Projet DRIVER du Fonds de Transition Energétique octroyé dans le cadre de l'appel de Novembre 2020

Délivrable 3 (D3) :

Rapport technique sur les simulations séparées et intégrées des étapes de la chaîne CCU (capture, purification, transport et conversion du CO_2)

Délivrable produit par : Université de Mons

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D3: Rapport technique sur les simulations séparées et intégrées des étapes de la chaîne CCU (capture, purification, transport et conversion du CO2)

Note : en accord avec les représentants du SPF Economie, il a été convenu lors de la kick off meeting du projet DRIVER qui s'est tenue le 25 Octobre 2021, que les délivrables du projet peuvent être rédigés soit en français soit en anglais moyennant un résumé en français. Le présent document comprend donc cette section introductive en français, qui résume le contenu du rapport technique qui correspond quant à lui à une synthèse des résultats valorisés à travers différentes communications scientifiques qui ont été réalisées dans le cadre du projet DRIVER.

1. Rappel des objectifs du projet DRIVER

Le projet DRIVER (**D**éveloppement d'un modèle de ma**R**ché, **I**nfrastructurel et régulatoire, du CO_2 comme **V**ecteur pour le stockage d'**E**nergie **R**enouvelable) vise le développement de modèles de chaînes de valeur incluant le CO_2 en vue de la production de fuels synthétiques défossilisés permettant de réduire la dépendance aux combustibles fossiles et à terme tendant vers une indépendance énergétique. Le projet intègre les volets économiques, infrastructurels et régulatoires, et prend en compte les spécificités belges tant au niveau énergétique que des infrastructures. Les modèles développés permettront *in fine* la définition d'une roadmap technique donnant les orientations à suivre pour le développement du « marché CO_2 belge », dont différents indicateurs (énergétiques, économiques, environnementaux, …) pourront servir de base en vue du développement ultérieur d'une plateforme digitale.

Le CO_2 étant au centre du projet DRIVER, une attention particulière se porte sur la chaîne de capture, purification et transport de CO_2, ce dernier pouvant ensuite servir à la production d'autres vecteurs énergétiques tel que par exemple le gaz naturel synthétique (SNG) ou encore le méthanol. Une telle chaîne de procédés est couramment appelée « CCU » (Carbon Capture & Utilisation). Le CO_2 est donc l'un des éléments d'un réseau énergétique global aux côtés des dispositifs de stockage d'énergie renouvelable, de la production et du transport d'hydrogène et de tous les éléments nécessaires pour fabriquer, à partir de ce CO_2, des e-fuels et les transporter.

Les différents Work Packages (WP) du Projet DRIVER sont illustrés à la Figure 1.

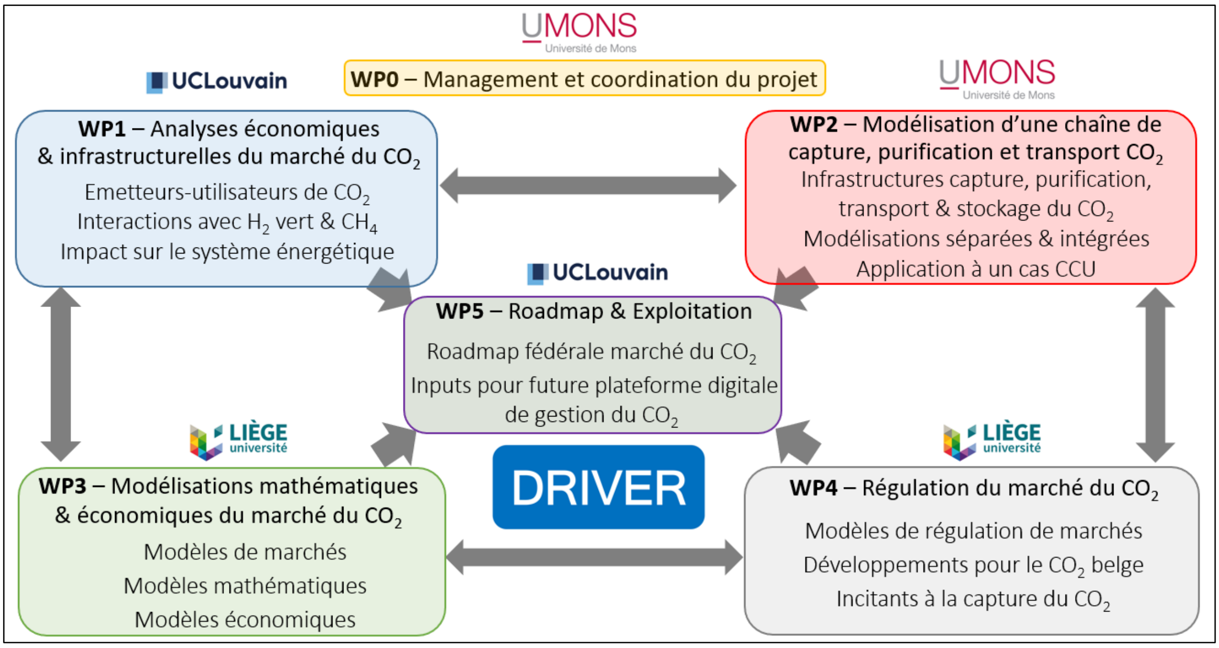

Figure 1 : Work Packages du Projet DRIVER

D'un budget total de 1 121 659 €, le projet DRIVER, a démarré au 1^er^ Octobre 2021 pour une durée de 4 ans.

Le consortium est composé de 3 universités belges qui mutualisent leurs expertises, à savoir l'Université de Mons (UMONS), l'Université de Liège (ULiège) et l'Université Catholique de Louvain (UCLouvain).

2. Résumé du rapport technique D3

Le présent rapport reprend une synthèse des communications scientifiques réalisées jusqu'à présent par l'UMONS dans le cadre du projet DRIVER concernant des simulations, séparées et combinées, d'étapes de capture, purification, liquéfaction et conversion du CO_2.

Les résultats de ces simulations ont permis de générer un certain nombre d'indicateurs techniques, économiques et environnementaux relatifs aux composantes des chaînes de valeur CCU.

Comme déjà indiqué dans le livrable D1, différentes voies de capture du CO_2 existent, à savoir la pré-combustion, l'oxy-combustion et la **post-combustion**, cette dernière (**la plus développée** actuellement) présentant l'avantage de ne pas nécessiter une modification des procédés en amont (technologie dite « end-of-pipe »). Au niveau des **technologies de capture du CO_2**, **quatre opérations unitaires** sont identifiées : procédés par absorption gaz-liquide, procédés par adsorption gaz-solide, l'utilisation de membranes séparatives (gaz-gaz) et enfin les procédés cryogéniques. La technologie par **absorption gaz-liquide**, et en particulier utilisant les **solvants aminés**, est **la plus mature** actuellement (TRL[1] de 9) et la plus disponible parmi les fournisseurs de technologie (dont plusieurs sont communiqués dans le rapport D1), bien que les autres technologies disposent d'un potentiel intéressant à moyen ou long terme, en particulier en termes de réduction des coûts et d'impacts environnementaux.
Dans tous les cas, que cela soit pour la capture, la purification ou la **liquéfaction du CO_2**, le développement de **systèmes cryogéniques** semble nécessaire.

Pour ce qui est du **transport du CO_2**, la pureté du CO_2 et l'impact éventuel des impuretés sur ses propriétés physico-chimiques sont des paramètres importants. Pour le transport continental, le CO_2 peut être transporté par **pipeline** (cf. les développements de Fluxys en la matière), par **barges fluviales**, en **train**s ou en **camions**, le transport off-shore se limitant bien évidemment aux canalisations et aux bateaux.

Concernant l'**utilisation du CO_2**, le marché mondial représentait déjà en 2018 plus de **230 Mt_{CO2} annuellement** dont **16% au niveau de l'Europe**. Près de **60% du CO_2 mondial** est actuellement utilisé dans la production d'**urée**, **34%** pour la **récupération assistée de pétrole** (EOR) et enfin tout ce qui concerne l'alimentaire et les **boissons gazeuses** (principales utilisations en Europe), ainsi que d'autres industries. Conjointement avec le développement de la filière hydrogène vert, d'**autres marchés** viendront à se développer dans le futur, tels que par exemple le **gaz naturel de synthèse (SNG)** et le **méthanol**, (qui ont fait l'objet d'études spécifiques), d'autres produits étant également envisagés tels que l'éthanol, l'e-kérozène, ainsi que des produits à plus hautes valeurs ajoutées mais dont les marchés sont sensiblement plus réduits comme ceux des polycarbonates, de l'acide formique, du polyuréthane, etc.

Enfin, mentionnons la **capture du CO_2 directe dans l'air ambiant (Direct Air Capture – DAC)**, qui pourrait avoir un rôle à jouer dans la décarbonation mondiale pourvu que tous les efforts soient réalisés en amont afin de réduire au maximum les émissions de CO_2 à la source.

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[1] TRL : échelle TRL (en anglais *Technology Readiness Level*) est un système de mesure employé pour évaluer le niveau de maturité d'une technologie. De 1 (plus bas niveau de maturité technologique) à 9 (application réelle de la technologie sous sa forme finale et en conditions réelles).

2.1. Résumé des principaux enseignements des simulations de capture de CO_2 par le procédé d'absorption-régénération

Plusieurs secteurs industriels, tels que par exemple les cimentiers et les producteurs de chaux, produisent des émissions de CO_2 dites « inévitables » car intrinsèquement liées au procédé industriel lui-même (décarbonatation du carbonate de calcium). Afin de réduire ces émissions, il est nécessaire d'implémenter une chaîne de Capture, Utilisation et/ou Stockage du CO_2 (CCUS), dont l'étape de capture, bien que déjà mature technologiquement (pour le procédé par absorption-régénération avec solvants aminés), entraine une **consommation énergétique fort importante**. Trois voies pour réduire cette consommation ont été investiguées à travers 4 communications scientifiques (expérimentalement et/ou via le développement de simulations Aspen Plus®), à savoir : (i) en amont du procédé via l'augmentation de la teneur en CO_2 des fumées à traiter (par oxy-combustion partielle et/ou recirculation des fumées), (ii) au sein du procédé (en utilisant des mélanges de solvants plus performants et innovants comme les **solvants démixants**), et (iii) au niveau configurationnel par implémentation de **configurations avancées du procédé de capture**. Il en est ressorti que l'utilisation d'un procédé démixant comme le mélange composé de diéthyléthanolamine (DEEA) et de méthyl-amino-propylamine (MAPA), ou l'implémentation d'une configuration avancée de procédé (Inter-Cooling Absorber + Rich Vapor Compression + Rich Solvent Splitting and Preheating, avec méthyldiéthanolamine (MDEA) + pipérazine (PZ) comme solvant) sont les voies permettant de réduire le plus fortement la consommation énergétique du procédé d'absorption-régénération, à savoir **de plus de 40% par rapport à un procédé classique utilisant la monoéthanolamine (MEA)**. De plus, d'un point de vue économique, et par rapport à une configuration de base avec la MEA, la technologie démixante présente l'avantage de pouvoir atteindre de telles performances énergétiques moyennant un investissement (CAPEX) plus limité (+1.6%) qu'avec des configurations de procédés plus avancées (+8.8%).

Les recherches concernant l'utilisation de solvants démixants afin de réduire la consommation énergétique du procédé de capture par absorption-régénération sont toujours en cours, en particulier pour trouver des alternatives au mélange DEEA+MAPA, encore plus économique et avec un risque moindre de dégradation.

Communications scientifiques réalisées sur ce sujet :

Costa A., Mouhoubi S., Dubois L., De Weireld G., Thomas D., « Kinetics in DEEA-MAPA-H2O-CO_2 Systems for the Post-combustion CO_2 Capture by Absorption-Regeneration Using Demixing Solvents », DA 2022 – 12th International conference on Distillation-Absorption Proceedings, 2022.

Dubois L., Costa A., Mouhoubi S., De Weireld G., Thomas D., « Post-combustion CO_2 capture process by absorption-regeneration applied to cement plant flue gases: techno-economic comparison between the use of a demixing solvent technology and an advanced process configuration », GHGT-16 Conference Proceedings, available on ssrn.com, 4271986, 2022.

Dubois L., Costa A., De Weireld G., Thomas D., « Study of pathways to reduce the energy consumption of the CO_2 capture process by absorption-regeneration », SFGP 2022 conference proceedings, MATEC Web of Conferences 379, 04002, 2023.

Dubois L., Costa A., Mouhoubi S., De Weireld G., Thomas D., « Techno-economic comparison of different configurations, including demixing solvent, for the absorption-regeneration process applied to cement plant flue gases », PCCC-7 (7th Conference on Post-Combustion Carbon Capture) Extended abstract, Pittsburgh (USA), 2023.

2.2. Résumé des principaux enseignements des simulations de capture-purification de CO_2 par voies cryogénique et hybrides membrane/adsorption-cryogénique

Les chaînes process CCUS font l'objet d'un intérêt croissant, et leur mise en œuvre massive à l'échelle industrielle est l'un des principaux moyens afin de réduire les émissions de CO_2. Dans ce contexte, l'**optimisation d'un processus de purification du CO_2 (CPU)** pour les gaz de combustion de cimenteries par **oxy-combustion** a tout d'abord été investigué. Cette optimisation est basée sur une étude multidimensionnelle des impacts énergétiques, exergétiques, économiques et environnementaux (analyse 4^E) du procédé. Les résultats des optimisations réalisées ont montré qu'il est **plus favorable d'augmenter le taux de récupération du CO_2 au-delà de 90%**, d'un point de vue énergétique, exergétique et économique. En outre, l'unité de purification du carbone avec membrane pour récupérer le CO_2, comparée à d'autres procédés cryogéniques développés dans la littérature, permet une réduction significative de la consommation d'électricité. L'analyse de l'évolution du coût de capture en fonction de la récupération du CO_2 montre que pour une taxe carbone donnée, il existe un minimum pour le coût total qui comprend la somme des contributions à la taxe carbone pour le CO_2 non capté et le coût de capture. Comme l'unité n'utilise que de l'énergie électrique, le coût et la production d'électricité auront un impact direct sur le coût de capture ainsi que sur le bilan global en termes de CO_2 évité. Lorsque le prix de l'électricité passe de 50 à 250 €/MWh, le coût de capture du CO_2 augmente de près de 250 %. Une analyse des incertitudes sur les paramètres permet d'observer leur impact sur les résultats, de définir un écart type par rapport aux points optimisés et de montrer la robustesse de ces derniers. En considérant les incertitudes paramétriques techniques, l'écart-type sur la consommation électrique (3,65 kWh/t_{CO2}), la récupération du CO_2 (0,09%) et l'efficacité exergétique (0,92%) est limité.

Dans une seconde étude, une **unité hybride combinant une unité d'adsorption modulée en pression sous vide (VPSA) et une unité de purification du carbone cryogénique (CPU)** a été évaluée pour améliorer la récupération et la pureté du CO_2 capturé dans les gaz de combustion contenant une concentration de CO_2 allant de 5% à 20%. L'unité VPSA préconcentre le CO_2 et la CPU complète la séparation et purifie le CO_2. L'étude a utilisé des modèles de substitution (« surrogate models ») pour l'optimisation multi-objectifs, en tenant compte de la consommation d'énergie, du coût et de la récupération du CO_2, ce qui constitue une approche efficace pour l'étude des processus exigeants en termes de calcul. Les résultats de l'étude indiquent que **le système hybride permet une récupération de plus de 90 %** du CO_2 pour la gamme de concentrations de gaz de combustion considérée, tout en assurant la **production d'un CO_2 de haute pureté (>99.99%)** adapté au transport. Les analyses réalisées révèlent l'équilibre entre la récupération, la consommation d'électricité et la viabilité économique. Une analyse de sensibilité a permis d'identifier les paramètres influençant la récupération et la consommation d'énergie, fournissant des orientations pour les efforts d'optimisation futurs. L'analyse technico-économique met en évidence l'**impact des prix de l'électricité et des taxes carbone sur les coûts totaux,** identifiant un optimum vers des valeurs de récupération plus élevées en cas d'augmentation des taxes carbone. En outre, la recherche met en évidence la faisabilité économique en fonction de la concentration, en soulignant l'attrait des concentrations supérieures à 10% par rapport à d'autres technologies, qui nécessitent des concentrations plus élevées. Pour un prix de l'électricité de 75 €/MWh, le coût total du système hybride de capture du CO_2, en tenant compte des émissions de CO_2 avec une taxe sur le carbone de 100 €/t_{CO2}, pour des concentrations allant de 10% à 20%, est de 123 à 80 €/t_{CO2} respectivement.

De manière générale, pour de telles technologies utilisant massivement de l'électricité, les analyses réalisées permettent de montrer l'**importance de disposer d'un mix électrique le plus bas carbone possible** de façon à maximiser la réduction nette des émissions de CO_2.

Communications scientifiques réalisées sur ce sujet :

Costa A., Coppitters D., Dubois L., Contino F., Thomas D., De Weireld G., « Energy, exergy, economic and environmental (4E) analysis of a cryogenic carbon purification unit with membrane for oxyfuel cement plant flue gas », Applied Energy, 357, 122431, 2024 (en collaboration avec l'UCLouvain).

Costa A., Henrotin A., Heymans N., Dubois L., Thomas D., De Weireld G., « Multi-objective optimization of a hybrid carbon capture plant combining a Vacuum Pressure Swing Adsorption (VPSA) process with a Carbon Purification Unit (CPU) », Chemical Engineering Journal, 152345, 2024.

2.3. Résumé des principaux enseignements des simulations de capture-conversion du CO_2

Une fois capture, le CO_2 peut être utilisé comme matière première pour produire des produits chimiques à valeur ajoutée. Le CCU a un rôle stratégique à jouer dans la décarbonisation des ressources énergétiques et la transition vers une économie climatiquement neutre. L'**e-méthanol**, le **gaz naturel synthétique (SNG)** et l'e-kérosène constituent des voies prometteuses pour convertir le CO_2 capturé. Dans ce contexte, l'objectif de l'étude réalisée a été de proposer un **procédé optimisé et intégré de conversion du CO_2** en méthanol et de le comparer au procédé de conversion du CO_2 en SNG d'un point de vue énergétique, économique et environnemental. Une configuration optimisée du réacteur dans l'unité de conversion du CO_2 en méthanol a été mise en œuvre avec succès dans le logiciel Aspen Plus® et conduit à une autosuffisance en énergie thermique de cette unité. Une **intégration thermique** avec une unité de capture avancée (cf. configuration avancée, non-démixante, telle qu'évoquée au point 2.1) a été réalisée. Il a été montré que dans le cas du méthanol, 5% des besoins en chaleur pouvant être fournis par l'unité de conversion tandis que 95% doivent être fournis via une source de vapeur externe. Notons que dans le cas du SNG, l'entièreté de la chaleur nécessaire pourrait être fournie via une telle intégration thermique du fait de la plus grande exothermicité de la réaction de conversion. L'évaluation technico-économique du processus optimisé a montré que le **méthanol est plus rentable lorsqu'il est utilisé comme matière première** pour synthétiser d'autres produits chimiques. En tant que **vecteur énergétique, le SNG reste le vecteur le plus intéressant**. Au niveau environnemental, par rapport au scénario de référence (pas de capture du CO_2, produits fournis par voie fossile comme actuellement majoritaire), une **réduction nette des émissions de CO_2 de 70% dans le cas de la conversion du CO_2 en SNG et de 60% dans le cas de sa conversion en méthanol** a pu être mise en évidence. En ce qui concerne l'impact sur l'épuisement des ressources fossiles, une réduction de plus de 60% a été observée dans les deux cas (environ 75 % pour la conversion du CO_2 en SNG et 61% pour la conversion du CO_2 en méthanol).

Globalement, l'étude a permis de montrer que d'une part **réfléchir en termes d'intégration énergétique entre des unités de capture et de conversion du CO_2 fait sens**, tant d'un point de vue énergétique, économique et environnemental, et d'autre part que l'un des éléments clés pour l'implémentation de telle chaine de valeurs reste l'**importance de disposer de grande quantité d'hydrogène vert** (d'où, de nouveau, l'importance d'un mix électrique le plus pas carbone possible) et à un prix le plus compétitif possible (lié au prix de l'électricité utilisée pour cette production).

Communication scientifique réalisée sur ce sujet :

Djettene R., Dubois L., Duprez M-E., De Weireld G., Thomas D., « Integrated CO_2 capture and conversion into methanol units: Assessing techno-economic and environmental aspects compared to CO_2 into SNG alternative », Journal of CO_2 Utilization, 85, 102879, 2024.

2.4. Résumé des principaux enseignements liés spécifiquement à la capture du CO_2 dans l'air ambiant (DAC)

Comme indiqué dans le rapport D1, la technologie de capture directe du CO_2 dans l'air ambiant (DAC – Direct Air Capture) a tout d'abord fait l'objet d'un travail spécifique. Pour rappel, à la différence de la capture du CO_2 appliquée aux fumées issues de points d'émissions (centrales électriques, cimenteries, fours à chaux, verreries, etc.) où celui-ci est concentré classiquement entre 3% et 30%, la concentration du CO_2 dans l'air ambiant est plutôt de l'ordre de 0.042%. Sa capture demande donc plus d'énergie (contrainte thermodynamique : travail maximum nécessaire à la séparation) et il convient dès lors de se poser la question si l'implémentation de cette technologie garde un sens, tant d'un point de vue économique qu'environnemental. La publication « Life cycle and techno-economic assessments of direct air capture processes: An integrated review » R. Chauvy & L. Dubois, Int J Energy Res. 2022;46:10320–10344, permet d'y apporter des éléments de réponse.

Il est ressorti de cette étude que les technologies DAC sont à des niveaux de maturité très différents (TRL de 1 à 3 pour certaines, jusque 9 pour d'autres) et impliquent diverses opérations unitaires (adsorption, absorption, …), utilisent différents types de matériaux (liquides ou solides) et types d'énergie (électrique et/ou thermique). La plupart des procédés utilisent l'adsorption (p.ex. Climeworks), l'absorption (p. ex Carbon Engineering), même si des solutions plus innovantes existent qui ne sont pas un niveau TRL suffisant pour envisager leur commercialisation.

En ce qui concerne les performances environnementales des technologies DAC, le caractère « **carbone-négatif** » de cette technologie a été souligné, en particulier lorsqu'elle est combinée à la séquestration du CO_2. Cependant, la construction de grandes installations de DAC a un impact sur d'autres aspects environnementaux concernant l'empreinte au sol, l'eau et l'utilisation des matériaux.

Pour ce qui est du volet économique, les études de la littérature fournissent de larges fourchettes de coûts, à savoir de 80 €/t_{CO2} à 1133 €/t_{CO2} pour les estimations actuelles, tandis que les coûts futurs des DAC devraient diminuer et se situer entre 34 €/t_{CO2} et 260 €/t_{CO2}.

Une autre étude, réalisée par l'UCLouvain en collaboration avec l'UMONS, a quant à elle concerné l'intégration d'un procédé DAC avec une unité de conversion en gaz naturel synthétique (SNG) (DAC – Power-to-Gas (PtG)) et l'analyse 4^E (énergétique, exergétique, économique et environnementale) associée. Cette étude a aussi mis en œuvre une quantification de l'incertitude. Les résultats de cette étude montrent que le système DAC-PtG est autothermique lorsqu'on introduit une unité de recompression mécanique de la vapeur à deux étages à la sortie du DAC. L'efficacité énergétique se situe entre 51.3 % et 52.6 % avec un écart-type de 3, l'incertitude étant due aux conditions ambiantes et à la chaleur de désorption. Le SNG issu du DAC-PtG a une empreinte carbone inférieure à celle du méthane fossile lorsque l'empreinte carbone de l'approvisionnement en électricité est inférieure ou égale à 0.12 kg_{CO2-eq}/kWh. Le coût nivelé du gaz naturel synthétique (LCSNG) varie entre 130 €/MWh et 744 €/MWh, en raison de l'incertitude du prix de l'électricité et des coûts liés au DAC et à l'électrolyse. Par conséquent, l'augmentation du volume de production, la poursuite de la maturation de ces technologies et davantage de projets de démonstration sont nécessaires pour réduire l'incertitude du LCSNG. Les travaux futurs prendront en compte les sources d'énergie renouvelables intermittentes.

Globalement, les leviers clés qui contribueront à améliorer les performances des DAC et à réduire leurs coûts sont liés aux développements technologiques (p. ex., l'utilisation de sorbants liquides ou solides, le contacteur gaz-liquide/solide), à la consommation d'énergie (p. ex. la possibilité d'utiliser la chaleur résiduelle, la disponibilité d'électricité à faible coût et à faible émission de carbone), ainsi qu'aux caractéristiques de mise en œuvre (p. ex., la modularité et la mise à l'échelle, l'intégration énergétique avec un ou d'autres procédés) ;

Au-delà de la récupération du CO_2 atmosphérique, les technologies DAC pourraient, à termes, fournir du CO_2 dans des zones où des industries (émettrices de CO_2) ne sont pas présentes mais où de grandes quantités d'énergie bas carbone sont produites (p.ex. solaire, éolien, géothermique, …), et permettraient à la fois de capturer le CO_2 dans l'air, mais également (par exemple) de produire de l'hydrogène vert, combinable au CO_2 afin de produire un vecteur énergétique plus facilement transportable et gérable, tel que le SNG.

Pour ce qui est de l'éventuelle application du DAC en Belgique, il semble clair qu'à l'heure actuelle la priorité doit être la limitation des émissions de CO_2 à la source (beaucoup plus concentrées, et donc aux performances de capture bien plus avantageuses), et donc la capture du CO_2 des fumées industrielles. Néanmoins, certaines technologies DAC pouvant s'ajouter à des installations existantes (p.ex. tours de refroidissement) ou profiter de chaleurs fatales actuellement perdues, il n'est pas à exclure que certains projets pourraient voir le jour dans le futur, en parallèle notamment des infrastructures relatives à l'hydrogène (production et transport) permettant alors d'utiliser ce CO_2 pour produire un autre vecteur énergétique.

Communications scientifiques réalisées sur ce sujet :

Chauvy R., Dubois L., « Life cycle and techno-economic assessments of direct air capture processes: An integrated review », International Journal of Energy Research, 2022;46:10320–10344, 2022.

