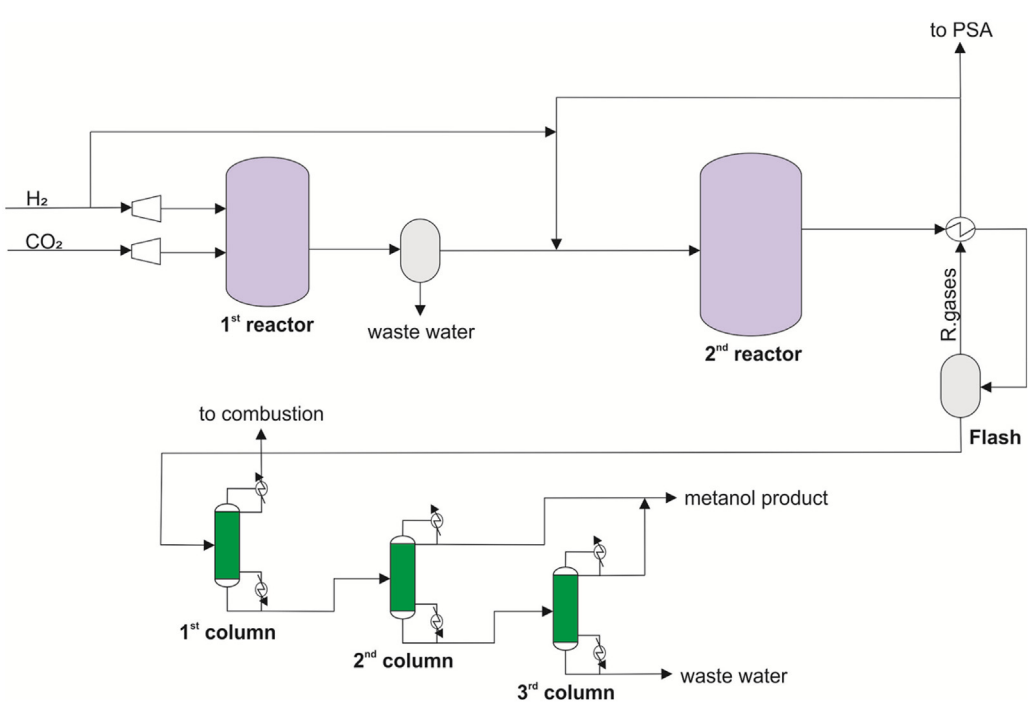

Fig. 1. Two-step methanol synthesis.

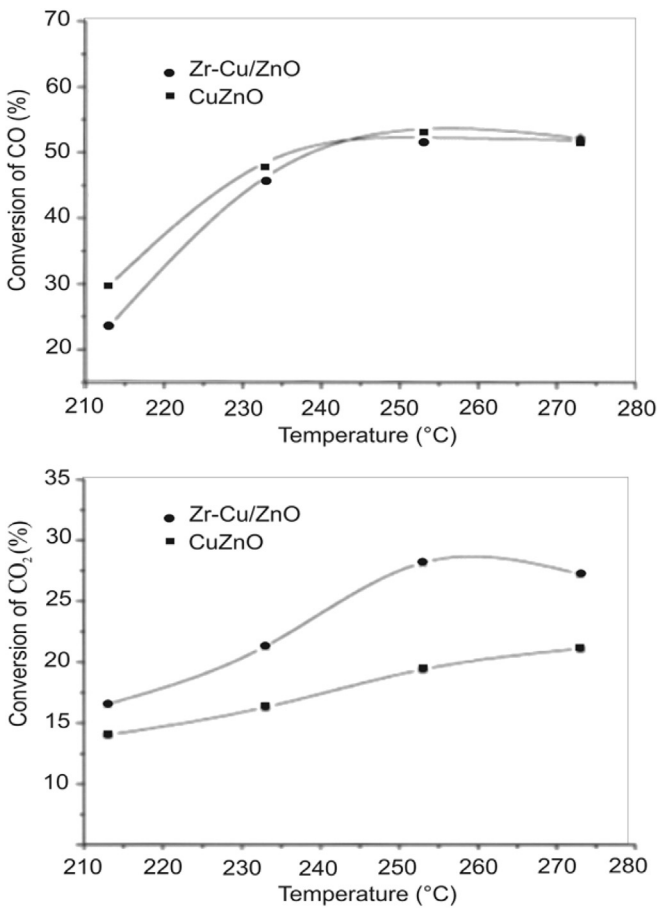

Fig. 3. Temperature dependence of CO_2 and CO conversions to methanol [6].

It can be seen that the addition of zirconium increases the conversion of CO_2, whilst the conversion of CO remains approximately the same. Even though the conversion is thermodynamically favoured at higher temperatures, thermal deactivation of the catalyst occurs at above 250 °C, and that is why the maximal conversions are observed at temperatures near 250 °C [7].

Three reactions occur simultaneously within the second reactor:

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \quad (2)$$

$$CO + 2H_2 \rightleftharpoons CH_3OH \quad (3)$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad (4)$$

The selectivity of the aforementioned catalyst exceeds 99%. Methane and DME (dimethyl ether) are observed as side-products and it is assumed that the side-products also include higher alcohols (ethanol, propanol) and higher alkanes (ethane, propane) [6]. Furthermore, it is assumed that the probability is lower of producing products with greater numbers of carbon atoms. The last assumption is taken into consideration when calculating the partial conversions of the reactants, for a particular product. All reactions with partial conversions of reactants are listed in Table 1.

The obtained mixture is further cooled to 30 °C and the gaseous and liquid phases are separated within a flash separator. The gaseous phase is then recycled back to the second reactor. Part of that phase, mainly consisting of non-reactive reactants (CO_2, CO and H_2) is purged from the synthesis loop and undergoes combustion. Before combustion the hydrogen is regenerated using PSA (pressure swing adsorption), with 90% recovery rate. The liquid phase consists of methanol, water, side-products, and dissolved gases (CO_2, CO). This phase enters the downstream process containing three distillate columns. The first column is used for separating those dissolved gases that are obtained as gaseous distillate, and undergo combustion together with natural gas and the purged stream from the synthesis loop after PSA. The energy released during combustion, is used for supplying the necessary amount of energy for the reversed water gas shift reactor. The needed amount of natural gas is 55 kmol/h. Carbon dioxide is produced during the mentioned combustion process and it can be separated from the exhausted gases using post-combustion carbon capture. The separated amount of CO_2 can then be used as starting material.

