CATO-2 Deliverable WP 1.1F6-D03B

Report on thermodynamic modelling outcomes of the hybrid membrane-solvent system

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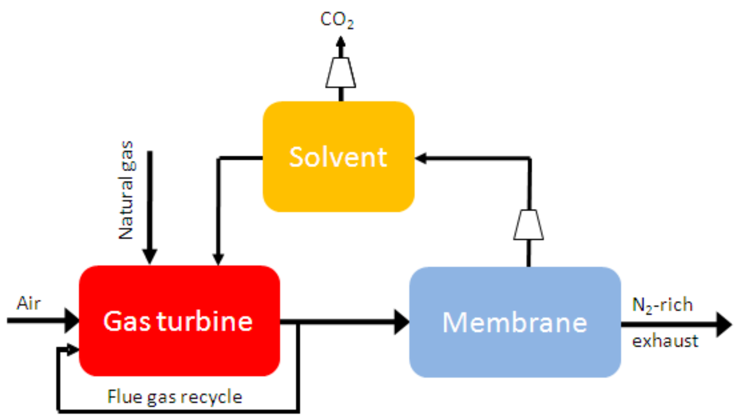
1. **Executive Summary**

Based on the previously established basic design and processes of post-combustion hybrid membrane-absorber carbon capture, membrane performance and system efficiency modelling have been carried out to chart the performance of such a system.



The following topics are treated:

- Approach to the modelling work;
- Case definition and selection including all input and output parameters
- Modelling outcomes of phase 1 (membrane modelling)
- Modelling outcomes of phase 2 (solvent system modelling) and combined overall results
- Analysis and conclusions

Nine membrane cases have been modelled of which four have been detailed out into values for the hybrid membrane-absorber system. Within the limits of the current accuracy, the model gives power consumptions for capturing CO_2 from gas-combusted flue gas for these cases in the range of 2.49 – 3.92 GJ_{th} per ton.

The modelling described in this report supports the validity of the hybrid CCS concept and is a basis on which to proceed with further conceptual and detailed system design, and later on experimental work.

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Document Change Record

(this section shows the historical versions, with a short description of the updates)

Version	Nr of pages	Short description of change	Pages

Table of Content

2. Applicable/Reference documents and Abbreviations

2.1 Applicable Documents

(Applicable Documents, including their version, are documents that are the "legal" basis to the work performed)

	Title	Doc nr	Version
~~AD-01a~~	~~Beschikking (Subsidieverlening CATO-2 programma verplichtingnummer 1-6843~~	~~ET/ED/9078040~~	~~2009.07.09~~
~~AD-01b~~	~~Wijzigingsaanvraag op subsidieverlening CATO-2 programma verplichtingennr. 1-6843~~	~~CCS/10066253~~	~~2010.05.11~~
~~AD-01c~~	~~Aanvraag uitstel CATO-2a verplichtingennr. 1-6843~~	~~ETM/10128722~~	~~2010.09.02~~
AD-01d	Toezegging CATO-2b	FES10036GXDU	2010.08.05
AD-01f	Besluit wijziging project CATO2b	FES1003AQ1FU	2010.09.21
AD-02a	Consortium Agreement	CATO-2-CA	2009.09.07
AD-02b	CATO-2 Consortium Agreement	CATO-2-CA	2010.09.09
~~AD-03a~~	~~Program Plan 2009~~	~~CATO2-WP0.A-D.03~~	~~2009.09.17~~
~~AD-03b~~	~~Program Plan 2010~~	~~CATO2-WP0.A-D.03~~	~~2010.09.30~~
~~AD-03c~~	~~Program Plan 2011~~	~~CATO2-WP0.A-D.03~~	~~2010.12.07~~
~~AD-03d~~	~~Program Plan 2012~~	~~CATO2-WP0.A-D.03~~	~~2011.12.12~~
AD-03e	Program Plan 2012b	CATO2-WP0.A-D.03	2012.06.08

2.2 Abbreviations

(this refers to abbreviations used in this document)

KPI	Key Performance Indicator

3. Introduction

In the previous deliverables of this work package on Hybrid Systems (WP1.1F6), the foundation was laid for the current performance quantification by modelling. Deliverable 1 explored the general concept of hybrid membrane-absorber CO_2 capture from gas-combusted flue gas, including the supporting flue gas recycling. Interfaces between the three key elements (gas turbine, membrane unit, solvent unit) were explored in terms of relevant parameter issues to be solved (e.g. temperature, pressure, connectivity issues, etc). Rough design constraints were extracted from this analysis.

