

Initial Assessment of Separation Train Design and Utilities Consumption for Cyclopentyl Methyl Ether Production [†]

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[†] Presented at the 4th International Electronic Conference on Applied Sciences, 27 October–10 November 2023; Available online: <https://asec2023.sciforum.net/>.

Abstract: Asymmetric ethers such as Cyclopentyl Methyl Ether (CPME) found their application as alternative solvents in technology; they are often labeled as “green solvents” as they can be prepared using renewable feedstock. They are almost immiscible with water and can be easily regenerated. Based on earlier experiments with CPME preparation in laboratory conditions and the estimated product yields, an initial assessment of the reaction mixture separation train was performed, for the chosen production capacity of 100 kg·h^{−1} of CPME. Following suitable thermodynamic model selection, basic analyses in Aspen Plus software were executed. Reactor effluent containing eight chemical species was subjected to multiple separation steps including extraction and several rectifications including one vapor phase compression step to yield saleable products with sufficient purity and unreacted chemicals recyclable to the reactor. Basic simulations were performed to find the optimal working conditions of individual columns and to estimate the associated energy needs. Basic design, without any heat or work integration measures, required a total heating duty of 787 kW and a total cooling duty of 614 kW. This yielded a specific heat consumption of 28.3 GJ per ton of the main product (CPME) which is unacceptably high as it represents around 70% of its chemical energy content (heating value). Further research will be devoted to reducing heating and cooling duty by integrated separation train design development to comply with the reduced carbon footprint mandatory for the syntheses and separations of green solvents.

Keywords: green solvents; separation; heating duty; rectification; carbon footprint



Citation: Variny, M.; Hlavatý, L.; Soták, T.; Magyarová, Z. Initial Assessment of Separation Train Design and Utilities Consumption for Cyclopentyl Methyl Ether Production. *Eng. Proc.* **2023**, *56*, 57. <https://doi.org/10.3390/ASEC2023-15307>

Academic Editor: Simeone Chianese

Published: 26 October 2023



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1. Introduction

Cyclopentyl Methyl Ether (CPME) is an asymmetric ether usable as a solvent in organic syntheses [1] with several advantages over other ether-based solvents such as practical immiscibility with water and good chemical stability [2]. It can be classified as an environmentally friendly solvent due to its easy regeneration from reaction mixtures and the possibility of synthesizing it from renewable feedstock [3]. Two synthesis pathways are used nowadays for CPME production: the Williamson synthesis utilizing cyclopentanol and methyl iodine [4] and the other one, based on methanol (MeOH) addition on cyclopentene in the presence of an acidic catalyst [2].

An alternative CPME production route was explored in our previous research [3,5], using zeolites for catalysis in the gas phase. Experimental investigation yielded an estimation of optimal reaction parameters: reaction temperature of 100 °C and feedstock flowrate of 0.1 g/h related to 1 g of catalyst. The resulting cyclopentanol (CYPol) conversion exceeded 80% and the selectivity towards CPME was as high as 82.5% [3]. Cyclopentene (CYPen) and dimethylether (DME) are among the important by-products, with CYPen being hydratable

back to CYPol and DME having its use as green coolant as an automotive fuel component [6,7]. Reactor effluent contains dicyclopentylether (DCPE), 1-cyclopentyl cyclopentene (CPCPen), and water as other noticeable by-products. Thus, a complex composition of reactor effluent is expectable, posing a challenge for efficient CPME separation.

An initial assessment of the reaction mixture separation is provided in this work utilizing simulations in Aspen Plus V12, dealing with a selection of suitable thermodynamic models and proposing a feasible configuration of separation steps and operation conditions. Basic operation parameters of separation equipment are estimated and its overall energy demand for heating and cooling is obtained for a production train capacity of 100 kg/h of CPME.

2. Materials and Methods

Table 1 provides the basic properties of components present in the reactor effluent [5]. Reaction selectivities are related to CYPol. Methanol excess related to theoretical consumption was set to 500% according to previous experimental investigation [5].

Table 1. Components in the reactor effluent and their basic properties.