Coppitters D., Costa A., Chauvy R., Dubois L., De Paepe W., Thomas D., De Weireld G., Contino F., « Energy, Exergy, Economic and Environmental (4E) analysis of integrated direct air capture and CO_2 methanation under uncertainty », Fuel, 344, 127969, 2023 (en collaboration avec l'UCLouvain).

2.5. Résumé des principaux enseignements des simulations de liquéfaction du CO_2

En vue de l'implémentation de chaînes CCUS, l'étape de transport du CO_2 a un rôle prépondérant. Dans le cas d'un transport terrestre (onshore), plusieurs analyses montrent que le transport par pipeline est la méthode préférée en raison de son coût inférieur, certaines études indiquant que le transport par train ou par camion pouvant être économiquement viable uniquement pour de petites quantités de CO_2. Les barges constituent également une solution envisageable si le site de captage est situé à proximité d'une voie fluviale. Le transport maritime devient plus avantageux que les pipelines au-delà d'une certaine distance, avec des transports optimaux à des pressions de 7 ou 15 bar selon le type de navire. Les impuretés dans le CO_2, provenant de divers procédés industriels et des performances variables des technologies de capture, augmentent la consommation d'énergie lors de la compression et peuvent entraîner des risques de corrosion. Les spécifications pour le transport maritime du CO_2, sous forme liquide, limitent la concentration de certaines impuretés par des seuils stricts. Des méthodes de purification du CO_2, telles que le système à deux flashs et la colonne de stripping, ont été proposées pour répondre à ces spécifications. Notons que de telles spécifications strictes sont également d'application pour le transport par pipeline (cf. spécifications fixées par l'opérateur Fluxys en Belgique). En vue de transporter le CO_2 sous forme liquide, il est donc nécessaire de s'intéresser à l'étape de liquéfaction du CO_2, ce qui a fait l'objet d'une étude spécifique, en prenant en compte la présence d'impuretés gazeuses ce qui est particulièrement innovant par rapport à ce qui est généralement considéré dans la littérature.

Les méthodes de liquéfaction du CO_2 étudiées montrent que les cycles hybrides, combinant un cycle ouvert avec une expansion Joule-Thompson et un cycle fermé avec une machine de refroidissement, permettent de réduire la consommation d'énergie et d'améliorer la récupération du CO_2 par rapport aux cycles ouverts ou fermés. En présence du seuil maximal d'impuretés dans le pipeline, la consommation d'énergie peut presque doubler, passant de 21 kWh/t_{CO2} à 40 kWh/t_{CO2}, avec une récupération maximale de 98 %.

Dans l'ensemble, le cycle hybride se positionne donc comme une solution polyvalente et efficace pour répondre aux complexités de la purification et de la liquéfaction du CO_2 à partir d'un pipeline.

Précisons que pour répondre aux spécifications du transport par bateau, il est nécessaire d'ajouter une colonne de distillation au processus de liquéfaction. En termes de coûts, cette étape de liquéfaction du CO_2 ajoute une contribution située entre 7 et 14 $€/t_{CO2}$ en fonction des impuretés présentes dans le CO_2, représentant néanmoins un coût entre 2 et 10 % de l'ensemble de la chaîne CCUS. Cette gamme de coûts met en évidence l'impact significatif que les impuretés gazeuses peuvent avoir sur le coût global de la liquéfaction du CO_2. Soulignons également que les impuretés gazeuses entraînent une perte de CO_2, qui sera facturée à l'opérateur de liquéfaction du CO_2.

Cette étude a donc permis de souligner l'importance d'optimiser les stratégies de transport et de liquéfaction du CO_2 pour faciliter le déploiement des technologies CCUS. L'une des perspectives de ce travail sera d'étudier la chaîne de manière plus complète afin de déterminer ce qui est le plus économiquement viable : être plus strict sur la pureté du CO_2 dans le pipeline et donc augmenter la purification du CO_2 à la sortie de l'unité de capture, ou s'en tenir aux spécifications actuelles, ce qui implique de traiter le CO_2 du pipeline pour répondre aux spécifications pour le transport par bateau.

Communication scientifique réalisée sur ce sujet :

Costa A., Dubois L., Thomas D., De Weireld G., « Optimization of liquefaction cycles applied to CO_2 coming from pipeline transportation », Carbon Capture Science & Technology, 13, 100280, 2024.

3. Conclusions et perspectives pour la suite du projet DRIVER

Le domaine du CCUS étant en continuelle évolution, un suivi et une veille technologique régulière s'avèrent nécessaires afin de pouvoir affiner les différents indicateurs générés (énergétiques, économiques et environnementaux). En outre, l'évolution du marché du CO_2 et sa régulation (ETS notamment), ainsi que l'évolution des projets CCUS et DAC en général (projets actuels et nouveaux projets), auront un impact important sur le déploiement de chaînes CCUS.

Au niveau des étapes de capture-purification du CO_2, deux grandes catégories de procédés sont étudiées, à savoir par **absorption-régénération utilisant des solvants aminés**, et des **technologies cryogéniques** (éventuellement hybrides, combinées avec l'utilisation d'adsorption gaz-solide (VPSA-CPU) ou de membranes en guise de préconcentration). L'enjeu pour la première catégorie reste d'en diminuer son coût (grande consommation d'énergie thermique) alors que pour la seconde de continuer l'optimisation du process afin d'en réduire sa consommation d'énergie exclusivement électrique. Le fait de considérer les techniques cryogéniques relève d'une importance primordiale. En effet, au-delà du taux de récupération du CO_2 en tant que tel, le fait de devoir respecter des **spécifications strictes de pureté pour l'injection du CO_2 dans un réseau de pipeline** (et/ou pour son transport liquéfié par bateaux) devrait très souvent nécessiter l'utilisation d'une telle technologie. L'investigation de la liquéfaction du CO_2 est également importante vu que son transport par bateau vers un hub de stockage géologique se déroulera sous forme liquide.

Pour ce qui est de l'étape de **conversion du CO_2**, éventuellement intégrée thermiquement avec une unité de capture (l'intérêt d'une telle opération a pu être démontré), une attention particulière a été portée sur les voies **méthanol** et **méthane**, ce dernier se positionnant comme le vecteur énergétique avec le potentiel le plus intéressant.

En complément d'investigations et de nouvelles simulations, la prochaine étape du projet DRIVER consistera à intégrer les résultats de ces simulations comme inputs dans des modèles de type **Remote Renewable Energy Hub (RREH)** développés à l'ULiège (cf. livrable D2). Conjointement avec les travaux réalisés à l'UCLouvain, l'objectif sera de pouvoir fournir une analyse plus globale des chaînes de valeur intégrant le CO_2 et divers vecteurs énergétiques. L'ensemble des résultats généraux permettront de constituer une roadmap technologique en vue de l'implémentation du CCUS en Belgique.

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Separate and integrated simulations of CCU process chains (CO_2 capture, purification, transport and conversion)

A. Costa, L. Dubois, D. Thomas and G. De Weireld

DRIVER

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1 Technological context regarding CCUS and DAC

On the road to greenhouse gas emissions reduction, and especially CO_2, such as for the defossilization of the economy, the implementation of a CCUS (Carbon Capture Utilization and Storage) process chain appears as a key component among the different measures such as renewables development, electrification, process efficiency improvement, etc. On the long term, the capture of the CO_2 in ambient air (Direct Air Capture – DAC) could also make sense in places where both a lot of area and green energy are available. The **DRIVER** project, whose scope is presented on Figure 1, positions itself in that context and comprises the **simulation of different CO_2 capture, purification, liquefaction and conversion processes**.

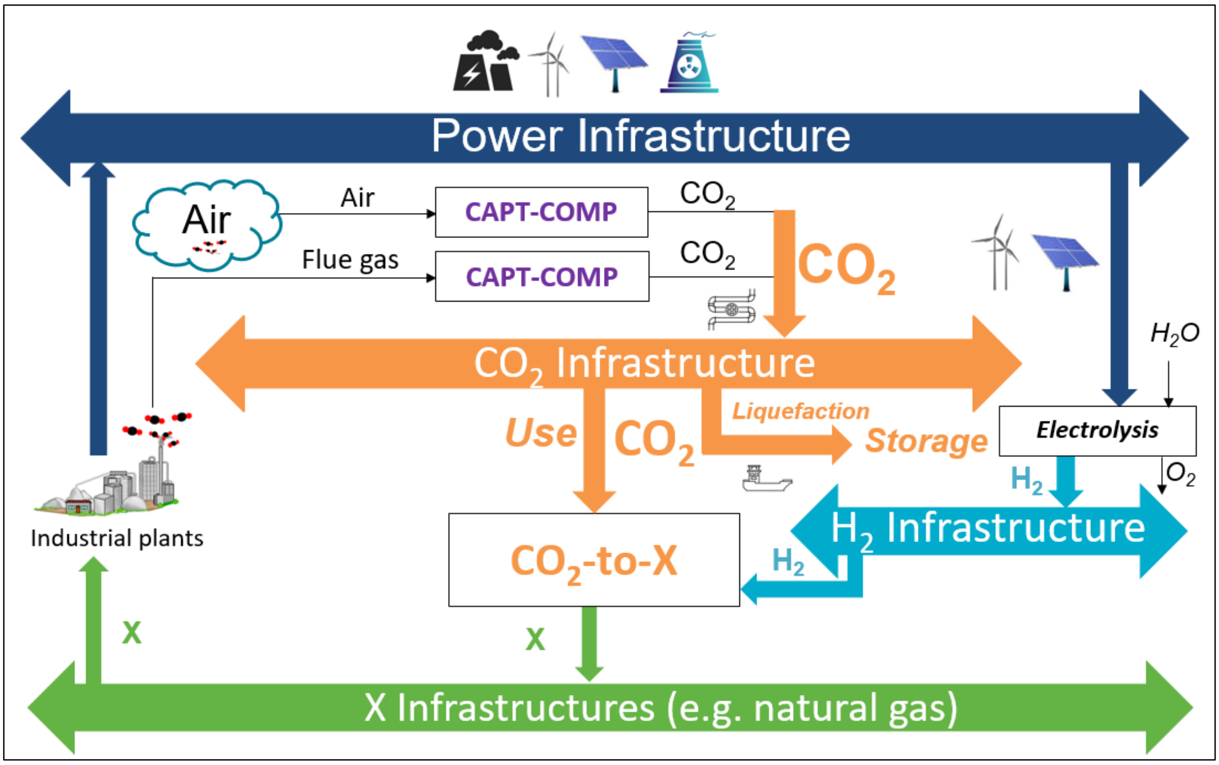


Figure 1: Illustration of the DRIVER project scope

As detailed in the first project deliverable (Deliverable-1 (D1): "Belgian and European CO_2 emitters and users, CO_2 capture, purification and transport infrastructures"), different **CO_2 capture ways** exist, namely:

- **pre-combustion:** where the carbon source is eliminated before the combustion step but which is not adapted for several industries where the major part of the CO_2 emissions is linked to the raw material decarbonation, such as in cement and lime industries;
- **oxyfuel-combustion:** which consists in the combustion with pure oxygen instead of air, leading to a CO_2-concentrated flue gas (>75%) needing the implementation of a Carbon Purification Unit (CPU). Such capture way needing a lot of adaptations in comparison with a conventional combustion (e.g. Air Separation Unit (ASU) for O_2 production, burners adaptation, etc.) it could make sense for new industrial units rather than in revamping cases;
- **post-combustion:** currently the most developed carbon capture way, also-called "end-of-pipe" technology, it corresponds to the CO_2 capture downstream of existing processes. It has the advantage of not requiring a lot of upstream process modification except a specific attention to other flue gas treatments (e.g. deSOx, deNOx, dedust, …).

In terms of **CO_2 capture-purification technologies**, especially for the post-combustion CO_2 capture application (or oxyfuel-combustion for CPU), four main unit operations have been identified as relevant to be investigated in the framework of the DRIVER project, namely:

- **gas-liquid absorption process:** the flue gas is put in contact with a liquid (solvent) that absorbs the CO_2 (generally accompanied with chemical reaction) in a first packing column, the solvent needing to be regenerated in a second column (stripper) that consumes a lot of thermal energy;
- **gas-solid adsorption processes:** in that case the CO_2 from the flue gas is captured thanks to the use of a solid materials (adsorbent), which can be regenerated using different ways, such as thermal energy (TSA – Temperature Swing Adsorption) or electrical energy ((V)PSA ((Vacuum)Pressure Swing Adsorption);
- **separation membranes (gas-gas):** the CO_2 is separated from the other gaseous components by passing through a membrane with specific characteristics allowing to be selective depending on the component that needs to be recovered;
- **cryogenic processes:** especially adapted for pre-concentrated flue gases (e.g. in combination with VPSA) or in the case of CPU applied to oxyfuel flue gases, it separates the CO_2 from the other flue gas compounds based on their different condensation temperatures. It also allows to generate CO_2 in liquid form (e.g. importance of CO_2 liquefaction step in a CCUS process chain application).

Gas-liquid absorption technology, and in particular the use of amine-based solvents, is currently the **most mature process** (Technology Readiness Level (TRL) of 9) and the most available among technology suppliers (several of which were mentioned in Deliverable D1), although the other technologies have interesting medium- to long-term potential, particularly in terms of cost reduction and environmental impact.

As presented on Figure 1, once captured, the CO_2 needs to be **transported** in view of its **geological storage** (CCS) or **utilization** (CCU). The purity of the CO_2 and the possible impact of impurities on its physicochemical properties are important parameters. For continental transport, CO_2 can be transported by **pipeline** (cf. Fluxys' developments in this field), river barges, trains or trucks, while off-shore transport is obviously limited to pipelines or **ship** transportation. In that last case, CO_2 needs to be **liquefied**.

Focusing on the **CO_2 utilization**, the global market already represented more than 230 Mt_{CO2} annually in 2018, of which 16% was in Europe. Nearly 60% of the world's CO_2 is currently used in urea production, 34% for enhanced oil recovery (EOR), and finally everything to do with food and soft drinks (the main uses in Europe), as well as other industries. In conjunction with the development of the green hydrogen sector, other markets will develop in the future, such as **synthetic natural gas (SNG)** and **methanol** which have been the subject of specific studies in the framework of the DRIVER project. Other products are also envisaged, such as ethanol and e-kerosene, as well as higher value-added products with much smaller markets, such as polycarbonates, formic acid and polyurethane.

Finally, as shown on Figure 1, the DRIVER project also considers that **DAC** could have a role to play in global decarbonization, provided that every effort is made upstream to reduce CO_2 emissions at source as much as possible.

Based on all these considerations, different **process simulation works** were performed in the DRIVER project with the following objectives:

- **post-combustion CO_2 capture by the absorption-regeneration process:** investigating other solvents (e.g. demixing solvents) and process configurations (e.g. Lean Vapor Compression (LVC)) in order to propose ways for reducing the thermal energy consumption of such process;

- **oxyfuel-combustion CO_2 purification and post-combustion CO_2 capture by hybrid VPSA-cryogenic/membranes processes:** optimizing the processes and performing their energy, exergy, economic and environmental impacts (4E) analyses;
- **CO_2 conversion processes:** optimizing and comparing CO_2-to-methanol and CO_2-to-methane processes, such as investigating their integration with a post-combustion carbon capture;
- **Direct Air Capture (DAC):** after having performed an overview on the different DAC technologies and their development status, performing a simulation study (together with UCLouvain) for investigating the integration of DAC with a CO_2-to-methane process;
- **CO_2 liquefaction process:** simulating and optimizing pipeline CO_2 liquefaction for ship transportation in view of offshore CO_2 storage.

The different studies performed on these topics are presented hereafter.

2 Post-combustion CO_2 capture by the absorption-regeneration process

2.1 Processes and pathways for the regeneration energy reduction

Several industrial sectors, such as cement and lime producers, produce so-called **“unavoidable” CO_2 emissions**, as they are intrinsically linked to the industrial process itself (calcium carbonate decarbonation). In order to reduce these emissions, it is necessary to implement a CCUS process chain. The capture step, although already technologically mature, especially the **absorption-regeneration process using amine-based solvents**, involves very **high thermal energy consumption** (see Figure 2).

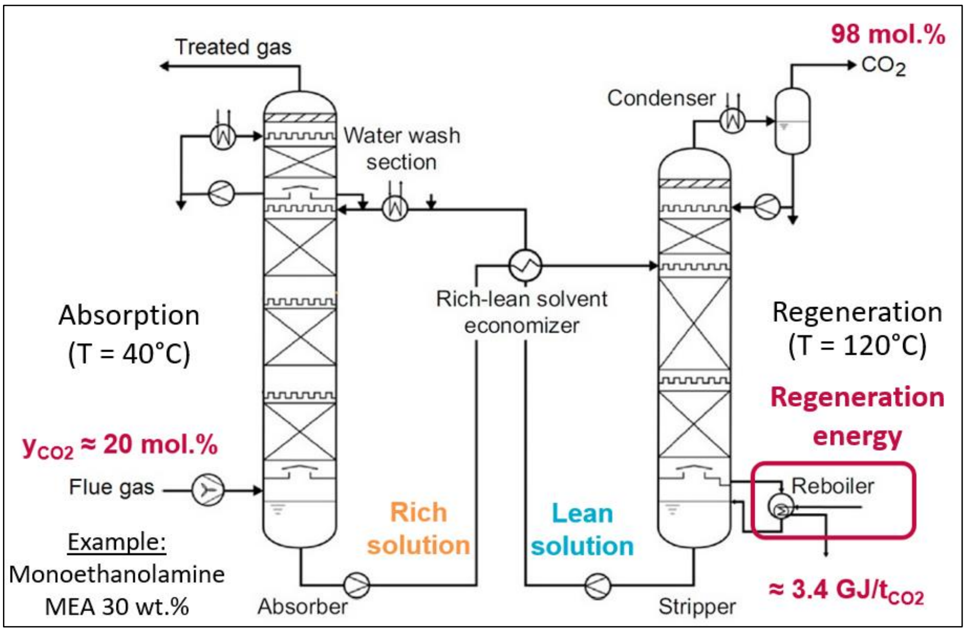


Figure 2: Typical absorption-regeneration CO_2 capture process using MEA 30 wt.% as solvent

The absorption-regeneration CO_2 capture technique comprises two steps: (i) the flue gas to be treated is sent to the bottom of an absorption column where the CO_2 is captured thanks to a counter-current contact with an amine-based solvent (an aqueous solution generally containing 30 to 60% by weight of amine(s)) (typical removal rate of 90%); (ii) the solvent containing the CO_2 (rich solution) is then regenerated in a second column where, by raising the temperature, the CO_2 is released from the solvent and recovered at high purity (>98 mol.%). The lean solution can then be returned to the absorption column. This second stage is the most energy-intensive (typically **3 to 4 GJ/t_{CO_2}** for a conventional 30% monoethanolamine (MEA) solution (van der Spek, 2017)).

Three ways of reducing this consumption were therefore investigated (experimentally and/or via the development of Aspen Plus® simulations, more details are available in (Dubois et al., 2023a)), namely (see Figure 3):

(i) **upstream of the process:** by increasing the CO_2 content of the flue gases to be treated (via partial oxy-combustion and/or flue gas recirculation);

(ii) **within the process:** by using more efficient and innovative solvent mixtures such as demixing solvents;

(iii) **at the configuration level:** by implementing advanced configurations of the capture process.

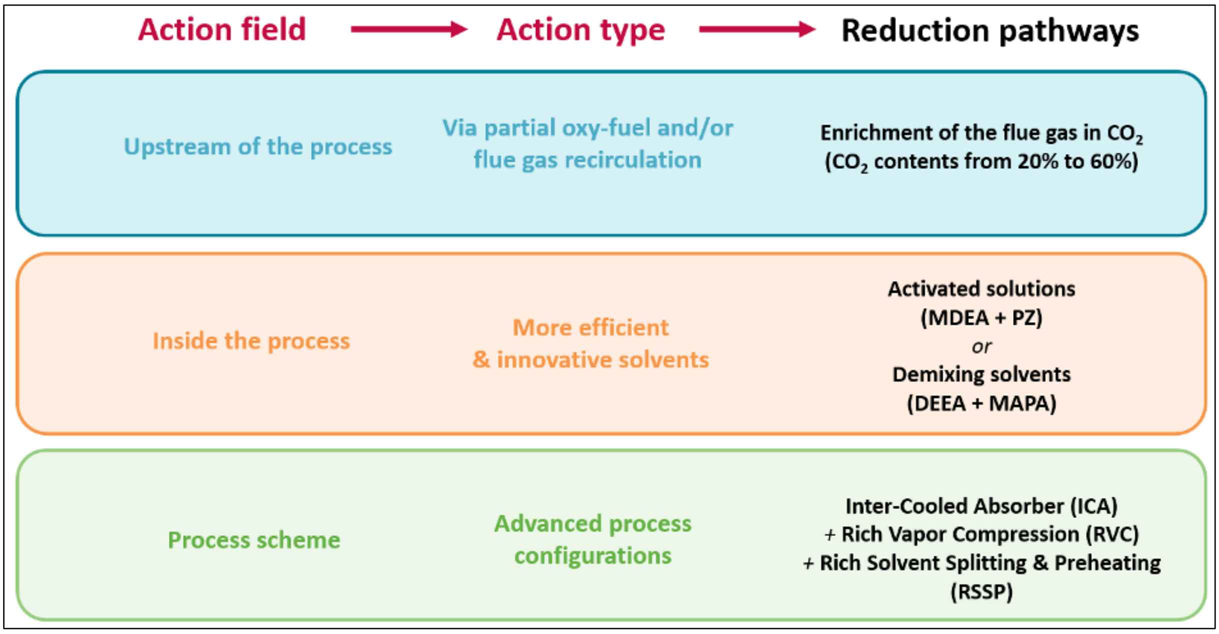


Figure 3: Regeneration energy reduction pathways investigated

As shown by (Dubois et al., 2022), the **demixing solvents technology** appears as a very promising option to significantly reduce the thermal energy consumption of the process without impacting too much the equipment investment. Indeed, thanks to the separation of the two immiscible phases formed after the CO_2 absorption, a demixing technology allows to regenerate a lower solvent flow rate with a higher CO_2 loading in comparison with non-demixing solutions. Such demixing solvent process could also be combined with a **process configuration** like L/RVC (Lean/Rich Vapor Compression), as represented on Figure 4.

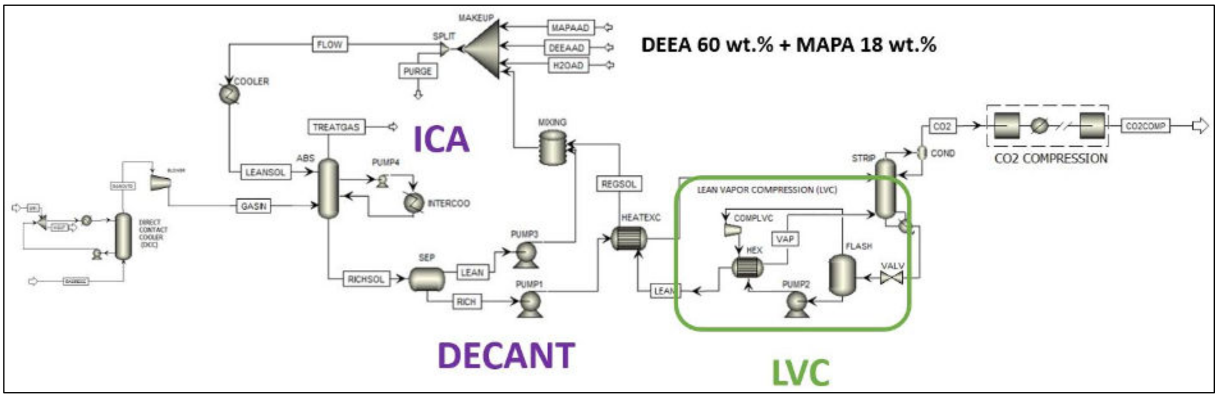


Figure 4: Aspen Plus® flow sheet of the demixing CO_2 capture process (DEEA+MAPA as solvent) combined with InterCooled Absorber (ICA) and Lean Vapor Compression (LVC)

2.2 Main conclusions drawn from the simulation works performed

As illustrated on Figure 5, it was found that the use of a demixing process such as the mixture of diethylethanolamine (DEEA) and methyl-amino-propylamine (MAPA), or the implementation of an advanced process configuration (Inter-Cooling Absorber + Rich Vapor Compression + Rich Solvent Splitting and Preheating, with methyldiethanolamine (MDEA) + piperazine (PZ) as the solvent are the most effective ways of reducing the energy consumption of the absorption-regeneration process, i.e. by over 44% compared with a conventional process using monoethanolamine (MEA) when both a demixing process is combined with a LVC configuration.

N°	Solvent	y_{CO2} (%)	Configuration	P_{abs} (bar)	P_{regen} (bar)	$(L/G)_{vol.}$	$\alpha_{CO2,rich}$ (mol/mol)*	$\alpha_{CO2,lean}$ (mol/mol)*	E_{regen} (GJ/t_{CO2})
1	MEA 30%	20	Base	1.2 bar	2 bar	$5.56\ 10^{-3}$	0.51	0.21	3.36
2	PZ 40%	20	Base	1.2 bar	6 bar	$3.16\ 10^{-3}$	0.73	0.18	3.14
3	PZ 40%	44	Base	1.2 bar	6 bar	$3.14\ 10^{-3}$	0.82	0.27	2.86
4	DEA 30% + PZ 15%	44	Base	1.2 bar	6 bar	$3.13\ 10^{-3}$	0.67	0.12	2.73
5	DEEA 60% + MAPA 18%	20	Demixing + ICA	1.2 bar	2 bar	$8.34\ 10^{-3}$	0.72	0.17	2.65
6	MDEA 10% + PZ 30%	20	RVC+ICA	1.2 bar	6 bar	$4.57\ 10^{-3}$	0.72	0.36	2.19
7	DEEA 60% + MAPA 18%	20	Demixing + ICA	1.2 bar	4 bar	$8.34\ 10^{-3}$	0.74	0.17	2.00
8	MDEA 10% + PZ 30%	20	Adv. configuration RVC + ICA + RSSP	1.2 bar	6 bar	$5.49\ 10^{-3}$	0.69	0.40	1.97
9	DEEA 60% + MAPA 18%	20	Demixing + ICA + LVC	1.2 bar	4 bar	$8.34\ 10^{-3}$	0.74	0.17	1.90

* For demixing solvent, the CO_2 loadings values are relative to the solutions at the inlet (after phase separation) and outlet of the regeneration column.

