# POLITECNICO DI TORINO

Collegio di Ingegneria Chimica e dei Materiali

# Corso di Laurea Magistrale in Ingegneria Chimica e dei Processi Sostenibili

Tesi di Laurea Magistrale

# Renewables-to-H2: Combined innovative processes for an efficient hydrogen production, storage and transport.



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#### <u>Sommario Esteso</u>

Negli ultimi tempi le fonti rinnovabili giocano un ruolo molto importante nell'ambito della produzione di energia, costituiscono una valida alternativa alle fonti energetiche non rinnovabili ormai prossime all'esaurimento, questo perché sono fonti di energia inesauribili e a basso impatto ambientale.

Tuttavia, sono fonti molto intermittenti e instabili, la crescente dipendenza da loro aumenta la necessita di sviluppare tecnologie più efficienti per lo stoccaggio di queste energie per andare a compensare la loro natura variabile e lampeggiante. La gestione dell'immagazzinamento rappresenta uno dei punti fondamentali nello sviluppo di un sistema economico/energetico futuro nel quale l'idrogeno potrebbe essere uno dei protagonisti.

L'idrogeno risulta essere promettente in quanto non solo è l'elemento leggero più abbondante dell'universo ma anche per il fatto che la sua reazione di combustione ha un potere calorifico elevato e inoltre produce solamente acqua, evitando la formazione di gas serra. Non va considerato come una fonte di energia, bensì come un vettore energetico, cioè un composto in grado di veicolare l'energia da una forma ad un'altra.

L'energia prodotta da fonti rinnovabili attraverso l'elettrolisi dell'acqua si può immagazzinare mediante la formazione di legami chimici che si formano dalla scissione della molecola di H<sub>2</sub>O. L'idrogeno prodotto può essere stoccato, trasportato, e a fini energetici può essere utilizzato in una cella a combustibile con lo scopo di produrre nuovamente elettricità.

La produzione di idrogeno verde ha un enorme potenziale nel fornire un ciclo di utilizzo dell'energia sostenibile e aprire un nuovo paradigma per diversi settori industriali che oggi dipendono principalmente dai combustibili fossili e per i quali la decarbonizzazione è altrimenti difficile. La produzione elettrolitica di idrogeno affronta sfide tecnologiche per sviluppare metodi che consumino il minor quantitativo di energia e siano in grado di farlo su gran scala. Migliorare l'efficienza e l'adattabilità agli input variabili come ridurre il costo dei materiali usati negli elettrolizzatori sono alcune di queste sfide.

L'elettrolisi è tecnologia che ha una certa maturità però richiede di operazioni a carichi costanti che consumano grandi quantità di energia, essendo una delle grandi sfide in uno schema da fonti rinnovabili. Oggi gli elettrolizzatori che possono funzionare in modo affidabile quando sono alimentati da fonti rinnovabili non sono ancora un commercialmente disponibile così sollecita la necessità di sviluppare nuovi approcci per sfruttare queste fonti di energia.

L'elettrolisi dell'acqua è un metodo ben studiato e diverse tecnologie sono disponibili da scala di laboratorio a larga scala. Principalmente si differenziano per il tipo di elettrolita utilizzato all'interno delle celle. Le tre principali tecnologie per l'elettrolisi dell'acqua che sono commercialmente disponibili sono la cella alcalina (AWE), la cella a membrana a scambio protonico (PEM) e la cella di ad ossidi solidi (SOEC). I primi due tipi lavorano in condizioni di temperatura ambiente (fino a 90 °C), mentre una SOEC di solito oscilla tra 700 e 950 °C.

# (Figura 1.1)

Poiché l'AWE è la tecnologia più predominante usata per la produzione su larga scala, ci riferiremo direttamente all'elettrolisi dell'acqua alcalina quando si parla di sistema di "elettrolisi dell'acqua commerciale". I sistemi di elettrolisi dell'acqua alcalina sono ampiamente disponibili, esibendo durata ottima e il costo di investimento relativamente basso.

Sfortunatamente la mancanza di flessibilità per lavorare con intermittenza porta anche a efficienze più basse a causa di diversi start-up e shutdown e colpisce la purezza del gas a causa del crossover a basse densità di corrente. Lo sviluppo si concentra sull'affrontare i problemi di densità di corrente, pressione operativa e progettazione per il funzionamento dinamico che influenza l'efficienza, la durata e le caratteristiche dell'idrogeno. I sovrapotenziali degli elettrodi e le perdite ohmiche sono principalmente al centro della ricerca per migliorare le prestazioni.

Per quanto riguarda allo stoccaggio, la situazione non è una mansione facile, anzi l'immagazzinamento dell'idrogeno è piuttosto impegnativo. L'idrogeno è il composto più leggero della terra. 1 kg di idrogeno gassoso, in condizioni ambientali, occupa 11 m<sup>3</sup>. Quindi, per rendere lo stoccaggio dell'idrogeno economicamente fattibile, la strategia è aumentare la sua densità. Questo potrebbe sembrare un compito facile, ma per farlo sono necessari metodi tecnologici, dove sono necessari alcuni input di energia come lavoro o calore, e a volte anche proprietà specifiche dei materiali che permettono di legare l'idrogeno o immagazzinarlo.

Per poter diventare una realtà occorre migliorare i processi di produzione, stoccaggio e trasporto dell'idrogeno i quali risultano essere i punti più critici. Per il superamento di queste criticità si è deciso di ricorrere ad una combinazione di due processi innovativi.

In primo luogo, si ha il disaccoppiamento dell'elettrolisi d'acqua per mezzo di un processo a due step in quanto la generazione di idrogeno non avviene contemporaneamente alla generazione di ossigeno. Questo comporta una riduzione dei tipici sovrapotenziali dell'elettrolisi convenzionale con un conseguente risparmio energetico. Il processo viene chiamato ETAC (in inglese) per ciclo elettrochimico-chimico termicamente attivato.

L'idrogeno prodotto successivamente viene immagazzinato in molecole organiche che posso alternare tra stati idrogenati e deidrogenati (mediante reazioni chimiche). Queste molecole vengono definite Liquid Organic Hydrogen Carriers (LOHC) perché a temperatura ambiente sono liquide, e risultano essere vantaggiose per quanto riguarda lo stoccaggio e il trasporto. Un'opzione di queste alternative è la coppia di idrocarburi ciclici Toluene-Metilcicloesano (TOL-MCH).