Component	Abbreviation/Formula	Reaction Selectivity [%]	Molar Mass [g/mol]	Normal Boiling Point [°C]	Reactor Effluent [mol/h]
Cyclopentanol	CYPol	-	86.13	139.85	540.94
Methanol	MeOH	-	32.04	64.6	23,634.99
Cyclopentylmethylether	CPME	65.8	100.16	106	1050.94
Cyclopentene	CYPen	21.7	68.12	43.85	346.59
Water	H ₂ O	-	18.02	100	3532.16
Dicyclopentylether	DCPE	11.4	154.25	207.83	91.04
1-cyclopentylcyclopentene	CPCPen	1	136.24	191.2	7.99
Dimethylether	DME	14.1 ¹	46.07	-24.85	2026.03
Soot	Approximated as C ₂₅ H ₄₀ [5]	0.1	340.60	-	0.32

¹ Methanol conversion to DME.

The reactor effluent composition provided in Table 1 results from the following chemical reactions, Equations (1) to (6).



In the initial design of the separation train, the following facts were considered: 1. The reactor effluent was to be cooled down at first to obtain two liquid phases (aqueous and organic) and a gaseous stream. 2. All three phases needed separate treatment ensuring the recirculation of unreacted reactants back to the reactor and obtaining product streams with sufficient purity. 3. The CYPen was to be hydrated to CYPol and recycled to the reactor. 4. The addition of water to the cooled-down reactor effluent helped form the aqueous phase and aided in extracting water-soluble components. 5. Separation of the DME required increased pressure if the cryogenic separation was to be avoided. 6. Additional purification could be achieved by absorption in cases when the rectification became difficult due to either low contaminant content or close boiling points of components in the mixture. However, the absorption units were not modeled but were included as mere component splitters.

Initial calculations included the estimation of reflux ratios and the number of theoretical plates for each considered rectification column via the Winn–Underwood–Gilliland method. Subsequent simulations of individual separation train configurations were performed in Aspen Plus V12. Selection of a suitable thermodynamic model was based on comparison of model-predicted binary vapor–liquid equilibria with experimental data recorded in the NIST database [8–11] and, in addition, on the ability of the model to describe the formation and composition of two liquid phases formed on reactor effluent cooling. In the end, the Soave–Redlich–Kwong–Kabadi–Danner (SRK-KD) model performed most satisfactorily and was implemented in simulations.

The number of theoretical plates for rectification columns was set to double compared to plate counts yielded from the Winn–Underwood–Gilliland method. The reflux ratio for columns was then adjusted to keep the required purity of product streams. Columns were set to operate at atmospheric pressure except for two columns where the DME was separated from the rest of the mixture that operated at 6 atmospheres. Heat losses were neglected.

3. Results

Figure 1 depicts the separation train configuration able to separate the reactor effluent into streams with suitable purity to be sold as commercial products. It contains six rectification columns, two adsorbers, and other auxiliary equipment and is partly integrated in terms of by-products and unreacted feedstock reuse.

