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Multi-stage membrane processes for CO₂ capture from cement industry

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Abstract

Capture conditions for cement plant flue gas differ substantially from other industrial flue gases due to the high partial pressure of CO₂, presenting an opportunity for polymeric membranes to compete with other capture technologies. In this work, two membrane processes are designed by applying a recently developed graphical methodology to identify promising membrane properties, number of stages and operating points for each stage. The net present values of cost and the CO₂ avoidance costs are compared with an MEA based capture unit when applied to a 0.7 Mt_{CO2}/year cement plant. The membrane designs are shown to have a significantly lower investment cost (32.6 M€ vs. 294 M€) and CO₂ avoidance cost (27 €/t vs 55 €/t) than the reference MEA based capture process. The investment cost for turbomachinery and the operating cost for electricity are also shown, in this particular case, to be more important than the membrane investment and replacement costs over the lifetime of the membrane capture plant. The present work underlines the importance of using a cost-based approach to balance the trade-offs in membrane process design.

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1. Introduction

In the transition to a low-carbon society, carbon capture technologies are considered for a range of industrial sectors. Post-combustion gas separation by permeation membranes is a promising alternative that has potential to

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reduce the capture cost in the short-term perspective. A variety of process layouts and membrane improvements have been studied for post-combustion capture in the power industry. However, due to the low driving force for separation from these flue gases, relatively complex membrane systems are needed in order to compete with chemical absorption on an energy efficiency basis.

When considering other industries, such as steel and cement production, capture conditions vary substantially from the power plant cases [1]. Specifically, the flue gas CO₂ concentration is higher, providing a higher driving force for separation. While chemical absorption is considered also for these cases, particularly using monoethanolamine (MEA), there is very little energetic benefit of increasing the CO₂ concentration beyond that of a typical coal power plant case (12 vol% CO₂) [2]. Membrane separators, on the other hand, benefit from the increased CO₂ partial pressure.

Significant work in literature is devoted to sensitivity analysis of single stage membrane units as inputs to process design. The trade-off between permeate purity and capture ratio can be explored by varying the membrane pressure ratio, area, permeation properties (flux and selectivity) and flow pattern (cross flow, co-current or counter-current flow). Single stage membrane separation is however infeasible with current membrane properties if stringent capture ratios and CO₂ purity requirements are to be met (e.g. 85-90% capture at 95% purity). The complexity for the design of a multi-stage membrane process increases as the process configuration and associated trade-offs at each stage must be considered.

Previous work on multi-stage process design for post-combustion capture involves establishing "good" process configurations based on insights from single-stage unit sensitivities for the case at hand. Global sensitivity studies for the multi-stage processes are then performed to find membrane properties and/or operating conditions which give a reasonable trade-off between membrane area and energy consumption. It is normally not known beforehand whether the process designed will achieve the targeted capture ratio and product purity simultaneously.

Merkel et al. used this methodology to establish optimal membrane properties and synthesize complex processes for post-combustion capture from a coal power plants [3] and natural gas combined cycle power plants [4]. Similar work has also been performed by other authors. Kundu et al. [5] investigated the use of dual stage membrane systems for post-combustion capture from a cement plant. A hybrid between membrane and solvent based capture units were also explored. Scholes et al. [6] built on the work of, among others, Merkel et al. [3], designing three different processes and comparing their energy use and cost. For the simplest layout, a parameter variation of the total stage cut of the first stage was used to find suitable operating parameters and membrane selectivity. All these studies, however, focus mainly on reducing power consumption while maintaining an acceptable membrane area. If economic results are included in the studies, they are calculated as a post-processing step.

For systems where energy and investment costs are of the same order of magnitude and follow opposing trends, overall process design need to address the economic tradeoff between these two costs in order to avoid sub-optimization. Membrane systems for CO₂ capture is an example of such a process, due to the high investment and replacement costs for the membrane and the high energy consumption associated with feed compression and vacuum pumping of the permeate. The trade-off between membrane area and pressure ratio must be dictated by a rigorous economic model for cost minimization.