ETAC: Ciclo Elettrochimico-Chimico Termicamente Attivato

Nell'elettrolisi convenzionale, l'idrogeno è prodotto al catodo mentre contemporaneamente l'ossigeno è generato all'anodo. In questo schema, i tassi di evoluzione di entrambi sono strettamente "accoppiati" nel tempo e nello spazio, con due moli di idrogeno per ogni singolo mole di ossigeno. Tuttavia, gli elettrolizzatori alimentati da fonti di energia rinnovabili variabili affrontano sfide operative come il crossover gassoso a basse densità di corrente: i tassi di  $H_2$  e  $O_2$  possono essere inferiori al tasso di permeazione attraverso la membrana.

Inoltre, AWE combatte contro una delle maggiori sfide nella produzione di idrogeno elettrolitico: I sovrapotenziali. Il trasferimento di quattro elettroni per la reazione di evoluzione dell'ossigeno, che avviene all'anodo, limita il tasso di generazione di ossigeno e di conseguenza di idrogeno. Questa resistenza viene visualizzata come un aumento del potenziale della cella (sovrapotenziale di attivazione) che mostra la differenza tra il potenziale definito termodinamicamente per metà reazione e il potenziale osservato sperimentalmente.

È con questo contesto che l'elettrolisi disaccoppiata è stata proposta ed è stata considerata come una strategia di scissione dell'acqua avanzata. Utilizzando un mediatore redox ausiliario (RM), è stato possibile tagliare a metà la reazione di elettrolisi collegando l'evoluzione dell'ossigeno a una riduzione reversibile del mediatore (accettore di elettroni) e successivamente riossidandolo (donatore di elettroni) mentre si genera dell'idrogeno al catodo. In questo modo, il tasso di evoluzione dell'ossigeno e dell'idrogeno possono essere completamente diversi e le reazioni potrebbero anche essere eseguite in tempi e spazi diversi, superando le problematiche menzionate sopra.

Nell'ambito di questo approccio, Dotan et al. [11] hanno proposto un'evoluzione disaccoppiata di idrogeno e ossigeno mediante un ciclo elettrochimico-chimico termicamente attivato a due step. Prima una fase elettrochimica che riduce l'acqua al catodo (generazione di idrogeno) e ossida l'anodo, seguita da una fase chimica spontanea che è guidata più velocemente a temperatura più alta, riducendo l'anodo di nuovo al suo stato iniziale ed ossidando l'acqua. (generazione di ossigeno).

# (Figura 1.2)

Il processo ETAC utilizza un mediatore redox solido che permette di operare senza membrana o separatore. In questo caso, il mediatore è l'anodo stesso che viene ossidato durante la generazione dell'idrogeno. L'idrossido di nickel ha un potenziale standard di riduzione superiore a quello dell'OER. Pertanto, la sua forma ossidata, NiOOH, può ossidare l'acqua e produrre ossigeno, in una reazione chimica spontanea.

NiOOH + H<sub>2</sub>O + 
$$e^- \rightarrow$$
 Ni(OH)<sub>2</sub> + <sup>1</sup>/<sub>4</sub> O<sub>2</sub> (E<sup>o</sup>= 0,19 V<sub>RHE</sub>)

#### (Figura 3.3.3)

Nonostante che il potenziale redox Ni(OH)<sub>2</sub> /NiOOH sia più alto del potenziale OER, è ancora adatto per il disaccoppiamento dell'elettrolisi poiché gli sovrapotenziali sono molto bassi in confronto al potenziale di attivazione per OER all'elettrolisi accoppiata. In questo schema, Ni(OH)<sub>2</sub> si comporta come un buffer che scambia protoni ed elettroni (ECPB) passando prima attraverso l'ossidazione (cioè la carica) mentre l'idrogeno viene prodotto al catodo; è poi a una reazione chimica spontanea per rigenerare l'anodo originale mentre produce ossigeno.

# (Figura 2.2)

Il vantaggio chiave dell'ETAC è che l'efficienza del processo è considerevolmente superiore a quella di altre applicazioni che utilizzano mediatori redox per disaccoppiare le reazioni di scissione dell'acqua perché, l'ossigeno viene generato spontaneamente senza la necessità di alcuna fonte di energia esterna per polarizzare gli elettrodi.

Inoltre, il processo ETAC presenta altri vantaggi chiave che lo rendono una nuova tecnologia con grandi prospettive di applicazione futura. È in grado di lavorare a basse densità di corrente esibendo potenziali di cella vicini alle condizioni termoneutrali. Il funzionamento disaccoppiato senza membrana potrebbe aprire la strada alla produzione ad alta pressione, evitando il crossover del gas che attualmente limita le pressioni di funzionamento negli elettrolizzatori alcalini convenzionali.

#### LOHC: Idrogeno Organico Liquido

Come precedentemente esaminato, una grande sfida nell'adozione dell'idrogeno per lo stoccaggio di energia (a lungo termine e su larga scala) è la mancanza di uno stoccaggio economico, efficiente e sicuro, così come l'infrastruttura e il trasporto di consegna. L'idrogeno è immagazzinato in uno

stato gassoso pressurizzato fino a 700 bar o in uno stato liquido a temperature inferiori a -253°C. Entrambi i sistemi sono critici per la sicurezza, tecnologicamente complessi e costosi per stabilire un'infrastruttura di distribuzione su larga scala.

Così l'immagazzinamento chimico dell'idrogeno si presenta come un'alternativa che evita le condizioni difficili per raggiungere densità più elevate legando chimicamente l'idrogeno a un atomo o a una molecola. I LOHC sono molecole organiche che possono passare da uno stato saturo in idrogeno ad uno libero di esso mediante processi di idrogenazione e deidrogenazione, rispettivamente, e consentono uno stoccaggio sicuro e a lungo termine con un'alta densità di energia. Il vantaggio dei LOHC è che entrambi forme sono liquide a condizioni normali, favorendo i processi di separazione dall'idrogeno quando viene rilasciato.

# (Figura 1.3)

Uno dei LOHC più studiati è il sistema metilcicloesano-toluene che ha una densità gravimetrica di stoccaggio del 6,1% in peso e una densità volumetrica di 47 kg/m<sup>3</sup>.La sua reazione di deidrogenazione è una tecnica ampiamente consolidata, soprattutto nell'industria petrolifera. I catalizzatori supportati a base di metalli nobili sono comunemente gli utilizzati. Termodinamicamente richiede almeno 68 kJ/mol (endotermica) con temperature che raggiungono i 350°C. Tuttavia, la reazione è abbastanza dipendente dalle proprietà del catalizzatore come l'attività, la selettività e la stabilità. Inoltre, la disattivazione e il coking devono essere presi in considerazione a causa delle alte temperature del reattore.