The distillation residue of the first column is then conveyed to the second column, where one part of methanol is obtained as distillate. The distillation residue of the second column is further led to the third column where the remainder of the methanol is recovered as distillate. The last two columns are used for methanol and water separation, which can also be done using a single column. However, the existence of two columns enables better heat integration. For this purpose it is very useful to observe that the pressure doesn't affect the purity of the product and heat consumption, so the pressures are chosen in such a way as to obtain better heat integration. The residual water is then conveyed to wastewater treatment whilst the distillates from the last two columns are combined in order to obtain the final product. The composition of the final product is represented in Table 2. The amount of carbon dioxide used is 44,000 kg/h, and total amount of hydrogen needed is 4,920 kg/h. It can be seen from Table 2 that the obtained methanol is very pure, and could be sold on the open market or used in other processes such as synthetic gasoline synthesis.

Table 1
Reactions within the methanol synthesis reactor.

Reaction	Fractional conversion	Reactant
$CO_2 + 2H_2 \rightleftharpoons CH_3OH$	0.4975	CO
$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$	0.2676	CO_2
$2CO + 4H_2 \rightleftharpoons CH_3CH_2OH + H_2O$	0.0010	CO
$5CO + 4H_2 \rightleftharpoons CH_3CH_2CH_2OH + 2CO_2$	0.0005	CO
$2CO + 5H_2 \rightleftharpoons CH_3CH_3 + 2H_2O$	0.0005	CO
$6CO + 4H_2 \rightleftharpoons CH_3CH_2CH_3 + 3CO_2$	0.0005	CO
$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$	0.0005	CH_3OH
$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$	0.0014	CO_2
$2CO_2 + 7H_2 \rightleftharpoons CH_3CH_3 + 4H_2O$	0.0014	CO_2

Table 2
Composition of final product.

Component	Mass fraction
H_2	0
CO	$1.135 \cdot 10^{-12}$
CO_2	$6.728 \cdot 10^{-4}$
H_2O	$2.917 \cdot 10^{-4}$
CH_3OH	0.998
CH_3CH_2OH	$9.970 \cdot 10^{-4}$
$CH_3CH_2CH_2OH$	$1.127 \cdot 10^{-6}$
CH_3CH_3	$6.830 \cdot 10^{-9}$
CH_4	$4.235 \cdot 10^{-13}$
$CH_3CH_2CH_3$	$9.857 \cdot 10^{-10}$
CH_3OCH_3	$1.642 \cdot 10^{-7}$
Total mass flow (kg/h)	25.319

3. Direct methanol synthesis

Together with the two-step process scheme, the process detailed scheme of the direct methanol synthesis is given in the Appendix, whilst simplified process scheme is represented in Fig. 4.

This process slightly differs from the two-step methanol synthesis. The reactants, a mixture of carbon dioxide and hydrogen at a ratio of 1:3, are directly led to the reactor for methanol synthesis [8]. A suitable catalyst, similar to the one for methanol production during the first process is used, in order to ensure proper conversion of the reactants. This catalyst is based on Cu/ZnO and is doped with ZrO_2. A significant amount of carbon monoxide is also produced during this process, but the selectivity of methanol is very high, above 99% without considering the carbon monoxide. The total conversion using this catalyst is 21%, and the selectivities of methanol and carbon monoxide are 68% and 31%, respectively [9]. The side-products associated with this reaction are DME and methane. Reactions and partial conversion of suitable reactants are presented in Table 3. It can be seen that the total conversion of CO_2 is low. It is reasonable to expect that this problem would be solved by the development of new catalysts, using novel materials and technologies. The stream coming from the first reactor mainly consists of non-reacted reactants, methanol, water, and carbon monoxide. The stream is then cooled and led to a flash-separator for separation over two phases, as in the first process. The gaseous phase is now split into three flows. The majority is recycled back to the first reactor whilst the second part is conveyed to a new reactor for additional methanol synthesis.

The smallest third part undergoes combustion but before that hydrogen is recovered using the PSA unit. This phase is divided in such a way as to ensure suitable composition of the stream going to the second reactor. This stream should be CO_2 rich syngas and the same composition is required as for the methanol synthesis reactor during the two-step process. The catalyst used within this reactor is identical to the one used in the first process and the list of reactions that occur in this reactor is presented in Table 1. The outlet stream of the second reactor is also cooled and is led to the same flash-separator that separates the gaseous and liquid phases. The liquid phase has similar properties to the liquid phase of the first process and the only difference is the greater amount of water present, as in this process water is not separated at the earlier stage. The downstream process also consists of three distillation columns but in this case the dimensions of the columns are slightly greater. The final product composition is represented in Table 4. In this process there is no natural gas needed as the energy requirements can be covered using heat integration.

The same level of purity is achieved as in the first process. Furthermore, a greater amount of product is obtained in this case; however, the consumption of hydrogen is also higher.

As can be seen, the two processes are similar, but they also differ in certain aspects. These differences are evaluated in the following chapters.

Table 3
Reactions within the first methanol synthesis reactor.

Reaction	Fractional conversion	Reactant
$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$	0.142800	CO_2
$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$	0.000340	CH_3OH
$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$	0.000085	CO_2
$CO_2 + H_2 \rightleftharpoons CO + H_2O$	0.065100	CO_2