A graphical methodology developed at SINTEF Energy Research [7] is used in the present work to design two near-cost-optimal membrane systems that fulfil requirements on CO₂ capture ratio (CCR) and product purity. The *attainable region* diagram is used to identify promising membrane properties, stage configurations and estimated capture cost for a typical cement case (~20% CO₂). The underlying membrane model and cost framework is then used to back-calculate operating conditions and break down the cost structure of the processes. Results on CO₂ avoidance cost and net present value of cost are finally compared to an MEA based solvent reference case.

2. Case study and benchmarking reference

The IEA case study [8] on CO₂ capture in the cement industry from 2008 is used as the foundation in the present work. This report presents detailed process simulations and economic evaluations of a hypothetical new-build 1Mt_{clinker}/year cement plant in Scotland, UK, with and without CO₂ capture.

The cement plant *without* capture is used in the present study to determine the flow rate and CO₂ concentration of the flue gas fed to the membrane units. The total CO₂ flow rate in the exhaust is 0.72 Mt_{CO2}/year, corresponding to

0.62 Mt_{CO2}/year captured with an 85% CCR. Since the membrane unit does not require any CHP plant for steam production, the CO₂ flow rate is significantly smaller than in the MEA case and the flue gas has a slightly higher CO₂ concentration. For consistent comparison, all economic assumptions in the membrane cost model of the present work is taken from the cement plant *with* capture and all data will be presented in 2008 euros, as in the IEA report.

The cement plant *with* MEA based CO₂ capture is used as the benchmarking reference to the developed membrane system. The annual operating costs, investment costs and emissions of CO₂ presented in the report are used to calculate the CO₂ capture cost and CO₂ avoidance cost consistently with the membrane cost evaluation. For comparison, the capture- and avoidance costs without flue gas desulfurization (FGD) and selective catalytic reduction (SCR) units are also calculated. These costs correspond to a case where these units would have to be included in the base plant without capture because of emissions regulations.

3. Design and modeling approach

3.1. Membrane properties

Three different membranes are considered for the present application: a) A dense polymeric membrane from literature with excellent permeation properties, b) a hypothetical polymeric membrane with a significantly higher selectivity but with the permeance scaled according to Robeson's upper bound relationship [9] and c) an ultra-thin facilitated transport membrane that combines a high selectivity with a permeance considerably exceeding Robeson's upper bound.

The parameters for the membrane model are given in Table 1. All membranes are modeled according to the solution-diffusion theory, implying that membrane properties are invariant to the pressure ratio. The membrane cost and lifetime are also assumed to be the same.

Table 1: Membrane properties

	$\alpha = P_{CO_2}/P_{N_2}$ -	P_{CO_2} m ³ (STP)m ⁻² hr ⁻¹ bar ⁻¹	Reference
Membrane A	50	5.94	[4]
Membrane B	200	0.108 ^a	[9]
Membrane C	200	1	[10]

^a Assuming the same membrane thickness as Membrane A

3.2. Design methodology

A graphical methodology for systematic and consistent design of membrane processes for post combustion capture has previously been developed at SINTEF Energy Research [7]. This methodology is now applied to the cement plant case to design simple, near-cost-optimal membrane processes with a high CO₂ capture ratio. The membrane separation task is divided into several stages, where each stage includes a membrane unit as well as its own rotating equipment and intercoolers (cf. Figure 1). The combination of a membrane model, a rotating equipment model and a cost model is used to calculate the technical and economic performance of each stage. An *attainable region* diagram is used to visualize the possible operating window of each membrane stage in addition to its optimal operating region. The number of stages and operating points are then easily identified using a step-wise approach similar to the McCabe Thiele diagram. Complex process features, such as retentate recycles or retentate heating before expansion, are not included in the graphical solutions generated.

The attainable region diagram is a plot of feed composition versus permeate/retentate purity and is drawn for a certain *stage* carbon capture ratio. This stage carbon capture ratio is in turn determined from the overall capture ratio