# (Figura 3.4.1)

Come la deidrogenazione, l'idrogenazione del toluene di solito coinvolge un catalizzatore di metalli nobili, in questo caso viene comunemente scelto il rutenio supportato (Ru), ma lo stesso catalizzatore per la deidrogenazione è ancora adatto a saturare le molecole di toluene variando le condizioni di reazione (temperatura e pressione). Questo ha creato un'opportunità vantaggiosa per un modo più diretto di immagazzinare e riutilizzare l'idrogeno. Inoltre, l'idrogenazione è esotermica, e le temperature tipicamente applicate vanno da 130-250°C. Le pressioni tendono ad essere più alte che nella deidrogenazione, nell'intervallo di 10-50 bar

Il MTH è in grado di raggiungere densità volumetriche pari a quelle dell'idrogeno liquido con un costo di funzionamento molto più basso dato che le spese di calore fornito sono inferiori a quelle dell'elettricità. È importante che non richieda un apporto considerevole di elettricità per liberare l'idrogeno, dato che lo scopo è quello di ridurre il costo dell'idrogeno prodotto per elettrolisi da fonti rinnovabili.

# (Figura 2.5)

In ogni caso, il calore ad alta temperatura deve essere generato per liberare l'idrogeno e se sono richieste grandi quantità di esso in un breve periodo di tempo, questo calore deve essere trasferito in modo efficiente e veloce. Tuttavia, nelle applicazioni industriali sembra possibile che queste richieste di energia termica possano essere soddisfatte senza grandi sfide tecniche, sia attraverso la integrazione termica con altri processi oppure tramite la combustione del MCH, un combustibile esterno, o parte dell'idrogeno rilasciato.

# Scopo ed obbiettivi del lavoro

Lo scopo del lavoro svolto è valutare la sinergia dei due processi illustrati e di confrontarli con un sistema convenzionale di elettrolisi alcalina e gas compresso. Gli obiettivi sono focalizzati sulla modellazione e l'analisi dei due processi innovativi nella catena di approvvigionamento

dell'idrogeno e come l'efficienza complessiva è influenzata dalla combinazione dei processi menzionati.

# Metodi

Per poter analizzare la affidabilità ed i vantaggi di entrambi le alternative, sono state eseguite delle simulazioni con Aspen Plus V.10 ed Office Excel. Grazie ai loro potenziale e i tools che permettono di integrarli, è stato possibile ricreare la reattoristica dei processi di elettrolisi che non sono disponibili nell'interface di Aspen Plus. La validazione dei modelli appositi è stata eseguita basandosi sui dati sperimentali dei processi innovativi descritti trovati in bibliografia.

Si suppone che entrambe le alternative funzionino con input di energia elettrica rinnovabile e si farà un'ulteriore analisi qualitativa per valutare la fattibilità e l'adattabilità. L'intero lavoro cerca di fornire idee su cui lavorare, così come offrire schemi, che possono essere un punto di partenza per soluzioni migliorate.

# Modellazione e simulazione

Aspen Plus ha diversi blocchi e opzioni in cui è possibile progettare e modellare routine specifiche attraverso Excel. Poi si danno al software le direttive per eseguire il calcolo che è necessario a seconda della funzione che si sta cercando di simulare.

Calculator è un'opzione di Flowsheeting che eseguirà una routine definita dall'utente per fare un calcolo specifico che non è disponibile in Aspen Plus. Questo è abbastanza vantaggioso dato che questo software non include codici per modellare le celle di elettrolisi.

Sono state effettuate quattro diverse simulazioni, una per ogni processo menzionato prima: Elettrolisi dell'acqua alcalina (3.1) e ETAC (3.3) per la produzione di idrogeno, e idrogeno gassoso compresso (3.2) e LOHC con toluene-metilcicloesano (3.4) per lo stoccaggio e il trasporto.

Per AWE, la modellazione dello stack è stata basata su una precedente ricerca di M Sanchez et al, [23,24] che fornisce le equazioni di base per la curva di polarizzazione del potenziale della cella in funzione della temperatura, della pressione e della densità di corrente e un tasso di idrogeno legato all'efficienza faradica.

# (Figura 3.1.3)

Invece per l'ETAC, è stato eseguito un modello basato su un ciclo elettrochimico termo rigenerativo (TREC) [3]. La fase di carica (anodo) è condotta a temperatura ambiente mentre l'idrogeno si evolve simultaneamente al catodo.

La carica dell'anodo può essere vista come il processo di carica di un circuito elettrico RC dove l'anodo si comporta come un condensatore e l'elettrolita come la resistenza ohmica. Quindi il potenziale applicato può essere visto come la somma della tensione reversibile, cioè la tensione minima perché la reazione avvenga, e una serie di resistenze.

# (Figura 3.3.2)

Poiché la carica viene trasferita all'anodo in un'operazione stabile, il numero di moli di  $Ni(OH)_2$ che sono state ossidate può essere calcolato dalla quantità di carica elettrica Q(t) secondo la legge di Faraday:

$$nNi(OH)_2 = \frac{Q(t)}{Fz}$$

Così, una volta completato il primo passo con un anodo completamente carico, il secondo passo è la rigenerazione dell'anodo per iniziare un nuovo ciclo. Questo passo è interamente chimico e dipende dalla cinetica delle seguenti reazioni. Dai dati sperimentali apportati da Dotan et al.[11] sono stati ottenuti i parametri della cinetica. La reazione è del primo ordine per il NiOOH.

$$4OH^{-} \rightarrow O_{2} + 2H_{2}O + 4e^{-}$$
 (E°= 1,23 V<sub>RHE</sub>)  
 $4NiOOH + 4H_{2}O + 4e^{-} \rightarrow 4Ni(OH)_{2} + 4OH^{-}$  (E°= 1,42 V<sub>RHE</sub>)

Per lo stoccaggio e trasporto nella prima alternativa invece l'idrogeno viene compresso tramite un compressore in cascata a due stadi per fornire idrogeno a 440 bar e 60°C; e anche idrogeno per veicoli a 880 bar e -40°C.

Siccome la compressione è una tecnologia già ampiamente sviluppata e solida, la simulazione ha permesso di ricreare le condizioni operative senza ulteriori complicazioni, in quanto diversi tipi di unità di compressione sono disponibili nel software.