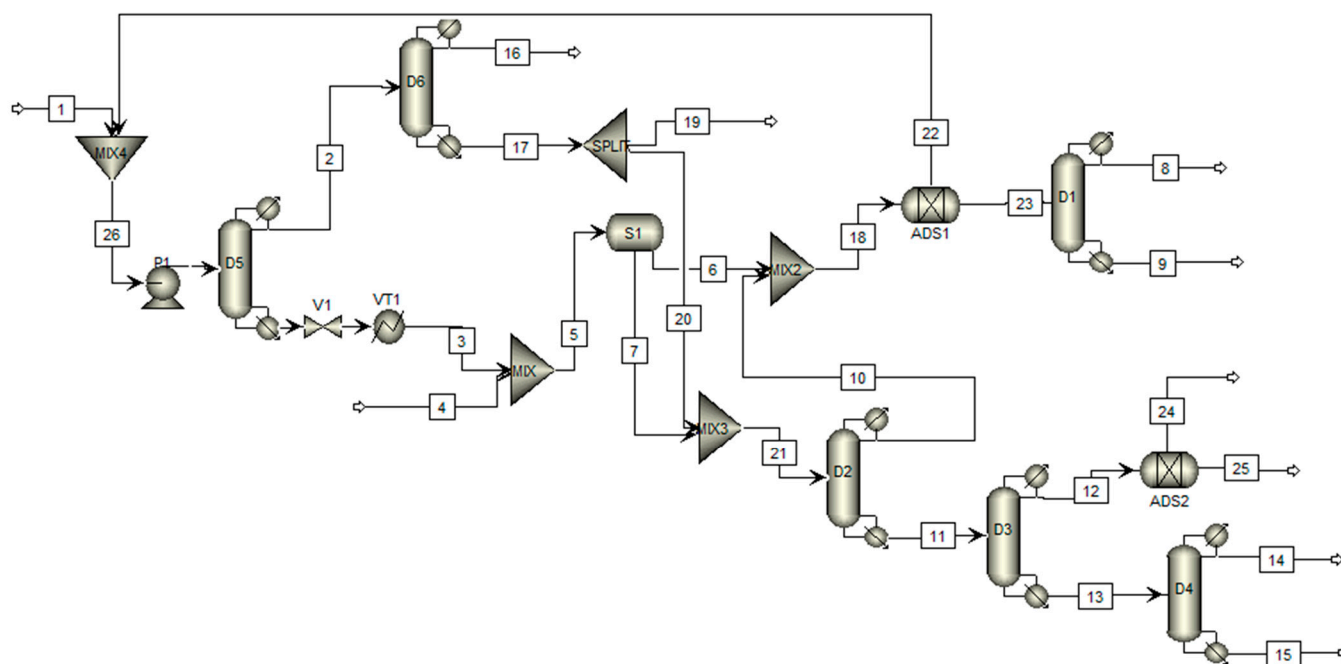


Figure 1. Selected separation train layout. Legend: ADS = adsorber, D = rectification column, MIX = stream mixer, P = pump, SPLIT = stream splitter, V = valve, VT = heat exchanger, 1 = reactor effluent, 4 = additional water, 22 = recycled valuable components; 8,9,14,15,16,19,24,25 = products streams, waste streams, and streams recycled to reactor (reactor not shown in the scheme); 2,3,5–7,10–13,17,18,20–23,26 = internal process streams.

Table 2 shows the overall mass balance of the considered separation train. As is obvious, the desired product CPME can be obtained with sufficient purity (99% mol., stream 25) and so does the valuable by-product DME (stream 16). Streams 8 and 14 are recycled to the reactor, reducing the need for fresh feedstock. Stream 19 could undergo hydration and could be sent as CYPol-rich stream back to the reactor. Streams 9 and 24 represent wastewater that could be partly recycled adequately replacing freshwater consumption (stream 4).

Table 2. Mass balance of the separation train.

Stream/Component	Molar Flow [kmol/h]									
	1	4	8	9	16	19	14	15	24	25
CYPol	0.541	0	0	0	0	0	0.540	0.001	0	0
MeOH	23.635	0	23.598	0.024	0	0.002	0	0	0	0.011
CPME	1.056	0	0	0	0	0	0.002	0	0.003	1.051
CYPen	0.347	0	0	0	0.0004	0.3461	0	0	0	0
Water	3.532	24.764	0.028	28.071	0	0	0	0	0.196	0
CPCPen	0.008	0	0	0	0	0	0	0.008	0	0
DME	2.023	0	0	0	2.021	0.002	0	0	0	0
DCPE	0.091	0	0	0	0	0	0	0.091	0	0
Sum	31.233	24.764	23.626	28.095	2.022	0.350	0.542	0.100	0.199	1.062

Table 3 provides insight into the basic design and operation parameters of the rectification columns. Column D2 exhibits by far the largest heating and cooling duty, coupled with both the comparatively high reflux ratio required for its operation and the large feed flow processed there. Column reboilers operate at temperatures common in industry and could be supplied by low- and middle-pressure water steam. Column condensers could, except column D6, be cooled by common industrial cooling water available at 15 to 25 °C.