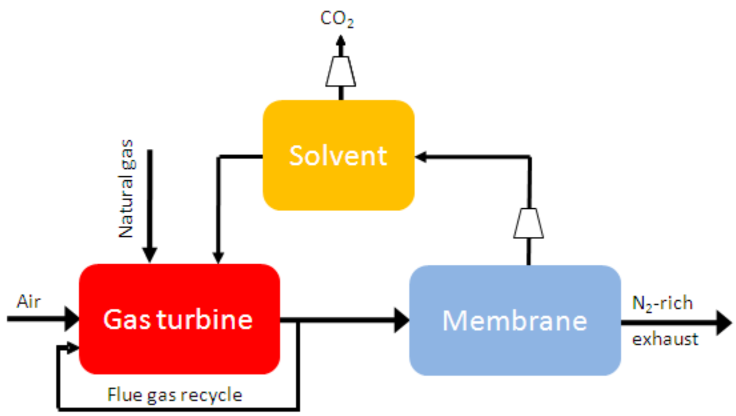

Figure 1. *The concept of hybrid membrane-absorber CO_2 capture from gas-combusted flue gas*

Deliverable 2 focused only on the solvent part of the system. Even though solvent-based CO_2 capture is a thoroughly characterised process for a vast set of conditions, the specific case for this concept is not standard in terms of e.g. pressure, RH and CO_2 content. Therefore, a solvent selection was carried out, yielding the most promising solvent for this process.

Proceeding from this point, a number of insightful and in-depth engineering sessions were spent detailing out the hybrid concept. Specific compression and vacuum concepts, heat integration, membrane area / recovery / purity optimisation and many more aspects were evaluated. It turned out to be exceedingly difficult to get to a detailed system design and good operating parameters, because of the many degrees of freedom involved in this concept consisting of three major tweakable system units. In other words, very many parameters or design choices all influence the system's technical and economical feasibility and KPI's, the latter primarily being CO_2 recovery and energy usage per ton of CO_2 captured.

It was ultimately agreed that performance modelling was the way forward. The idea was to investigate the influence of a number of parameters (e.g. vacuum pressure) and design choices (e.g. number of stages, water removal). The results would paint a clearer picture of where to go. Possibly an iterative process of modelling and design revision/refinement would follow.

The current document reports the first outcomes of the hybrid membrane-absorber CO_2 capture modelling, serving not so much as a definitive result, but rather a first intermediate one upon which to base further maturation of the concept.

4. **Approach**

General approach

The general approach to the modelling reported here on hybrid membrane-absorber CO_2 capture from gas-combusted flue gas can be described as follows, in order of execution:

1. Definition of cases. A preselection has to be made of which scenarios (parameter values, system layouts) will need to be calculated. A representative set of parameters was selected, correlating to a number of system design questions.
2. Membrane unit *separation* modelling. Hybrid systems being a novel concept, no comprehensive model exists covering incorporating all relevant aspects and outputting our KPIs of choice. Hence, a stand-alone newly-developed KEMA membrane performance model is used as a first step.
3. Membrane unit *energy usage* modelling. Although the aforementioned novel model is currently being integrated with KEMA's state-of-the-art power technology model SPENCE, this process is not finished yet. The models are complementary in outputting separation performance or energy usage, respectively. Therefore, the relevant calculated separation parameters were fed into SPENCE, from which the energy usage of the membrane unit was calculated.
4. Absorber unit *comprehensive* modelling. The results of the membrane unit modelling are used as input for the separate, unrelated model Pro2Sim (operated by Procede) that can, among other things, model absorber systems including separation performance and energy usage. Separation performance and energy usage of the absorber process can be simultaneously calculated. Combining this with the membrane unit modelling results, the overall performance of the hybrid system is determined as well.

All of these elements will be discussed in turn.

Case definitions

After much deliberation about which set of parameters would be an optimal starting point for performance calculation and most suitable for optimisation, the following was decided. Note that this is not a best-case scenario, but rather an average and currently realistic case. In other words, should calculations infer a positive feasibility for a scenario, then optimisation should bring further performance advances – but it will already be interesting and possible currently, without such further work. The planned practical tests of this concept are therefore more relevant too.