Figure 5: Simulation (a) and economic (b) results for different regeneration energy reduction pathways investigated, available in (Dubois et al., 2023a) and (Dubois et al., 2023b), using kinetic model developed in (Costa et al., 2022)

Moreover, from an economic point of view, in comparison with a basic configuration using MEA, demixing technology offers the advantage of being able to achieve high energy performance at a more limited investment (CAPEX) (+1.6%) than with more advanced process configurations (+8.8%), leading to a lower CO_2 capture cost (-24%).

The researches about the use of demixing solvents to reduce the energy consumption of the absorption-regeneration CO_2 capture process are still ongoing (PhD Thesis of Mr D. Verdonck, funded as Research Fellow by the F.R.S./F.N.R.S), in particular to find more economical and environmentally friendly alternatives to the DEEA+MAPA mixture. Another option that also started to be investigated at UMONS (PhD Thesis of Mrs C. Pasté, funded by ATLANTIS F.R.S./F.N.R.S Research Project) is the use of a catalyst allowing to facilitate the CO_2 desorption and reducing the solvent regeneration temperature, leading to a significant decrease of the energy consumption.

3 CO_2 capture and purification process using cryogenic technology

3.1 CO_2 purification unit (CPU) for oxy-combustion flue gases

3.1.1 Description of the CPU process simulated

As alternative to post-combustion CO_2 capture, implementing **oxyfuel combustion** followed by a **CO_2 Purification Unit (CPU)** is an interesting option, especially when designing new industrial units (e.g. cement plants). In this context, (Costa et al., 2024a) investigated the optimization of a CPU for oxy-combustion flue gases from cement plants. This optimization was based on a **multidimensional study of the energy, exergy, economic and environmental impacts (4E analysis)** of the process. Among the different capture-purification units available in the literature, it appears that for flue gases with a CO_2 concentration higher than 70% (Lockwood, 2014), the **cryogenic carbon purification unit** is the most suitable technology. As illustrated on Figure 6, the principle of this process is to separate the CO_2 from the other gaseous components by liquefying the carbon dioxide after dehydration and eventual flue gas pre-treatments (e.g. de-dusting, de-NOx, etc.).

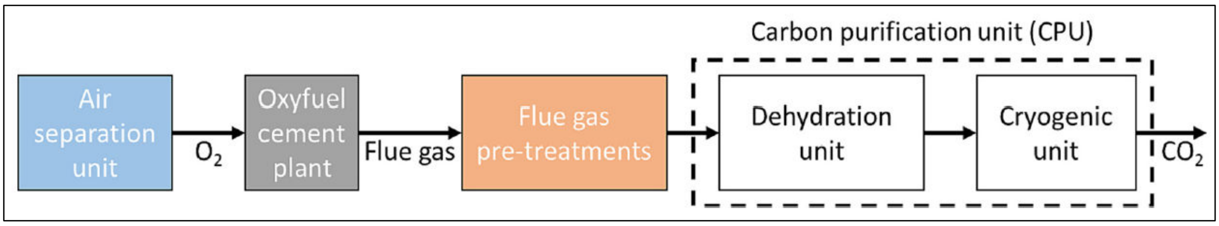


Figure 6: Block diagram of an oxy-combustion cement plant comprising a CPU (Costa et al., 2024a)

As reviewed in (Costa et al., 2024a), the **targeted purity of the purified CO_2** depends on the CO_2 transport mode and/or utilization and it has an influence on the CPU design and optimization. In the present work, the objective was to consider a very restrictive case which corresponds to the specification given by the Northern Lights project, world's first open-source CO_2 transport and storage infrastructure. The data from (ZEP/CCSA, 2022) was considered for transport by ship to a terminal in western Norway for intermediate storage, before being transported by pipeline for permanent storage in a reservoir 2600 m under the seabed. Therefore, a CPU capable of generating a high purity CO_2 was modelled. In addition, to reduce the electrical consumption of the system, which directly influences the process operation costs, a **hybrid system with a membrane was studied**. The CPU process considered is presented on Figure 7 and the corresponding Aspen Plus® flowsheet developed is provided on Figure 8. Such configuration also increases the maximum CO_2 recovery of the process compared to a standard one for a similar flue gas. The modelling of a CPU with membrane and its optimization was addressed. Moreover, a multidimensional study, an energy, exergy, economic and environmental (4E) analysis was carried out by considering an oxy-combustion flue gas coming from a cement plant as a base case. In addition, a further analysis of the source and electricity price in the system was performed. The CPU performance is subjected to a considerable number of uncertain parameters. In this framework, **uncertainty quantification (UQ)** allows the uncertainty on a quantity of interest to be quantified (e.g., the electrical consumption) with respect to the random environment (e.g., the compressor efficiency). Finally, a variation of the CO_2 content linked to the possibility of a higher or lower air entrance was also considered.

Focusing on the process presented on Figure 7, considering a flue gas coming from an oxy-combustion cement kiln, it combines a membrane unit to increase the CO_2 recovery with a cryogenic unit to reduce the power consumption of the compressors (lower pressure) and, at the same time, a compression unit for sending the CO_2 in a supercritical state into a pipeline.

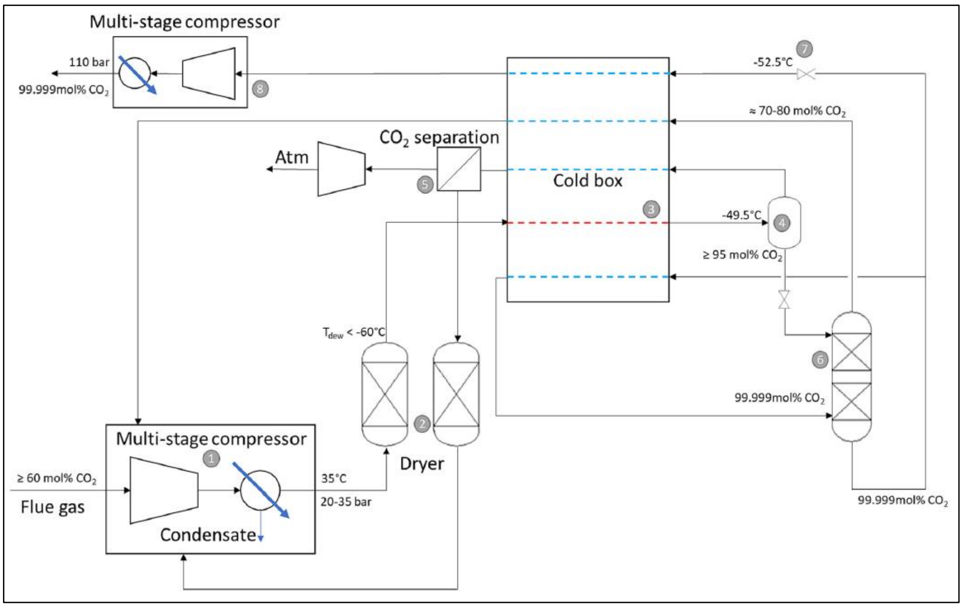


Figure 7: CPU process considered including membrane (Costa et al., 2024a)

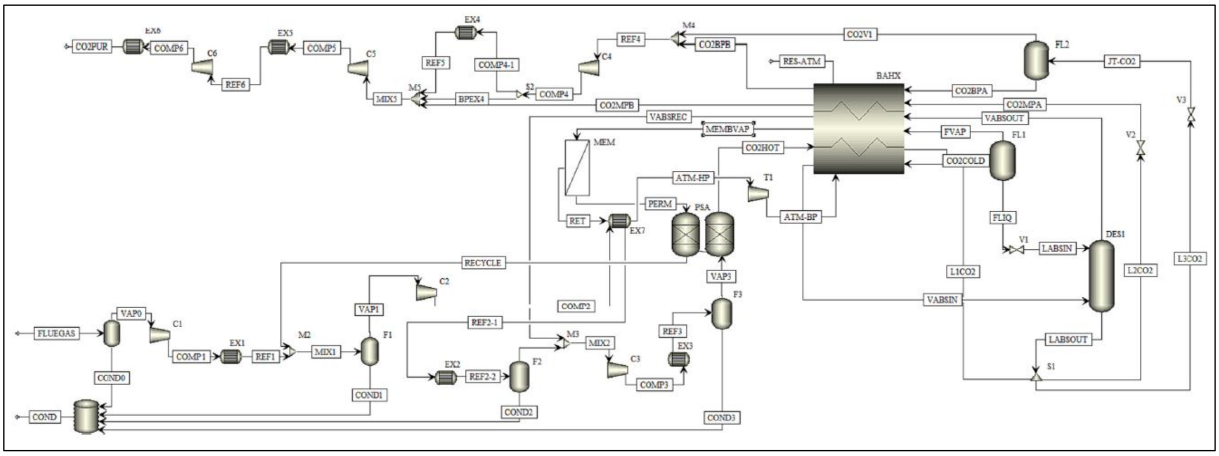


Figure 8: Aspen Plus® flowsheet of the CPU process simulated (Costa et al., 2024a)

The process can be divided into eight subsystems (see Figure 7): (1) flue gas compression, (2) flue gas drying, (3) flue gas cooling, (4) CO_2 vapor-liquid separation, (5) CO_2 recovery of the vapor from flash, (6) CO_2 purification, (7) cold generation and (8) CO_2 compression. The objective of the cryogenic unit is to cool the flue gas to recover CO_2 with high purity. This cooling is applied close to the triple point temperature for pure CO_2 (-56.6 ◦C) but without going below it to avoid any dry ice in the installation. A limit of -54 ◦C is fixed to avoid any issues with the triple point. The flue gas enters the multistage compression chain to reach the working pressure, allowing at least 90% CO_2 recovery (1). The gas is compressed in 3 compressor stages to get the compression ratio between 2 and 5 by stage, and to limit gas warming below 200 ◦C. The stream is dried by an adsorption column containing silica gel or alumina to a dew point temperature below -60 ◦C (2). The stream is then cooled in the cold box before entering the flash at -49.45 ◦C. The multi-stream heat exchanger technology is a brazed aluminum heat exchanger (BAXH). The cooled flue gas is sent to a flash to separate liquid CO_2 from the incondensable gases (4). The cold duty of the vapor phase coming from the flash is recovered in the cold box, before being sent to the membrane to recover CO_2 that will be used to regenerate the dryer and being recirculated through multistage compression. The non-condensables are expanded in a turbine (5). The desorption column extracts the impurities of the liquid CO_2 coming from the flash by means of a pure CO_2 vapor (6). The desorption of impurities allows a CO_2 purity of 99.999 mol% to be reached. The liquid obtained at the bottom of the column is separated into two streams. The first one is heated to generate the CO_2 vapor used in the column. The second one is expanded in a Joule-Thomson valve (7) to generate a stream at -52.45 ◦C to obtain a pinch of 3 ◦C with the stream to be cooled. At the end of this process, the CO_2 is compressed in order to be injected into the pipeline distribution at 110 bar.

All the details regarding the modeling and costs calculation assumptions are provided in (Costa et al., 2024a).

3.1.2 Results of the CPU process optimization

The results of the optimizations carried out are completely described in (Costa et al., 2024a). It was shown that it is more favorable to increase the **CO_2 recovery rate above 90%**, from an energy, exergy and economic point of view. In addition, the carbon purification unit with membrane for CO_2 recovery, compared with other cryogenic processes developed in the literature, enables a significant reduction in electricity consumption. The analysis of the evolution of the cost of capture as a function of CO_2 recovery shows that for a given carbon tax, there is a minimum for the total cost, which comprises the sum of the carbon tax contributions for uncaptured CO_2 and the cost of capture (see Figure 9).

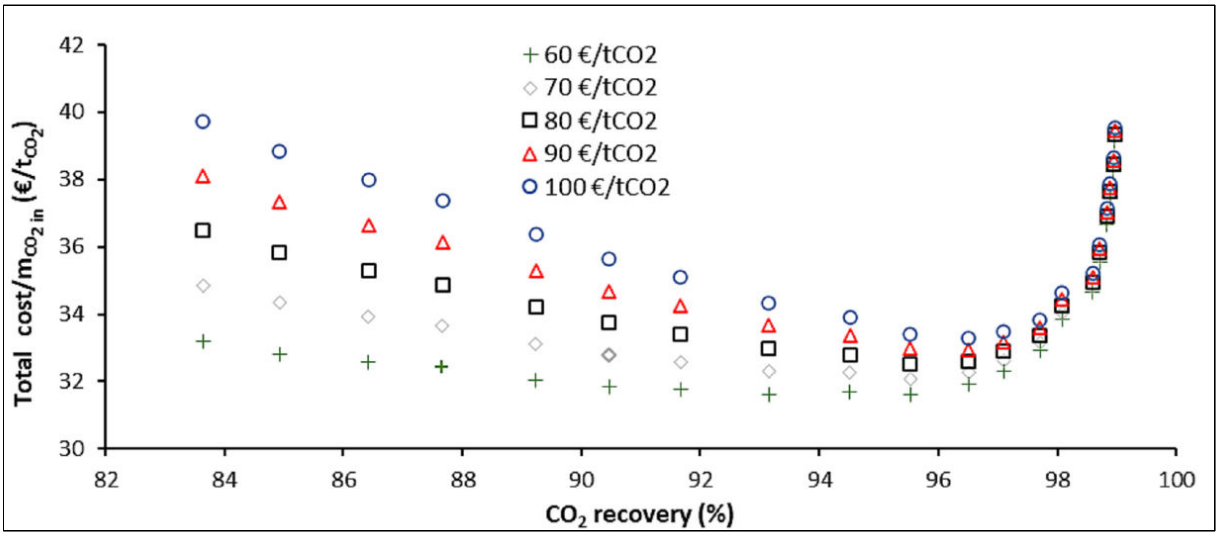


Figure 9: Total CO_2 costs for different carbon tax values (Costa et al., 2024a)

Figure 9 shows different curves depending on the value of the carbon tax. Thus, considering an interval of 60 to 100 €/t_{CO2}, a minimum of the total CO_2 cost for a 60 €/t_{CO2} carbon tax appears from a CO_2 recovery of 93% with a tendency towards a higher CO_2 recovery for a higher tax. For an allowance of 100 €, it is interesting to capture around 96.5% of the CO_2.

As the unit uses **only electrical energy**, the cost and production of electricity will have a direct impact on the cost of capture. When the price of electricity rises from 50 € to 250 €/MWh, the cost of CO_2 capture increases by almost 250%. An analysis of parameter uncertainties enables us to observe their impact on the results, to define a standard deviation in relation to the optimized points, and to demonstrate the robustness of the latter. Considering the technical parametric uncertainties, the standard deviation on power consumption (3.65 kWh/t_{CO2}), CO_2 recovery (0.09%) and exergy efficiency (0.92%) is limited.

Moreover, as well illustrated on Figure 10, the source of the electricity will also impact the **overall balance of avoided emissions**. The percentage of CO_2 avoided compared to an initial CO_2 recovery of 94.9% is 94.7% for wind power generation (0.011 kg_{CO2e}/kWh) and can degrade to 82.8% for coal power generation (1 kg_{CO2e}/kWh). In Europe (ENTSO-E), the electricity mix emits 0.399 kg_{CO2e}/kWh which gives an avoided CO_2 rate of 90.1%. Taking emissions factor from the European electricity mix as an example, the impact of these emissions on the total carbon footprint of the process is not negligible.

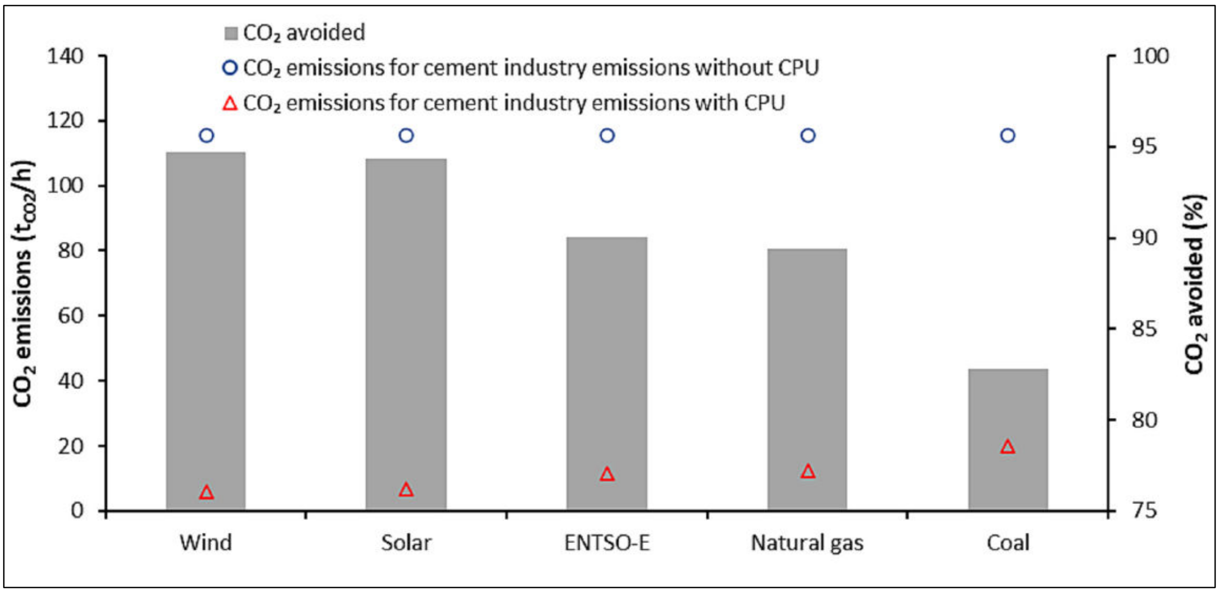


Figure 10: CO_2 emissions and CO_2 avoided considering several sources of electricity production (Emissions factor of electricity (kg_{CO2e}/kWh): wind = 0.011; solar = 0.044; European Network of Transmission System Operators (ENTSO-E) = 0.399; Natural gas = 0.450; Coal = 1.000) (Costa et al., 2024a)

Figure 11 shows the evolution of different KPIs (Key Performance Indicators) for a 90 and 95% CO_2 recovery considering different CO_2 concentrations in the flue gas. As shown in this figure, electrical consumption follows a very similar trend as for the capture cost. For a CO_2 concentration of 74%, the exergy efficiency shows that it is more energetically (and therefore economically) interesting to have a CO_2 recovery of 95%. It can be reminded that exergy is based on a combination of the first and second laws of thermodynamics to consider both the quantities of energy used and their quality, allowing the calculation of the energy useful for the work (exergy) and the energy lost and degraded during the process.

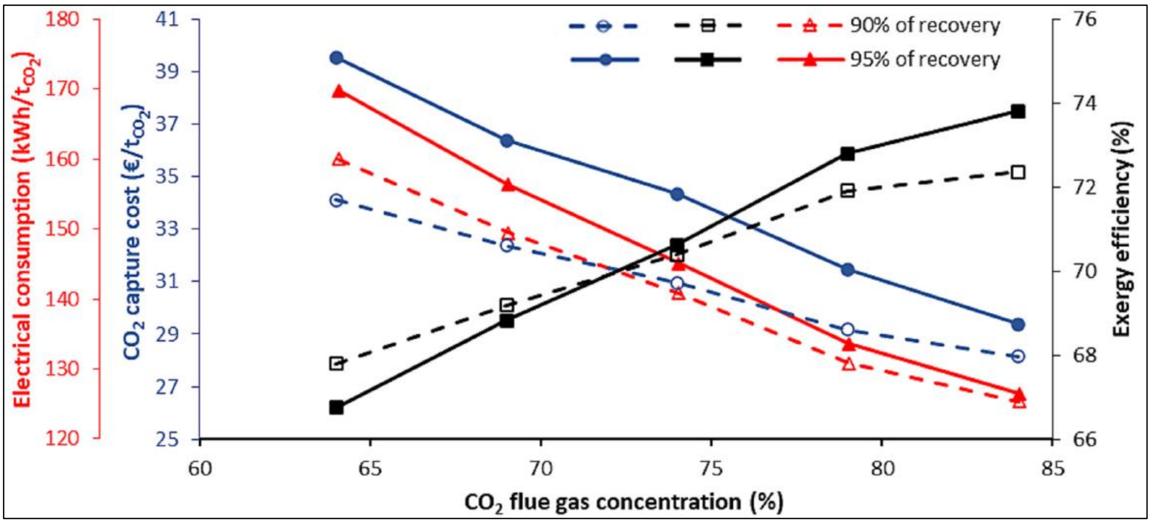


Figure 11: Variation of the CPU electrical consumption, CO_2 capture cost and exergy efficiency as function of the CO_2 flue gas concentration for CO_2 recovery of 90% and 95% (Costa et al., 2024a)

Regarding the capture cost, it can be observed that the difference between both CO_2 recoveries decreases when the concentration in the flue gas is higher. That means that in the case of oxyfuel combustion, a good maintenance of the process, thus avoiding the air inlets (decreasing the CO_2 flue gas concentration), can make it possible to have better performances for a slight difference from an economic point of view.

3.2 Hybrid VPSA-cryogenic CPU applied to flue gases with CO_2 content from 5% to 20%

3.2.1 Introduction on the VPSA-CPU hybrid combination

In this second study (Costa et al., 2024b), a **hybrid system combining a Vacuum Pressure Swing Adsorption (VPSA) unit and a cryogenic CPU** was evaluated to improve the recovery and purity of CO_2 captured from flue gases containing CO_2 concentrations ranging from 5% to 20% (see Figure 12). The VPSA unit preconcentrates the CO_2 and the CPU completes the separation and purifies the CO_2. The combination of these two technologies makes it possible to mix high CO_2-recoveries of VPSAs and high CO_2-purities of CPUs, resulting in an optimized capture process that combines both qualities.

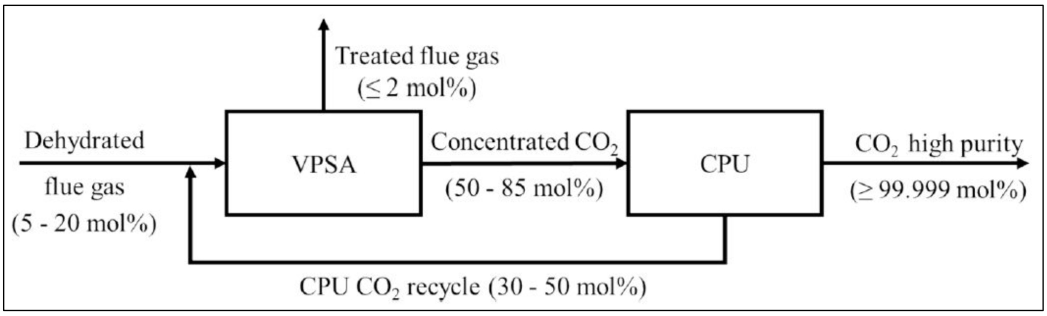


Figure 12: Block diagram of the hybrid VPSA-CPU CO_2 capture process (Costa et al., 2024b)

Adsorption has already demonstrated its effectiveness in gas treatment, whether in refineries to purify hydrogen produced by Steam Methane Reforming (SMR), or in natural gas extraction to purify methane from carbon dioxide. PSA allows to perform rapid cycle compared to TSA (Temperature Swing Adsorption) which limits the investment costs. The main drawback of PSA process is the electrical energy required. Therefore, the optimization of energy consumption is an essential point to design an efficient separation unit. In the literature, numerous PSA processes have been developed for CO_2 capture. Since the flue gas is already at atmospheric pressure, VPSA processes are preferred due to the better selectivity at low adsorbent loading. Several adsorbent and cycle configurations have been studied for CO_2 capture with VPSA process. Among the numerous materials available (active carbon, zeolite, MOF, etc.), zeolite 13X is one of the most interesting materials, exhibiting high CO_2 adsorption capacity and selectivity at low and moderate partial pressure of CO_2 (0.05–0.5 bar) and ambient temperature. For a 15/85 % CO_2/N_2 mixture at 1 bar and 25°C, the CO_2 adsorption capacity is around 2.5 to 3.5 mmol/g with a selectivity between 150 and 850 and for 5 % CO_2 at 1 bar et 25°C, the selectivity remains higher than 100 with a capacity higher than 1 mmol/g. Nevertheless, zeolite 13X is sensitive to contaminants such as NOx or SOx reducing the CO_2 adsorption capacity of the material. Water is also a concern for this material since zeolite is a hydrophilic material, making the adsorption of water preferential instead of CO_2. Presence of water vapor in flue gas leads to a drastic reduction of the CO_2 adsorption capacity of the zeolite, and a reduction of performance in VPSA cycle. Therefore, a pretreatment line is required to remove contaminants and water before the VPSA unit. VPSA processes can be operated with different cycle configurations depending on the number of adsorption beds used, and the sequence of steps performed (more information are provided in (Costa et al., 2024b)).