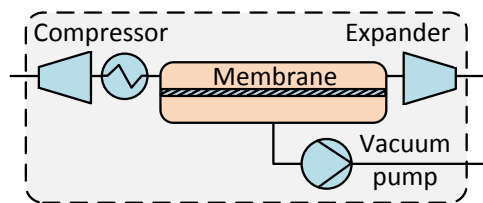


Figure 1: Membrane unit used to create the attainable region diagram

to be attained and an assumption on the number of stages. The overall capture ratio can be subject to economic optimization, but is set to 85% in this work in line with the IEA report [8]. Additionally, the minimum allowable permeate side vacuum must be set. In this work, 0.2 bar is used. The *minimum cost* curve (locus of permeate/retentate purities) is then calculated for the entire range of feed CO₂ mole fractions (0-1), using the cost model to determine the membrane pressure ratio and area which gives the lowest cost for each point. In addition, curves of constant cost can be drawn as a function of feed composition. These curves intersect the minimum cost curve at the lowest feed composition for which the given separation can be attained to the required specifications. The envelope formed by the iso-cost curves represents the attainable region for a given membrane and indicate the ranges of purity which are attainable without unreasonable increases in cost for a given feed composition.

The total specific capture cost (CC, in €/t CO₂) for *n* separation stages can be calculated from the stage capture costs and the stage capture ratios:

$$CC_{total} = \frac{CC_{stage}^1}{CCR_{stage}^1} + \dots + \frac{CC_{stage}^{n-1}}{CCR_{stage}^{n-1}} + CC_{stage}^n \quad (1)$$

3.3. Membrane model

The design methodology requires robust models for the membrane separator, the rotating equipment. A membrane model for two gas components, after Saltonstall [11], is adopted for the present work. The model assumes a membrane unit in cross-flow configuration with plug flow on the feed side and no mixing with the bulk stream on the permeate side. These assumptions allow analytical solution of all model equations, which is favorable in terms of robustness and computational speed. A disadvantage of this approach is that water vapor permeation cannot be modeled. As a result, the cost and/or power consumption of drying units before or after the membrane unit(s) cannot be included in the present analysis. To ensure that the analysis is conservative with respect to membrane performance, the water vapor is treated as an inert gas contributing to reducing the partial pressure of CO₂ in the exhaust. It should be noted that although a multicomponent model could have included water in the performance analysis, experimentally validated membrane permeation constants in the presence of water vapor are scarce in open literature.

3.4. Cost assessment methodology

The additional cost of equipping a cement plant with membrane CO₂ capture is evaluated for an 85% capture ratio and compared to the additional cost of a cement plant with MEA CO₂ capture. This study assumes costs of a "NOAK" (Nth Of A Kind) plant to be built at some point in the future, when the technology is mature. Investment and operating costs are given in 2008 prices which correspond to the reference year for costs in the IEA report [8].

The costs for the MEA capture facility and FGD/SCR units are adopted from the IEA report [8]. The costs of the membrane capture process is evaluated using cost function based on Aspen Process Economic Analyzer following the IEA cost methodology in order to obtain consistent and comparable costs estimates. For membrane unit equipment costs, more details can be obtained in Roussanaly et al. [12]. The average direct and indirect cost factors, the maintenance costs and utility costs of the cement plant with MEA CO₂ capture considered in the IEA report are used to evaluate the investment cost of the cement plant with membrane capture considered in this paper.

The technical characteristics and costs associated with CO₂ conditioning from 1 to 150 bar are modelled using the BIGCCS transport modules previously presented and illustrated [13,14].

The CO₂ avoided cost (€/t_{CO2}), presented in Equation (2) is here used as a key performance indicator to measure the unitary cost of capturing CO₂ from a cement plant. The CO₂ avoided cost approximates the average discounted CO₂ tax or quota over the project duration that would be required as income to match the net present value of additional capital and operating costs due to the CCS infrastructure. The calculations are performed considering a real discount rate of 10%, 7 884 operating hours per year and an economic lifetime of 25 years [8]. To be consistent with the IEA report, the CO₂ avoided is calculating considering only the direct electricity linked emissions with a climate impact of 520 kg_{CO2}/MWh_{consumed}.

$$\text{CO}_2 \text{ avoided cost [€}/\text{t}_{\text{CO}_2}] = \frac{\text{Annualized investment} + \text{Annual OPEX}}{\text{Annual amount of CO}_2 \text{ captured} - \text{Annual direct emission}} \quad (2)$$

