Analysis of Energy-Saving Schemes for the Purification of Raw Biomethanol

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Biomethanol can be used as a clean biofuel or as a chemical feedstock. Its production process includes a section for its purification downstream the conversion unit, which is generally carried out by distillation, with relevant energy consumption that may significantly impact on the costs of the whole process.

This work analyzes different configurations for the biomethanol purification section, for which no works in the literature focusing on this topic have been found, with the aim of determining the best one which allows for a reduction of the energy consumptions and, thus, of the operating costs.

The base scheme is composed of two main sections, one for removing the low boiling impurities present in the mixture mainly composed of biomethanol and water and the second one for separating water and other components so to increase the concentration of methanol to the required high purity (99.85 % wt.), with water content < 0.1 % wt., for obtaining an A grade product.

Simulations have been carried out by using the commercial software ASPEN Plus® V11.0, with the thermodynamic method Non-Random Two-Liquid (NRTL), suitable for this system and for the low pressure conditions, and by considering a rate-based approach for the simulation of the columns.

On the basis of the obtained results, the scheme which favors a reduction of the total (investment and operating) costs of the plant has been determined.

1. Introduction

The "methanol economy" was highly supported by the chemist George Andrew Olah, who thought of it as a possible substitute to natural oil and gas (Olah, 2005; Olah et al., 2018) because of the capability of methanol to provide an efficient mean to store energy and to be employed as a convenient fuel or as a raw material for synthetic hydrocarbons and related products. As an energy carrier, methanol can be employed in the marine, automotive and electricity sectors (Ptasinski et al., 2002).

The main methanol production routes starts from fossil (Lange, 2001) or renewable sources, that have attracted a great interest in recent years (De Guido et al., 2021; Lodi et al., 2018; Pellegrini et al., 2015). Green methanol is produced by biomass gasification or reforming or by electrolysis for production of a green hydrogen-rich stream, which is mixed with renewable carbon dioxide for producing a species with the same characteristics of the grey or brown methanol though with a lower carbon intensity.

CO_2 from bio-origin or obtained by direct air capture is considered renewable, CO_2 from fossil origin and from industry is considered non renewable. Carbon dioxide removed from gaseous streams as flue gas exiting a power plant (Moioli and Pellegrini, 2020) can be used for producing methanol (Van-Dal and Bouallou, 2013), therefore enhancing possible uses of the CO_2, whose concentration and related Earth's temperature increase must be limited into the atmosphere according to the international agreements (COP26, 2021; UN, 2015), and retarding its emissions to the atmosphere.

The methanol price is characterized by high fluctuations within few months, which depend on the market conditions and on the market locations, with values ranging from about 150 $/metric ton to more than 500 $/metric ton in the last two years (Methanol Institute, 2021). It follows that, in order to support the methanol economy, a low-cost production is fundamental.

For all the production routes, the purification of the raw methanol stream to obtain a product with the specifications required by the market is fundamental, and is based on distillation, with relevant energy consumptions (Zhang et al., 2010). Moreover, the treatment of a raw methanol stream from bio-sources may be more challenging because of additional species which could be present as co-products due to the initial starting material.

The overall production path of methanol has been extensively studied in the literature (Zhang et al., 2016), considering different raw materials (Rivarolo et al., 2016), with also sugarcane bagasse (Renó et al., 2011) or renewable hydrogen (Galindo Cifre and Badr, 2007), and adding CO_2 removed from other industrial processes (Abdelaziz et al., 2017; Szima and Cormos, 2018).

Only few papers focused on a reduction of the economics of the process through the analysis and the comparison of different schemes (Shahandeh et al., 2014; Shahandeh et al., 2015) and without focusing on the purification of a biomethanol raw stream. In particular, Douglas and Hoadley (Douglas and Hoadley, 2006) performed a thermal and economic comparison of schemes with two and three columns, with enhanced heat integration, considering a raw methanol stream from steam methane reforming. A 5-column heat integrated distillation scheme and the comparison of its performances with the 4-column scheme were studied by Sun et al. (Sun et al., 2012).