- Membrane: one commercial membrane module will be modelled. The CO_2 separation behaviour of the selected module lies under the current levels attained in various R&D projects, but is reasonable and adequate for our cases and experiment.
    - Material: asymmetric self-supported PPO
    - Module: commercial Parker
    - Selectivity: around 20
    - Permeance: 5,8 m^3 / (m^2 h bar).
    - Stages: for simplicity in most cases one stage is used. In two cases, a second stage with an identical membrane unit will use the first unit's permeate stream as CO_2-enriched feed stream (after pressure adjustment to atmospheric level)

- CO_2 recovery of the membrane subsystem: first, three different crude values for the overall membrane-solvent system were set, being 50%, 60% and 70%. Assuming the solvent system will have an 85% recovery, the membrane subsystem's recovery needs to be 60%, 70% and 80%, respectively.

- Driving force: the driving force generation concept selected is application of permeate vacuum. More options are available such as feed compression, a combination of feed compression and permeate suction, and using a sweep gas, but this was considered less practical. Some optimisation can be done in this area later, to optimise energy usage and/or membrane area used.

- Flue gas parameters: these parameters are based on a gas turbine with flue gas recycling applied, and a heat exchanger to reduce temperature to a safe working range for polymer membranes (see Deliverable 1: ' Report on basic design and process descriptions'). The values of the flue gas parameters are given below.

    - Feed flow 300 kg/s = 869,806 Nm^3/h
    - Feed pressure 1012 mbar
    - Feed temperature 55 °C
    - Feed composition
        - N_2 73% v/v
        - O_2 5% v/v
        - CO_2 7%
        - H_2O 15%

- Under the conditions above, the flue gas RH is 96.5%. It is possible that this has a negative effect on the compressors applied (in terms of durability and efficiency). Therefore, one case was included in which 40% of the feed water is removed with SPEEK water capture membrane technology, before regular CO_2 capture.

- Although the membrane area is an input parameter, it is not fixed. Rather, it is adjusted in such a way that overall recovery matches the target value set in the particular case.

Membrane modelling output parameters

Output parameters will be:
- Permeate flow
- Permeate composition
    - N_2 v/v
    - O_2 v/v
    - CO_2 v/v
    - H_2O v/v

The CO_2 recovery and purity are key output parameters, and can be calculated from the permeate composition, feed and permeate flow.

Absorber modelling input parameters

The values of the aforementioned conditions and output parameters will be used as input values for the absorber modelling in Pro2Sim. Additionally, the following parameters and key design choices are used:

- The vacuum pump is a diaphragm pump with the following specs:
    - efficiency 80%
    - compression factor of maximum 10
    - pressure increase 0.1 bar to 1 bar
- No water removal
- No intercooling (but: heat exchanger)
- Solvent: DEPG
- CO_2 recovery of this step: adjust other parameters to have this approximate 90%.

The system setup for the absorber step could be called 'worst case', as many parameters could most definitely be optimised. It was chosen not to do so at this stage, to simply get a crude impression of the validity of the overall hybrid concept. If feasible, more detailed investigation is warranted.

Absorber modelling output parameters

Again, CO_2 recovery and purity will be key output parameters. The overall CO_2 recovery over the entire hybrid process is obviously calculated as the product of the two components' individual recovery.

Case overview

In table 1 below, the 9 cases defined are represented, with their distinguishing parameters.

***Table 1**. Case overview.*

Case	CO_2 recovery	Vacuum pressure	Stages
1	60%	100 mbar	1
2	70%	100 mbar	1
3	80%	100 mbar	1
4	60%	150 mbar	1
5	70%	150 mbar	1
6	80%	150 mbar	1
7	60%	100 mbar	2
8	70%	100 mbar	2
10**	70%	100 mbar	1*

** 1 CO_2 capture stage, after 1 water capture stage*
*** Case 9 does not exist as a CO_2 capture case*

5. **Membrane performance modelling**

Membrane separation performance model

Description

For this CATO2 work, a membrane separation performance model was developed. This model follows the dedicated membrane separation theory outlined by Melin[1]. Gas permeation mathematically is governed by differential equations with (except in particular cases such as simple binary gas mixtures) have no analytical solution. However, the formulas below can provide a solution by iteration. For a membrane and certain set of local conditions, the concentration of one component is 'guessed' and adjusted until a solution is found, after which a second formula yields all other components.