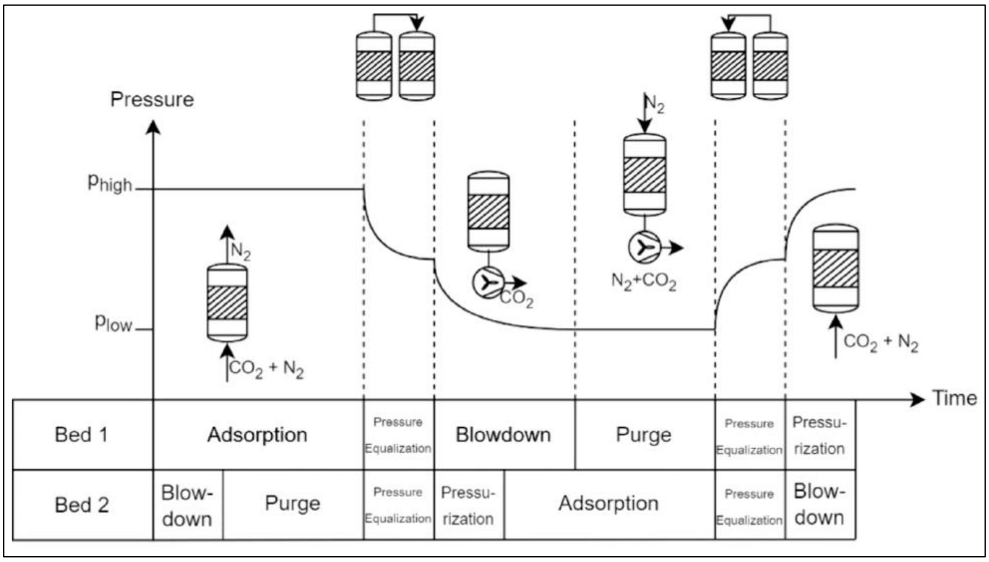
Regarding the CPU technology, as investigated in the DRIVER project, several studies have shown its interest and adaptability to different oxy-combustion flue gas compositions with CO_2 concentrations ranging from 75 to 95 mol% (dry basis). Remarkably, CPU can achieve CO_2 recovery rates as high as 90 %, although the potential exists for even higher recoveries, depending on the initial CO_2 concentration at the system inlet. Achieving the desired purity levels depends largely on the inclusion of unitary operations in the CPU process, such as a distillation column or a desorber. There are two main types of CPUs: medium purity CPU and high purity CPU. The medium purity CPU, often equipped with 1 or 2 flash separators, can deliver CO_2 with a purity of 95 mol%. The high purity CPU, on the other hand, is equipped with a column system that allows it to consistently exceed the coveted 99 mol% purity level and even achieve food-grade CO_2 quality. In terms of energy consumption, it should be noted that the high purity CPU typically consumes 10 to 15 % more electrical energy compared to its medium purity counterpart. This discrepancy in energy consumption results from the more complex separation processes required to achieve high CO_2 purity. Consistent with the general principles of carbon capture, it's also important to recognize that the **energy required for CO_2 capture decreases as the initial CO_2 concentration in the flue gases increases** (as shown in section 3.1.2). Values range from about 164 kWh/t_{CO2} for flue gases containing 75 mol % CO_2 (Li et al., 2013) to a more efficient 112 kWh/t_{CO2} for flue gases containing 94 mol% CO_2 (Magli et al., 2022). This progressive reduction in energy demand highlights the potential energy saving benefits of CPU systems, particularly when used in environments with higher CO_2 concentrations, and contributes to more sustainable and economically viable carbon capture solutions.

In the present work, a **2-bed VPSA** was chosen to generate pre-concentrated CO_2 flux at a minimum of 50 mol%. This value corresponds to the entry level at which the CPU becomes energetically interesting. For the CPU, a **purity of 99.999 mol%** is targeted in order to avoid any trace of undesirable compounds for CO_2 transport or conversion operations. Aspen Plus® and Aspen Adsorption® V14 were used to model cryogenic and VPSA units, respectively. Surrogate models, which convert process simulations into mathematical representations, are employed to facilitate the optimization of the process, aiming to analyze diverse performance indicators including energy consumption, cost, and CO_2 recovery. These models play a pivotal role in identifying the most advantageous operational parameters for the processes. The application of such tools in a hybrid setup stands as a noteworthy innovation, offering substantial time savings in investigating simulated processes that entail computationally demanding calculations. Optimizing two processes simultaneously provides an advantage over optimizing each process individually to ensure finding the optimum point. This work provides a detailed energetic and economic study of this innovative process, and a methodology for performing multi-objective optimization of a complex, fully integrated process.

3.2.2 Description of the VPSA-CPU process simulated

The studied process is a hybrid combination of a PSA and a cryogenic CPU used to capture the CO_2 from flue gases with a CO_2 concentration between 5–20 mol% and a flow rate of 70,000 Nm3/h corresponding to around 1000 t/d of clicker production. To prevent deterioration of the adsorption performance and ice formation in the CPU, the flue gas is considered as dehydrated upstream of the process. To achieve the dehydration required for the VPSA and the CPU, TSA with silica gel or alumina must be used to dry flue gas before the CO2 capture unit. It is also necessary to consider potential treatments on a larger scale to remove pollutants that could degrade the material, such as dusts, NOx, SOx, Hg, etc. In this study, a preliminary assumption is to focus solely on nitrogen and carbon dioxide. The VPSA is used to concentrate CO_2 from the flue gas at least 50 mol% CO_2 before remove the rest of the impurities in the CPU. The CPU purifies the CO_2 through the liquefaction of the flue gas, allowing to separate liquid CO_2 from the incondensable gases. These are sent back to the VPSA to recover the CO_2 that has not liquefied in the CPU. Finally, a minimum purity of 99.999 mol% is obtained at the output of the CPU. The total process CO_2 recovery depends on the impact of CPU recycle on the VPSA. Traditionally, the target for capture processes is to achieve 90 % recovery even if in recent papers, this target increases to reach a value of 95 % or more. Nevertheless, this value could be higher while remaining economically viable. That's why in this study, recovery will be an optimization objective. The **objective of this work is to minimize the electrical consumption of the CO_2 capture process** by globally optimizing the hybrid process, VPSA and CPU. Each process can be optimized for a specific CO_2 recovery and purity by minimizing the electrical consumption that is associated with a large part of the capture process cost. When the two processes are combined, the CO_2 recovery is fixed at the VPSA level, and the final CO_2 purity is determined with the CPU performance. This means that there is flexibility in the purity of the CO_2 at the VPSA output, which will have an impact on the electrical consumption. At fixed recovery, the more concentrated the CO_2 is, the higher the electrical consumption of the VPSA will be, but the lower the electrical consumption of the CPU will be. It is important to retrieve the right balance between the CO_2 purity and the electrical consumption of the VPSA and CPU in order to minimize the overall electrical consumption of the entire CO_2 capture process. Moreover, the recycled flux to the VPSA can modify the performances of the adsorption unit leading to different results in terms of purity, recovery, and energy consumption.

More precisely, the first part of the process is a 2-bed VPSA unit performing the Skarstrom cycle with pressure equalization step. Sequence of steps for one bed, in addition with the pressure profile is represented on Figure 13.



Bed 1	Adsorption		Pressure Equalization	Blowdown		Purge	Pressure Equalization	Pressu-rization
Bed 2	Blow-down	Purge	Pressure Equalization	Pressu-rization	Adsorption		Pressure Equalization	Blow-down

Figure 13: Sequence of steps and pressure profile for the cycle used in the VPSA unit (Costa et al., 2024b)

The first step of the cycle is the adsorption where the flue gas is sent to the column to adsorb mainly the CO_2 and to obtain a nitrogen-rich gas at the outlet of the column. The column is then connected to the second column which is at lower pressure to equalize the pressure and save mechanical work of compression and vacuum. The pressure is further reduced in the blowdown step to desorb the CO_2 in the column and retrieve it. A part of the nitrogen-rich stream of the column in adsorption step is used during the purge step to flush the CO_2 from the second column and increase the amount of CO_2 retrieved. Finally, the two columns are connected for the equalization of pressure, followed by a pressurization from the flue gas until the adsorption pressure is reached. In this cycle, the time of the blowdown step and the purge step must be equal to time of the adsorption step and pressurization step to keep the synchronization between the two beds. As indicated in section 3.2.1, zeolite 13X was chosen for its good CO_2/N_2 separation performance in dry conditions (CO_2 adsorption capacity, selectivity, etc.), the results already proven in simulation and pilot scale VPSA process for post-combustion CO_2 capture, and its commercial availability. It has to be noted that to process the 70 000 Nm^3/h of flue gas, five VPSA units are working in parallel to treat initially 14 000 Nm^3/h of flue gas.

The second part of the process is the CPU. This unit is inspirited by the Air Liquide Callide project in Australia and based on the study performed by (Costa et al., 2024a) described in Section 3.1. A schematic of this process is proposed on Figure 14 and the corresponding flow sheet developed in Aspen Plus software is provided on Figure 15. Six fundamental steps are present: (1) flue gas compression, (2) flue gas cooling, (3) CO_2 vapor–liquid separation, (4) CO_2 purification, (5) cold generation and (6) CO_2 compression. This unit purifies the CO_2 pre-concentrated by the 5 VPSA units. The minimum concentration at the inlet of the CPU is 50 mol% CO_2 to stay energetically interesting. The cryogenic unit plays a crucial role in purifying CO_2 and removes incondensable gases. This separation process is achieved by utilizing the unique properties of cryogenics, particularly the liquefaction of CO_2.

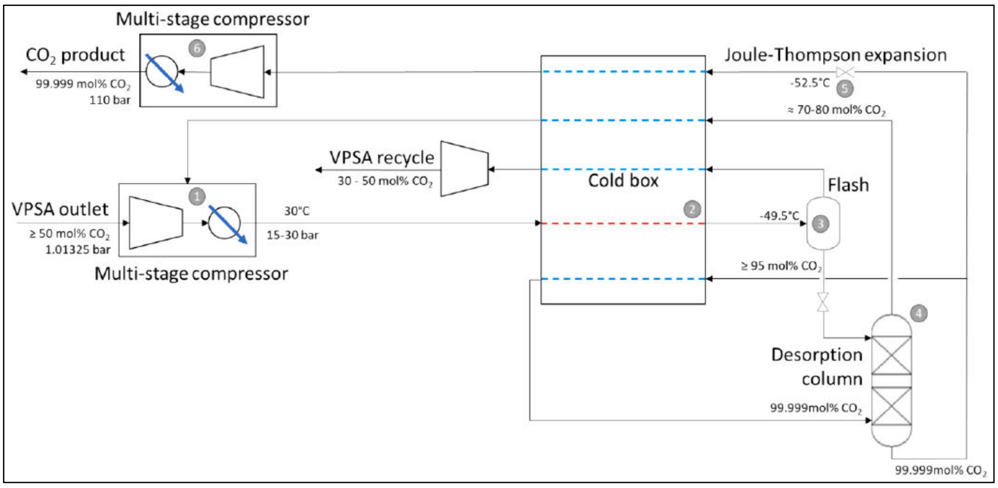


Figure 14: Schematic plan of the CPU (Costa et al., 2024b)

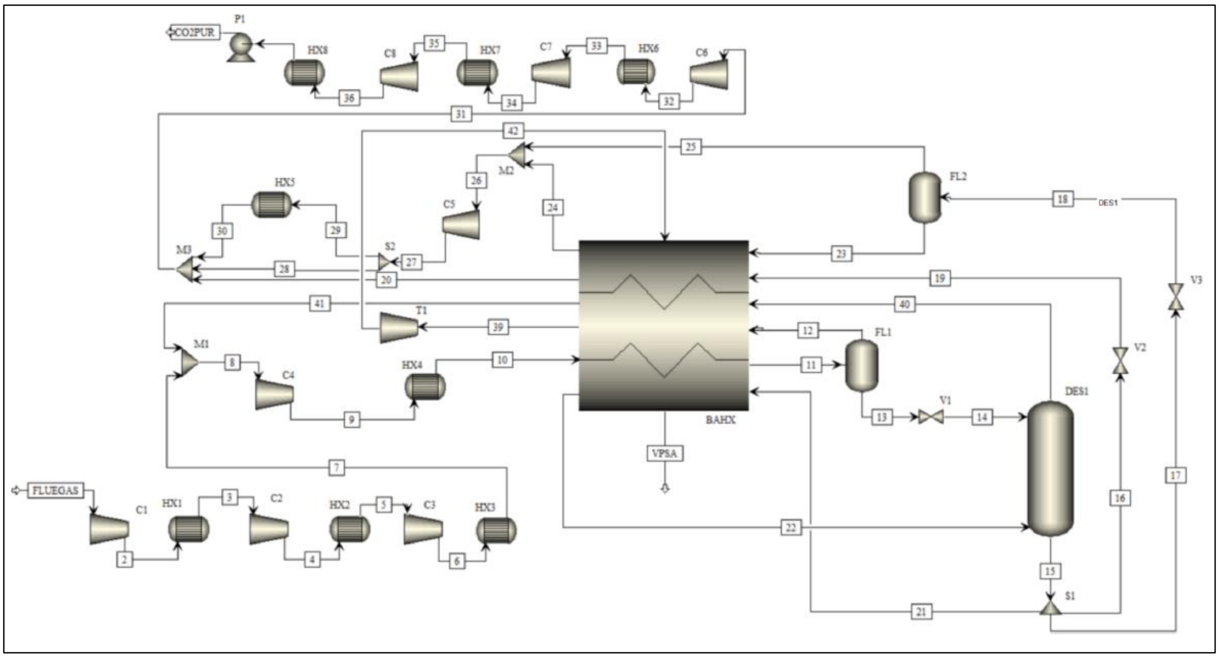


Figure 15: Aspen Plus® flowsheet developed for the CPU (Costa et al., 2024b)

To ensure efficient separation without the formation of dry ice (solid CO_2), a carefully controlled temperature limit of -54 ◦C is established. This temperature is deliberately kept just above the triple point of -56.6 ◦C at which CO_2 transitions between its solid, liquid, and gaseous phases. The concentrated CO_2 from the 5 VPSA units passes through a multistage compression system that includes intercooling with water (1). To achieve the flue gas liquefaction, multi-stream brazed aluminum heat exchanger (BAHX) is employed.

After liquefaction step, the liquid CO_2 is separated from non-condensable gases by using a flash separator (3). This separation step ensures that liquid CO_2 (>95 mol%) enters the process. To avoid losing the coldness from these gases, it can be efficiently recovered and utilized through BAHX. These gases are then expanded to generate energy before being returned to the VPSA processes, optimizing the overall efficiency of the plant. The liquid CO_2 is then fed into the desorption column (4). In this column, the impurities are effectively stripped by pure CO_2 vapor. This desorption process is fundamental to achieving a high CO_2 purity of 99.999 mol%. To further increase the efficiency of the plant, a fraction of the product liquid CO_2 is heated to provide pure CO_2 vapor to the column, while the remaining fraction is subjected to Joule-Thompson expansion (5). Then, the product CO_2 is compressed to reach the required supercritical pressure for injection into the pipeline distribution network, typically 110 bar (6). The expansion process generates the refrigeration required for liquefaction, contributing to the overall energy efficiency of the system.

All the details regarding the operating conditions, modeling parameters and costs calculation assumptions are provided in (Costa et al., 2024b).

3.2.3 Results of the VPSA-CPU process optimization

First of all, the surrogate model of the VPSA unit was used to evaluate the pareto of VPSA recovery and purity at different CO_2 concentrations in the inlet flue gas for a flow rate of 14 000 Nm³/h. Pareto plot is given in Figure 16 for a CO_2 concentration of 5, 10,15 and 20 %.

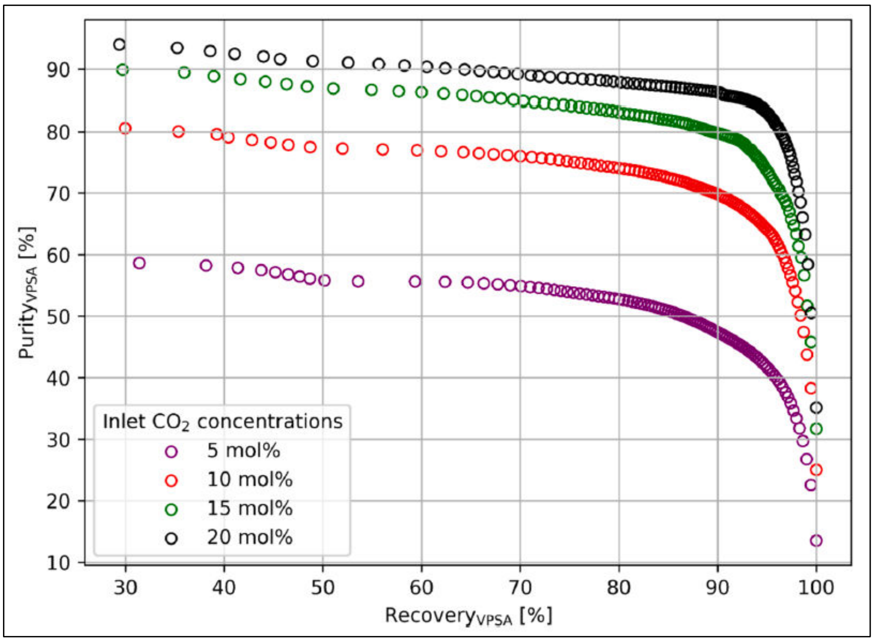


Figure 16: Pareto plot of the VPSA unit for different CO_2 molar fractions in the flue gas with a flow rate of 14000 Nm³/h (Costa et al., 2024b)

As observed, the VPSA unit can reach high recovery for all CO_2 concentrations. The maximum CO_2 purity obtained in the unit increases with the inlet CO_2 concentration. For all CO_2 inlet concentrations, a sharp decrease of purity is observed as the VPSA recovery increases. The decrease of purity is stepper between 95 and 100 % recovery for the VPSA due to an increase of purge time to recover all the CO_2 adsorbed.

Optimizing the CPU with an inlet flow rate of 10 000 Nm³/h and varying concentrations ranging from 50 to 85 mol% CO_2 demonstrates an interesting trend (see Figure 17). Indeed, as the CO_2 concentration in the feed from the VPSA increases, the electrical consumption of the CPU is decreasing, which presents a promising energy-saving prospect for this unit. These findings are in line with the broader observations made across various capture units, all of which point towards reduced electrical consumption as CO_2 concentrations rise. Furthermore, an interesting correlation emerges in terms of the recycled flow. This flow is directly linked to the decreasing concentration of nitrogen within the system. The reducing nitrogen concentration implies a reduction in the volume of non-condensable components exiting the cold box during the flash separation process from the liquid CO_2. By definition, the higher the concentration of CO_2 in the VPSA feed, the more energetically advantageous it becomes for the CPU. However, in our quest for optimization, it remains crucial to determine the precise threshold at which these two processes, VPSA and CPU, reach their optimal balance, ensuring the most efficient and energy-effective operation.

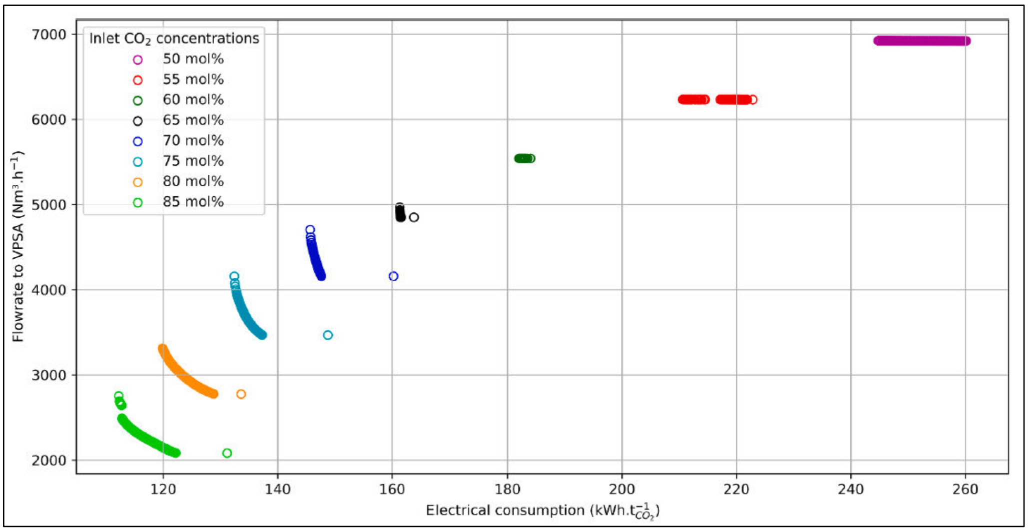


Figure 17: Pareto plot of optimization between electrical consumption and flow rate to VPSA for a stream of 10000 Nm³/h at different inlet CO_2 concentrations (Costa et al., 2024b)

After analyzing the parameters used for optimizing CPU performance, some interesting trends emerge regarding electricity consumption: **(i)** when the pressure in the cold box decreases, the electrical consumption also decreases, while the flow rate towards the VPSA unit increases, **(ii)** the cooling temperature of the flue gas is constant and **(iii)** thanks to the higher pressure operation, more CO_2 turns into a liquid form resulting in a lower flow rate to the VPSA unit. This comprehensive analysis reveals intricate relationships between various parameters and electrical consumption in CPU optimization. These findings highlight the importance of carefully tuning these parameters to strike a balance between process performance and energy efficiency.

Once both surrogate models were effectively established and validated, the optimization for the VPSA + CPU coupling was performed. The focus was on optimizing both recovery and electrical consumption. The primary objective is to maximize the recovery process while concurrently minimizing electrical consumption. A range of inlet concentrations, varying from 5 to 20 mol% with 5 mol% increments, for a flue gas of 70 000 Nm³/h was examined. Figure 18 displays the results of the combined process optimization. The higher the concentration of CO_2 the inlet flue gas, the less electricity is consumed.

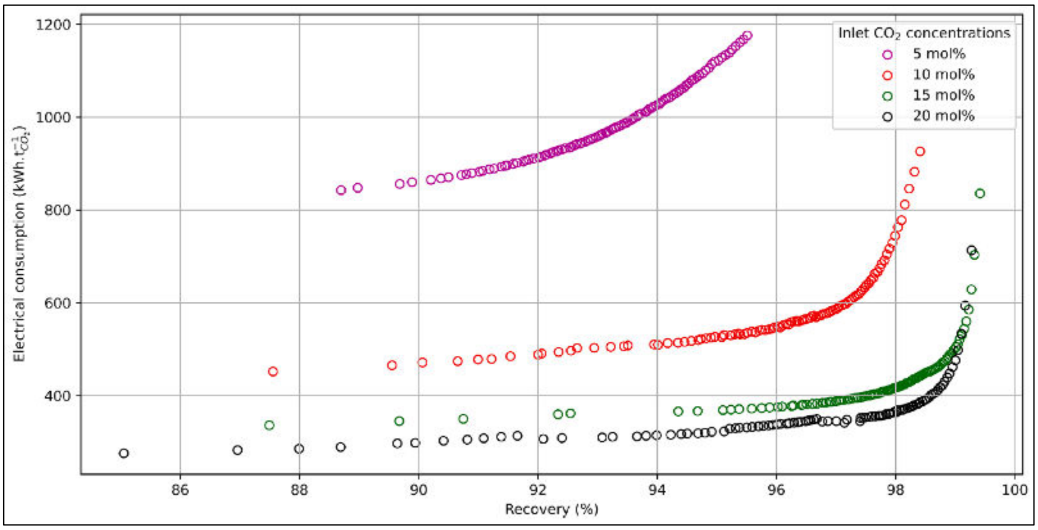


Figure 18: Pareto plot of the optimization between electrical consumption and global CO_2 recovery for different inlet CO_2 concentrations (Costa et al., 2024b)

To achieve the highest recovery rates, it is therefore necessary to increase electrical consumption. As the results demonstrate, recovery rates approaching 99 % are achievable thanks to VPSA technology. Therefore, it is reasonable to inquire about the desired recovery rate. To address this question, it is essential to consider the electricity prices and carbon taxes in order to determine the optimum recovery point. Indeed, the fluctuation of electricity prices is a topic of utmost importance in the fields of energy and economics. This variability is influenced by a multitude of complex factors, including the availability of energy resources, the production costs, the demand, the government policies, the international energy market fluctuations, and the technological advancements. In this study, the process under investigation consumes only electricity. To examine the impact of electricity prices on the total process cost, it was varied from 50 to 200 €/MWh. Electricity price variation will have an important impact on the optimum recovery at minimal total cost. Figure 19 displays the minimum total cost of the VPSA-CPU unit as a function of carbon tax and CO_2 concentration within this range of electricity prices.

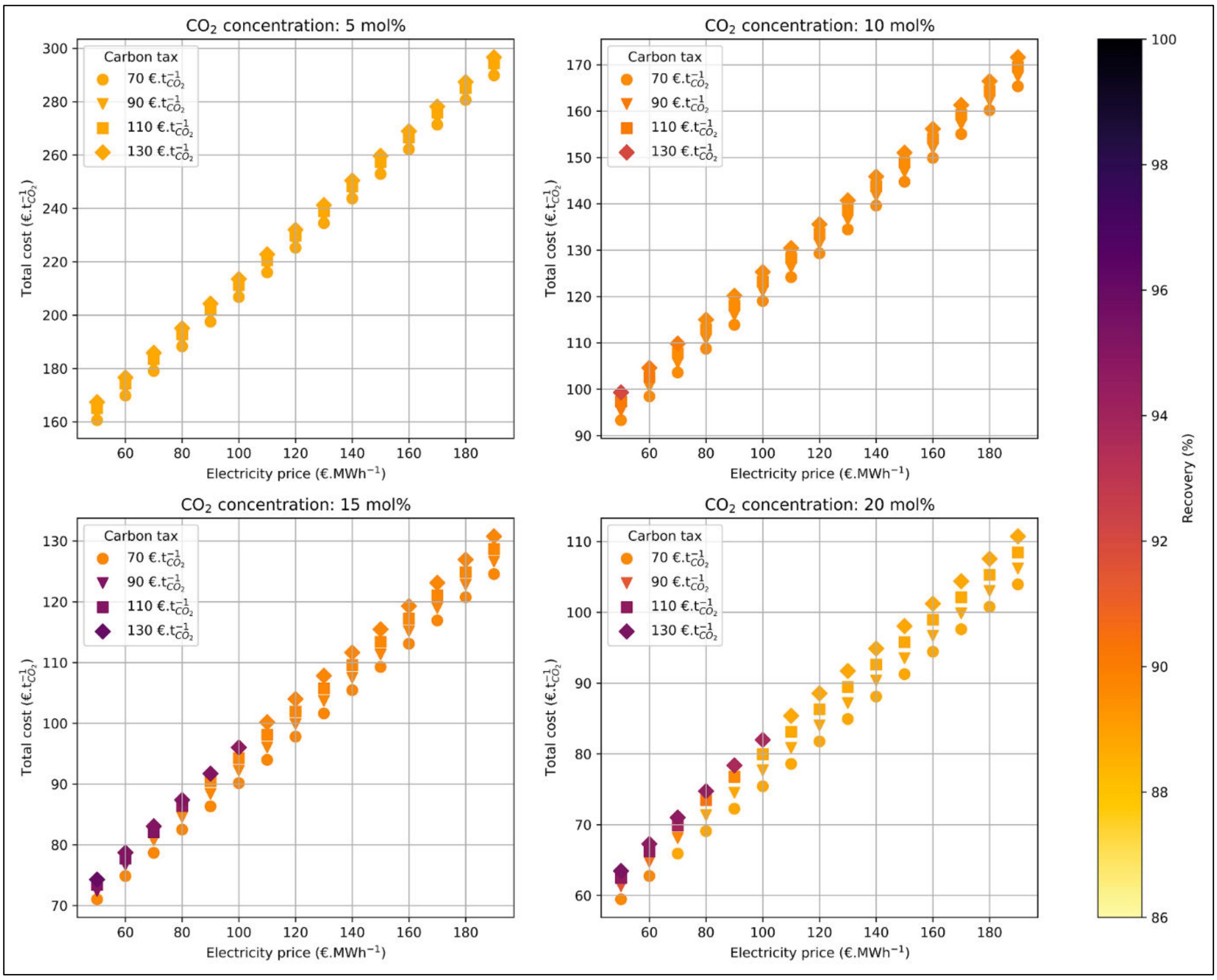


Figure 19: Optimum total cost for several carbon taxes in function of the electricity price and the CO_2 inlet concentrations (Costa et al., 2024b)

Notably, the optimal recovery rate is higher for lower electricity prices. For the 5 % concentration, this technology demonstrates a substantial cost disadvantage over the carbon tax. Consequently, it is presently not prudent to consider such installations for concentrations at this low level. This process becomes interesting for 10 % concentration for a high carbon tax (>130 €/t_{CO2}) and a low electricity price (<50 €/MWh). However, for other concentrations, if the electricity cost remains below 100 €/MWh and the carbon tax is at least 100 €/t_{CO2}, this technology proves to be relatively compelling. Furthermore, **achieving a recovery rate exceeding 90 % remains economically viable and attractive**. Naturally, as highlighted in Section 3.1 for the CPU process applied to oxyfuel flue gases, the choice of the electricity mix will also influence the global CO_2 balance of the installation and the effective amount of CO_2 avoided. This aspect was also investigated in the DRIVER project by (Costa et al., 2024b).