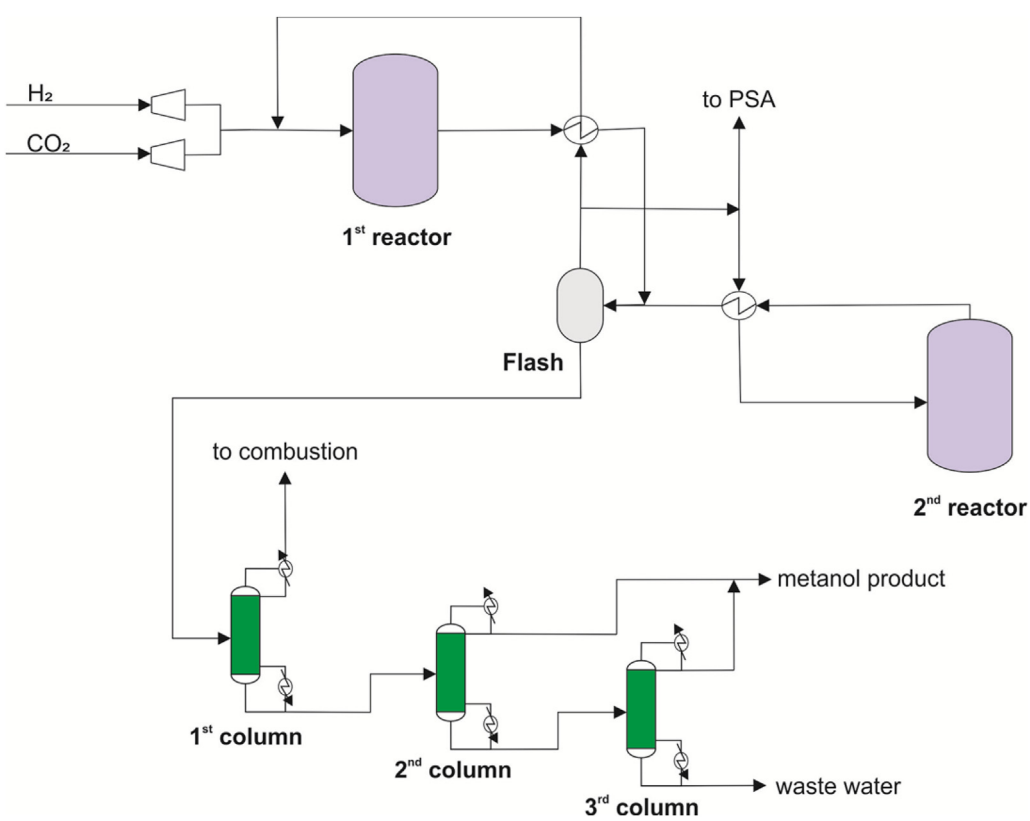

Fig. 4. Direct methanol synthesis process.

Table 4
Composition of final product.

Component	Mass fraction
H_2	0
CO	0
CO_2	$2.883 \cdot 10^{-8}$
H_2O	$9.390 \cdot 10^{-4}$
CH_3OH	0.999
CH_3CH_2OH	$4.280 \cdot 10^{-4}$
$CH_3CH_2CH_2OH$	$4.850 \cdot 10^{-4}$
CH_3OCH_3	$1.740 \cdot 10^{-4}$
Total mass flow (kg/h)	28,757

4. Econimical efficiency

The main cost of methanol production, in both cases, is hydrogen production. In our case it is assumed that hydrogen is produced via water electrolysis, and a huge amount of electricity is needed for that purpose. It is well-known that the electricity price is lower during nights and weekends. Therefore, in order to decrease the cost of methanol production it is essential to develop a process that can only operate at full capacity during those periods of lower electricity costs. This can be achieved in different ways. For example, the process can be designed in such a way as to operate at warm-start during day, and then at full capacity during the nights, *i.e.* during periods of lower electricity prices. Studying this process flexibility is beyond the scope of this paper, and will be the subject of further studies. The process of methanol production can also be combined with some of the technologies for CO_2 capture. A huge amount of oxygen is produced during hydrogen production via water electrolysis. This oxygen can be used for fossil fuel combustion within a power plant. As pure oxygen is applied for combustion, only CO_2 and water are present in flue gases. The water can be separated easily and very pure CO_2 can be obtained for methanol production. This technology is also known as oxy-fuel technology [10]. Once again, the flexibility of methanol production would be crucial, as electricity produced from fossil fuel during the day could be sold on the electricity market, and during the night when the price is low, electricity can be used for hydrogen production and further methanol production.

The economic efficiency comparison between both methods of methanol production from CO_2 is based on the NPV (net present value) and is evaluated further in this chapter.

4.1. Analysis of electricity market

An electricity market analysis was carried out in order to estimate the number of hours during which the process could operate at full capacity. Electricity has been traded as any other goods at the stock market since electricity market liberation. The biggest exchange of this kind is the European Energy Exchange in Leipzig, Germany. The prices of electricity during the days, weeks, and years are represented in Figs. 5–7 respectively [11].

The contract price changes every day. The price on the free market is represented by the red line. It can be seen that each day there are approximately 8 h-long periods during which the price of electricity is lower. This is a very reasonable approximation as in many countries there are 8 h-long periods, starting from 10 p.m. to 6 a.m. when the price is at the lower tariff. It can be seen from Fig. 4 that the price also decreases during weekends, and that this period lasts approximately 42 h from Saturday 12 a.m. to Monday 6 a.m. The total number of hours with the lower electricity price per week is equal to 82 h, which amounts to 4264 h per year.

When developing the model it was assumed that the off-peak electricity price during the nights was 15% greater than during weekends. It then follows that:

$$\mathrm{PE_{we}} = \frac{\mathrm{PE}_n \times 40 + \mathrm{PE_{wn}} \times 42}{82} = 1.073 \times \mathrm{PE_{wn}} \tag{5}$$

Where PE_n is the price for electricity during the night, $\mathrm{PE_{wn}}$ is the price during weekends, and $\mathrm{PE_{we}}$ is the average off-peak price that varies during the year.

The mean off-peak price value for the one year period was estimated using the data from Fig. 7. It can be easily concluded that each down peak represents the price of electricity during weekends (there are 52 such peaks, matching the number of weekends in one year). The variation of $\mathrm{PE_{wn}}$ during one year is represented in Fig. 8.

The calculated mean value is $\overline{PE_{we}} = 31.84$ EUR/MWh. The transport is excluded in this price because it is assumed that the methanol plant would be placed near an electricity source in order to minimise the electricity transport costs.

4.2. Calculation of net present value

Net present value is one of the more widely used methods for determining economic efficiency. This method provides some very important parameters such are break-even point and internal rate of return, which can be further used for comparison between two or more processes. The values of capital and operating costs, prices of products, and the annual discount rate should be estimated in order to determine these parameters.

4.2.1. Estimation of capital costs

Capital costs are estimated using several parameters and indexes. The equation that is used for this purpose is the equation $C = n^e C_0 (S/nS_0)^f$ [12], where C is the cost of a process unit, n is the number of equally-sized units, C_0 is the cost of a reference unit, S is the capacity of a process unit, S_0 is the capacity of a reference

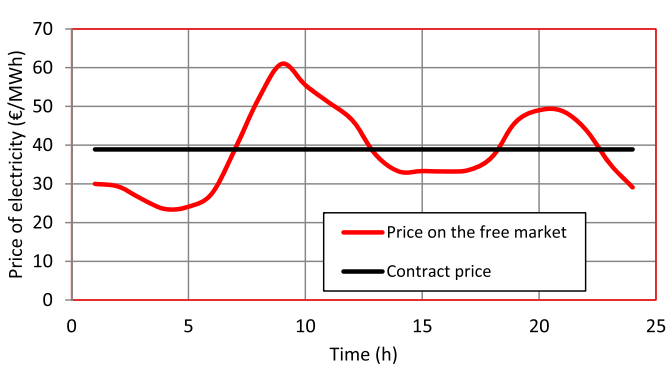

Fig. 5. Daily variations in electricity prices [11].