$$1 - \sum_{i=1}^{n} \frac{x_i * y_1 * \frac{Q_i}{Q_1}}{x_1 - y_1 * \frac{P_p}{P_F} * (1 - \frac{Q_i}{Q_1})} = 0 \qquad y_i = \frac{x_i * y_1 * \frac{Q_i}{Q_1}}{x_1 - y_1 * \frac{P_p}{P_F} * (1 - \frac{Q_i}{Q_1})}$$

Figure 2*. Membrane separation performance key formulas. The leftmost formula can be used to iteratively calculate the concentration of a single component y_1, after which the second formula yields the concentrations of the other components y_i.*

A more detailed mathematical – physical description of the model's inner workings would be beside the point of this report. What is interesting perhaps is to note that the iteration process is performed for a sufficiently large number of sufficiently small (limiting towards an infinite number of infinitesimal) slices of the membrane area, as the feed and permeate stream change after every slice.

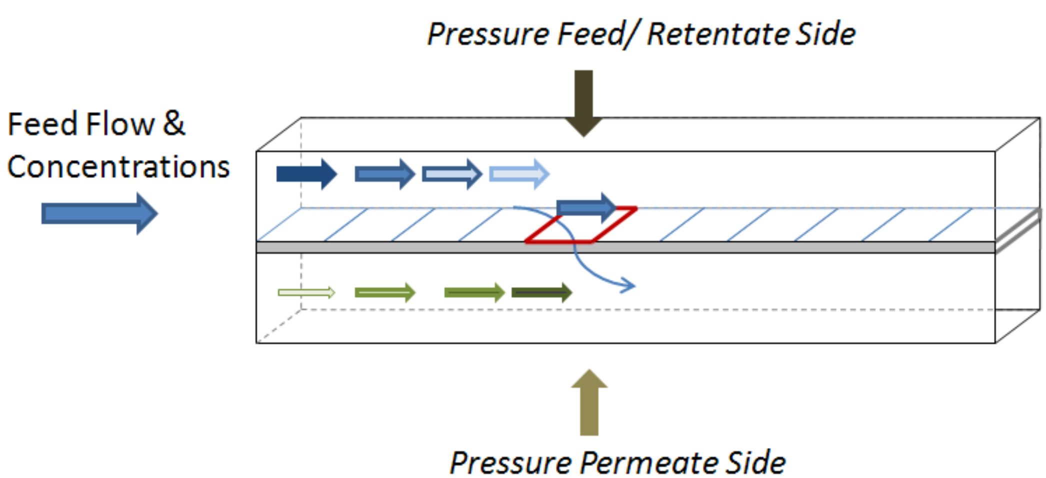

Figure 3*. Schematic representation of the working mechanism of the membrane separation performance model. The horizontal segmented plane in the middle represents the membrane. For each slice, based on the local concentration of components in the gas stream on both sides, sequentially new concentrations and permeation are calculated.*

[1] *Thomas Melin, Robert Rautenbach "Membranverfahren", **2007**, chapter 14.*

SPENCE model

Description

KEMA has developed a software package called SPENCE® for simulation of processes for energy conversion and electricity production. SPENCE® is intended to support thermodynamic and chemical engineers employed within electricity companies or industry.
SPENCE® supports are used in:

- system and feasibility studies
- basic design
- design reviews
- process optimization
- upgrading and re-powering
- exergy analyses
- technical and functional specifications
- development of on-line conditioning monitoring modules.