The results of this study indicate that the hybrid system achieves over 90% CO_2 recovery for the range of flue gas concentrations considered, while ensuring the production of high-purity CO2 (>99.99%) suitable for transport.

Generally speaking, for CO_2 capture-purification technologies using electricity on a massive scale, the analyses carried out show the importance of having the lowest possible carbon electricity mix in order to maximize the net reduction in CO_2 emissions.

4 CO_2 capture and conversion to methane or methanol

4.1 Context of the study and simulated CCU processes

Once captured, CO_2 can be used as a raw material to produce value-added chemicals. Carbon Capture and Utilization (CCU) has a strategic role to play in the decarbonization of energy resources and the **transition to a climate-neutral and defossilized economy**. **E-methanol**, **synthetic natural gas (SNG)** and e-kerosene are promising ways of converting captured CO_2. In this context, the aim of this study was to propose an optimized and integrated process for converting CO_2 into methanol, and to compare it with the process for converting CO_2 into SNG from an energy, economic and environmental point of view.

The power to methanol system investigated in this work is combined with carbon capture and utilization (CCU) chain where a flue gas emitted from a conventional cement plant (see Figure 20) is treated. In this chain, three units are included: the water electrolysis unit for the green hydrogen production, the post-combustion CO_2 capture unit, and the CO_2 conversion consisting in a catalytic CO_2 to methanol conversion unit.

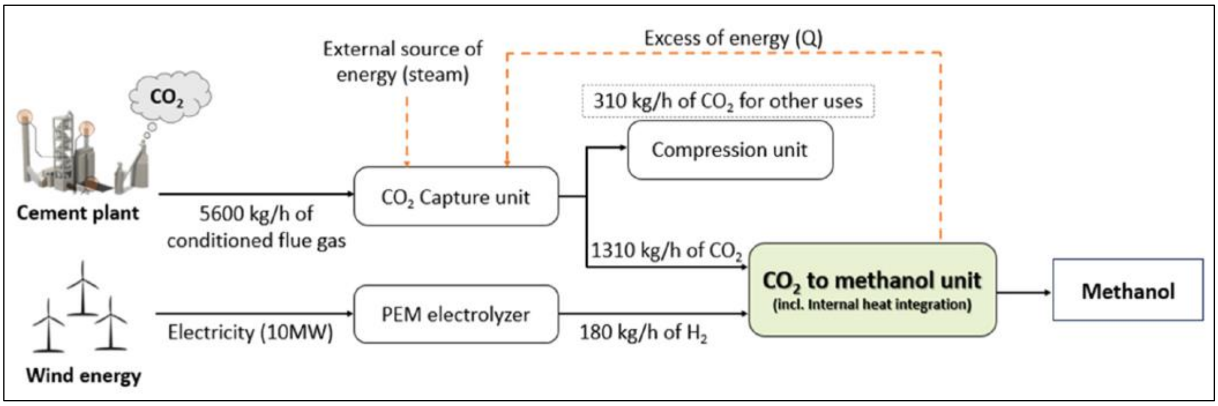


Figure 20: Conceptual power-to-methanol system combined with CCU process (Djettene et al., 2024)

To generate green hydrogen, a polymer electrolyte membrane electrolysis (PEM) was considered in this work due to its high potential for cost reduction, durability, and efficiency improvement. It is assumed that a 10 MW PEM stack (biggest single stack scale currently commercialized), linked to a wind park, corresponds to approximately 180 kg/h of hydrogen production (with an associated oxygen production of 8 kg_{O2} per kg_{H2}). It is worth noting that the process for producing H_2 was not within the focus of the present study (literature data used). The entire process, including the carbon capture unit, was scaled based on the hydrogen production one.

The integrated flowsheet of the CCU unit, developed in Aspen Plus® software, is provided in Figure 21. Concerning the CO_2 capture unit, the present study considers an advanced post-combustion capture unit based on the work outlined by (Chauvy et al., 2021). The selected solvent is an aqueous blend composed of 10 wt% of methyl diethanolamine (MDEA) and 30 wt% of Piperazine (PZ).

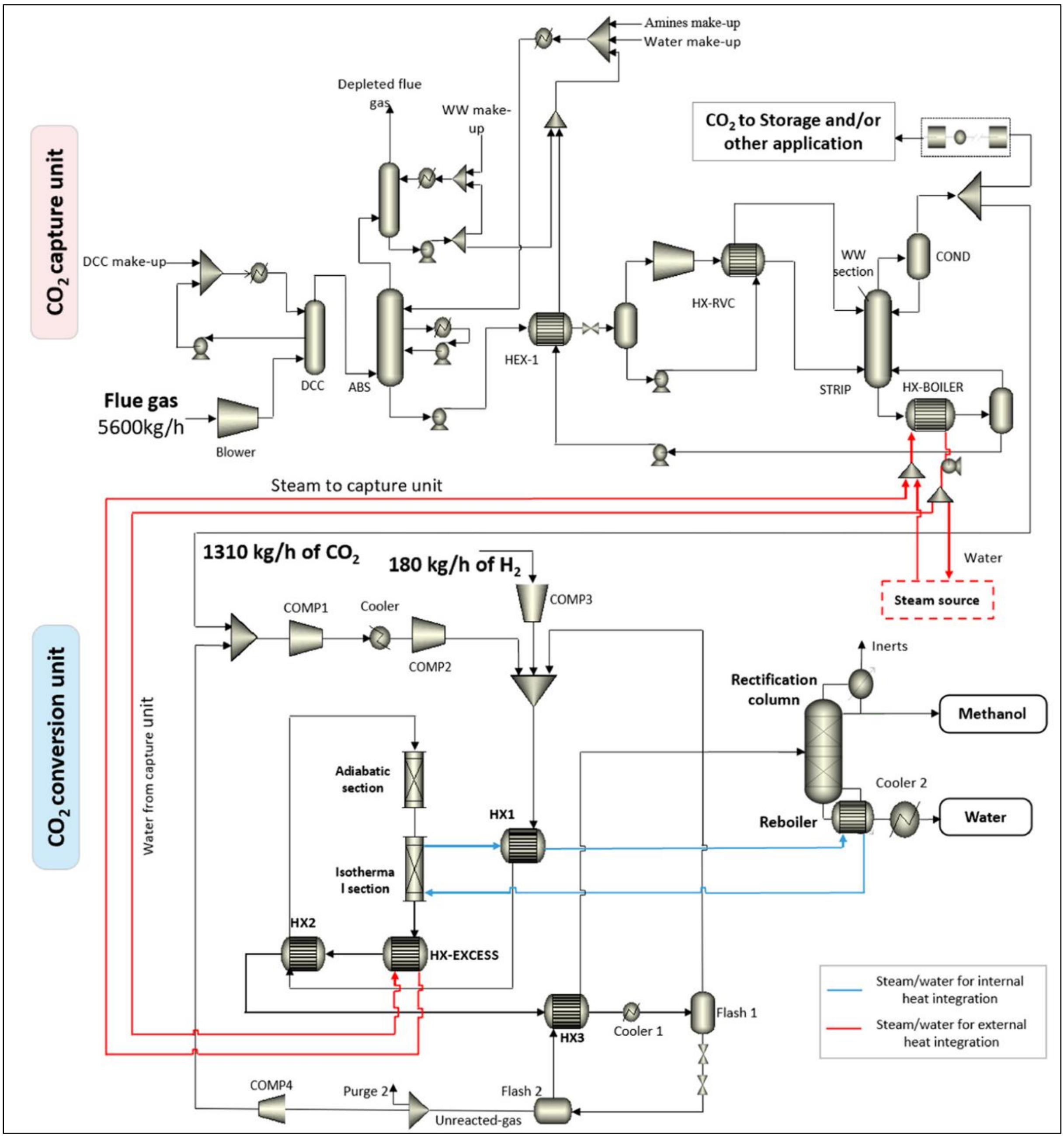


Figure 21: Aspen Plus® flowsheet of the integrated CO_2 capture-conversion to methanol plant (Djettene et al., 2024)

As represented on Figure 21, the implemented CO_2 capture process includes a Rich Vapor Compression (RVC) process combined with an Inter-Cooled Absorber (ICA) and two Water-Wash (WW) sections, interconnected with a conventional absorption-regeneration process. Such kind of process configuration and solvent has shown his interest as illustrated in Section 2. In order to compare the CO_2 to methanol process and the CO2 to SNG one, the size of the capture unit, directly linked to the realistic scale of a single stack (namely 10 MW) for the H_2 production unit, is the same as considered in the work of (Chauvy et al., 2021). They verified that the surplus energy reclaimed from the methanation unit is allocated to solvent regeneration within the capture unit, maintaining self-sufficiency in thermal energy within the conversion unit. This results in a possibility to treat 10 % of the global cement plant's flue gas (5600 kg/h). Considering the Brevik cement plant's flue gas in Norway as case study, the gas to be treated is injected at 1.2 bar and 146.6◦C. Its constituents include N_2, CO_2, O_2, and H_2O at percentages of 64.7, 20.4, 8.6, and 6.3 mol% respectively. It has to be noted that the CO_2 absorption ratio is equal to 90 mol.% resulting in a mass flow rate of 1620 kg of captured CO_2 per hour (with a purity of 98 mol.% at 4.96 bar and 45°C). The captured CO_2 and green H_2 are sent to the conversion unit with a stochiometric ratio H_2/CO_2 equal to 3 at the inlet of the installation, which means that 1310 kg/h of CO_2 is used by the process. The residual portion of the captured CO_2 (310 kg/h) undergoes compression up to 110 bar through a three-stage compressor with intercooling down to 40°C. This step is essential for transporting the CO_2 to alternative utilization sites or for storage purposes.

Regarding the CO_2 conversion unit, the Redlich-Kwong equation of state was employed for computing gaseous properties, while the gas-liquid equilibrium calculations within the rectification column were based on the UNIFAC model. As illustrated on Figure 21, the H_2 and CO_2 are fed with a pressure of 30 and 4.96 bar respectively. They are compressed up to 65 bar using one compressor for H_2 and three stages compressor with intermediate intercooling for CO_2. They are then mixed and preheated to 230°C (Heater 1) before entering in a plug-flow reactor comprising a first adiabatic section followed by a second isothermal section operating at 250°C. The model of Graaf has been considered to describe the reaction kinetics. This model was established using $CuO/ZnO/Al_2O_3$ solid catalyst where all reactions are presumed to follow a dual-site Langmuir-Hinshelwood- Hougen-Watson (LHHW) mechanism. Three reactions are involved: (1) the CO_2 hydrogenation, (2) the Reverse Water Gas Shift (RWGS) and (3) the hydrogenation of CO. The RWGS reaction is endothermic while the reactions of CO and CO_2 hydrogenation are exothermic. The Gas Hourly Space Velocity (GHSV) value has been set at 10000 h^{-1} while ensuring a temperature of 250°C at the exit of the adiabatic section, which corresponds to the operating temperature of the isothermal section. The product stream leaving the reactor is subsequently cooled to 40°C and directed into a sequence of flashes. These flashes are employed to separate unreacted gases, which are recycled back to the reactor inlet after undergoing compression and preheating. To avoid the inert gases and by-products accumulation within the reaction loop, a portion of the recycled gases is removed (Purges 1 and 2) (1.5 % for each). The liquid phase, consisting of methanol and water, is heated to 90°C and conveyed to a rectification column. This step aims to separate the components, ensuring a high purity level of 99.85 wt% for methanol (adhering to the standard in the methanol market) and 99.9 wt% for water, thus avoiding its post-process treatment. To minimize the energy demand of the rectification column, a parametric optimization has been performed. A Design of Experiments conducted using JMP software and Aspen Plus® simulations was performed to identify the best parameters combination (reflux ratio, reboiler duty, temperature of crude methanol, temperature, number of stages and feed stage number). The aim is to strike a balance, seeking optimal purities for methanol and water while minimizing the energy consumption of the rectification column's reboiler.

Finally, to systematically integrate heat between processes (CO_2 capture and conversion) and determine the recoverable surplus energy from the CO_2 conversion unit, a comprehensive pinch analysis was conducted. The methodology consists in collecting the hot and cold streams data, passing through the exchangers (coolers and heaters) to build the hot and cold curves which represent the released and required heat respectively (composite curves). For the evaluated system, a minimum temperature difference (ΔT_{min}) has been set at 10°C. The heat released by the exothermic reactions is recovered from the isothermal reactor using a medium pressure steam (at 174°C and 8 bar) as utility stream. The results of the pinch analysis were used to efficiently integrate the conversion unit in a first stage (internal heat integration) by recovering a maximum energy. Additionally, according to these analysis results, if an excess energy is available, it could be used for the capture unit in a second stage (external heat integration).

All the details regarding the operating conditions, modeling parameters and costs calculation assumptions are provided in (Djettene et al., 2024) for the CO_2-to-methanol case and in (Chauvy et al., 2021) for the CO_2-to-methane case (developed in a previous study at UMONS).

4.2 CCU simulation results for the CO_2-to-methanol and CO_2-to-SNG cases

4.2.1 Techno-economic and environmental results

The Levelized Cost of the Plant (LCoP) for the optimized processes, expressed as the sum of annualized CAPEX (CAPital Expenditures) and OPEX (OPEration EXpenditures) divided by the annual production of methanol or SNG (on a mass quantity basis (ton of product) or an energy basis (GJ of the product, on a LHV (Low Heating Value) basis) are compared on Figure 22 (a) and (b) respectively considering three cases: (i) excluding expenses of hydrogen production, (ii) incorporating expenses associated with hydrogen production and (iii) considering the costs linked to hydrogen production and revenues from oxygen and methanol/SNG selling (87.4 €/ton of O_2, 71.83€/MWh for natural gas and 510 €/ton of methanol).

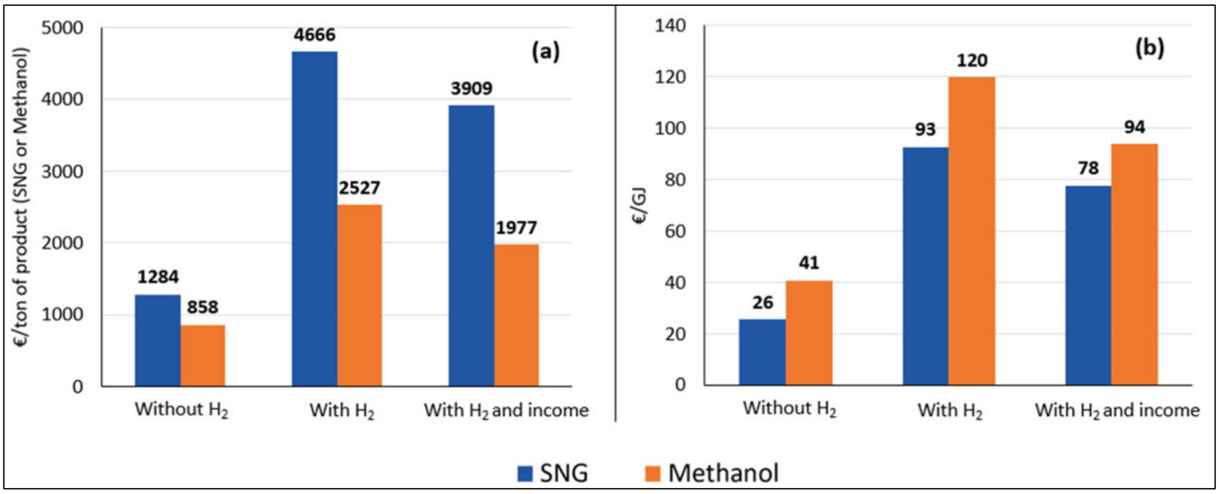


Figure 22: LCoP related to the CO_2 to SNG and CO_2 to methanol plants expressed in: (a) €/ton of product and (b) €/GJ. (Djettene et al., 2024)

It is worth noting that the annual production is assumed to reach 7124 ton of methanol against 3512 ton of SNG per year for each plant. This difference leads to a **lower LCoP of the CO_2 to methanol plant when considering the cost per ton of product**. Considering the **cost of MJ (LHV basis)**, this trend is reversed and the **LCoP of SNG is lower thanks to its higher LHV comparing with methanol**. The most attractive option is therefore dependent on the final application of the product. When the costs of H_2 production are considered, the LCoP of each plant is increased by 280 % and this highlight the weight of the H_2 production costs on such processes. Even if the revenues are considered, both plant remaining costs are not fully compensated. It is interesting to note that the production costs of both plants are almost identical when considering the cost per ton of converted CO_2. However, when considering hydrogen production (and the resulting incomes from SNG/methanol such as O_2 selling), the cost of the SNG plant becomes higher than that of the methanol plant (due to the stoichiometry $H_2/CO_2 = 3$ for methanol case and 4 for the SNG one).

Figure 23 shows the sensitivity analysis results applied to the LCoP of both systems. The **major cost driver of the LCoP in each case is the electricity price** which affects mainly the hydrogen production. Variations in steam price affect the LCoP of CO_2 to methanol process especially at the upper boundary. The steam price has no effect on the CO_2 to SNG one (steam generated internally through heat integration). Among other parameters, the electrolyzer cost (CAPEX PEM) has the most substantial impact on the economic feasibility of both processes.

Concerning the environmental assessment, the CO_2 capture and conversion steps were included in the system boundaries along with the hydrogen generation process. Therefore, all processes are accounted for on-site, taking into consideration heat integration, while disregarding the environmental impacts and energy needs associated with transportation and storage. Infrastructures were not included in the study.

The **functional unit (FU)** is defined as the production of one ton of the product. Two scenarios were defined to get conclusive results regarding the environmental impacts (see Figure 24):

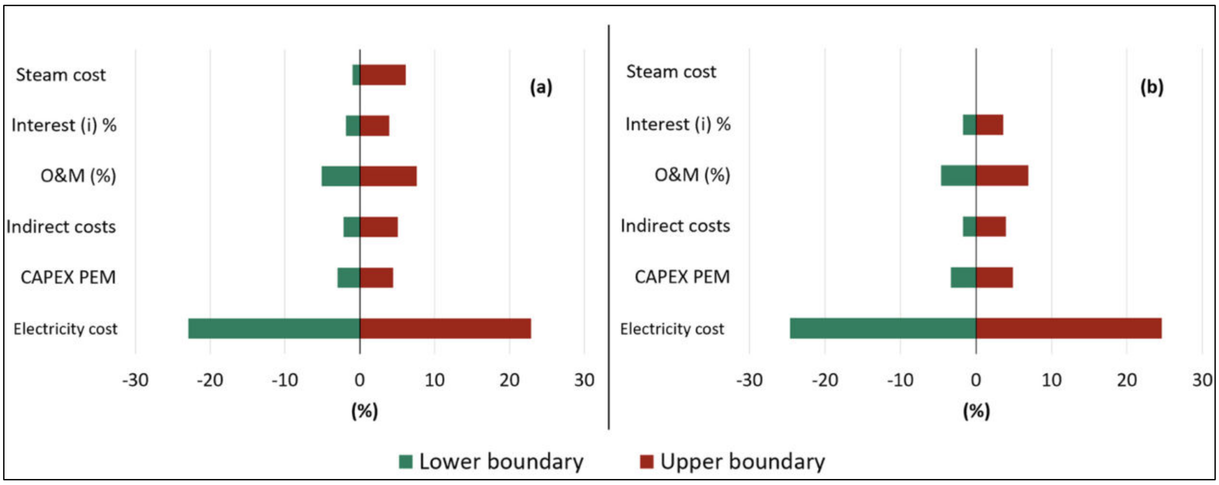


Figure 23: Sensitivity analysis on the cost of production of methanol (a) and SNG from CO_2 (b) (Djettene et al., 2024)

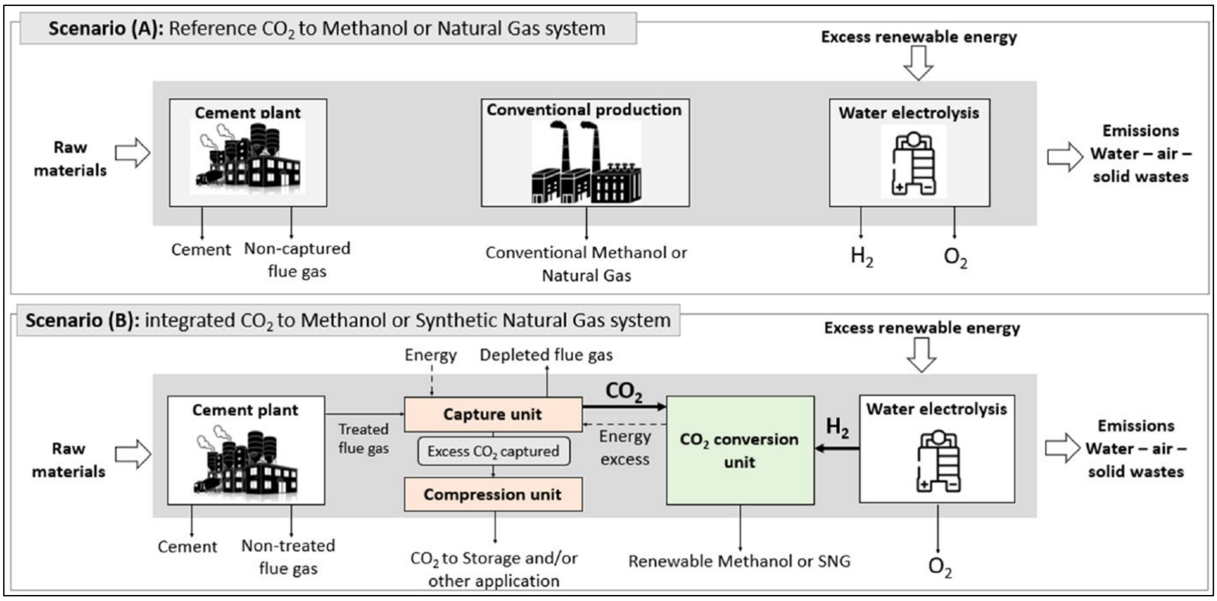


Figure 24: Defined scenarios for the environmental assessment (Djettene et al., 2024)

- **Scenario (A):** this reference scenario includes a cement plant without CO_2 capture nor conversion units. The assessment considers a methanol production unit reliant on fossil resources, while hydrogen production is assumed to utilize surplus renewable energy generated fk,rom wind turbines. The BAT cement plant relies on aggregated data obtained from the EcoInvent database and literature sources. Data concerning conventional methanol production from natural gas is sourced from the EcoInvent database.

- **Scenario (B):** an integrated scenario combining CO_2 capture and conversion to methanol, a portion of the captured CO_2 is used onsite to produce methanol, utilizing renewable hydrogen. The rest of the captured CO_2 is compressed for transport to storage or alternative applications. The system also integrates thermal energy between the capture and conversion units.

It should be noted that the environmental assessment results reported by (Chauvy et al., 2021) and carried out for the CO_2 to SNG case were updated (in terms of calculation methods and data base) in order to highlight the main differences with the CO_2 to methanol case, the same methodology being applied to both cases. Life Cycle Assessment (LCA) has been performed focusing on two impact factors: Climate Change (CC) and Fossil Depletion (FD). The technological parameters of the CO_2 capture and conversion units standardized to the production of one-ton of methanol are presented in Figure 25.

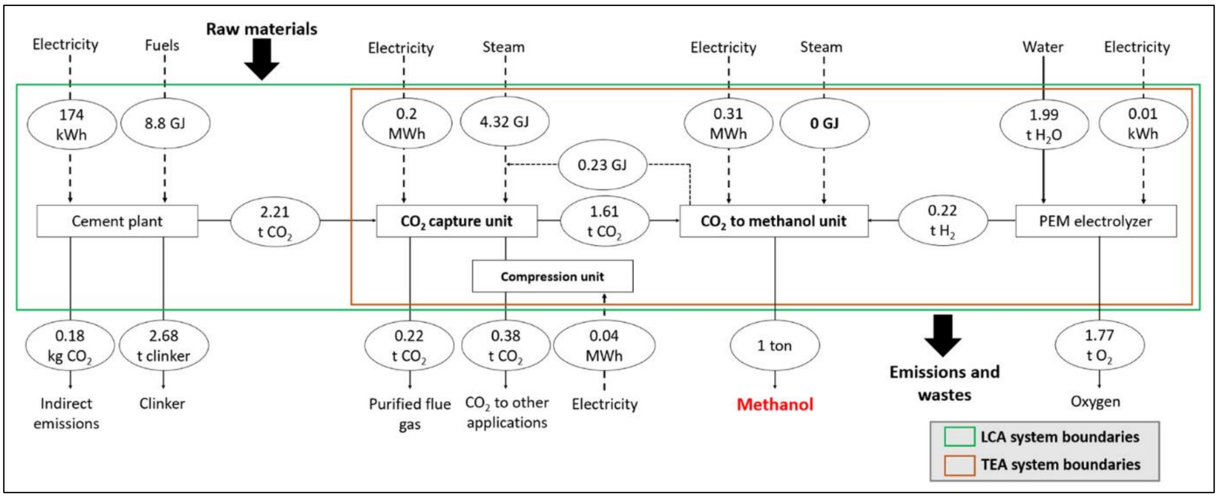


Figure 25: Parameters of the CO_2 to methanol plant standardized to the production of one-ton methanol (FU) (Djettene et al., 2024)

Regarding the climate change impact, a **net CO_2 emission reduction by 70 %** between scenario (A) and scenario (B) is seen in the CO_2 to SNG route and a reduction by 60 % in the methanol route (see Climate change results on Figure 26 (a) and (b) respectively).