No papers focusing on the study of different configurations for the post-production treatment to obtain a biomethanol product with the characteristics required by the final users and by the market have been found. This work, then, focuses on the purification section of the raw methanol stream and aims at studying alternative schemes to select the one which reduces the overall costs on the basis of a techno-economic analysis.

2. Case studies

The feed stream comes from the section of methanol production from syngas obtained from biomass, after drying, gasification and reforming following the process presented in a previously published work (Poluzzi et al., 2022). It is composed mainly of methanol and water, with traces of ethanol and other light gases. The temperature, pressure, flowrate and composition are detailed in Table 1.

As stated by Sun et al. (Sun et al., 2012), the reduction of the energy consumption of the column for obtaining the methanol product is the key to save energy. The study has focused on the process design of the base scheme and on the study of alternative configurations for the section of purification of raw methanol, in particular considering the possibilities of vapor recompression, with and without heat recovery.

2.1 The baseline scheme

Figure 1a) reports the base scheme considered for the process of purification of raw methanol. The FEED stream is fed to a first distillation column (T-101) that has the aim of removing most of the incondensable gases, so to produce a bottom product (BOTTOMS1) rich in methanol and water that can be fed to a second distillation column (T-102) for obtaining a methanol stream with high purity (MeOH PRODUCT), in addition to a water-rich stream (WATER) exiting from the bottom and a stream of vapor distillate (INCOND), composed of the incondensable gases that have not been removed in the T-101 unit. The use of a flash unit instead of the first distillation column does not reduce significantly the amount of incondensable gases in the liquid stream exiting from the bottom of the unit, that are fed to the second distillation column and impact on the maximum possible recovery of methanol in the product of interest that can be obtained (about 90% instead of more than 99%).

2.2 Alternative configurations

Vapor recompression is a heat pumping method used for exploiting the low grade heat content available in the process by increasing the temperature of the stream of interest to a value for which heat transfer between process fluids is feasible. In particular, as drawn in Figure 1b), in this work it has been applied to the second distillation column, that is the one with the highest reboiler duty, to avoid employing steam at the reboiler of T-102 for the operation of the process. The vapor stream exiting from the top of the unit T-102 is compressed to a pressure so that the stream DIST-HT has a temperature higher of at least 5 °C than the maximum temperature occurring in the reboiler of the second distillation column (a future development of this work is evaluating the option of a difference in the temperature of at least 10 °C). By providing thermal power to the bottom stream of the distillation column and partially vaporizing it, stream DIST-HT exits from the unit at a lower temperature and partly condensed. The following units, in particular the heat exchanger E-102 and the Flash drum have the aim of completing the cooling and separating the incondensable gases from the MeOH rich stream, that is split into a stream REFLUX and a stream MeOH PRODUCT, with the same characteristics of the corresponding streams in the base case.

Two configurations have been considered for the vapor recompression scheme, one alternative (named Scheme VRC) with the stream BOTTOMS1 directly fed to the unit T-102 (not reported in Figure 1) and one