Per l'immagazzinamento chimico di idrogeno è stata effettuata una simulazione del ciclo completo considerando una fase di stoccaggio in serbatoio e una fase di trasporto per stimare le spese.

#### (Figura 3.4.1)

Come menzionato prima, il nostro ciclo LOHC è basato sull'idrogenazione/deidrogenazione rispettivamente di Toluene-Metilcicloesano su catalizzatori a base di platino Entrambe le unità sono reattori tubolari catalitici di flusso a pistone. La cinetica è basata su ricerche sperimentali di Usman et al. [25] per 1% wt. Pt/ $\beta$ -Zeolite e le condizioni operative sono basate sullo studio di simulazione di Hamayun et al. [19] per un sistema simile.

Delle simulazioni entrambe le reazioni contenevano una grande proporzione di sottoprodotti, fatto che è stato anche riportato da Usman et al. [25]. Tuttavia, le condizioni di reazione sono state ottimizzate al fine di massimizzare la selettività del prodotto principale e la conversione del reagente sulla base dei dati sperimentali e di modelli simili di idrogenazione/deidrogenazione di LOHC.

# (Figura 3.4.4)

# <u>Risultati</u>

I risultati ottenuti fanno riferimento a diverse condizioni operative, mettendo in risalto la variabilità delle risorse rinnovabili. Per poter confrontare dettagliatamente i sistemi, l'analisi dei risultati è stata divisa per funzionalità.

Per quanto riguarda la generazione di idrogeno, in termini energetici, ETAC significherebbe un incremento di efficienza, nonché di versatilità operativa. Inoltre, si ha la possibilità di operare con minori carichi energetici. A basse densità di corrente, l'idrogeno si produce ad una velocità accoppiata alla carica dell'anodo, mentre per AWE non sarebbe possibile raggiungere i livelli energetici minimi per far procedere la reazione.

Per i sovrapotenziali invece, entrambi simulazioni mostrano che man mano si incrementa la corrente nella cella, i potenziali aumentano. Nonostante, le celle dell'ETAC si mantengono sotto il potenziale al quale occorrerebbe generazione di ossigeno, mentre le celle AWE a parità di corrente applicata mostrano potenziali ben maggiori.

(Figura 5.2.1)

Per l'AWE, le alte pressioni causano un aumento della permeazione dell'idrogeno attraverso il diaframma di separazione che limita la pressione di funzionamento poiché il limite di infiammabilità potrebbe essere raggiunto. Mentre per l'ETAC l'ossigeno si produce in quantità trascurabili parassitariamente a causa dell'auto scarica dell'anodo alla corrente di steady-state durante la HER, quindi il rapporto OTH rimane costante con la pressione. Questo permette di operare senza membrana ad alta pressione e risulta essere un vantaggio di questa tecnologia in quanto non porta al rischio di incorrere in miscele esplosive.

(Figura 5.2.2)

Rispetto allo stoccaggio per l'immagazzinamento chimico, le spese energetiche (in termini di consumo elettrico) diminuiscono notevolmente. Di solito si lavora con flussi liquidi in pressioni sotto i 10 bar (invece che con compressori sopra i 700 bar).

Il tasso di stoccaggio dell'idrogeno è di 0,7 mol per mol di idrogeno all'alimentazione con una resa di metilcicloesano dell'80,6%. Il tasso di stoccaggio dell'idrogeno è di 0,7 mol per mole di idrogeno all'alimentazione. Nonostante l'eccesso di  $H_2$  viene ricircolato, dato che il rapporto idrogeno/Toluene superiore al rapporto stechiometrico ha effetto positivo sull'attività e la selettività.

Come menzionato, l'idrogenazione del toluene è una reazione esotermica che genera circa 2,04 MJ/kg LOHC (9,08 kWh/kg H2). Questo calore potrebbe essere integrato con la fase di rigenerazione anodica all'ETAC che ha una domanda di calore di circa 2,04 kWh/kg H<sub>2</sub> o utilizzato in un'altra applicazione.

La deidrogenazione del MCH viene eseguita a 360°C e a pressione atmosferica. Trattandosi di una reazione endotermica, essa è favorita da alte temperature, ma non da alte pressioni a causa degli intermedi di reazione e dell'equilibrio di adsorbimento. La presenza di idrogeno nel feed ha dimostrato di avere un effetto positivo aumentando la velocità di reazione e la selettività di MCH verso il Toluene.

(Tabelle 4 e 5)

Per quanto riguarda la generazione di calore per il processo di deidrogenazione, esso deve essere fornito ad un tasso di 28,25 kW, comportando ad installare un sistema apposito di generazione del calore. Gravimetricamente, rappresenta 2,01 MJ/kg di LOHC alimentato, essendo leggermente inferiore a quello generato nella fase di idrogenazione. Questo crea un'opportunità se si potesse implementare una tecnologia di immagazzinamento del calore quando entrambe le unità sono situate alla pari, assorbendo e rilasciando il calore a seconda della richiesta di elettricità.

In fine dai risultati ottenuti si garantisce una certa ciclabilità del processo con alta selettività del MCH verso il Toluene. Nonostante questo, si dovrebbero fare ulteriori separazioni e riciclaggio durante il ricircolo del LOHC esaurito, data la percentuale di sottoprodotti risultanti alla fine del ciclo.

Analisi Energetica

È stata effettuata un'analisi energetica con lo scopo di valutare le efficienze energetiche all'interno dei processi. Esse vengono calcolate secondo la seguente equazione e sono basate sul potere calorifico superiore dell'idrogeno (HHV).

$$Efficenza = (HHV_{H_2})/(Elettricita + Calore)$$

Sia l'AWE che l'ETAC funzionano a condizioni vicine a quelle ambientali, quindi non viene fornito calore per la fase di generazione dell'idrogeno. Invece per la fase di rigenerazione dell'anodo, le efficienze sono state determinate sia considerando una fornitura di calore esterna che l'integrazione termica con il processo di idrogenazione. La variazione delle efficienze energetiche lungo la linea viene presentata nelle tabelle 6 e 7.

#### Analisi Economica

La valutazione economica è divisa nelle tre fasi della catena di approvvigionamento di idrogeno per entrambe le alternative I costi di produzione, stoccaggio e trasporto sono stati presi dalle informazioni disponibili online e da altre analisi. [13,18]. La posizione dei sistemi per i calcoli è un parco eolico preinstallato in Abruzzo, Italia, con una capacità di 10 MW, composto da 5 turbine eoliche ed un'operabilità annuale di 5000 ore.