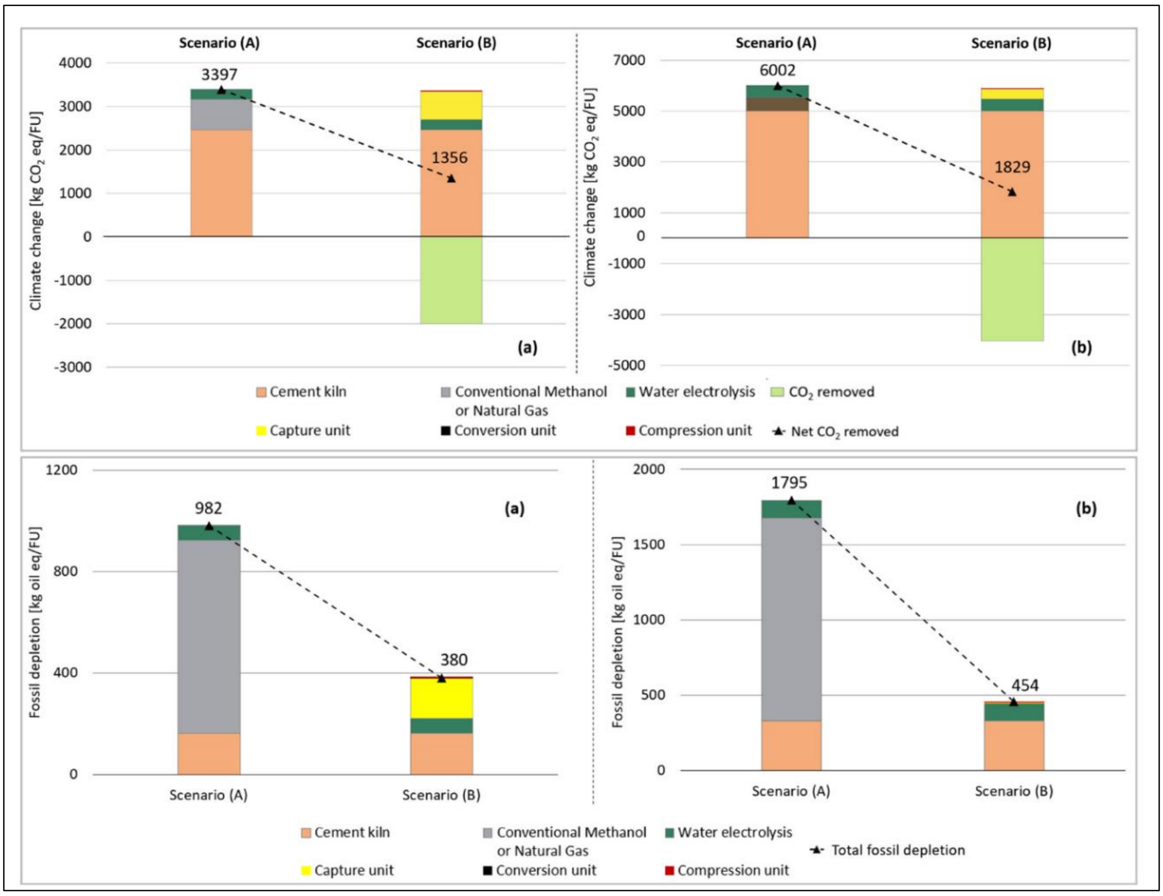


Figure 26: Climate change and fossil depletion impacts of both scenarios and routes: (a) CO_2 to methanol and (b) CO_2 to SNG (Djettene et al., 2024)

It is worth noting that the global thermal energy required for solvent regeneration in the capture unit is supplied by the heat surplus from the conversion unit. In the CO_2 into methanol case, only a small part, approximately **5 %, of the heat demand for the solvent regeneration is provided**. A **complete energetic integration can be achieved in the SNG route**. This is due to the methanation process being significantly more exothermic compared to the CO_2 to methanol process. Therefore, for this latter, the steam required for solvent regeneration must come from an external source. For the environmental performance assessment, a generic data from the EcoInvent database was utilized, which considers the average European fuel mix used in the chemical and petrochemical industry: approximately 57 % natural gas, 14 % coal, 12 % oil, 10 % refinery gas, with the remainder from other sources. Regarding the fossil depletion impact, results for both scenario in the case of CO_2 to methanol and CO_2 to SNG are also presented in the lower part (FD results) of Figure 26 (a) and (b) respectively. A reduction of more than 60 % was noticed (75 % in SNG route and 61 % in methanol route). Therefore, the **environmental benefits of integrating CO_2 capture and conversion to either SNG or methanol have been demonstrated**. This advantage primarily stems from the advanced CO_2 capture process considered, enabling the capture of a significant amount of CO_2 with a fixed energy input. In the case of conversion to SNG, there is an additional benefit from recovering the thermal energy released during the methanation process, leading to higher savings in terms of fossil depletion in comparison with the conversion to methanol where a large quantity of steam must still be provided by an external source.

4.2.2 Summary of the CCU simulations of the CO_2-to-methanol and CO_2-to-SNG cases

An optimized reactor configuration in the CO_2-to-methanol unit was successfully implemented in Aspen Plus® software, leading to thermal energy self-sufficiency for the conversion unit. Thermal integration with an advanced capture unit (cf. advanced, non-demixing configuration, as discussed in section 2.1) was carried out. It was shown that in the case of methanol, 5% of the heat requirement could be supplied by the conversion unit, while 95% had to be supplied via an external steam source. It should be noted that in the case of SNG, the entire heat requirement could be supplied via such thermal integration, due to the greater exothermicity of the conversion reaction.

It could be seen that **methanol is most cost-effective on a mass basis than SNG**, corresponding to the case of the CO_2-based product is used as a feedstock to synthesize other chemicals. As an energy carrier, and therefore **on an energy basis, SNG remains the most attractive**.

On an environmental point of view, compared with the reference scenario (no CO_2 capture, products supplied by fossil fuels as currently in the majority), a net reduction in CO_2 emissions of 70% in the case of conversion of CO_2 to SNG and 60% in the case of its conversion to methanol has been demonstrated. As for the impact on the depletion of fossil fuels, reduction of around 75% for the conversion of CO_2 to SNG and 61% for the conversion of CO_2 to methanol were noticed.

Globally, the study showed that, on the one hand, thinking in terms of energy integration between CO_2 capture and conversion units makes sense from an energy, economic and environmental point of view, and, on the other hand, that one of the key elements for the implementation of such a value chain remains the importance of having large quantities of green hydrogen available (hence, once again, the importance of an electricity mix that is as carbon-free as possible) and at the most competitive price possible (linked to the price of the electricity used for this production).

5 Direct Air Capture: technological review and integration with CO_2-to-methane process

5.1 Summary of the technological review on Direct Air Capture

5.1.1 Introduction on DAC context and technologies

The Intergovernmental Panel on Climate Change (IPCC) regularly point out that atmospheric CO_2 concentrations have been higher than ever since at least 2 million years, increasing from 315 ppm in the late 60s to more than 420 ppm in 2024. The IPCC also indicates that the rise of atmospheric CO_2 concentration over the industrial era is unequivocally due to emissions from human activities. Although emissions reductions were observed in 2020, mainly associated with measures to prevent the spread of COVID-19, global and regional climate responses to these temporary reductions were undetectable and above natural variability. To this extent, **immediate actions are essential to reduce both anthropogenic CO_2 emissions and atmospheric CO_2 concentration**, to keep global average temperatures from increasing 1.5 to 2°C above pre-industrial levels as stated in the Paris Agreement.

Regarding the CO_2 emissions limitations, several measures must be taken, such as the decrease of the energy consumption both by the industrial sector and the population, the use of other fuels (e.g., coal substitution biomass use), or the use of low-carbon energy sources (e.g., renewable energies, such as solar, wind, hydraulic, geothermal, and nuclear electricity production). Complementary to these actions, Carbon Dioxide Removal (CDR) processes can be applied with the motivation to reduce CO_2 emissions rapidly enough to keep within the carbon budget. Specifically, in the case of industrial CO_2 emissions coming from power plants and hard-to-abate facilities, such as cement and lime plants, implementing Carbon Capture Utilization and/or Storage (CCUS), as shown in previous sections of the current report, appears as a necessity to reduce CO_2 emissions from these sectors significantly. Over and above the deployment of technologies for reducing or avoiding new emissions, recent years have seen increased interest in "net negative CO_2 emissions" strategies for removing CO_2 from the atmosphere to reach the goals in terms of global temperature increase. As defined by the International Energy Agency, being carbon negative requires removing more CO_2 from the atmosphere than it is emitted. Different negative emissions approaches exist, such as afforestation, biochar, Biomass Energy use with Carbon Capture and Storage (BECCS), enhanced weathering, ocean liming, and Direct Air Capture (DAC). The present study, which led to a paper publication by (Chauvy & Dubois, 2022), was focused on the DAC approach.

DAC, also named DACC(U)S when combined with geological storage and/or utilization of the captured CO_2, refers to man-made technologies for selectively extracting CO_2 from ambient air and making it available in a concentrated form for future use or storage (see illustration on Figure 27). As a reminder, CO_2 is a minor component of air (only ~ 0.04 mol.% of dry air is carbon dioxide), while other air's constituents are nitrogen (~78 mol.%), oxygen (~21 mol.%), argon (~0.9 mol.%), a variable amount of water vapor, and other minor compounds including neon, helium, methane, ozone, and nitrous oxide.

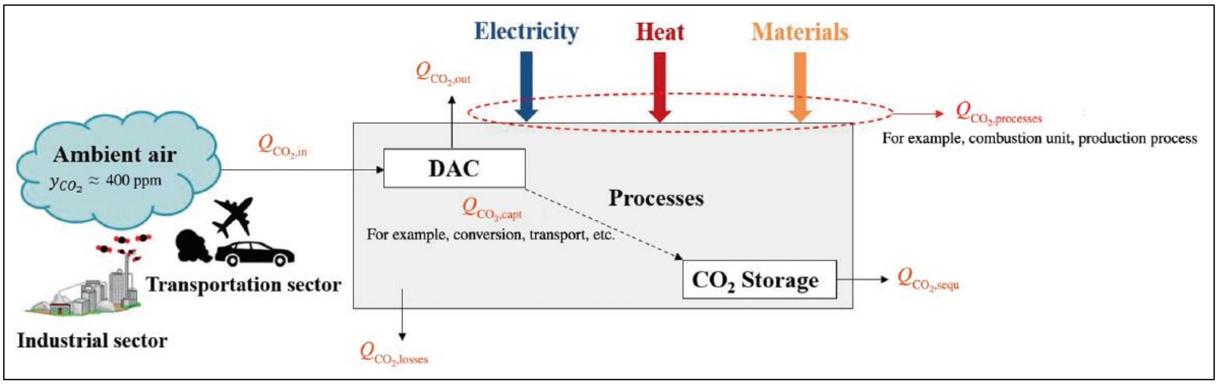
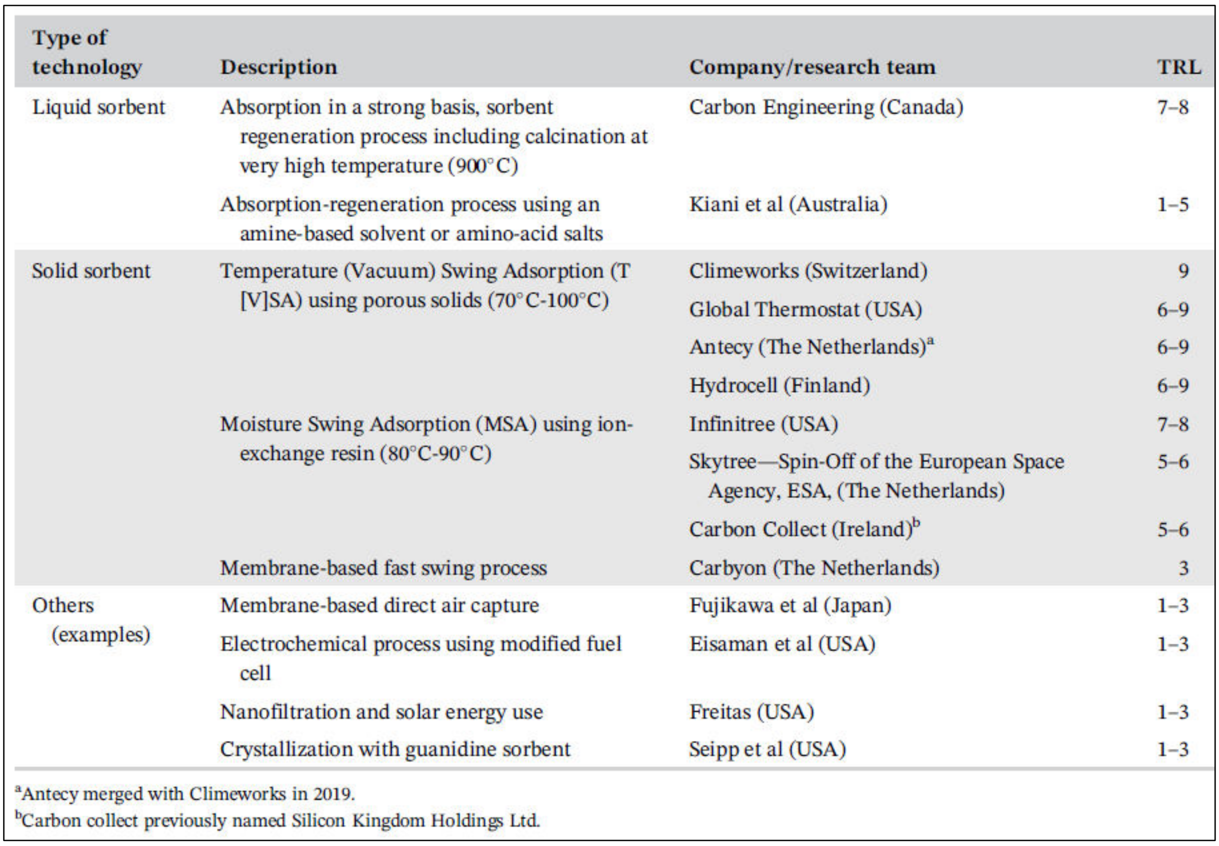


Figure 27: Generic illustration of a process chain including a DAC process and CO_2 storage (Chauvy & Dubois, 2022)

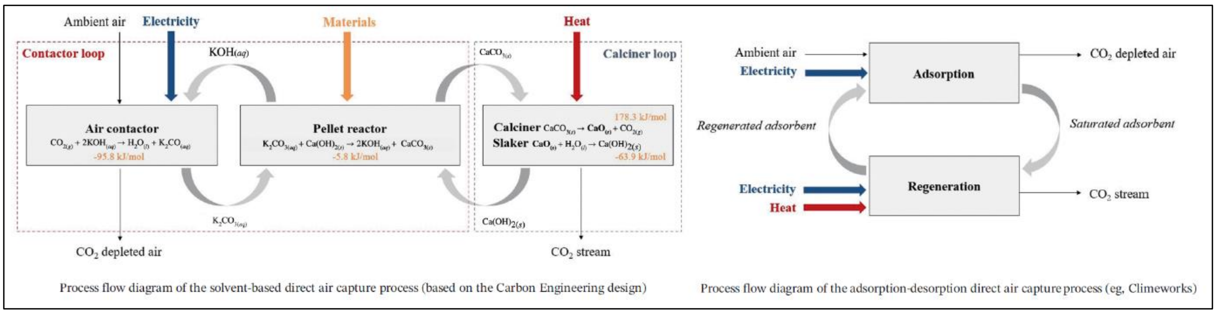
Among the variety of promising DAC technologies (listed in Figure 28), they are currently **two main processes** reaching the commercial stage, based on a **liquid solvent** or a **solid sorbent** (see Figure 29). One of the main interests of DAC is that it allows for location-independent sourcing of CO_2 so that it can be located in favorable areas, considering the availability of renewable energy, space, seasonal and geographical variability of temperature, humidity, wind, and air composition, CO_2 valorization option, etc. (Ozkan, 2021). This also supposes that energy demand (i.e., electricity and heat) is met.



Type of technology	Description	Company/research team	TRL
Liquid sorbent	Absorption in a strong basis, sorbent regeneration process including calcination at very high temperature (900°C)	Carbon Engineering (Canada)	7–8
	Absorption-regeneration process using an amine-based solvent or amino-acid salts	Kiani et al (Australia)	1–5
Solid sorbent	Temperature (Vacuum) Swing Adsorption (T[V]SA) using porous solids (70°C-100°C)	Climeworks (Switzerland)	9
		Global Thermostat (USA)	6–9
		Antecy (The Netherlands)[a]	6–9
		Hydrocell (Finland)	6–9
	Moisture Swing Adsorption (MSA) using ion-exchange resin (80°C-90°C)	Infinitree (USA)	7–8
		Skytree—Spin-Off of the European Space Agency, ESA, (The Netherlands)	5–6
		Carbon Collect (Ireland)[b]	5–6
	Membrane-based fast swing process	Carbyon (The Netherlands)	3
Others (examples)	Membrane-based direct air capture	Fujikawa et al (Japan)	1–3
	Electrochemical process using modified fuel cell	Eisaman et al (USA)	1–3
	Nanofiltration and solar energy use	Freitas (USA)	1–3
	Crystallization with guanidine sorbent	Seipp et al (USA)	1–3

[a] Antecy merged with Climeworks in 2019.
[b] Carbon collect previously named Silicon Kingdom Holdings Ltd.

Figure 28: Summary of DAC technologies (non-exhaustive list) (Chauvy & Dubois, 2022)



Process flow diagram of the solvent-based direct air capture process (based on the Carbon Engineering design)

Process flow diagram of the adsorption-desorption direct air capture process (eg, Climeworks)

Figure 29: Process flow diagrams of the two main DAC technologies (Chauvy & Dubois, 2022)

Based on the generic process chain including a DAC unit and the CO_2 storage as illustrated on Figure 27, different parameters can be defined. The amount of CO_2 captured ($Q_{CO_2,capt}$), in kg/h, corresponds to the difference between the CO_2 quantity entering the DAC unit ($Q_{CO_2,in}$) and the outlet ($Q_{CO_2,out}$) of this unit, Eq. (1) :

$$Q_{CO_2,capt} = Q_{CO_2,in} - Q_{CO_2,out} \tag{1}$$

The captured CO_2 must be transported to a storage site and/or converted into another product. These operations can lead to residual CO_2 emissions ($Q_{CO_2,losses}$), in kg/h, such as carbonation processes that cannot mineralize all the CO_2 captured. The effective amount of CO_2 sequestered is therefore defined by Eq. (2):

$$Q_{CO_2,sequ} = Q_{CO_2,capt} - Q_{CO_2,losses} \qquad \textbf{(2)}$$

Finally, all the processes used for capturing, transporting, converting and/or storing the CO_2 use electricity, heat, and materials, that could potentially lead to other CO_2 emissions ($Q_{CO_2,processes}$), in kg/h, need to be considered for calculating the net amount of CO_2 removed ($Q_{CO_2,removed}$), in kg/h, Eq. (3):

$$Q_{CO_2,removed} = Q_{CO_2,sequ} - Q_{CO_2,processes} \qquad \textbf{(3)}$$

A net-negative global DACCS process chain in terms of direct CO_2 emissions means that more CO_2 will be sequestered than emitted by the other processes ($Q_{CO_2,removed}>0$). In general, CO_2 equivalent emissions are also considered to compare emissions from various greenhouse gases on the basis of their Global Warming Potential (GWP), by converting amounts of other gases to the equivalent amount of CO_2. The main objectives of such process chain are not only to capture CO_2 from the air, but to ensure that it is net-negative in terms of carbon emissions, and also that the CO_2 will remain stored for a long period of time. Nevertheless, the production of carbon-neutral e-fuels (e.g., e-kerosene, SNG, etc.) can also be promising alternatives to support the energy transition to a low-carbon society.

Based on these considerations, the purpose of this study was to propose an up-to-date review of the current status of both Life Cycle Assessments (LCA) and Techno-Economic Assessments (TEA) on DAC(CS) processes, which are essential methodologies for a systematic evaluation to guide research and development towards commercialization, while ensuring the sustainability of promising technologies. The need for such review is also supported by a bibliometric analysis performed by (Zolfaghari et al., 2022) that emphasizes the lack of comprehensive systematic and impacts assessment research on DAC technologies.

5.1.2 Summary of the main information coming from the technological review performed

First of all, it is important to remind that unlike CO_2 capture applied to flue gases coming from emission points (power plants, cement plants, lime kilns, glass kilns, etc.), where the concentration is typically between 3% and 30%, the concentration of CO_2 in ambient air is closer to 0.042%. **Its capture therefore requires more energy** (thermodynamic constraint: maximum work required for separation, see Figure 30), and the question arises as to whether it makes sense to implement this technology, both economically and environmentally. The works performed by (Chauvy & Dubois, 2022) in the framework of the DRIVER project provides some answers.

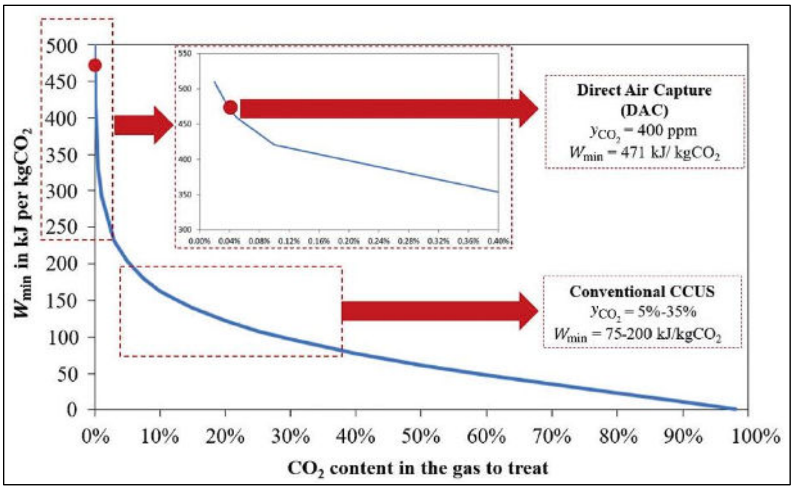


Figure 30: Minimum thermodynamic work for separating the CO_2 as a function of the inlet stream CO_2 content (Chauvy & Dubois, 2022)

The environmental impacts of DAC systems are by far related to energy consumption, mainly associated with the initial concentration of CO_2. Figure 31 presents the specific energy consumption provided in the literature, including the electricity demand (Figure 31-left) and the heat demand (Figure 31-right). Although the figures are not directly comparable since they were determined for specific system configurations, they show that the electricity requirement for the Climeworks DAC system is higher compared with the Carbon Engineering system. However, the heat demand for the Climeworks DAC system is generally lower, and can be covered from waste heat due to the low-temperature level. Some other DAC systems could potentially have lower energy requirement but they are still in the research and development phase. It is worth noting that little information is available regarding the energy requirements of other commercial units, including the Global Thermostat and Hydrocell DAC systems.

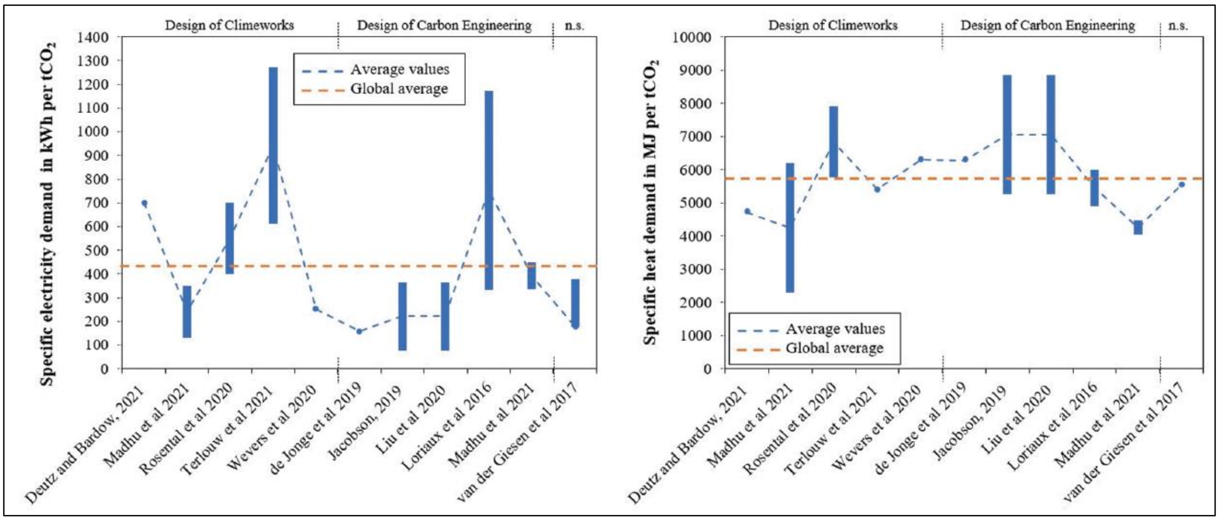
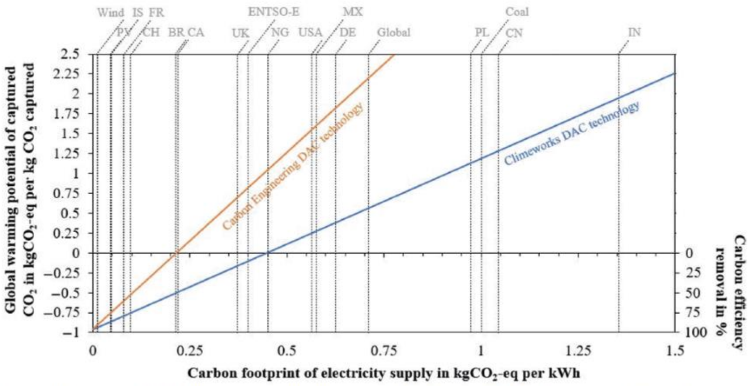


Figure 31: DAC specific energy consumption from different sources (left) electricity demand, (right) heat demand (Chauvy & Dubois, 2022)

Figure 32 presents the cradle-to-grave carbon footprint of a DACCS system including the contribution of the DAC equipment, the materials (adsorbents), the electricity and heat supply, as well as the subsequent storage. It can be seen a linear trend in the relationship between the carbon footprint of the captured CO_2 and the **carbon footprint of the electricity supply**. To this extent, such analysis confirms that the energy source is of significant importance to effectively help mitigate climate change and achieve negative emissions.