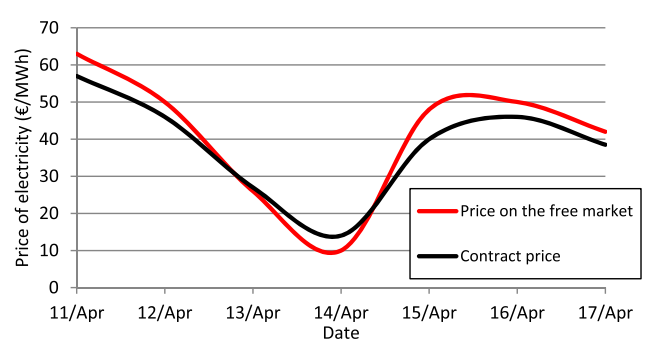

Fig. 6. Variations in electricity prices over one week [11].

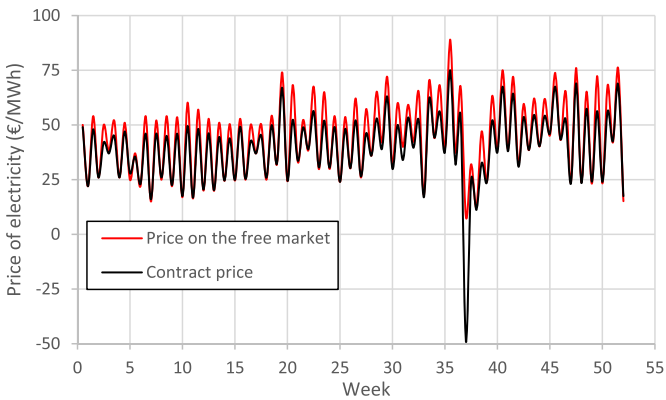

Fig. 7. Price changes of electricity during last year [11].

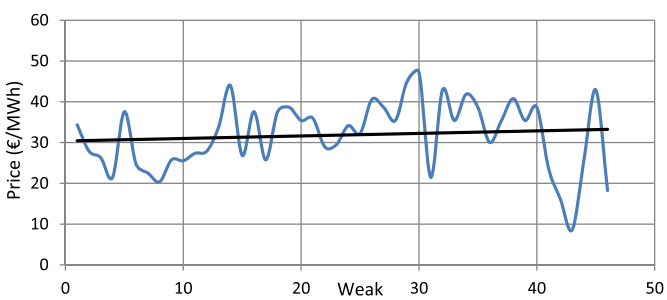

Fig. 8. Variation of average weekly price during last year.

process unit, e is the cost scaling exponent for different numbers of equally-sized units, and f is the cost scaling factor. The mentioned equation is used for calculating the costs regarding the majority of the equipment, except for calculation of the compressor's price. The equation for the estimation of capital cost regarding compressors is used for this purpose [13].

The costs of process units are taken from different literature and consequently from different years; therefore the CEPCI (chemical engineering price cost index) must be taken into account, in order to calculate the present value of the reference unit cost using equation $C'_0 = C_0 \cdot i/i'$ [14]. Where, i' is the present value of CEPCI, and i is the value of CEPCI at the time when determining the reference's cost.

Both methanol production processes are divided into several parts and the total capital cost is represented by the sum of the costs of individual parts. The calculations of capital costs for two-step methanol synthesis and direct methanol synthesis are represented in Table 5 and Table 6, respectively.

In order to obtain these results some approximations and assumptions have to be made due to the lack of information. Firstly, it is assumed that the price of heat exchangers is negligible compared to the price of a methanol reactor. Secondly, it is assumed that the prices of methanol synthesis reactors for these processes are the same as the price of a methanol synthesis reactor for methanol production from syngas. This assumption is very reasonable as a similar reactant's composition and the same types of reactors are used. Furthermore, as the value of the CEPCI index for 2013 is unavailable as yet, the 2012 value is taken as the present value [15,16].

It can be seen that the capital cost for the two-step process is higher and that the main reason for this is the combustion unit necessary for obtaining suitable temperature within the first reactor.

4.2.2. Estimation of operating costs and prices of reactants

The operating costs are usually calculated for one year of production and they are associated with energy consumption, catalyst usage, prices of reactants and raw materials, maintenance costs, etc.

The first part of the operating costs is the electricity consumption for the compressors, and production of hydrogen. The total consumption of electricity together with its annual price and the price for the catalyst, for both processes, is also given in Table 7. The price of the catalyst for RWGS reaction is not taken into consideration, due to the lack of information. Since its price is low, it wouldn't have any great influence on the final result. Furthermore, the energy consumption of distillation columns is not used during calculation of the operating costs, as that energy can be provided by heat integration.

The second part of the operating costs is the prices of reactants and raw materials. In both methanol syntheses the main reactants are hydrogen and carbon dioxide, whilst in the two-step process natural gas is also considered as a raw material.

The highest cost element during methanol production is hydrogen production via water electrolysis. The electrolysis process with the highest available efficiency (73%) was chosen for this particular study, due to the huge consumption of hydrogen [22]. A very important aspect of hydrogen production is the pressure of the produced hydrogen. The pressures of water electrolysis can vary, and the variation would have very little impact on the voltage used and on process efficiency [23,24]. The usage of compressors can be avoided by choosing the appropriate pressure. The needed amounts of hydrogen for both processes are represented in Table 8, and the amount of electricity needed for hydrogen production has already been stated in Table 7.

It can be seen that a greater amount of hydrogen is needed for the direct methanol synthesis, and consequently the costs are also higher. On the other hand, the amount of carbon dioxide entering the process is the same in both cases. One way of CO_2 capture (oxy-fuel technology), has already been mentioned, and the other commercially-available technologies are post and pre-combustion captures of CO_2. The prices of CO_2 capture that don't include the costs of transport and storage are given in Table 9 [25]. These prices are the prices of the liquid (condensed) carbon dioxide.

Table 5
Calculation of capital costs for two-step methanol synthesis.