(Tabelle 8,9,10,11 e 12)

Dai risultati si può vedere che gli investimenti di capitale saranno maggiori per l'ETAC in quanto per una capacità produttiva uguale richiede un numero maggiore di celle. Tuttavia, gli OPEX sono maggiori per AWE+CGH2 a causa degli alti consumi elettrici per l'elettrolisi e la compressione. L'idrogeno da ETAC+MTH potrebbe essere più economico delle tecnologie disponibili in commercio in un intervallo da 0,3 a 0,6 €.

# Discussione

Come visto in precedenza, l'elettrolisi dell'acqua alcalina affronta alcune sfide tecnologiche. Il carico minimo richiesto e il tempo di funzionamento limitato portano a un numero elevato di cicli di avvio e di arresto, che potrebbero superare il limite del produttore e aumentare il degrado dell'elettrodo. Produrre idrogeno ad alta pressione e ad alta purezza da fonti rinnovabili intermittenti e aumentare l'efficienza energetica per essere più competitivi sono compiti importanti nello sviluppo.

Il processo ETAC può affrontare queste sfide. Ha dimostrato di essere il 15% più efficiente dal punto di vista energetico e abbastanza flessibile nel funzionamento. Supera AWE per i carichi parziali ed è in grado di lavorare a basse densità di corrente a partire da 100 mA/cm2 permettendo un funzionamento per tutto il giorno senza compromettere la domanda di elettricità.

Lo stoccaggio di idrogeno con alta densità affronta barriere puramente tecniche. l'idrogeno compresso ha le più basse densità volumetriche di stoccaggio delle tecnologie disponibili e tuttavia è il più utilizzato fino ad oggi, influenzando direttamente i costi di investimento poiché determina la dimensione dello stoccaggio.

Anche per un'alta pressione di stoccaggio di 700 bar, il sistema mostra alcune limitazioni. CGH2 aumenta anche le spese perché la maggior parte del costo operativo è legato all'uso dell'elettricità, essendo generalmente prodotto e immagazzinato durante i periodi di basso prezzo dell'elettricità.

I LOHC riuniscono diverse caratteristiche che li rendono molto attraenti per lo stoccaggio di idrogeno. Sono liquidi sia in forma idrogenata che deidrogenata a condizioni ambientali, hanno un'alta densità gravimetrica e volumetricamente quasi corrispondono alla densità dell'idrogeno liquido senza passare attraverso un processo ad alta spessa energetica come la liquefazione.

Le simulazioni hanno rivelato l'importanza del catalizzatore e delle condizioni di reazione in entrambe le reazioni, suggerendo la necessità di successivi passaggi di purificazione in base alla frazione di sottoprodotti. La realtà invece ha dimostrato che l'idrogenazione del Toluene e la deidrogenazione del MCH sono processi altamente selettivi su vari catalizzatori eterogenei. Inoltre, è il MTH è il sistema LOHC più riconosciuto e come tecnologia ha già superato la fase dimostrativa.[4]

Occorre sempre considerare che un punto di criticità nel processo sia la generazione del calore necessario per la reazione. L'adozione di LOHC come carrier di idrogeno e di conseguenza vettore energetico richiederà lo sviluppo di sistemi più efficienti termicamente e cataliticamente per il rilascio di H<sub>2</sub>.

#### Conclusione

In questo lavoro viene fornita una descrizione di una combinazione di due processi innovativi. Le loro prestazioni sono simulate e viene effettuata un'analisi dei loro limiti e opportunità. I risultati vengono confrontati con tecnologie mature e commercialmente disponibili e vengono presentate le principali sfide per valutare la fattibilità di questa soluzione all'avanguardia.

Il processo ETAC mostra la possibilità di una scissione dell'acqua a bassa corrente (vicino a condizioni termoneutrali ) con una maggiore efficienza energetica e purezza dell'idrogeno. Tecnologicamente è meno complesso delle tecnologie disponibili in commercio e richiede meno materiali costosi e con costi di assemblaggio inferiori. Inoltre, soddisfa la necessità di essere più flessibile ed è adatto al funzionamento a carico parziale. Il processo ETAC accoppiato con le energie rinnovabili potrebbe fornire un migliore bilanciamento della rete grazie al suo potenziale di evoluzione dell'idrogeno a basse tensioni.

I LOHC sono un'alternativa molto attraente poiché le attuali soluzioni di stoccaggio e trasporto dell'idrogeno non sono redditizie e non sono sicure a causa delle basse densità, delle alte pressioni o dell'eccessivo consumo di elettricità. Le caratteristiche che rendono i LOHC molto simili al petrolio greggio offrono un'opportunità unica per l'uso dell'infrastruttura esistente e specialmente il sistema MTH mostra un potenziale molto alto per la produzione su grande scala e il mercato internazionale.

I processi esaminati hanno una sinergia positiva e diversi vantaggi rispetto alle tecnologie disponibili in commercio. Dovrebbero essere anche considerati in una fase iniziale per la sua applicazione, almeno a livello regionale, in quanto hanno il potenziale per incoraggiare altri attori a muoversi in una direzione simile.

L'idrogeno sarà il modo di incanalare l'elettricità rinnovabile a diversi settori per i quali la decarbonizzazione sarà altrimenti difficile. Sviluppare nuove tecnologie e migliorare quelle esistenti deve essere il motore del cambiamento per un futuro sostenibile basato sulle fonti rinnovabili.

#### Abstract

Water splitting will be the most reliable and sustainable way of producing hydrogen. In order to make hydrogen an applicable reality, actual production cost and storage-transport limitations must be overcome. Models of a conventional water splitting plant that provides compressed hydrogen and the combination of two innovative processes to replace de previous ones, were proposed in order to analyze and compare the performance and capability of the alternatives. The strategy proposed is a two-stage electrochemical-thermally activated chemical (ETAC) process to decouple electrolysis followed by a reversible hydrogenation of liquid organic molecule , commonly known as Liquid Organic Hydrogen Carrier (LOHC), so as to chemically storage the produced hydrogen.

For this reason, simulations of both alternatives were carried out using Aspen Plus due to its great potential and flexibility enhanced with Office Excel integrated tools. This work searches to assess the operation under a renewable power source scheme and review advantages as limitations. As well as discuss possible solutions to address actual challenges towards an overall efficient renewable-to- $H_2$  future.