alternative (named Scheme VRC+HR) with the addition of a process-process heat exchanger (E-101) for the recovery of the heat content of the bottom stream rich in water (WATER), reported in Figure 1b).
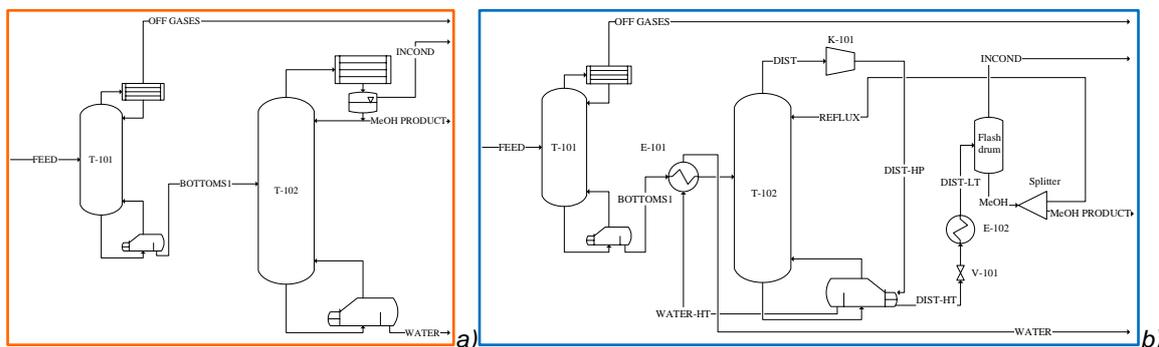
Figure 1: Scheme of the a) base configuration and b) advanced configuration with vapor recompression and pre-heating (Scheme VRC+HR).

3. Methodology

The purification section must produce a methanol-rich stream of fuel grade (A grade), considering a minimum weight fraction of methanol in the product stream of 0.9985 and a water content lower than 0.1 % wt. As additional specification, in this work a recovery of the methanol entering the purification section of at least 99% has been considered.

The simulations for the design and the evaluation of the performances of the different schemes have been carried out in ASPEN Plus® V11.0 (AspenTech, 2021), considering a γ / ϕ method, based on the Non-Random Two-Liquid (NRTL) theory (Renon and Prausnitz, 1968) for the description of the liquid phase, which is accurate for the representation of the phase equilibria of this system (Allocca, 2020). The columns, supposed to be packed with Sulzer Mellapak 252Y, have been simulated as rate-based units, taking into account the mass transfer resistances, with 50 stages for simulation (of which 1 for the condenser and 1 for the reboiler).

The results from the simulation have been used as input for the economic analysis, for the estimation of the investment costs (CAPEX) and operating costs (OPEX) and of the Net Present Value (NPV) for the evaluation of equipment alternatives (Turton et al., 2012), with different CAPEX and OPEX, to obtain the same production. The CAPEX have been determined on the basis of the Preliminary Design Estimate method and the OPEX have been estimated considering the cost of cooling water and the cost of steam reported in Turton et al. (2012). As for the cost of electricity, that has been significantly increased in the last period (year 2022), the study has focused on different values for the price of electricity as representative of the cost of electricity in the first semester of year 2022 (Eurostat, 2023) and in the first semester and in the second semester of year 2021 (European Commission, 2023) in Italy, equal to 0.2525 Euro/kWh, 0.1403 Euro/kWh and 0.0939 Euro/kWh.

The NPV for the evaluation of equipment alternatives has been calculated as:

$$NPV = \sum_{k=0}^{25} \frac{C_k}{(1 + d)^k} \tag{1}$$

with C_k being the cost at year k and d = 0.10, assuming 25 years for the operation of the plant. The less negative NPV provides the best alternative.

In order to identify the optimal configuration, a techno-economic analysis has been carried out so that for the baseline scheme the characteristics of the two columns (height, feed stage, bottom-to-feed ratio) have been optimized with the aim of fulfilling the required specifications while maintaining the lowest investment and operating costs. To determine the values of the height, feed stage and bottom-to-feed ratio variables an iterative procedure has been applied, since the result of one variable depends on the value of the other ones. Then, for the selected distillation columns, the advantages to the plant of providing a vapor recompression system and a process-process heat exchanger for thermal recovery have been determined.

4. Results and Discussion

Table 1 reports the characteristics of the streams for the base case. More than 99% of methanol is recovered in the MeOH PRODUCT stream, that contains also the ethanol present in low amount in the stream fed to the plant. The incondensable gases exit in the OFF-GASES and INCOND streams and 99.65% of water is recovered

in stream WATER with high purity (> 99.25 % mol.). For reasons of space, in this paper only the main results are reported.