Process/unit	Scaling parameter	S	S_0	C_0(M$)	Reference/year	C'_0(M$)	n	f	e	C (M$)
Water electrolysis	MW based on LHV	259.9	220	33.00	[17]/2010	35.02	2	0.67	0.9	45.93
RWGS	CO (kg/s)	4.6	2	7.00	[17]/2010	7.43	3	0.67	0.9	17.29
Methanol reactor	MeOH (tonne/day)	607.6	5000	81.96	[13]/2005	102.30	1	0.67	0.9	24.93
Methanol distillation	MeOH (tonne/day)	607.6	5292	19.20	[18]/2008	21.36	1	0.67	0.9	5.01
PSA	H_2 (kg/h)	55.6	23	0.02	[19]/2001	0.03	3	0.67	0.9	0.07
Combustion unit	MW based on LHV	19.7	20	12.82	[20]/2010	13.61	1	0.67	0.9	13.61
Price of compressors										0.85
Total capital cost										84.18

Table 6
Calculation of capital costs for direct methanol synthesis.

Process/Unit	Scaling parameter	S	S_0	C_0(M$)	Reference/year	C'_0(M$)	n	f	e	C (M$)
Water electrolysis	MW based on LHV	309.3	220	33.00	[17]/2010	35.02	2	0.67	0.9	51.61
1st methanol reactor	MeOH (tonne/day)	420.9	5000	81.96	[13]/2005	102.30	1	0.67	0.9	19.49
2nd methanol reactor	MeOH (tonne/day)	318.7	5000	81.96	[13]/2005	102.30	1	0.67	0.9	16.18
Methanol distillation	MeOH (tonne/day)	690.2	5292	19.20	[18]/2008	21.36	1	0.67	0.9	5.46
PSA	H_2(kg/h)	210.0	23	0.02	[19]/2001	0.03	9	0.67	0.9	0.19
Price of compressors										0.45
Total capital cost										72.94

The pre-combustion capture of carbon dioxide is the cheapest technology and, as was mentioned previously, there is a possibility of combining oxy-fuel capture and methanol production. Carbon tax should also be taken into account when calculating the total costs of CO_2 production. This tax is set by governments. In our case it would decrease the cost of CO_2 production as in our process CO_2 is used and not emitted. The values of carbon taxes vary from country to country, from 13 € per ton of CO_2 in Denmark, to 114 € per ton in Sweden [26]. The current rate in Slovenia is 14.4 € [27]. The total price of carbon production for both processes is presented in Table 10. The price of pre combustion capture is taken into account for calculating the price of CO_2 production. In order to calculate the price of CO_2 capture and the value of carbon tax, the amount of carbon dioxide used for methanol production is taken into account. Also the current value of the tax in Slovenia was used for the calculation.

As stated above, in the two step methanol synthesis natural gas is used for obtaining the needed amount of energy for the first reactor. This means that the natural gas is also considered as a reactant for that process. The calculated price is 0.149 € per kg of natural gas [28]. The needed amount is approximately 900 kg/h, in line with its annual cost of 0.566 M€.

Finally, the total operating costs can be calculated. The total operating cost of the two-step methanol synthesis process is $O_t = 38.93$ M€, and the total operating cost of direct methanol synthesis is $O_t = 45.16$ M€.

At the very end maintenance cost should also be estimated. Its value, for this kind of investment, varies between five and six % of the total capital costs [29]. The value used in our work is 5%, and the calculated values for the two-step and the direct methanol synthesis are 4.167 M€ and 3.625 M€, respectively.

4.2.3. Prices of products

The main product from both processes is methanol. A very important side-product is the oxygen produced during water electrolysis. The price of methanol has been constantly increasing since 2009, and that trend can be seen in Fig. 9 [30]. The current methanol price of 0.390 €/kg is taken into account for calculating the total profit of methanol production. The amounts of methanol and its values for both processes are represented in Table 11.

As already stated, the side-product of these processes is oxygen. Due to the stoichiometric ratio, for each kg of hydrogen produced 8 kg of oxygen is produced. The price of oxygen taken into consideration for calculating NPV is equal to 0.085 € per kilogram of oxygen [31]. The amounts and prices of oxygen produced are also represented in Table 11.

4.2.4. Net present value

The last parameter needed for calculation of the net present value is the annual discount rate. Its current value in Slovenia is 1.75%. The current value is very low due to the present economic crisis. In our work, the value before the global economic crisis had to be taken into consideration as it is reasonable to expect economic recovery in the coming years, when the annual discount rate may also increase. The Slovenian value before the economic crisis was 4%.

In order to calculate the net present value, annual profits (A_p) for both processes are calculated. $A_p = P_m + P_o - O_t - M_t$, where P_m is the price of the total amount of methanol produced, P_o is the price of the total amount of oxygen produced, and M_t is the maintenance cost.

The calculated annual profits for the two-step and the direct methanol syntheses are 12.02 M€ and 14.56 M€, respectively. The values of capital costs, annual profits, and annual discount rates are used for calculating the net present value over 30 years. The results are graph-represented in Fig. 10 and Fig. 11.

From Figs. 10 and 11, it can be seen that direct synthesis has higher economic efficiency as its break-even point is approximately 6 years compared to 8 years for the two-step synthesis. The main reasons for this trend are the higher capital cost of the two-step process on the one hand, and greater annual profit (due to the greater amount of methanol produced) of the direct synthesis process, on the other hand. Furthermore, one of the reasons is the usage of natural gas in the two-step synthesis.

The net present value after 30 years is 171.9 M€ for the direct methanol synthesis, and 119.1 M€ for the two-step methanol synthesis. It is reasonable to expect that the net present values can be increased in both cases. Firstly, it is obvious that the methanol price is constantly increasing and that could increase the profit. Secondly, the value of carbon tax in Slovenia is taken into account whilst doing calculations. This value is one the lowest values in the

Table 7
Annual operating costs for both methanol synthesis processes.

		Price	Amount		Annual cost (M€)
Two–step methanol synthesis	Electricity consumption	31.84 €/MWh	For compression 1.939 MW	For hydrogen 259.9 MW	34.9
	Methanol catalyst	56.8 €/m^3 of methanol [21]	0.133 E06 m^3		0.5
Direct methanol synthesis	Electricity consumption	31.84 €/MWh	For compression 1.070 MW	For hydrogen 309.3 MW	41.2
	Methanol catalyst	56.8 €/m^3 of methanol [21]	0.152 E06 m^3		0.6

Table 8
Hydrogen demand and price for both processes.

	Direct methanol synthesis	Two step methanol production
F_{H_2} [a](kg/h)	6000	4920
PSA_{H_2} [b](kg/h)	189	50
Net amount (kg/h)	5811	4970

[a] Amount of hydrogen entering process.
[b] Amount of hydrogen regenerated from PSA.

Table 9
Price of CO_2production.

Technology	Price of CO_2 avoided (€/tonne)
Pre combustion capture	33.11
Post combustion capture	44.66
Oxy-fuel	40.04

Table 10
Net price of CO_2 production for both processes.