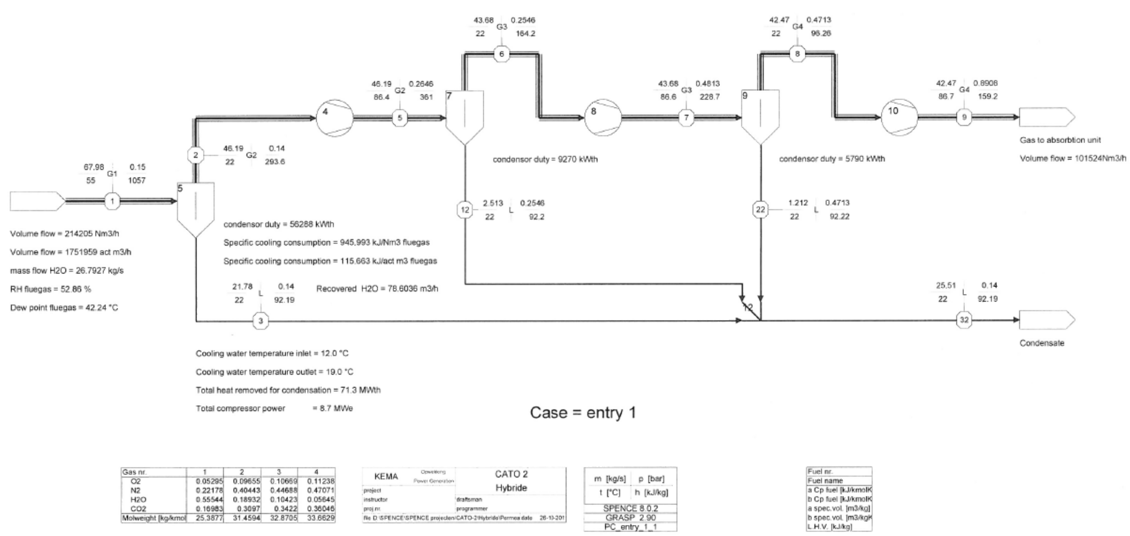

Figure 4. *Example SPENCE scheme, showing the scheme for one set of conditions (case 1, 150 mbar vacuum pressure).*

SPENCE® is a static flow sheet simulator based on thermodynamics to determine the technical data and merits of energy conversion systems, including:

- efficiency
- environmental impact
- cost/benefits

The membrane performance separation data have been fed into a SPENCE process scheme containing adequate vacuum generation systems and any other elements necessary (e.g. intercooling).

Results

Table 2 below summarises the membrane separation performance results for the cases described. For clarity, the following should be pointed out:

- For the two-stage calculations in case 7 and 8, case 3 was taken as the first stage. The feed flow and feed composition was adjusted accordingly.
- Case 9 is no CO_2 capture case, but a calculation of water capture, as pretreatment for case 10 (feed flow and composition adjusted accordingly).

Table 2. *Membrane performance modelling results.*

Case	Input				Output			Permeate					checked
	Stage	Area	Pperm	Sel CO_2/N_2	Rec. Stage	Rec. Overall	Purity	Flow	CO_2	N_2	O_2	H_2O	checked
	-	m^2	mbar	-	%		% (dry)	Nm^3/h	%	%	%	%	
1	1	191,500	100	19.3	60%	**60%**	**38%**	214,205	17.0%	22.2%	5.3%	55.6%	OK
2	1	260,000	100	19.3	70%	**70%**	**35%**	245,407	17.3%	26.6%	6.0%	50.2%	OK
3	1	354,000	100	19.3	80%	**80%**	**31%**	282,985	17.1%	31.7%	6.7%	44.5%	OK
4	1	245,000	150	19.3	60%	**60%**	**34%**	216,033	16.8%	26.9%	5.9%	50.3%	OK
5	1	338,000	150	19.3	70%	**70%**	**30%**	256,132	16.6%	31.6%	6.5%	45.3%	OK
6	1	470,000	150	19.3	80%	**80%**	**26%**	305,706	15.9%	37.2%	7.0%	39.9%	OK
7	2	44,100	100	19.3	75%	**60%**	**71%**	78,772	46.2%	11.0%	8.0%	34.8%	OK
8	2	66,000	100	19.3	87%	**70%**	**65%**	92,773	45.7%	14.8%	9.7%	29.8%	OK
					Rec CO2Ret	Rec H2OPerm	Pur CO2Ret						
9	0	10,000	100		99,9%	40,1%	7,4%	52,445	0.2%	0.0%	0.0%	99.8%	OK
10	1	271,000	100	19.3	70%	**70%**	**34%**	198,390	21.4%	34.5%	7.6%	36.4%	OK

Table 3. *Overview of cooling water capacity and compressor energy usage.*

Case*	Stages	Permeate pressure *mbar*	Area m^2	Recovery %	Purity %	Flow Nm^3/h	Cooling water capacity MW_{th}	Compressor energy usage MW_e
1	1	100	191,500	60%	17.0%	214,205	**73.2**	**11.2**
2	1	100	260,000	70%	17.3%	245,407	**77.1**	**14.4**
3	1	100	354,000	80%	17.1%	282,985	**80.8**	**18.5**
4	1	150	245,000	60%	16.8%	216,033	**66.4**	**9.7**
5	1	150	338,000	70%	16.6%	256,132	**71.9**	**12.6**
6	1	150	470,000	80%	15.9%	305,706	**77.2**	**16.6**
7	2	100	44,100	60%	46.2%	78,772	**18.7**	**6.0**
8	2	100	66,000	70%	45.7%	92,773	**19.7**	**7.6**