Table 1: Temperature, pressure, molar flowrate and composition of the streams of the base case ("traces" refers to mole fractions lower than 1e-12).

	MIXTURE	OFF-GASES	BOTTOMS1	INCOND	MeOH PRODUCT	WATER
Temperature [° C]	40.94	35.55	80.65	64.56	64.56	100.51
Pressure [bar]	2.00	1.50	1.51	1.01	1.01	1.08
Molar flowrate [kmol/h]	818.66	18.83	799.83	5.28E-4	527.89	271.94
Mole fractions						
DiMethylEther	2.83E-05	0.001229	1.37E-10	2.13E-08	2.07E-10	traces
H_2O	0.330868	0.007946	0.338470	0.000602	0.001495	0.992598
H_2	0.002108	0.091638	Traces	Traces	0.00E+00	0.00E+00
CO_2	0.014853	0.645801	3.08E-12	6.67E-10	4.66E-12	6.49E-20
CO	5.51E-05	0.002396	Traces	Traces	0	0
Methanol	0.649746	0.162063	0.661227	0.999104	0.998047	0.007399
CH_4	0.001325	0.057603	Traces	Traces	0	0
C_2H_4	3.10E-11	1.35E-09	Traces	Traces	0	0
Ar	4.83E-10	2.10E-08	Traces	Traces	0	0
N_2	0.000719	0.031290	Traces	Traces	0	0
Ethanol	0.000298	3.40E-05	0.000303	0.000294	0.000458	2.53E-06

The investment cost of the base scheme is significantly lower than the ones of Scheme VRC and of Scheme VRC+HR, due to its simpler configuration (Figure 2a)). The addition of the compressor significantly increases the CAPEX, though favouring a saving in the OPEX (Figure 2b)). In particular, for the period related to 2021 the operating costs for the Scheme VRC and the Scheme VRC+HR result to be reduced of at least 46.7 % in the second semester of 2021 and for at least 60.9 % in the first semester of 2021 (this consideration can be extended also to the previous years, when the cost of electricity was not as high as in 2022). Considering the operating life of the plant, for these alternative schemes, the obtained reduction of the OPEX is much higher than the increase in CAPEX, resulting in a reduction of the NPV (Figure 3) of at least 33.5 % for the period 2021 S2 and of 46.5 % for the period 2021 S1.