	Direct methanol synthesis	Two step methanol production
F_{CO_2} [a](kg/h)	44,000	44,000
C_{CO_2} [b](kg/h)	2989	6439
Price of CO_2 capture (€/h)	1357	1243
Value of carbon tax (€/h)	591	541
Annual cost (M€)	3.2	2.9

[a] Amount of carbon dioxide entering the process.
[b] Amount of carbon dioxide in streams undergoing combustion.

EU, and if for example the value of Swedish taxes were to be taken into account, the profit would be much higher. Nevertheless, the value of carbon taxes is increasing in all countries and it is approaching the value before the global economic crisis (app. 35 € per ton). Furthermore, as a huge amount of oxygen is produced, it would be good to investigate the possible ways of oxygen distribution in order to increase the profit. On the other hand, some changes can have a negative influence on the net present values. For example, during the 30 year long period, it is reasonable to expect recession periods, and during these periods the prices of all energy products, including methanol, can decrease, thus having a negative influence on NPV. Furthermore, the price of electricity has been constantly increasing over recent years and that would increase the cost of production, leading to a decrease in the NPV value.

To sum up, the economic analysis showed that direct methanol synthesis is more profitable. The other, very important comparison is based on comparing energy efficiency and that principle is presented in the following chapter.

5. Energy efficiencies

Energy-efficiencies can be compared in several ways and two such ways are presented in this paper. It has already been stated that the main energy source for this process is electricity. Both reactants are obtained using electricity and that is why it would be very useful to calculate the electricity needed per 1 kg of methanol

Table 11
Amounts and prices of products.

	Methanol		Oxygen		
	X_{met} [a](kg/h)	Price (M€/a)	X_{H_2} [b](kg/h)	X_{O_2} [c](kg/h)	Price (M€/a)
Direct methanol synthesis	28,757	46.90	5790	46,320	16.44
Two step methanol production	25,320	41.29	4864	38,917	13.83

[a] Amount of methanol produced.
[b] Net amount of hydrogen produced.
[c] Net amount of oxygen produced.

produced. The three ways for producing carbon dioxide and their prices have been explained in the previous chapter. All these ways are closely related to electricity production (power plants) and carbon dioxide capture would reasonably decrease the net outputs of power plants. Furthermore, 0.194 kWh of electricity is needed for capturing 1 kg of carbon dioxide during the pre-combustion process [32]. Using this data, calculations can be performed as to how much electricity is needed for the production of 1 kg of methanol, the results being in Table 12.

Before making any conclusions it should be stated that in this calculation the amount of natural gas used during the two-step process is not taken into consideration. This is the main reason why less electricity is needed during that process. The data calculated in Table 12 are very useful but because of the mentioned fact it cannot be used for determining which process is more energy-efficient.

The other aspect from which energy efficiencies can be compared is the usages of LHVs (lower heating values) and HHVs (higher heating values). LHV is usually used for comparing process efficiencies, representing the total heat released during the combustion minus the heat from the vapourisation of water [33]. The ratio between the LHV of the reactants and products is defined as cold gas efficiency. These values are calculated for both processes. The overall cold gas efficiencies based on lower and higher heating values for both processes are presented in Table 13. The values for each component of the reactants and products are given in the Appendix [33].

It is reasonable to expect the HHV values to be greater than LHV and that fact can also be observed in Table 13. As stated previously, LHVs are used for determining cold gas efficiency and for that purpose the following equation is used: Cold gas efficiency $= (LHV)_p/(LHV)_r$. where $(LHV)_p$ is the lower heating value of products, and $(LHV)_r$ is the lower heating value of reactants. In the case of two-step synthesis, the amount of the needed natural

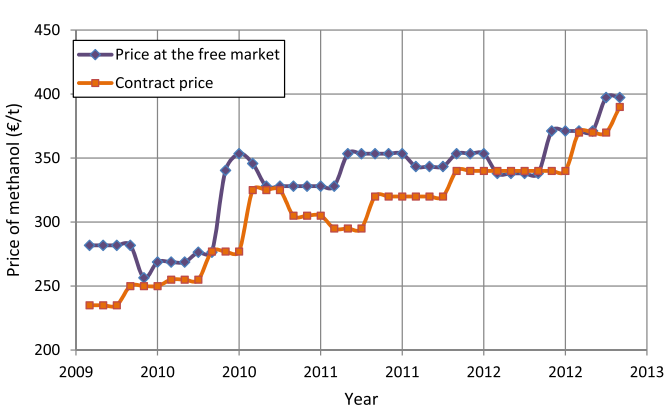

Fig. 9. Price of methanol over the last 4 years.

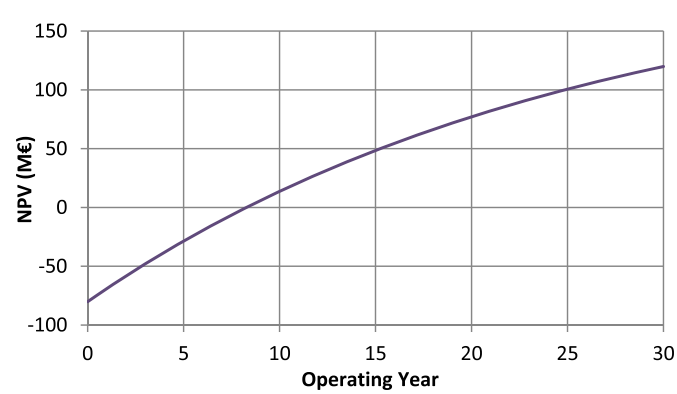

Fig. 10. Net present value for two-step process.

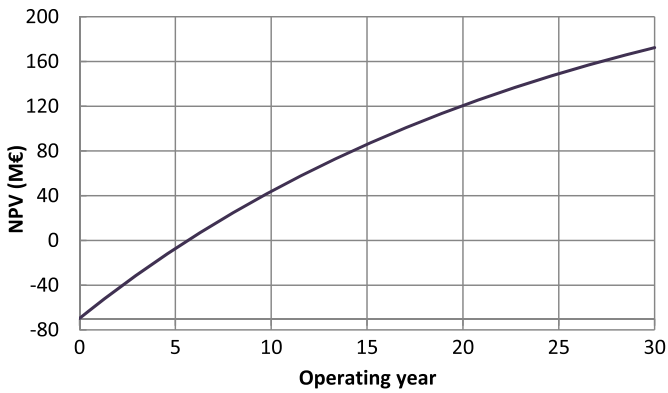

Fig. 11. Net present value of direct synthesis process.

gas is included in the lower heating value of reactants. As can be seen from Table 13, the cold gas efficiency is slightly higher for the direct synthesis. In this comparison the amount of natural gas is taken into consideration, and that is why this method is more relevant when deciding which process is more energy efficient.