Global warming potential of captured CO_2 from ambient air when including subsequent CO_2 storage, according to the carbon footprint of the electricity supply. Figure based on data from Deutz and Bardow,[43] Terlouw et al,[49] and Madhu et al,[47] using linear regression (see these references for more details related to the systems involved). BR, Brazil; CA, Canada; CH, Switzerland; CN, China; DE, Germany; ENTSO-E, European energy mix; FR, France; Global, Global energy mix; IN, India; IS, Iceland; MX, Mexico; NG, natural gas; PL, Poland; PV, photovoltaics; UK, United Kingdom; USA, United States

Figure 32: Global Warming Potential (GWP) of DACCS systems for different carbon footprint of the electricity supply (Chauvy & Dubois, 2022)

Similar analysis for DACCU systems (combination of DAC with CO_2 conversion to synthetic fuel) is provided in (Chauvy & Dubois, 2022).

Finally, concerning the **economic aspect of DAC, current costs estimations are very uncertain** as many DAC sorbents need more tests in real ambient conditions to demonstrate their viability for commercialization. Nevertheless, DAC costs estimations from different sources are illustrated in Figure 33, including the recent costs estimations (2011-2021 period, see Figure 33-left) and the future costs estimations (2030-2050 period, see Figure 33-right).

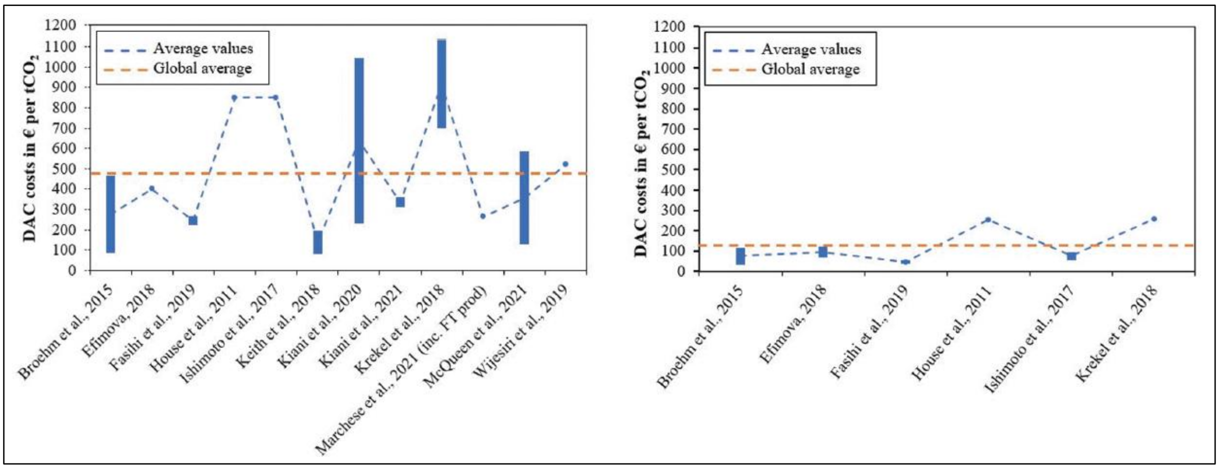


Figure 33: DAC costs estimations from different sources (left) recent costs estimations (2011-2021), (right) future costs estimations (2030-2050) (Chauvy & Dubois, 2022)

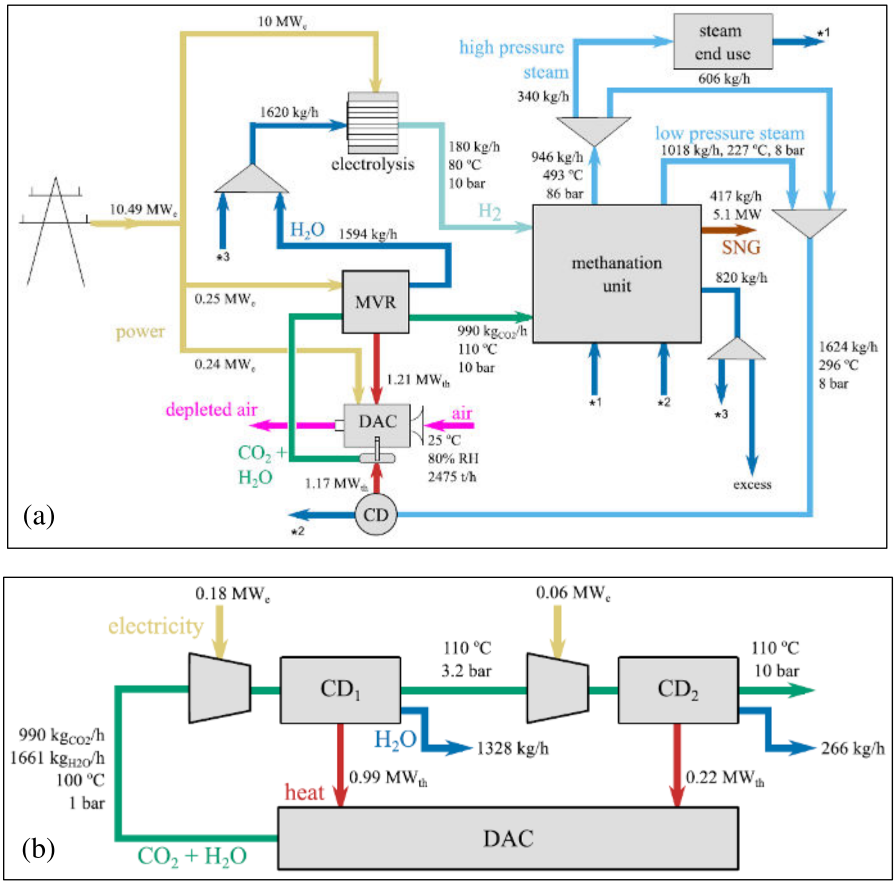
It can be pointed out that the **current DAC costs estimations vary from 80 €/t_{CO2} to 1133 €/t_{CO2}**, while the **future DAC costs are expected to be lower**, in the range from 34 €/t_{CO2} to 260 €/t_{CO2}. Considering the global average costs (see dotted lines on Figure 33), these are currently estimated to be 483 €/t_{CO2} (actual technology costs) and 135 €/t_{CO2} (future technology costs). It is also important to highlight that the variability in the DAC costs estimations could be associated with the calculation methods (eg, costs contributions considered such as total costs including indirect costs or only direct costs, etc., the data scarcity in capital and operation and maintenance costs for different DAC technologies, etc.). The source of the data used (eg, literature, simulation, lab-scale or pilot plant experimental data, or a combination of these) and divergent assumptions of energy demand may also play a significant role in this wide variability. Moreover, similarly to LCA studies, the definition of the costs system boundaries is also a very important factor influencing the economic performances of the system (eg, heat recovery included or not, full implications of the energy system investigated or not, CO_2 conversion process integrated or not, etc.). Further harmonization in terms of consistency is required to compare the TEA results.

To summarize, the study revealed that **DAC technologies are at very different levels of maturity** (TRL from 1 to 3 for some, up to 9 for others, see Figure 28) and involve various unit operations (adsorption, absorption, etc.), using different types of materials (liquid or solid) and types of energy (electrical and/or thermal). Most processes use adsorption (e.g. Climeworks) or absorption (e.g. Carbon Engineering), although more innovative solutions exist which are not at a TRL level high enough to be marketed. Regarding the environmental performances of DAC technologies, the **"carbon-negative" nature of this technology has been emphasized, particularly when combined with CO_2 sequestration**. However, the construction of large-scale DAC plants has an impact on other environmental aspects concerning land footprint, water and materials use. Moreover, the emission factor of the energy used for operating the DAC units has a direct impact on the effective atmospheric CO_2 concentration reduction. Concerning the economic aspect, it was shown that literature studies provide wide cost ranges, but future DAC costs are expected to fall thanks to technological development.

5.2 Heat integration of a DAC process with a CO_2-to-SNG conversion unit

5.2.1 DAC-CO_2-to-SNG processes simulated

Another study, carried out by (Coppitters et al., 2023) at UCLouvain in collaboration with UMONS, looked at the **integration of a DAC process with a synthetic natural gas (SNG) conversion unit** (DAC - Power-to-Gas (PtG)) and the associated 4E analysis (energy, exergy, economics and environment). The study also included a quantification of uncertainty. The processes simulated are represented on Figure 34.



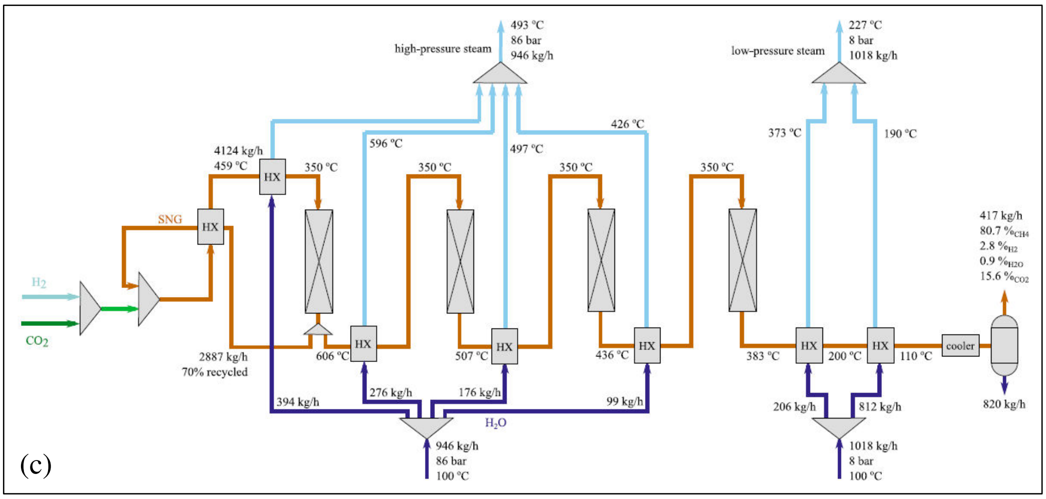


Figure 34: Global DAC-to-SNG processes simulated (a), including the two-stage mechanical vapor recompression (MVR) (b) and the CO_2-to-methane catalytic conversion unit (c) (Coppitters et al., 2023)

These systems modeling were developed in Python. For each unit, a validated model was adopted from the literature. These component models were integrated into a Python script that directs the energy, exergy and mass transfers between the components and quantifies the performance indicators. To quantify the energy, exergy and mass balances, the thermodynamic properties at each state were calculated using the Python package CoolProp.

As represented on Figure 34, **the modeled system includes a solid sorbent DAC unit, an electrolyzer for hydrogren production and a catalytic methanation unit**. The DAC unit is used to adsorbs CO_2 and water from the ambient air. The co-adsorbed water is used as a feedstock for the electrolyzer, which converts water into hydrogen and oxygen. The CO_2 and hydrogen react in a methanation unit and form raw SNG, i.e., SNG with a methane mass fraction of around 80%. The methanation unit consists of a typical four series-connected adiabatic fixed bed reactors, to reach a sufficient CO_2 conversion into CH_4, based on the design completely described in (Chauvy et al., 2021).The waste heat released by this exothermic reaction (typically around 350 °C) is recovered as steam to comply with the heat demand of the DAC unit. As the primary goal of this study is to evaluate the effect of the component synergies on the overall system performance, an SNG upgrading unit for grid injection is not included. It can be highlighted from Figure 34 that for recovering the water desorption heat spent during the DAC process, a Mechanical Vapor Recompression (MVR) unit was connected to the DAC outlet stream. Indeed, in such MVR unit, the gas is compressed and cooled consecutively to recuperate the latent heat from the vapor and remove the condensed water.

All the details regarding the operating conditions, modeling parameters and costs calculation assumptions are provided in (Coppitters et al., 2023).

5.2.2 Summary of the DAC-CO_2-to-SNG 4E results

The results of this study show that the **DAC-SNG system is autothermal when a two-stage mechanical steam recompression unit is introduced** at the DAC outlet. The energy efficiency ranges from 51.3% to 52.6% with a standard deviation of 3, the uncertainty being due to ambient conditions and heat of desorption.

In addition to the flows and energy values already indicated in Figure 34, Figure 35 (left) provides the Grassman diagram (evaluating the exergy destruction in each component of the global unit) and the costs breakdown (Figure 35 (right)) of the entire DAC-CO_2-to-SNG processes. It can be seen that electrolysis results in the highest exergy destruction (3.96 MW). The DAC unit with MVR results in an exergy destruction of 0.94 MW, due to preheating of the sorbent and condensation in the MVR.

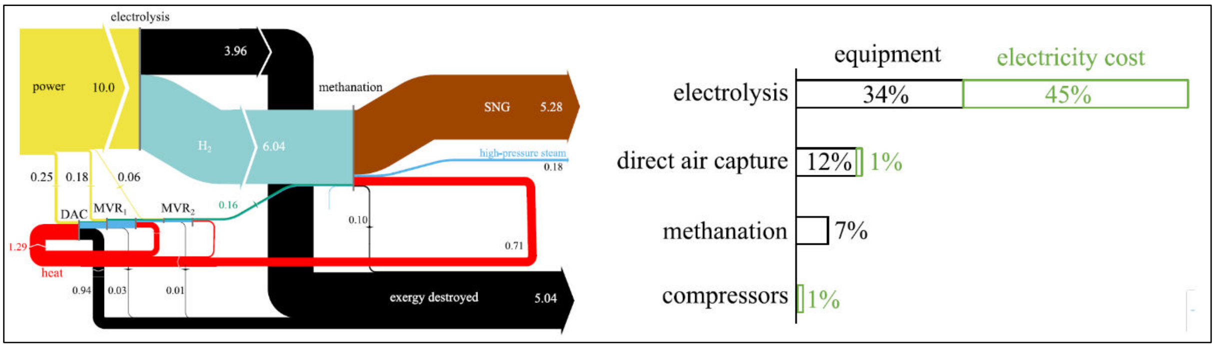


Figure 35: Grassmann diagram (values in MW) (left) and costs breakdown (right) of the entire process (Coppitters et al., 2023)

Nevertheless, the exergy destruction in the DAC unit with MVR is limited (19%) when compared to the overall exergy destruction in the DAC-SNG system (5.04MW). The produced raw SNG carries an exergy content of 5.28MW, while the excess high-pressure steam carries 0.18MW. Combining the exergy in the raw SNG (5.28MW) and steam (0.18MW), the DAC-SNG system reaches an exergy efficiency of 52.2%. Due to the overpotentials in the PEM electrolyzer, a significant amount of heat is released into the environment (1.52MWth). Considering that the waste heat has a temperature of 80 °C, the cooling water to recover that heat can be heated up to 75 °C. As the water temperature is rather low, the amount of exergy recovered from PEM electrolysis is small (0.22MW). Consequently, introducing PEM waste heat recovery improves the exergy efficiency of the DAC-SNG system by only 2%abs. Nevertheless, the low-grade heat can be supplied to, e.g., district heating networks, which typically operate near 75 °C.

Concerning the cost breakdown (Figure 35 (right)), it can be seen that **the main cost is related to electrolysis for hydrogen production**. Not that the equipment cost corresponds to the CAPEX + OPEX, while the electricity cost corresponds to the cost for electricity to run the unit. Due to the high power demand for electrolysis, **nearly half of that cost (45%) relates to buying electricity to produce hydrogen**. In contrast, **34% corresponds to the PEM electrolyzer equipment cost**, i.e., indirect cost, investment cost and operating and maintenance cost. The DAC unit cost is noticeable (13%) but clearly lower than electrolysis one. As the total cost is dominated by the cost related to electrolysis, the choice of technology to provide the CO_2 for methanation has a limited effect on the cost of producing SNG.

(Coppitters et al., 2023) shows that the **levelized cost of synthetic natural gas (LCSNG) varies between 130 €/MWh and 744 €/MWh, due to the uncertainty of electricity prices and the costs associated with DAC and electrolysis.** Consequently, increased production volume, further maturation of these technologies and more demonstration projects are needed to reduce the uncertainty of LCSNG.

Figure 36 (left) presents the carbon capture efficiency and the climate change as environmental indicators with respect to the carbon footprint of the electricity supply. It can be pointed out that **an electricity supply with a carbon footprint below 0.12 kg_{CO2-eq}/kWh results in a carbon-reducing system**, as the corresponding impact remains below the climate change impact of fossil methane (58.3 g_{CO2-eq}/MJ_{SNG}). This is achieved by the energy mixes of Norway (NO), Iceland (IS) and France (FR). Instead, the global energy mix and the energy mix of Germany (DE), the United States of America (USA) and the European Network of Transmission System Operators (ENTSO-E) would result in a carbon increasing system.

Finally, regarding the evolution of the water self-sufficiency ratio and flows of exergy with respect to the ambient air relative humidity (see Figure 36 (right)), the results illustrate that below 42% of relative humidity, the system is not water self-sufficient. However, a reduced humidity in the ambient air reduces the power and heat demand of the compressors and Direct Air Capture (DAC) unit, respectively.

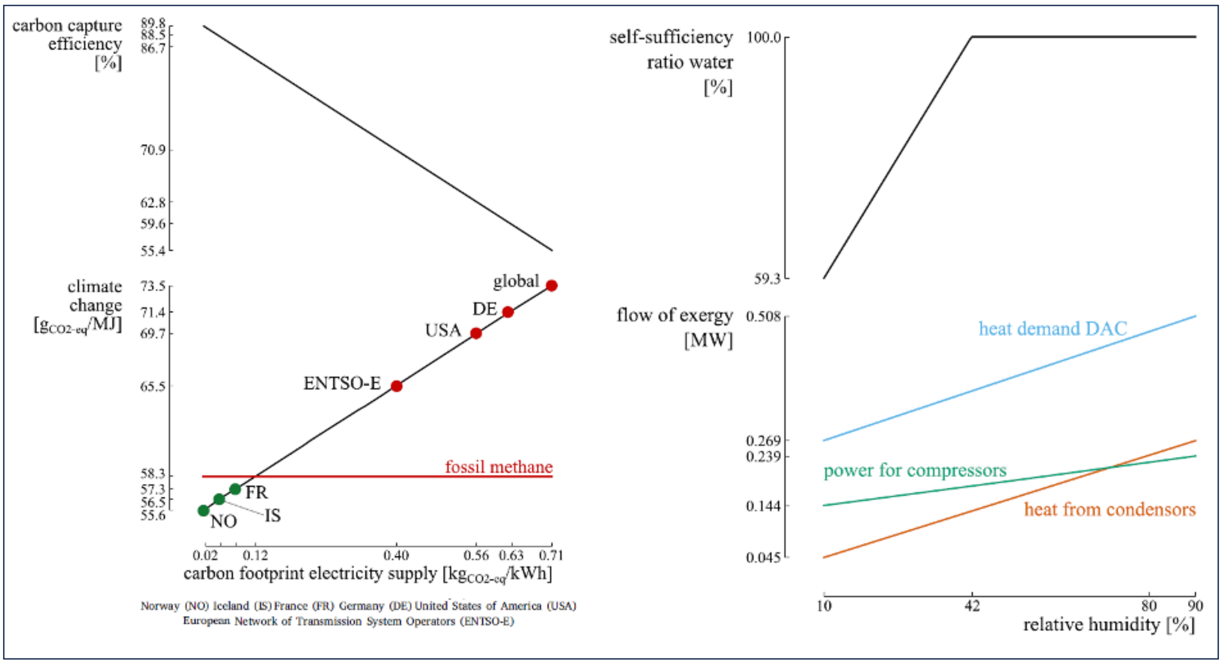


Figure 36: Environmental indicators (carbon capture efficiency and climate change) as function of the carbon footprint of the electricity supply (left), and water self-sufficiency ratio and exergy flows as function of air relative humidity (right) (Coppitters et al., 2023)

5.3 Conclusions regarding the DAC studies

The studies performed on DAC in the framework of the DRIVER project indicated that the **key levers** that will help to improve DAC performance and reduce costs are related to: **technological developments** (e.g., the use of new solid or liquid sorbents to reduce the cost of DACs), the development of **new technologies** (e.g., new gas-liquid/solid contactors), the **energy consumption** (e.g., the possibility of using waste heat, the availability of low-cost, low-carbon electricity), and the **implementation features** (e.g., modularity and scalability, energy integration with other process(es)). One very important factor is the **carbon footprint of the electricity used by the DAC process** (e.g. it was shown that SNG from DAC would have a lower carbon footprint than fossil methane if the carbon footprint of the electricity supply is less than or equal to 0.12 $kg_{CO2\text{-}eq}$/kWh).

Beyond the recovery of atmospheric CO_2, DAC technologies could eventually supply CO_2 to areas where (CO_2-emitting) industries are not present but where large quantities of low-carbon energy are produced (e.g. solar, wind, geothermal, ...), and would enable both the capture of CO_2 from the air, but also (for example) the production of green hydrogen, combinable with CO_2 to produce a more easily transportable and manageable energy carrier, such as SNG as investigated in the DRIVER project.

As far as the possible application of DAC in Belgium is concerned, it seems clear that, for the time being, **the priority must be on limiting CO_2 emissions at source** (which are much more concentrated, and therefore offer much better capture performance), and therefore to capture CO_2 from industrial flue gases. Nevertheless, as certain DAC technologies can be added to existing installations (e.g. cooling towers) or take advantage of waste heat currently lost, it is possible that certain projects could arise in the future, notably in parallel with hydrogen infrastructures (production and transport), enabling this CO_2 to be used to produce other energy carriers.

6 CO_2 liquefaction processes

6.1 CO_2 liquefaction study framework and processes simulated

For the implementation of CCUS process chains, the **CO_2 transport stage plays a key role**. In the case of onshore transport, several analyses show that pipeline transport is the preferred method due to its lower cost, with some studies indicating that rail or truck transport may only be economically viable for small quantities of CO_2. Barges are also an option if the capture site is located close to a waterway. Sea transport becomes more advantageous than pipelines beyond a certain distance, with optimal transport at pressures of 7 or 15 bar depending on the type of vessel. Impurities in CO_2, arising from various industrial processes and the variable performance of capture technologies, increase the energy consumption during compression and can lead to corrosion risks. Specifications for the maritime transport of CO_2, **in liquid form**, limit the concentration of certain impurities by strict thresholds. CO_2 purification methods such as the two-flash system and the stripping column have been proposed to meet these specifications. It should be noted that such strict specifications also apply to pipeline transport (cf. specifications set by the operator Fluxys in Belgium). In order to transport CO_2 in liquid form, it is therefore necessary to investigate the CO_2 liquefaction step, which has been the subject of a specific study, taking into account the presence of gaseous impurities, which is particularly innovative compared with what is generally considered in the literature. The main objectives of the work are to explore the intricacies of CO_2 liquefaction processes, considering constraints and assumptions for transportation that significantly influence system behavior. While the usual choice for onshore CO_2 transport is transportation in supercritical state by pipelines, the reconditioning of existing pipelines introduces a distinctive challenge. In such cases, CO_2 is not conditioned into a supercritical state, and instead, it is transported as a gas within the maximum pressure limits set by the existing pipeline infrastructure (e.g. 30–35 bar).

Two ways to liquefy CO_2 are available. The first involves leveraging the significant Joule-Thompson coefficient of CO_2 (1 K/bar at 303 K). The CO_2 is pressurized to reach the minimum pressure required for liquefaction with the cooling water. Liquid CO_2 is expanded to the desired pressure generating a vapor-liquid equilibrium. Vapor is recycled to be recompressed. This cycle is known as the **Linde-Hampson or CO_2 -open cycle** (see Figure 37 (a)). The second method employs a refrigeration machine to provide the necessary cold duty for liquefying CO_2 at the chosen pressure (see Figure 37 (b)).

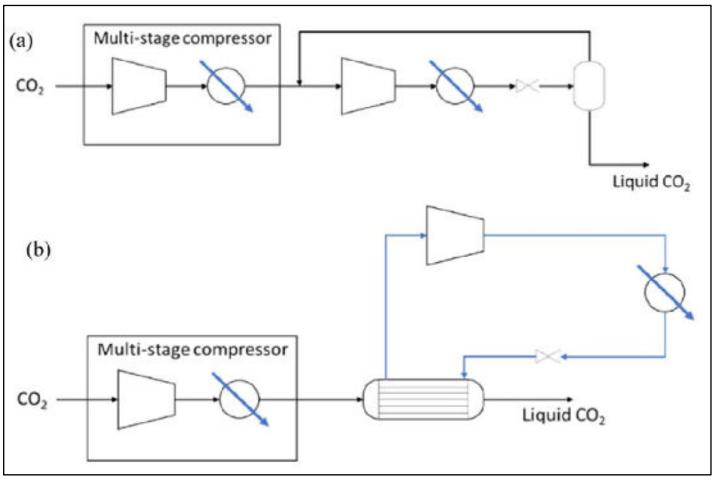
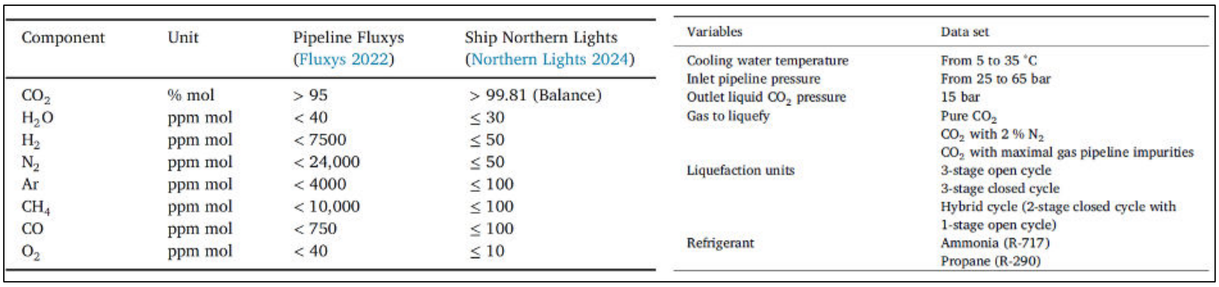


Figure 37: Illustration of (a) CO_2 -open and (b) closed cycle liquefaction (Costa et al., 2024c)

The liquefaction machine is the classic process with refrigerant that is compressed up to the high pressure. This pressure depends on the outlet cooling water temperature used to liquefy the refrigerant through the heat exchanger before its expansion to generate vapor-liquid equilibrium. The refrigerant is expanded to the pressure corresponding to the temperature necessary to cool and liquefy the CO_2. The flow rate of the cycle is related to the total amount of cooling required to generate steam at the outlet of the heat exchanger, which then enters the compressor **to close the loop**. The operating conditions (pressure and temperature) in these cycles are dependent on the properties of the cooling water system and the heat exchangers, such as the inlet temperature, the temperature rise, and the pinch of the exchanger associated with its performance.