4. Results

4.1. Dense polymeric membranes

Figure 2 shows the attainable region diagram for membrane A and B, representing the trade-off between permeance and selectivity normally seen in polymeric membranes. Due to its high permeance, membrane A has a relatively wide attainable region (the convex hull which encompasses all iso-cost curves). The iso-cost curves also extend far down in feed gas CO₂ concentration for the same reason. Membrane B on the other hand, has an extremely narrow operating window, and can in practice only reach one particular permeate purity for a given feed gas. In addition, the cost level of a membrane B system is much higher than for a membrane A system, as indicated by the iso-cost curves, mainly due to the need for larger membrane area and greater feed compression. Membrane B can indeed be used in a single stage configuration since it can reach 95% purity with a cement flue gas feed, but it will require massive feed compression (16.2 bar) in addition to a large membrane area ($> 2 \cdot 10^5 \text{ m}^2$). This leads to a prohibitively large specific cost for separation (33 €/t without final compression). Membrane B is therefore not considered further.

The number of stages for membrane A is determined by first considering a design using the minimum cost curve alone. Adhering strictly to the minimum cost, three separation stages is required to reach 95%+ purity, since the permeate from the second stage will only be about 90% CO₂. Since the third stage will reach far beyond 95% purity, a three stage design will either separate the components excessively or be operated *below* the minimum cost curve to reach the desired separation. In practice, it is never desirable to operate any stage below the minimum cost curve, since this implies a higher cost, lower purity and a larger number of units than necessary. Two stages are therefore chosen, with operating points determined by the iso-cost curves.

By considering the gradient of the iso-cost curves, it is clear that a two-stage design should aim for a high purity in the permeate from the first stage to avoid an excessively expensive second stage. The indicated Design I is not optimal, since it operates quite far away from the minimum cost in the first stage but very close to it in the second stage. Design III does not represent a good trade-off either – the second stage cost is too high since it ends up in a region with a large gradient in the cost function. Design II is the design of choice for the present application.

The two-stage design of Scholes et al. [6] is plotted in the attainable region for comparison with the present work. This design uses minimal feed compression, presumably in an attempt to limit power consumption, and is therefore unable to combine a high stage capture ratio with a decent permeate purity. Significant energy is wasted through the vacuum pumping of nitrogen/water, and a larger area than necessary is used. Consequently, the second stage becomes prohibitively expensive due to the low intermediate purity. This example shows why a consistent, cost-based approach is needed to design membrane systems even as "simple" as a two stage design.

Finally, the potential for recycling the retentate stream from the second stage is evaluated for Design II. As indicated by the dotted line, the retentate purity is only about 15% CO₂. It is therefore not judged likely that recompressing this stream and mixing it with the feed stream will contribute to reducing the cost for capture.

4.2. Facilitated transport membranes

Figure 3 shows the attainable region diagram of membrane C, modelled as a solution-diffusion governed membrane. Compared to the curves for membrane B in Figure 2, the attainable region is significantly wider and the costs are lower. However, the process based on membrane C (Design IV) must be operated above the minimum cost for the cement feed, leading to a significant feed compression (7 bar). The cost is in a reasonable range due to the smaller number of units compared to a two-stage design and the smaller required area. It should however be noted that the operating point is in a region with a large gradient in the cost function, indicating that the cost results are sensitive to changes in underlying assumptions or errors in the membrane model (e.g. feed composition or permeate purity).