a)   b)
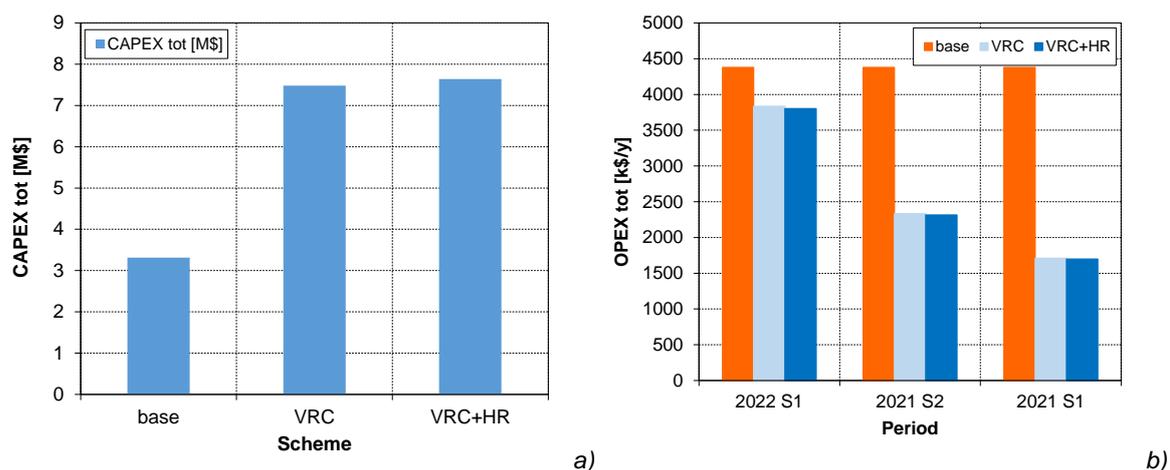
Figure 2: a) Total investment costs (referred to column T-101 and to column T-102) and b) total operating costs due to the consumption of the main utilities for the three considered schemes and taking into account the different price of electricity in semester 1 of 2022 (2022 S1), semester 2 of 2021 (2021 S2) and semester 1 of 2021 (2021 S1).
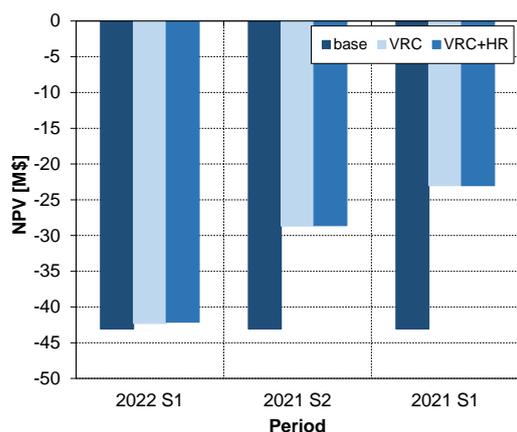
Figure 3: NPV for the three considered schemes and taking into account the different price of electricity in semester 1 of 2022 (2022 S1), semester 2 of 2021 (2021 S2) and semester 1 of 2021 (2021 S1).

With the increase in the cost of electricity, in particular in 2022, the OPEX of the alternatives result to be in any case lower than the ones required in the base scheme (at least 12.4 %), though the reduction of the NPV is at maximum 2.2 %, because the reduction in the OPEX compensates the increase in the CAPEX for the two more complex configurations. However, it is to be considered that this work has been conservative as for the estimation of the cost of steam. After 2022, the cost of all the energy sources has increased, so a higher cost of steam would be more realistic and would influence the OPEX and the NPV of the base scheme. For instance, by taking into account a cost of steam equal to 100 €/t instead of 14.05 $/GJ (corresponding to about 29 $/t), the OPEX of the base scheme results equal to 14412 k$/y and the NPV equal to -148.857 M$, so the alternative configurations, that employ steam only for the first distillation column, are much more advantageous also with the increased price of electricity of 2022.

The addition of a heat exchanger (E-101) for pre-heating the feed stream to T-102 has a negligible influence on the NPV in this case. Indeed, the reduction in the operating costs obtained by using the heat content of the WATER stream for heating the BOTTOMS1 stream compensates the additional capital investment needed for the E-101 unit, also considering that the reboiler of T-102 is slightly reduced because of the lower duty needed. The low improvement obtained in Scheme VRC+HR, if considering the application of heat recovery to other process schemes, is due to the fact that the water stream has a flowrate that is lower than 35% of the BOTTOMS1 stream and does not favour a significant increase in the enthalpy of this stream before its entrance in the second distillation column.

5. Conclusion

This work focused on the techno-economic evaluation of two Vapor Recompression schemes as possible alternatives to the base configuration consisting of two distillation columns, for the process of purification of raw biomethanol produced from syngas obtained from biomasses.

Different prices for the steam, the main utility consumed in the base case, and for the electricity, the main utility needed for the alternative schemes, have been considered, taking into account the steep increase in the energy costs in the last year.Scheme VRC and Scheme VRC+HR result advantageous because they provide a low NPV related to the CAPEX and OPEX, for all the considered prices of electricity, despite the more complex configuration of the plant.The future development of this work will focus on the analysis of the same schemes considering a difference between the temperature of the hot fluid and the one of the cold fluid in the heat exchanger equal to at least 10 °C and on the evaluation of other process alternatives for the reduction of the cost of production of purified methanol.

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