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#### UNITS OF MEASUREMENT

A ampere

bar bar

- C coulomb
- °C degree Celsius
- cm<sup>2</sup> square centimeter
- g gram
- **h** hour
- **kg** kilogram
- kJ kilojoule
- **kW** kilowatt
- kWh kilowatt hour
- kPa kilopascal
- m meter
- MJ megajoule
- **mol** mol
- MPa megapascal
- Nm<sup>3</sup> normal cubic meter
- sec second
- V volt

#### ABREBIATIONS

AWE	Alkaline Water Electrolysis		
BEV	Battery Electric Vehicle		
CGH2	Compressed Gas Hydrogen		
ЕРСВ	Electron Proton Couple Buffer		
ETAC	Electrochemical - Thermal Activated Chemical		
FCEV	Fuel Cell Electric Vehicle		
HER	Hydrogen evolution reaction		
HHV	High Heating Value		
НТО	Hydrogen to oxygen ratio		
LH <sub>2</sub>	Liquid Hydrogen		
LHV	Low Heating Value		
LOHC	Liquid Organic Hydrogen Carrier		
МСН	Methylcyclohexane		
MTH	Methylcyclohexane-Toluene-Hydrogen System		
OER	Oxygen evolution reaction		
ОТН	Oxygen to hydrogen ratio		
PEM	Proton Exchange Membrane		
RHE	Reversible Hydrogen Electrode		
RM	Redox mediator		
SOC	State of charge		
SOEC	Solid Oxide Electrolyzer Cell		
SOFC	Solid Oxide Fuel Cell		
TOL	Toluene		

# **1.Introduction**

The increasing reliance on renewable generated electricity brings the need of developing more efficient ways of storing this energy to mitigate the variable and intermittent nature of these power sources. Water splitting through electrolysis is one of the most attractive ways of transforming these renewable inputs, storing them by chemical bond formation and producing fuels such as hydrogen that can be therefore used in a fuel cell to produce electricity again.

As world population increases tremendously along with a higher demand for better living standards, future energy need will have to be met in order to comply with society expectations. In the actual scenario, energy use ,mainly for transportation and heating, relies on nonrenewable sources that results in an increase in  $CO_2$  and greenhouse emissions. Thus, the current system is not sustainable and will have to change to an ecofriendly state in order to assure integrity.

Green hydrogen production has a tremendous potential in providing a sustainable energy usage cycle and open a new paradigm for decarbonization of the chemical industry which nowadays relies principally on hydrogen form fossil fuels. Hydrogen is an ideal energy carrier with the highest energy density of 120 MJ/kg and as it mentioned before its burns clean.

However, hydrogen is not an energy source and it has to be produce spending less energy than the one it provides from using it. Therefore, the need of a system that makes use of hydrogen, as an energy carrier, in the cycle for energy supply, known as Hydrogen Economy, must be achieved and in order to do it difficulties must be overcome.

Electrolytic hydrogen production faces technological challenges to develop methods that would consume the least energy amounts and be able to do it on large scale. Improving efficiency and adaptability to variable inputs as reducing cost of materials used in electrolyzers are few of those challenges. Today electrolysers that can function reliable when driven by intermittent power inputs such as renewables are not still a commercially available so the need of developing new approaches to exploit these power sources is urgent.

Storage and transportability require readily availability, short charge/discharge times and enough gravimetric/volumetric density. Nowadays a big part of industry and on-vehicle applications rely on compression or liquefaction of hydrogen which has relatively good charging/discharging times but very low energy density. In addition, safety is very important aspect to this due to high pressures and flammability. Thereby, it is imperative to develop safer and higher energy dense ways of transport and store H<sub>2</sub> that take advantage of preinstalled capacity rising the viability as energy carrier.

This work will try to approach these two important aspects in Hydrogen Economy by proposing the combination of two innovative processes that could provide to society clean and safe energy to many applications. By decoupling electrolysis, we will be able to consume less power to drive water splitting at low voltages with lower current densities. Subsequently, by chemically bonding that hydrogen to an organic compound suitable for hydrogenation/dehydrogenation (Liquid Organic Hydrogen Carrier) we facilitate its transportation as it does not require any higher pressures or lower temperatures. Thereby, hydrogen would be supplied on-site and on-demand by desorbing it from the carrier.

Renewables-to- $H_2$  could be the way of moving towards a carbon neutral or carbon free economy in the short and medium term. By improving efficiencies, increasing versatility, and reducing

energy losses we will be able to maximize the recovery from primary sources and provide society with a sustainable way to satisfy present and future demands.

#### 1.1 Electrolysis

In early 1800, Alessandro Volta built up the first voltaic pile able to provide a continues current flow. In the same year, W. Nicolson and A. Carlisle used it to discover water electrolysis using copper electrodes which, a month later, lead J. Ritter to perform the first "real" water splitting collecting hydrogen and oxygen separately.

Today, water electrolysis is a well-investigated method and several technologies are available from lab-scale to large-scale. Principally they differ on type of electrolyte use within the cells. The three major technologies for water electrolysis that are commercially available are alkaline water electrolysis (AWE), proton exchange membrane cell (PEM) and solid oxide electrolysis cell (SOEC). The first two types work under near ambient temperature conditions ( up to 90°C), whereas a SOEC usually ranges between 700 and 950 °C.[22]

Alkaline water electrolysis (AWE) is consolidated as the most mature technology commercially available for large-scaled hydrogen production. It consists in two Ni-based electrodes immersed in basic solution (usually 30-35% wt KOH) separated by a porous diaphragm. As mentioned, before it operates with temperatures between 60 and 90 °C and below pressures of 30 bar achieving a purity in the range of 99,5-99,9%. The key to this technology is its availability and low specific cost compared to other technologies.

PEM electrolysis was first introduced to overcome the limitation of AWE electrolysis. It allows high current densities and much more flexible than the other technologies. It is a very compact technology and very suitable for small applications and achieves good cell efficiency. In addition is capable of operating under pressures providing highly pure and compressed hydrogen. However, several disadvantages have held this technology back such as expensive platinum catalyst, membrane materials, high system complexity and water purity requirements.

SOEC, is the least developed technology and has not reached commercially availability as the previous ones. Nonetheless several companies are bringing it to the market giving its advantages like high energy efficiency, low material cost and the possibility of reverse mode operation as a fuel cell or syngas production through co-electrolysis from steam and carbon dioxide.