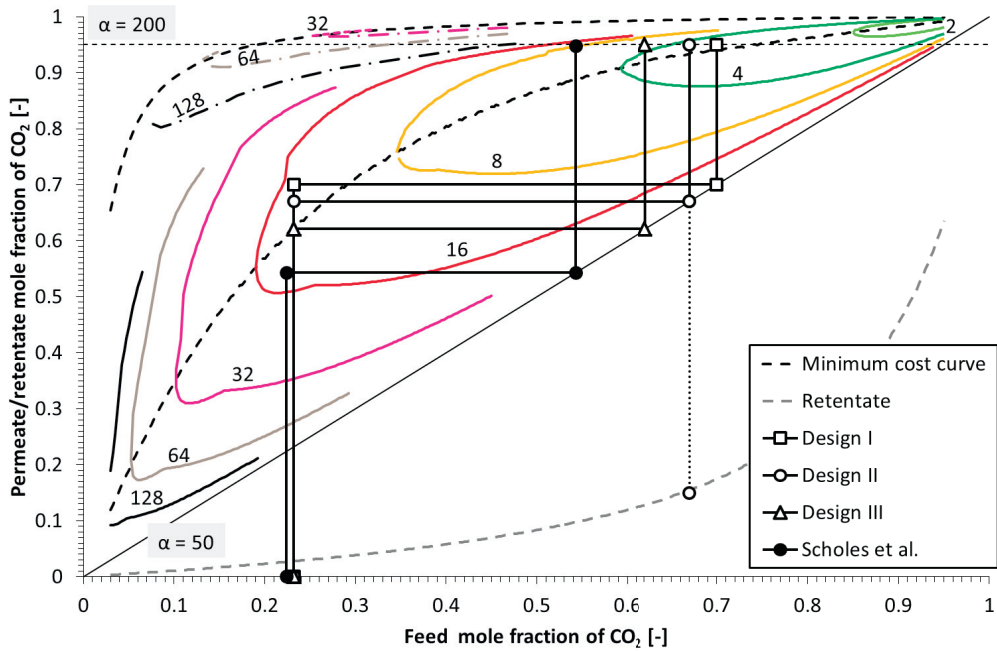


Figure 2: Attainable region diagram for membrane A (CCR: $\sqrt{0.85}$, $\alpha = 50$) and B (CCR: 0.85, $\alpha = 200$). Numbers in plot area indicate iso-curve for specific capture cost (€/t) without final compression to transport conditions. Total specific capture costs without compression: Design I – 18.6 €/t; Design II – 18.0 €/t; Design III – 18.6 €/t

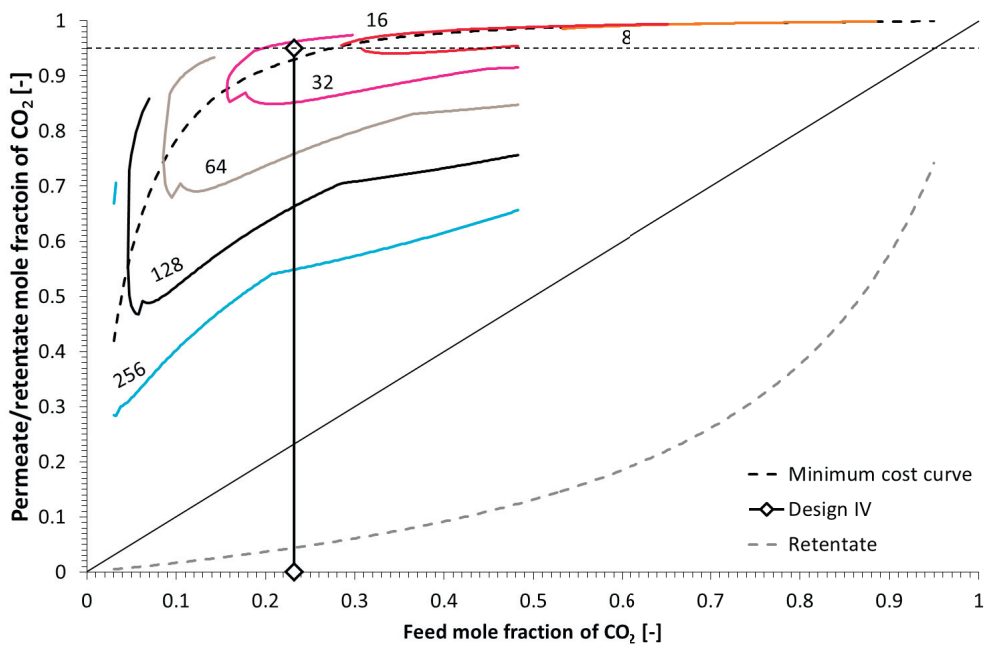


Figure 3: Attainable region diagram for membrane C (CCR: 0.85, $\alpha = 200$). Numbers in plot area indicate iso-curve for specific capture cost (€/t) without final compression to transport conditions. Total specific capture cost without compression: Design IV – 22.7 €/t

4.3. Economic comparison

A summary of the key results from the economic evaluation is given in Table 2. The membrane processes of the present work represent a major improvement in investment and operating costs over the base case MEA process, since they avoid building and operating a CHP plant. The CO₂ avoidance costs of the membrane systems are therefore also superior to the MEA case, despite the significant climate impact of the consumed electricity.