The present study examines a **range of pressures** including critical pressure for transition phase. A **key variable in this analysis is the impurities content within CO_2**, influenced by the emission source. These **impurities significantly impact phase equilibrium, consumption rates, and the necessary purification steps for CO_2 transport via ships**. Figure 38 (left) presents the typical specifications for a pipeline transport in gas phase and a ship. Permanent gases such as CO, H_2, or O_2 may require liquid distillation to meet the specified standards. SOx, H_2S, and NH_3 are not included in the table as the pipeline specifications are equal to or lower than those set for the ship transportation. In this study, one of the key points of interest is the non-condensable gases, which result in higher consumption and CO_2 losses associated with purge streams. At the end, the objective is to compare a **3-stage optimized system** with various possible refrigerants (ammonia and propane), an optimized open CO_2 cycle, and a hybrid system of both processes for gaseous and supercritical CO_2, as well as CO_2 with specifications for pipeline transport, aiming to meet the requirements of transportation by ship. An investigation of the influence of cooling water temperature is also presented by (Costa et al., 2024c). Figure 38 (right) provides the different data investigated in the present study.



Component	Unit	Pipeline Fluxys (Fluxys 2022)	Ship Northern Lights (Northern Lights 2024)
CO_2	% mol	> 95	> 99.81 (Balance)
H_2O	ppm mol	< 40	≤ 30
H_2	ppm mol	< 7500	≤ 50
N_2	ppm mol	< 24,000	≤ 50
Ar	ppm mol	< 4000	≤ 100
CH_4	ppm mol	< 10,000	≤ 100
CO	ppm mol	< 750	≤ 100
O_2	ppm mol	< 40	≤ 10

Variables	Data set
Cooling water temperature	From 5 to 35 °C
Inlet pipeline pressure	From 25 to 65 bar
Outlet liquid CO_2 pressure	15 bar
Gas to liquefy	Pure CO_2 CO_2 with 2 % N_2 CO_2 with maximal gas pipeline impurities
Liquefaction units	3-stage open cycle 3-stage closed cycle Hybrid cycle (2-stage closed cycle with 1-stage open cycle)
Refrigerant	Ammonia (R-717) Propane (R-290)

Figure 38: Pipeline and ship CO_2 specifications (left) & investigated data in the liquefaction study (right) (Costa et al., 2024c)

The impurities present in CO_2 have an **influence on its thermodynamic and physicochemical properties compared to pure CO_2**. Figure 39 shows the vapor-liquid equilibrium for the different cases studied.

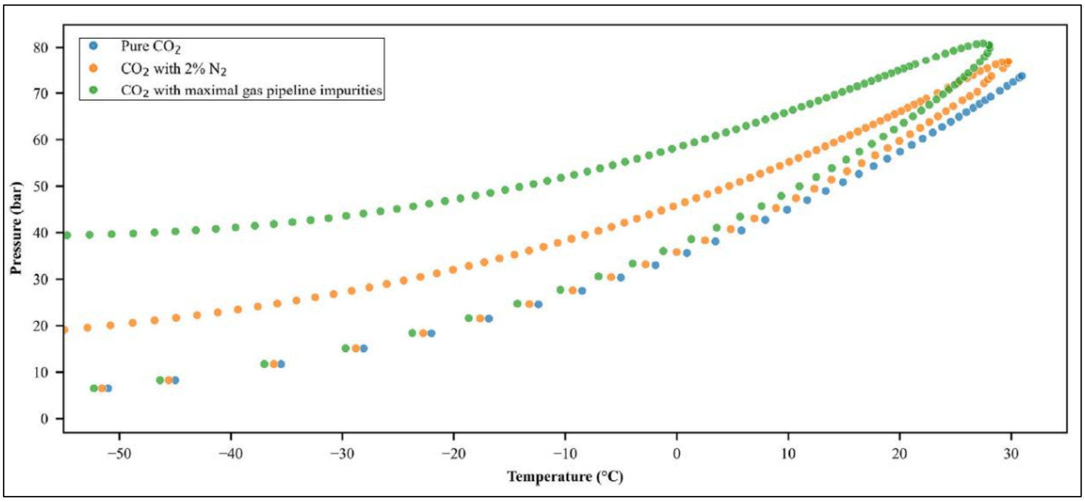


Figure 39: Vapor-liquid equilibrium for the different studied cases (Costa et al., 2024c)

It can be observed that pure CO_2 is liquid at -28 °C for a minimal pressure of 15 bar. However, at the same temperature, the liquefaction pressures for the other two cases are approximately 26 bar and 44 bar. This is particularly evident when comparing pure CO_2 to CO_2 with impurities, as the last one required higher pressure at fixed temperature or lower temperature respectively at fixed pressure. Therefore, it is necessary to purify the CO_2 to achieve complete liquefaction.

As noted in Figure 38 (right), **different configuration of the CO_2 liquefaction process were simulated** in Aspen Plus® v14 software, including **3-stage open and close cycles**, but also **hybrid cycle (2-stage closed cycle with 1-stage open cycle)** and **hybrid cycle including a distillation column** (see Aspen Plus flow sheets on Figure 40).

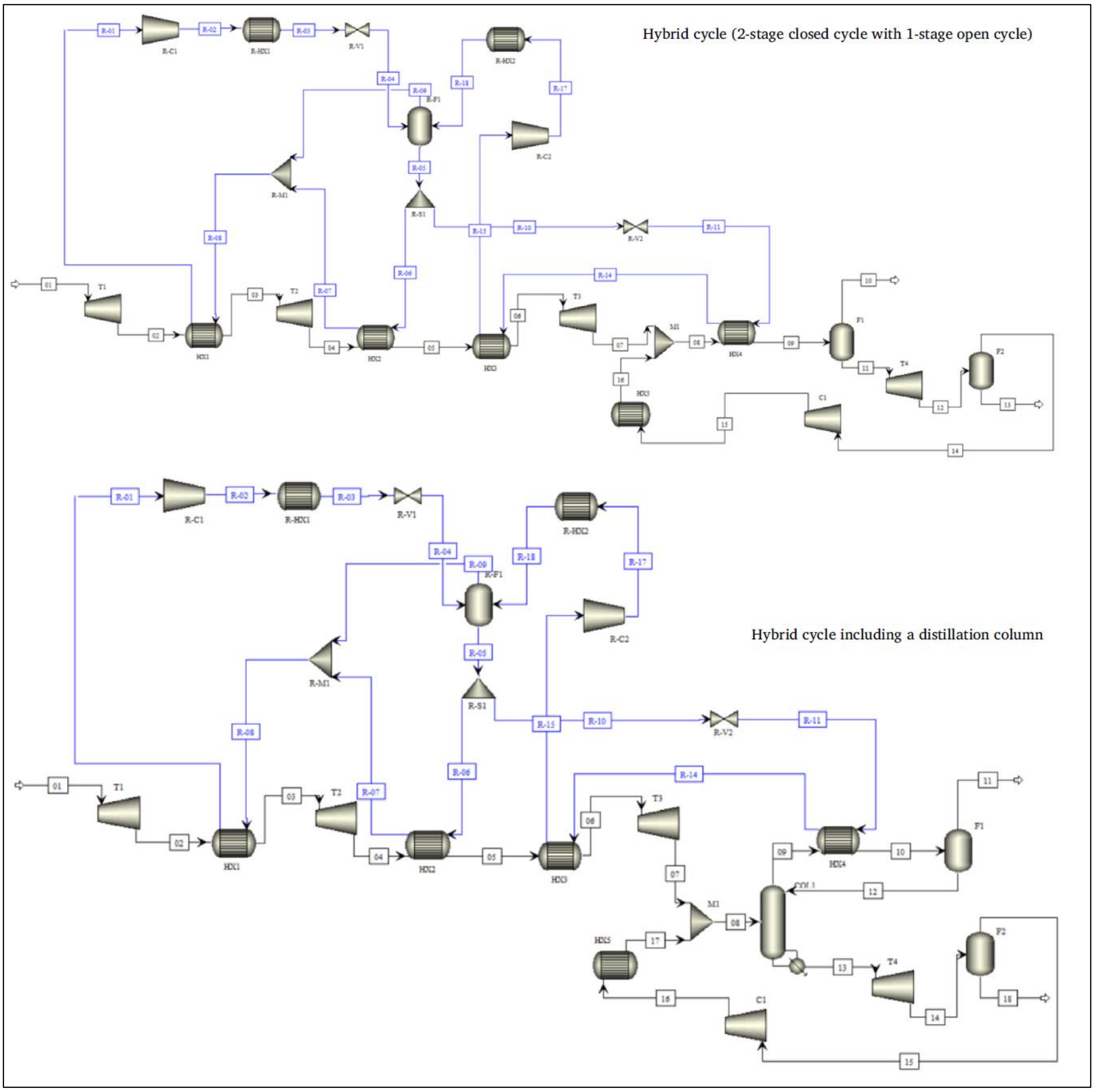


Figure 40: Aspen Plus® flow sheets of the hybrid cycle (2-stage closed cycle with 1-stage open cycle) and hybrid cycle including a distillation column (Costa et al., 2024c)

The hybrid cycle is a combination of the closed-cycle and open-cycles. The 2-stage closed cycle allows the liquefaction of CO_2 at an intermediate pressure before expanding liquid CO_2 to the transport pressure, generating both the liquid phase (the final product) and a vapor phase. The vapor phase is recompressed and sent back before the heat exchanger, where CO_2 is liquefied in conjunction with the refrigeration cycle. A purge is added at the liquefaction outlet to extract impurities from the CO_2 in the pipeline. For these different cycles, the pressure at the outlet of the first turbine (T1) is set to produce a saturated liquid stream. The last turbine (T4) determines the outlet pressure. The intermediate turbine pressures (T2 and T3) are optimized to minimize the total electrical consumption of the process. This optimization is performed using the integrated optimization tool in Aspen Plus. In the case where CO_2 from the pipeline is in a gaseous state, the first turbine is removed. In the open cycle, CO_2 enters the system before compressor C1 if the pressure is below the liquefaction pression of CO_2 with the cooling water. Since the permissible impurities in liquid CO_2 are very strict, distillation of the CO_2 may be necessary to purify it for transportation.

An advanced process including a **distillation column** is suggested for one of the cycles (hybrid cycle in this case, see second flow sheet on Figure 40). The column is fed by the stream coming from turbine T3 and the recycle from compressor C1. This stream is in a vapor-liquid state. The distillation column is modeled using the RadFrac block in Aspen Plus in rate-based mode. A structured packing, the Mellapack 250Y, is considered as internal in the contactor. The condensation is partial, and condenser is fed by the last stage of the refrigeration unit (HX4). The vapor stream (stream 11) corresponds to the process purge. The liquid is returned to the column as reflux.

All the details regarding the operating conditions, modeling parameters and costs calculation assumptions are provided in (Costa et al., 2024c).

6.2 Simulation results of the CO_2 liquefaction processes

First of all, as already shown several times in the DRIVER project studies, the **impact of electricity prices on the process costs** (liquefaction in the present case) is a crucial aspect to consider in the processes optimization. Fluctuations in electricity prices can significantly influence operational expenses and ultimately affect the economic viability of CCUS chains. To assess this impact, a sensitivity analysis was conducted, varying electricity prices within a realistic range from 50 to 250 €/MWh. The results presented on Figure 41 indicate a direct correlation between electricity prices and liquefaction costs across the different liquefaction cycles studied.

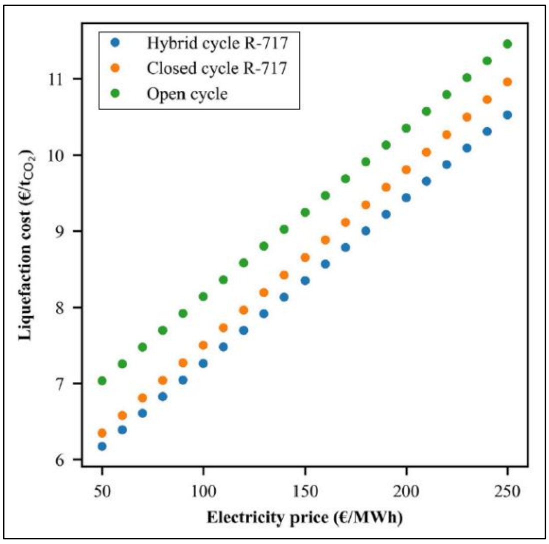


Figure 41: Impact of the electricity price on the liquefaction cost for several cycles (Costa et al., 2024c)

Higher electricity prices lead to increased operational expenses, resulting in higher liquefaction costs per ton of CO_2 liquefied. Relative to the base case at 100 €/MWh, the liquefaction cost for the hybrid process exhibits a variation ranging from -15% to -40% for the two extremes considered for the electricity price. It can also be noticed that the closed cycle closely approaches the hybrid cycle as the electricity price decreases, but the liquefaction costs with the hybrid cycle remains the lowest.

These findings underscore the **importance of considering electricity price dynamics in the design and operation of liquefaction facilities**. Strategies such as demand-side management, renewable energy integration, and energy storage solutions may offer avenues for mitigating the impact of electricity price volatility on liquefaction costs, thereby enhancing the economic feasibility of these technologies.

Focusing on the hybrid cycle, Figure 42 represents the electrical consumption in function of the inlet pressure, the refrigerant and the cooling water temperature. It can be seen that the **electrical consumption are quite similar with the two refrigerants, namely R-717 (ammonia) and R-290 (propane),** the most visible different being observed with the highest cooling water temperature (35°C). Moreover, Figure 42 also allows to see the decrease of the electrical consumption with a lower cooling water temperature. The same observation can be made with the inlet pressure: the electrical consumption of the liquefaction unit is decreasing as the inlet pressure is increased from 25 bar to 65 bar.

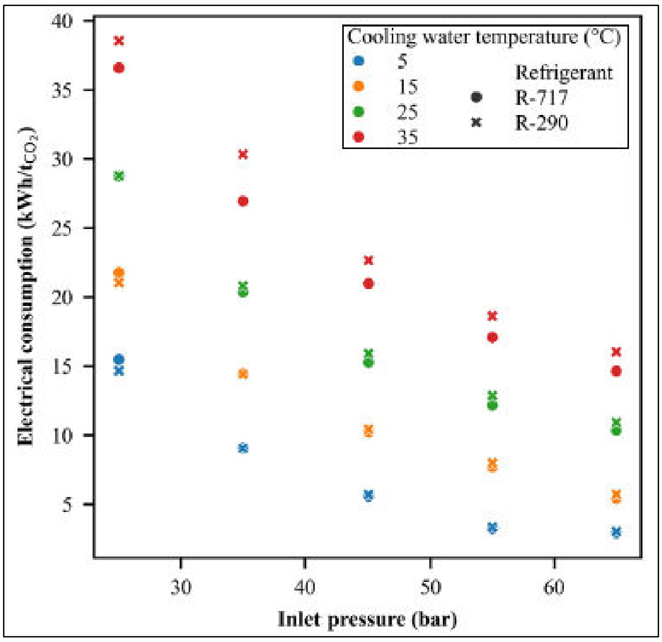


Figure 42: Electrical consumption for hybrid cycle in function of the inlet pressure, the refrigerant and the cooling water temperature (Costa et al., 2024c)

Figure 43 illustrates the various consumptions as a function of the recovery for the different cases studied in this work. It can be observed that distillation of CO_2 achieving the specified targets for transportation by ship for case 2 consumes up to 16 % more electricity than for the initial process with flash, which results in out-of-spec liquid CO_2. Looking at the figures obtained for the same conditions (inlet pressure, cooling water temperature, outlet pressure), it can be noticed that the consumption is almost double when seeking to minimize CO_2 losses.

Considering the case with different impurities in the CO_2 during transportation by pipeline, there is a loss of at least 2 % of the CO_2 regardless of the energy consumption. This limit is related to the minimum achievable temperature for CO_2. The condenser temperature tends to decrease from -30 °C to -54 °C as the recovery rate increases, implying higher electrical consumption to reach these colder temperatures at the refrigeration unit. Conversely, the column pressure is quite low for lower recoveries and increases for higher recoveries, ranging from 16 bar to 25 bar. For other column parameters, their variations tend to increase or decrease depending on the recovery rate, with the boil up rate ranging from 0.11 to 0.18, the packing height ranging from 1 to 8 m, and the feed stage varying between 5 and 7 considering a discretization of 20 stages. The vapor fraction at the outlet of the first liquefaction stage decreases from 0.24 to 0.17 for high recoveries (> 95 %).

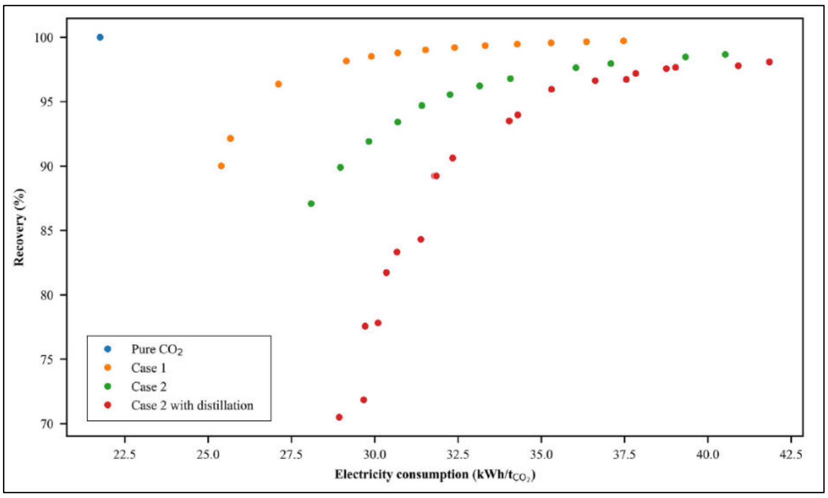


Figure 43: Recovery in function of electrical consumption of hybrid cycle for the different cases (Costa et al., 2024c)

Finally, the evolution of the liquefaction total cost for the more stringent gas operator specification case as a function of recovery and carbon tax for various concentrations is presented on Figure 44. For the case at 60 €/t_{CO2}, the economic optimum is around 2.5 % loss of CO_2 during liquefaction. For case 1, the trend to minimize losses is the same, with however an optimum at 0.8 % loss for 100 €/t_{CO2}.

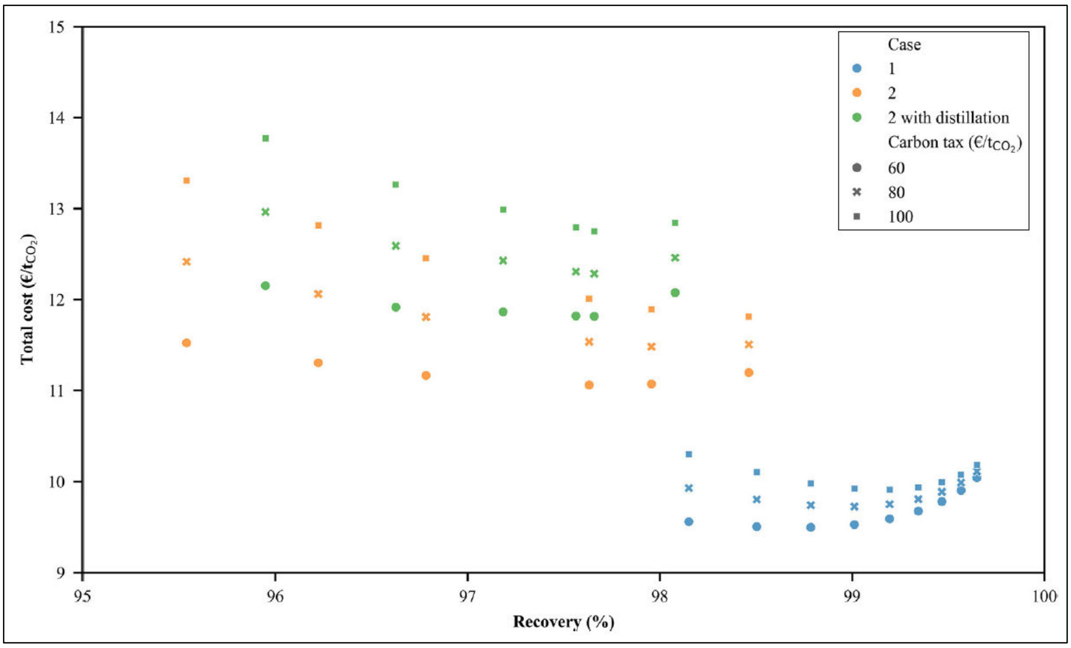


Figure 44: Evolution of total cost as a function of CO_2 recovery and carbon tax for both case (Costa et al., 2024c)

This analysis demonstrates that it is interesting, knowing that the carbon tax will inevitably increase to achieve zero carbon emissions objectives, to minimize losses by increasing performance and therefore the cost of the process. When comparing the costs associated with case 2, both with and without a distillation column, there is an observed increase in pricing ranging from approximately 7 % to 10 %. This upward cost trend can be attributed to the heightened electrical consumption and an additional investment, namely the inclusion of the distillation column. The price range for case 2, incorporating distillation, fluctuates between 12 and 13 €/t_{CO2}. In contrast, the cost for a pure CO_2 stream under identical conditions stands at 7.3 €/t_{CO2}. The increase is noteworthy. This prompts a critical examination of the pipeline specifications, raising the question of whether they should align more closely with those typically associated with shipping methods.

Globally, the CO_2 liquefaction methods studied show that **hybrid cycles**, combining an open cycle with a Joule-Thompson expansion and a closed cycle with a cooling machine, **reduce energy consumption and improve CO_2 recovery compared with open or closed cycles. In the presence of the maximum impurity threshold in the pipeline, energy consumption can almost double**, from 21 kWh/t_{CO2} to 40 kWh/t_{CO2}, with a maximum recovery of 98%. Overall, the hybrid cycle is therefore a versatile and efficient solution to the complexities of purifying and liquefying CO_2 from a pipeline. It should be pointed out that, in order to meet shipping specifications, it is necessary to add a distillation column to the liquefaction process. In terms of costs, this CO_2 liquefaction step adds a contribution of between 7 € and 14 €/t_{CO2}, depending on the impurities present in the CO_2, representing nevertheless a cost of between 2% and 10% of the entire CCUS chain. This range of costs highlights the significant impact that gaseous impurities can have on the overall cost of CO_2 liquefaction. It should also be noted that gaseous impurities lead to a loss of CO_2, which will be invoiced to the CO_2 liquefaction operator.

This study has therefore highlighted the **importance of optimizing CO_2 transport and liquefaction strategies** to facilitate the deployment of CCUS technologies. One of the perspectives of this work will be to study the chain more comprehensively in order to determine what is most economically viable: to be stricter on the purity of CO_2 in the pipeline and therefore increase the purification of CO_2 leaving the capture unit, or to stick to current specifications, which implies treating CO_2 from the pipeline to meet specifications for transport by ship.

7 Conclusions and next steps

The CCUS (Carbon Capture Utilization and/or Storage) domain constantly evolving, regular monitoring and technology watch are necessary in order to generate relevant and up-to-date indicators: energitcal, exergetical, economical and environmental ones. Moreover, the evolution of the CO_2 market and its regulation (ETS (Emissions Trading Scheme) in particular), as well as the evolution of CCUS and DAC projects in general (current and new projects), will have a major impact on the deployment of CCUS chains needing processes simulations and optimization as performed in the framework in the DRIVER project.

Regarding the **CO_2 capture-purification technologies**, two main categories of processes have been studied, namely absorption-regeneration using amine-based solvents, and cryogenic technologies (possibly hybrid, combined with the use of gas-solid adsorption (VPSA-CPU) or membranes as pre-concentration). The challenge for the first category is to reduce its cost (high thermal energy consumption), while for the second to continue optimizing the process in order to reduce its exclusively electrical energy consumption. Consideration of cryogenic techniques is of paramount importance. Indeed, over and above the CO_2 recovery rate as such, the need to meet strict purity specifications for injecting CO_2 into a pipeline network (and/or for its liquefied transport by ship) should very often necessitate the use of such a technology. The investigation of CO_2 liquefaction is also important, given that its transport by ship to a geological storage hub will take place in liquid form. Globally, it was shown that thanks to these technologies, high recovery rate (>95%) and high CO_2 purity (>99%) are achievable thanks to the optimization of process configuration and operating parameters.

Focusing on the **CO_2 conversion processes** and their possible thermal integration with a capture unit (the interest of such an operation has been demonstrated, also in combination with Direct Air Capture (DAC)), particular attention has been paid to the methanol and methane routes, the latter being positioned as the energy carrier with the most interesting potential while methanol has an interest as chemical building block.

Globally, one **key factor** that has been highlighted among all the works performed is the **importance of the electrical mix** and its associated network. Indeed, all the CCUS processes will use electricity and some of them will use exclusively electricity (e.g. cryogenics ones). That will imply to have an **electrical mix with the lowest carbon intensity possible** in order to have a favorable environmental balance.

As perspectives, in addition to further investigations and simulations that are still under progress, the next step of the DRIVER project will involve integrating the results of these simulations as **inputs into Remote Renewable Energy Hub (RREH) models** developed at ULiège (see Deliverable D2). In conjunction with the work carried out at UCLouvain, the aim will be to provide a more global analysis of the value chains integrating CO_2 and various energy carriers. The overall results will be used to draw up a technological roadmap related to the CCUS implementation in Belgium.

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