Table 3. The design and operation parameters of columns and heating and cooling duty required. D = rectification column.

Column/Parameter	D5	D6	D1	D2	D3	D4
Reflux ratio	3.79	0.49	0.67	3.01	0.83	0.73
Number of theoretical plates	33	27	14	81	35	20
Condenser duty [kW]	73.2	15.8	72.6	419.8	21.7	10.7
Reboiler duty [kW]	182.5	17.0	78.2	475.2	22.8	11.1
Column head temperature [°C]	38.8	30.7	49.6	65.4	77.4	138.8
Column bottom temperature [°C]	127.2	115.0	92.1	98.6	143.6	196.5

4. Discussion

The selected separation train layout depicted in Figure 1 is far from being optimal, despite its complexity and the achieved product stream purity documented in Table 2. It is a result of mathematical modeling and relies on assumptions applied and the thermodynamic model used. An industrial counterpart to compare it with is, unfortunately, not available. Apart from material reuse, another layer of complexity would be added when attempting to reduce heating and cooling duty. This could be realized in two ways—implementing heat-integrated design and heat pumps or developing and applying separation methods other than rectification, which is energy-intensive. This will be the goal of our further research.

Table 3 shows that most of the heating and cooling duty is consumed in column D2. This column serves to separate methanol and other volatile components from less volatile ones. Large methanol excess (500% compared to theoretical consumption) coupled with its comparatively high latent heat of evaporation (over 1 MJ per kg) and the required reflux ratio of more than 3 are the reasons for this observation. Further studies on reaction mechanisms and conditions that would lead to the required methanol excess reduction are required.

The total heating duty of the separation train is 787 kW, or 7.87 MWh (28.3 GJ) per 1 t of CPME product. If the DME is considered as another valuable product, total heating duty reduces to around 14 GJ per ton of (CPME + DME) product which, nevertheless, is unacceptably high as it still constitutes a large fraction of their heating value. Additional energy would be required to cover the cooling duty and pumping work, contributing to final energy requirements and greenhouse gas emissions. Assuming the required heating duty is provided by natural gas (49 MJ/kg lower heating value) combustion with 85% heating

efficiency, around 680 kg of natural gas would be combusted, releasing almost 1.9 t of CO₂ by its combustion considering its emission factor of 2.75 t_{CO₂}/t. This cannot be accepted, neither from an economic and energetic nor from an environmental point of view. Further research will be directed towards reducing the energy requirement and the related carbon footprint of CPME production.

5. Conclusions

The presented study bears on developing the design of a separation train for the production of 100 kg/h CPME and on assessing its basic design and operation features, striving to find a viable and industrially acceptable alternative for its separation from the reaction mixture. Considering the complex composition of reactor effluent, several distillation steps are required in conventional rectification columns, aided by adsorption units to reach desired product purity and to both ensure the recycling of valuable streams to the reactor and minimize waste stream formation. Initial assessment of energy consumption in the developed separation train design indicates a specific heating duty of over 28 GJ per ton of main product (CPME) and of over 14 GJ per ton of product if DME is counted as a valuable by-product. The related carbon footprint reaches almost 2 t of CO₂ per ton of CPME and hinders labeling the produced CMPE as a “green solvent”. Process design and operation modifications are required to lower the associated energy intensity substantially. This poses a challenge for our further research.

Author Contributions: Conceptualization, M.V. and T.S.; methodology, L.H. and Z.M.; software, L.H.; validation, T.S. and Z.M.; investigation, M.V. and L.H.; resources, Z.M.; data curation, L.H.; writing—original draft preparation, M.V. and L.H.; writing—review and editing, T.S. and Z.M.; visualization, M.V. and L.H.; supervision, M.V. and T.S.; funding acquisition, M.V. and T.S. All authors have read and agreed to the published version of the manuscript.

Funding: This study was supported by the Slovak Research and Development Agency under contract no. APVV-18-0134 and by the Slovak Scientific Agency, grant no. VEGA 1/0374/23.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All available data are shown in the paper.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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