Figure 4 presents a breakdown of the Net Present Value (NPV) of the capture unit cost for the four cases. It is clear that the membrane systems are favorable compared to the MEA case not only due to the lower total NPV, but due to the much smaller investment cost compared to the operating cost.

Figure 5 compares the cost structure of the two different membrane process designs in the present work. Compressors and electricity dominate the cost, particularly for the facilitated transport membrane. It is clear that the Design II is preferable over Design IV for two reasons: Even if it were possible to fabricate membrane C at the same cost and with the same lifetime as membrane A, this combination of selectivity and permeance requires too much feed compression to be competitive with multi-stage systems. Increased permeance is not expected to change this, since the membrane area represents a small share of the total cost for this particular case. Moreover, designing for a slight overcapacity with membrane C is much more costly, since Design IV already operates at a point with a steep gradient in the cost function with respect to e.g. feed composition and target purity.

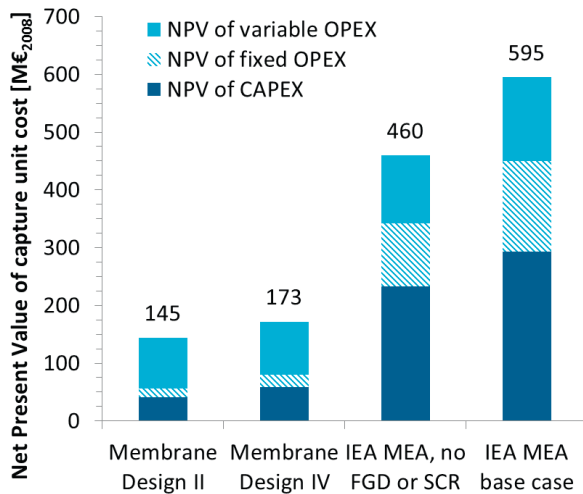


Figure 4: Comparison of cost types for the membrane processes and the reference MEA capture unit [8]

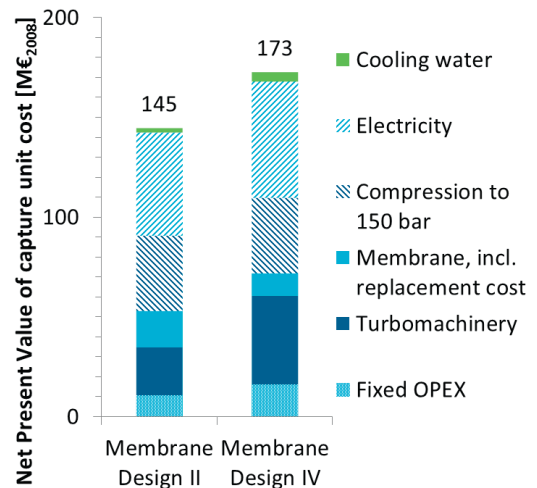


Figure 5: Breakdown of costs of the membrane processes

Table 2: Summary of key results

		Design II	Design IV	MEA without FGD/SCR	Base case MEA
Specific energy penalty	MJ/kg CO ₂ captured	0.91	0.98	-	-
Specific capture cost	€/t CO ₂ captured	24	29	45	58
Climate impact of electricity	Mt _{CO2} /year	0.056	0.097	-0.054 ^a	-0.054 ^a
Specific avoidance cost	€/t CO ₂ avoided	27	32	43	55
CAPEX	M€	33	50	234	294
OPEX	M€/yr	7.7	8.8	23	31

^a The electricity produced in the CHP plant has a lower climate impact than the average grid electricity

Conclusions

Two cost competitive membrane processes for CO₂ capture from a cement plant have been designed based a recently developed graphical methodology. The designs are shown to have a significantly lower CO₂ avoidance cost than the reference MEA based capture process, even when disregarding SO_x and NO_x removal units. Moreover, the investment cost for turbomachinery and the operating cost for electricity are shown to be, in this case, more important than the membrane investment- and replacement cost over the lifetime of the capture plant. The present work underlines the importance of using a cost-based approach to balance the trade-offs in membrane process design.

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