** For clarity and comparison, some values from table 2 were included. As noted before, case 9 was membrane-based water removal as pretreatment and is not included in this table. Case 10 was erroneously left out and will be included in the next round of modelling if required.*

Apart from obvious conclusions, such as deeper vacuum requiring more energy and higher recovery requiring a larger membrane area (other things being equal), no more analysis of these intermediate results is presented here. What matters are the results over the entire hybrid system.

6. **Solvent and system performance modelling**

Pro2Sim model

Description

An advanced modelling tool called Pro2Sim (using advanced thermodynamics in a rigorous numerical model) was developed by Procede to support the research for (new) advanced absorption processes such as under study here. Pro2Sim supports both ideal and non-deal thermodynamics (thermodynamic model ElecEOS) and both equilibrium based and rate-based column models. The simulator will support many unit operations (absorbers, strippers, flash drums, heat exchangers, pumps, compressors, etc.).

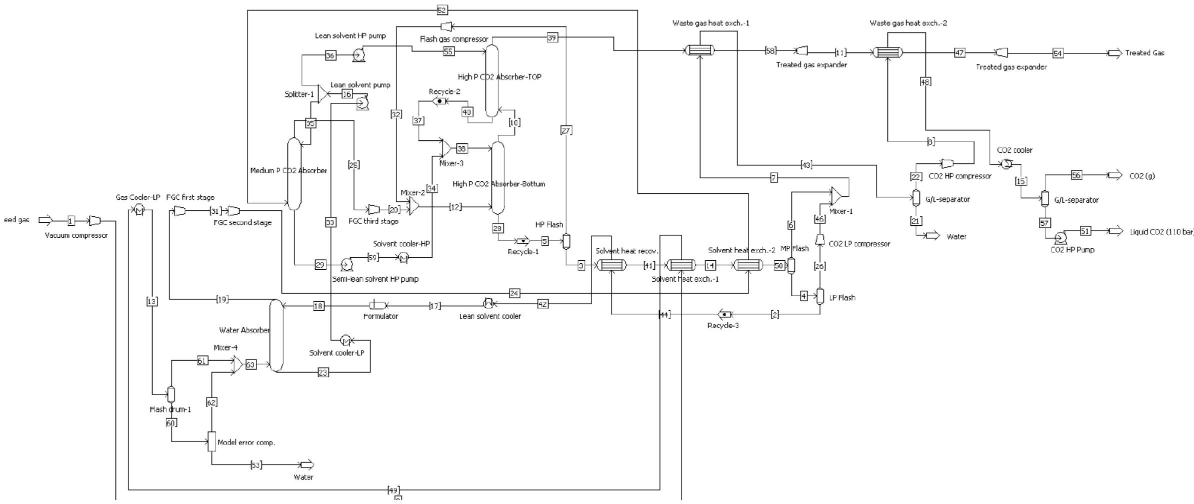

Figure 5. *Pro2Sim process scheme for this work.*

Results

Table 4. *Pro2Sim simulation outcomes for overall hybrid system.*

Process element	Duty (MWe)						
	Case 1 Procede	Case 1 KEMA	Case 4 Procede	Case 4 KEMA	Case 8 Procede	Case 8 KEMA	Case 10
CO_2 HP pump	0.062	0.062	0.0593	0.059	0.118	0.118	0.069
Lean solvent HP pump	0.268	0.268	0.267	0.267	0.276	0.276	0.321
Lean solvent pump	0.375	0.375	0.374	0.374	0.386	0.386	0.448
Semi-lean solvent HP pump	0.682	0.682	0.666	0.666	0.797	0.797	0.797
CO_2 HP compressor	2.655	2.655	2.323	2.323	3.455	3.455	2.721
CO_2 LP compressor	0.149	0.149	0.162	0.162	0.25	0.25	0.184
FGC first stage	3.012	3.012	3.436	3.436	2.06	2.06	4.027
FGC second stage	4.523	4.523	5.18	5.18	3.022	3.022	6.073
FGC third stage	3.099	3.099	3.639	3.639	1.657	1.657	4.26
Flash gas compressor	0.171	0.171	0.171	0.171	0.228	0.228	0.195
Vacuum compressor	23.31	*11.2*	18.392	*12.6*	9.952	*7.6*	21.68
Second stage vac. compr.	N/A	N/A	N/A	N/A	*18.5*	*18.5*	N/A
Treated gas expander 1^{st}	-2.597	-2.597	-2.583	-2.583	-0.76	-0.76	-3.253
Treated gas expander 2^{nd}	-2.464	-2.464	-2.708	-2.708	-1.139	-1.139	-3.253
Total	**33.245**	**21.135**	**29.378**	**23.586**	**38.802**	**36.45**	**34.269**
Product flow (ton/h)	52.64	52.64	50.46	50.46	66.98	66.98	58.92
CO_2 capture % absorber	89.64	89.64	86.55	86.55	97.94	97.94	86.03
Power consumption* (GJ_{th}/ton)	**3.92**	**2.49**	**3.61**	**2.90**	**3.60**	**3.38**	**3.61**

** in primary heat equivalent at 58% plant efficiency.*

Analysis and discussion of these results can be found in the next chapter. The following remarks should be kept in mind before proceeding:

- At this point, Procede opted to only model what was considered the most promising cases. The conclusions drawn so far, already dependent on the specific 10 cases selected and the design of the system as implemented in the two models, was made in a somewhat subjective way.
- As it turns out, Procede not including intercooling in their compression step, makes a very large difference. The result column labelled “KEMA” contains the Procede calculation with the vacuum compression element replaced by a SPENCE simulated vacuum compression element, triple intercooled from 102 °C maximum to 22 °C. The intercooled calculated energy usage values are more realistic and fortunately also lower.