*Figure 1.1 : Water electrolysis technologies*: *AEC : Alkaline Electrolytic Cell ; PEMEC : Polymeric Exchange Membrane Electrolytic Cell ; SOEC : Solid-Oxide Electrolytic Cell* 

Since AWE is the incumbent technology used for large scale production, in this research, "commercial water electrolysis" refers directly to alkaline water electrolysis. Alkaline water

electrolysis systems are widely available, exhibiting durability and relatively low investment cost. The use of nickel-based electrodes for AWE has drawn the cost of using noble metal electrodes such as the platinum group metals that also suffered dissolution during Oxygen Evolution Reaction (OER) leading to a quicker loss of activity. Nickel is the most active non-noble metal and proved to be more stable during OER. In addition, high surface area has been achieved by dealloying Ni-Zn or Ni-Al alloys in alkaline solution, commonly known as Nickel Raney obtaining high catalytic activity. In addition, the lower dissolution of anodic catalyst and the electrolyte exchangeability consent to a higher durability.

Alkaline electrolysis does not need to use a membrane like the PEM. However, this is a drawback that limit operation under pressure and impact negatively on the hydrogen cost. In addition, the lack of flexibility to work with intermittent lead also to lower efficiencies due to several start-up and shutdown and affects gas purity due to cross-over at low current densities.

Development are focused on addressing the current density issues, operating pressure and design for dynamic operation which influences efficiency, durability and H<sub>2</sub> characteristic .Electrode overvoltage and ohmic losses are mainly on the focus of research in order to improve performance.

# 1.2 Storage and distribution

The store of hydrogen is quite challenging. Hydrogen (H<sub>2</sub>) is the lightest compound on earth. 1 kg of gas hydrogen at room ambient conditions occupies  $11 \text{ m}^3$ . So, to make hydrogen storage economically viable, the key is to increase its density. This might sound like an easy task but in order to do so technological methods, where some **energy inputs** as work or heat, are needed and sometimes even specific **material properties** that allow to bind hydrogen or store it.

The goal of having hydrogen stored stationary is to reduce the cost of delivery and availability on demand. Consequently, storage is cost-related to the applications that use the hydrogen due to investment cost as for operating costs and to rate of use. There are several technologies for hydrogen storage and in the last years research have been focused on hydrogen storage for mobility.

Because of that, compressed hydrogen (CGH<sub>2</sub>) is the "mainstream" option when talking about storing and distributing hydrogen, especially for the automotive sector due to rapid refueling capability and well-developed and established infrastructure. Compression from the atmospheric pressure to 30 MPa or higher needs a large amount of energy and can be realized by adiabatic or by isothermal compression. In case of adiabatic compression, the process occurs without heat exchange between gas and the surrounding environment and safety conditions must be assured. During isothermal compression the temperature remains constant and such cooling of the gas has to be taken into consideration.

Mostly CGH<sub>2</sub> in pressurized vessels is available up to 300 bar and in order to achieve higher energy density for on-vehicle applications high pressure tanks are being developed to resist up to 700 bar, being one of greatest challenges in construction when selecting materials not only for the containers but also safety and balance of components as pipelines, valves and regulators.

Nevertheless, compressed hydrogen has the lowest volumetric energy density and leads to safety issues of operating with a flammable at high pressure. In addition, materials must also resist corrosion and avoid hydrogen diffusion.

Another available technology is liquefaction of hydrogen. Cryogenic hydrogen (LH<sub>2</sub>) has a density nearly twice that of compressed hydrogen at 70 MPa. Liquid hydrogen is stored in specially insulated cryogenic tanks under pressure. However, liquefaction is an energy-intensive process consuming about 12.5-15.0 kWh/kg compared to about 6.0 kWh/kg for compression to 70 MPa (J.W. Sheffeld et al., 2014).

High-pressure cryogenic tanks are also being explored to alleviate the requirement for very low temperature storage. New approaches are needed to reduce the cost of liquefaction and make it more energy efficient. The storage capabilities of current technologies, such as gas and liquid hydrogen storage in containers are far from the requirements for viable onboard automotive storage. Simple, incremental improvements in these technologies will not allow researchers to meet the rigorous storage requirement. Discovering new materials and technics to storage hydrogen in a more efficient way are the present and future challenges if hydrogen is to become the center of our economy.

# 1.3 Actual and future challenges.

#### 1.3.1 Production

Today hydrogen is a fundamental agent in the production of base chemicals as ammonia or methanol, petroleum products and many other materials and compounds. The industrial sector relies on its supply mostly by steam reforming of fossil hydrocarbons, resulting in air and atmosphere pollution if following protecting steps are not taken into account (Carbon Capture).

To create a carbon-free and environment-focus economy in the near term, it is by all means that water splitting is the key technology in order to achieve it and to develop solutions for distributed on-demand and on-site generation.

Various water splitting technologies are already widely available, few of them even at industrial scale. The major types of electrolyzers differ principally on the type of electrolyte used in the cells and they all present very high efficiencies for **high current densities** (Appendix 3). They are already implemented as an on-site solution for gas chromatography, welding and metallurgy, pharmaceuticals and food & beverage industry, glass, and electronic production. In the energy sector, electrolytic hydrogen is used as a cooling fluid for turbines and also in bubble chamber of nuclear power plants.

However conventional electrolyzers are designed for operation at fixed process conditions and the implementation of fluctuating and highly intermittent renewable energy, such as solar and wind, is challenging. Each component of a hydrogen energy system has to be optimized in order to increase the operation time and system efficiency. Only in this way, hydrogen produced by water splitting can be competitive with the conventional fossil fuel-based path.

At low power availability AWE shows a limited part-load range due to an increased gas impurity resulting in explosive mixtures of hydrogen and oxygen that must be prevented to avoid safety

shutdown when reaching certain gas contamination. Although when working with high currents ,the energy losses reduce energy efficiency and excessive overpotentials are displayed. Catalysts are required to address these issues and also seek to increase the rate of the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER).

Many researchers have aimed for the replacement expensive noble-metal electrodes that directly influences the costs of production and capex when projecting or revamping a medium-large scale plant. Attention should be focused when considering scale-up of such systems.

Others for instance are also considering how to "deconstruct" traditional electrolysis technology to sidestep the issues that arise when using intermittent power sources, including the mixing of hydrogen and oxygen, and poor efficiency. Is under these premises that a **two-stage electrolysis** system, where hydrogen and oxygen are generated in separate steps with high efficiency could result in a sustainable and more advantageous way of harvesting hydrogen from renewable power inputs.

Photovoltaic panels and wind turbine efficiencies are also to be improved as capex and opex to be reduced if we think of an energy power matrix based on these primary energy sources. The process of water splitting is defined by current–voltage characteristics and photovoltaic panels and wind turbines should be operated at the maximal power point in order to guarantee possible modulation.