It can be concluded that the direct methanol synthesis process is more thermodynamically efficient, mainly because the operating temperatures are moderated during the direct methanol process, in contrast to two-step synthesis using a high-temperature RWGS reactor. The only reason why the differences in energy efficiencies are not greater is the significant amount of hydrogen needed for the direct methanol synthesis. As can be seen in the Appendix the heating values of hydrogen are very high, and this has the greatest influence on the final results.

6. Conclusion

This paper provided a comparison between two methods for methanol syntheses using carbon dioxide as the starting material. It has been shown that direct synthesis has higher economical and energetic efficiency, but the difference is fairly insignificant, especially in the case of energy efficiency.

It can be said that these technologies are promising, as they can be used for the reduction of CO_2 emissions. The reduction of greenhouse gases' emission is essential in order to obtain reasonable standards of living for our world [34]. Both technologies have similar disadvantages but it is reasonable to expect that these could be overcome by future developments. When deciding which process would be suitable for application in practice, a significant amount of facts should be considered. Firstly, the location of the plant would play an important role. For example, if the plant were to be placed within an area with a large amount of available cheap electricity, the two-step process could be more economically efficient. On the other hand, if the plant were to be placed within an area within strict environmental laws, the direct synthesis would be more appropriate as it would provide better consumption of reactants.

There is room for improvements for both processes and these could be done over future years. The economic feasibility and energy-efficiency could be increased by initiating these improvements, whilst investment costs could be decreased. For example, instead of selling oxygen on the free market it could be used for some other chemical process in order to increase its value. Furthermore, heat integration of the overall process is possible (including CO_2 capture, water electrolysis, methanol production and separation). . The possible improvements of the process would be examined in future studies. It would be reasonable to expect that one of these processes would find its way into practise and with the mentioned improvements this possibility would be even higher.

Table 12
Calculation of electricity needed per kg of methanol produced.

		Direct methanol synthesis	Two step methanol production
Electric power needed	CO_2 capture (MW)	7.956	7.275
	H_2 production (MW)	309.3	259.9
	Compressors (MW)	1.070	1.939
Methanol production(kg/h)		28,757	25,320
E_{met}[a](kWh/kg)		11.07	10.63

[a] Electricity needed for the production of one kg of methanol.

Table 13
HHVs and LHVs of reactants and product.

	Two step methanol synthesis	Direct methanol synthesis
HHV of reactants (MJ)	740,580	823,999
LHV of reactants (MJ)	629,311	697,087
HHV of product (MJ)	574,379	655,624
LHV of product (MJ)	504,056	572,417
LHV ratio	80.1%	82.2%

Appendix

Table A1
Calculation of HHV and LHV for two step mechanism.

Component	HHV (MJ/kg)	LHV (MJ/kg)	Mass flow of component in reactant (kg/h)	Mass flow of component in product (kg/h)
H_2	141.8	119.9	4871	0
CO_2	0	0	44000	17.04
CO	10.1	10.1	0	0
CH_4	55.5	50	854	0
CH_3OH	22.7	19.9	0	25270
CH_3CH_3	51.9	47.8	50	0.0001
CH_3CH_2OH	29.7	26.8	0	25.23
CH_3OCH_3	31.7	28.9	0	0.004
$CH_3CH_2CH_3$	50.3	46.3	0	0
$CH_3CH_2CH_2OH$	33.6	29.7	0	0.03
H_2O	0	0	0	7.39
HHV (MJ)			740,580	574,379
LHV (MJ)			629,311	504,056

Table B1
Calculation of HHV and LHV for direct synthesis.

Component	HHV (MJ/kg)	LHV (MJ/kg)	Mass flow of component in reactant (kg/h)	Mass flow of component in product (kg/h)
H_2	141.8	119.96	5811	0
CO_2	0	0	44000	0
CO	10.1	10.1	0	0
CH_4	55.5	50	0	0
CH_3OH	22.7	19.92	0	28714
CH_3CH_3	51.9	47.8	0	0
CH_3CH_2OH	29.7	26.81	0	12.31
CH_3OCH_3	31.681	28.882	0	0
$CH_3CH_2CH_3$	50.35	46.35	0	0
$CH_3CH_2CH_2OH$	33.6	29.7	0	3.21
H_2O	0	0	0	26.91
HHV (MJ)			823,999	656,624
LHV (MJ)			697,087	572,417