- Note that, incorrectly, the input flow was assumed to be in actual cubic meters, while normal cubic meters should have been used instead. This does not cause a large discrepancy here.

7. Conclusions and outlook

Conclusions

First and foremost, it can be concluded that the compression step is the most energy-intensive step of the hybrid process; depending on case and calculation method, between 53% and 70% of process energy is used in this step. The membrane part of the hybrid process is therefore the bottleneck in terms of energy usage, at least with current parameters (including membrane performance). Optimisation of the membrane step, particularly of the compression step, could yield the most benefits energetically.

Intercooling is an excellent example of such an optimisation. Comparing Procede modelling (currently without intercooling in the compression step) with KEMA modelling (with intercooling, numbers in italics in Table 4) immediately and clearly demonstrates the point, up to halving the compression energy.

Unfortunately, at this stage nothing can be said about the effects of recovery, vacuum pressure or the number of membrane stages – the main parameters varied – on the results. Main reasons for not being able to are the limited number of cases that have been fully modeled at this point (membrane plus absorber system), and the currently unoptimised nature of the absorber modeling. Also, nothing can be concluded yet on effect of water removal.

Last but not least, the results presented may not be definitive in terms of number and optimisation level, yet at this stage they show the concept of hybrid membrane-absorber CO_2 capture is promising. Based on the current work, the power consumption per ton of CO_2 captured is competitive; below 3 GJ/ton is already possible, even at low CO_2 concentration and with little-optimised membrane and absorber systems. Further refining, improvement, and broadening of modelling work as carried out here might very well lead to even better results.

Outlook

A number of steps forward can be identified from the results and conclusions above. The obvious first conclusion is that more cases are to be modeled. Although a good and encouraging start, more information is needed to support the concept, as well as to prepare and support upcoming practical experimentation. Some existing cases have not been fully modeled yet (e.g. 2, 3, 5, 6, 7, 10). Additionally, a significantly larger number of cases should be modeled at all, enabling a clearer and more comprehensive look at the influence of various parameters (especially pressures, purity, recovery, and number of stages). A particular point of interest would also be to model a membrane with a higher (yet realistic) performance.

The modelling for the absorber part should be refined with at least intercooling for the compression step, as substantial savings are expected based on theory and comparison calculations. Adding intercooling will have some indirect effects though, as through heat integration temperature changes will be induced elsewhere in the system, but this will be relatively minor and easily handled. A practical issue of (inter-)cooling can be the formation of acidic condensates, harmful to system components, which needs to be looked into. Perhaps this is another incentive for (more) water removal, e.g. by membranes, as in case 9 / 10.