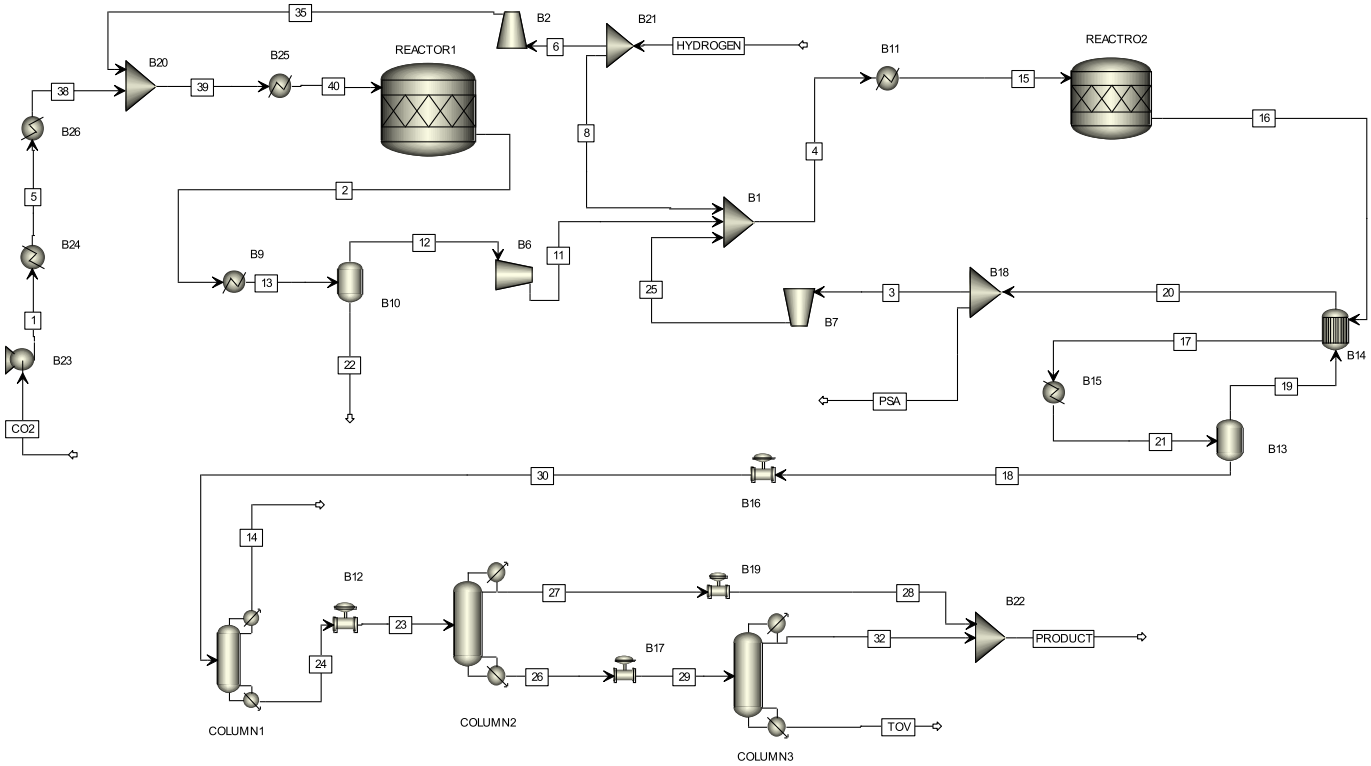

Fig A1. Process scheme for two-step methanol synthesis.

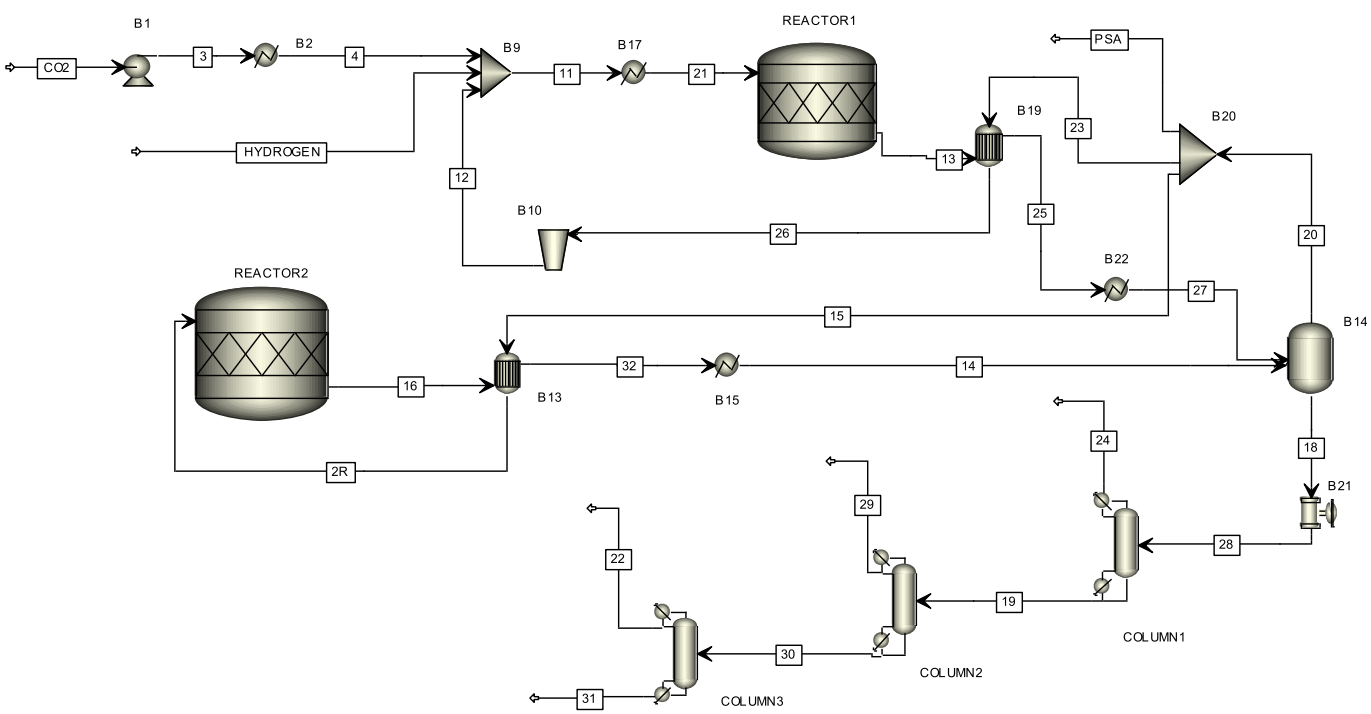

Fig B1. Process scheme for direct synthesis of methanol.

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Nomenclature

RWGS: reverse water gas shift reaction
CAMERE: carbon dioxide hydrogenation to methanol via reverse water gas shift reaction
CCS: carbon capture and storage
WGS: water gas shift
DME: dimethyl ether
PSA: pressure swing adsorption
NPV [M€]: net present value
PE_n *[€/MWh]:* price of electricity during night
PE_{wn} *[€/MWh]:* price of electricity during weekends
PE_{we} *[€/MWh]:* average off-peak price of electricity
C [M€]: cost of a process unit
C_0 *[M€]:* cost of reference process unit
S: capacity of process unit
S_0*:* capacity of reference process unit
e: cost scaling factor for different numbers of equally-sized units
n: number of equal size units
f: cost scaling factor
CEPCI: chemical engineering price cost index
i: value of CEPCI index
F_{H_2} *[kg/h]:* amount of hydrogen entering process
PSA_{H_2} *[kg/h]:* amount of hydrogen regenerated from PSA
F_{CO_2} *[kg/h]:* amount of carbon dioxide entering the process
C_{CO_2} *[kg/h]:* amount of carbon dioxide in streams undergoing combustion
X_{met} *[kg/h]:* amount of methanol produced
X_{H_2} *[kg/h]:* amount of hydrogen produced
X_{O_2} *[kg/h]:* amount of oxygen produced
O_t *[M€]:* total operating costs
A_p *[M€]:* annual profit
P_m *[M€]:* price of total amount of methanol produced
P_0 *[M€):* price of total amount of oxygen produced
M_t *[M€]:* total maintenance costs
E_{met} *[kWh/kg]:* electricity needed for the production of one kg of methanol
LHV [MJ]: lower heating value
HHV [MJ]: higher heating value