The need of a more versatile and reliable technology commercially available which allows operation on fluctuant amounts of energy and possible grid integration is indispensable. Integration of water electrolysis and renewable energy for sustainable hydrogen production is an essential step towards the decarbonization of industrial processes and the transport sector.

# 1.3.2 Storage and Transport

Despite extensive research toward clean hydrogen production, hydrogen storage of high density is still a challenge for stationary applications as for portable ones ,being even a significant issue for transportation applications.

Safe and cost-effective storage and transportation are a major task in the development of a sustainable hydrogen economy. Compressed gaseous and liquid hydrogen are the two solid storage techniques commercially available and typically require large-volume systems or instead operation under very high pressures or near absolute zero temperatures.

Storage is still regarded as one of the most critical points, which must be solved before a technically and economically viable hydrogen fuel system can be established. In fact, without effective storage systems, a hydrogen economy will be difficult to achieve.

Transportation has already seen some viability in the past years, and it is available for gaseous and liquid hydrogen distribution by trucks or pipelines depending on demand. Technical and economic competitiveness of each transport option depend on volume and delivery distances. Pipelines are the preferred option for large quantities and long distances. Liquid hydrogen trailers are for smaller volumes and long distances and compressed gaseous hydrogen trailers are suitable for small quantities over short distances.

Economically, pipelines are characterized by a very low operating cost but high capital investment while liquid hydrogen has very high operating cost due to liquefaction but lower capital costs

depending on the quantity of hydrogen and the delivery distance. In addition, hydrogen suitable pipelines must be made of non-porous, high quality materials such as stainless steel.

Therefore, investments in a hydrogen pipeline are up to two times higher than those for natural gas pipelines. But on the other hand, costs could be considerably reduced if the natural gas built up infrastructure could be adapted to hydrogen. Unfortunately this would be a short-medium term solution as hydrogen would need to be blend up with natural gas, pipelines coated internally to avoid diffusion and in particular valves, manifolds and compressors would need to be modified as optimal work point is under certain range of conditions such as gas composition.

So still urges the development of applicable long-term solutions able to overcome the previous challenges. Reorient the investment in developing new suitable distribution lines by resettle the actual built up infrastructure of fuel supply and distribution. Hydrogen should be transported in safe and easy way as **liquid hydrocarbons** fuels are today, aiming for the highest energy density without compromising the energy supply. The advantages of making use of the already existent infrastructure will make hydrogen a possible and applicable reality bypassing one of the most critical bottlenecks of hydrogen economy.

# 1.3.3 <u>Renewable electricity</u>

By nature, the production of electricity from renewable energy sources is pretty different from conventional coal, gas, or nuclear power plants. The intermittence of most renewable added to the limited human capacity to forecast their behaviors is the main limitation on the road to a fully renewable energy dependability.

Unlike the conventional power stations, the scale of renewable power plants is smaller than the first ones. Most renewable power production units are connected to distribution networks instead of transmission networks due to the power levels. However, because of their variability sometimes more energy is injected to the power grid this could cause complications along the network if actions are not taken. While the distribution structure has been thought to be top to down, the increasing of power injection into distribution networks raises technical issues and complicated management of the networks.

Is by these facts that there are benefits on introducing energy storage in our electrical networks to face an increase in productions or a decrease in consumption by absorbing and releasing available power allowing production level to be maintained.

# 1.4 Research & Development

# 1.4.1 When producing hydrogen

In conventional electrolysis, hydrogen is produced at the cathode while simultaneously oxygen is generated at the anode. In this scheme, the rates Oxygen Evolution Reaction (OER) and Hydrogen Evolution Reaction (HER) are tightly "coupled" in time and space, with two moles of hydrogen for every single mole of oxygen. However, electrolyzers run by variable renewable energy sources face operational issues such as  $H_2/O_2$  crossover at low current densities. For instance, when powered by solar energy, rates of  $H_2$  and  $O_2$  may be lower than the permeation rate though

membrane/diaphragm. This not only impacts on the amount of hydrogen that could harvested but sets dangerous scenarios or even could cause damage to cell materials and components because of the formation of reactive oxygen species.

Moreover, AWE battle against one of the major challenges in electrolytic grade hydrogen production: The overpotentials. The four-electrons transfer for Oxygen Evolution Reaction, which take place at the anode, limits the rate of generation of oxygen and consequently hydrogen. This resistance is displayed as a cell potential increase (activation overpotential) that show the difference between half-reaction thermodynamically defined potential and experimentally observed potential.

Is because of this background that decoupled electrolysis was proposed and has been considered as a strategy of advance water splitting. By using an auxiliary redox mediator (RM), it has been possible to cut in half the water splitting reaction by linking the oxygen evolution to a reversible reduction of the mediator (electron acceptor) and subsequently reoxidizing it (electron donor) while generating hydrogen at the cathode. In this way, rate of oxygen and hydrogen evolution can be completely different and could even been performed in different time and space overpassing the problematics mentioned above. When these mediators also buffer the pH during electrolysis, they are known as electron-coupled-proton buffers (ECPBs).

Decoupled evolution of  $H_2$  and  $O_2$  can be already found in photosynthesis and thermochemical water splitting. By stepping electrolysis, it will be possible to make renewables-to- $H_2$  more efficient and economical avoiding high overpotential and gas mixture. Then the key concept here is a suitable redox mediator that acts as a scissor for the input voltage of conventional electrolysis. However, some essentials requirements must be satisfied. The redox potential of the RM must be situated between the OER and HER onset potential with a fast and reversible wave. In addition, it must be stable in electrolyte conditions when changing it state of oxidation and should guarantee high reversibility, kinetics, and cycle stability.

Up today many realizations of decoupled water splitting were made using soluble redox mediator which have advantages as they can be easily adapted to redox flow batteries but suffer difficulties with high pH electrolytes and gas crossover. For these reasons, solid-state ECPBs were introduced allowing cell operation without a membrane. The redox mediator is the electrode itself behaving as anode for hydrogen evolution and cathode for oxygen generation in a completed cycle.

Under this approach is that Dotan et al. [10] proposed a decoupled hydrogen and oxygen evolution by a two-step electrochemical-chemical cycle. First an electrochemical step that reduces water at the cathode and oxidizes the anode, followed by a spontaneous chemical step that is driven faster at higher temperature, which reduces the anode back to its initial state by oxidizing water.(Figure 1.2)



Figure 1.2: E-TAC Cycle steps. Hydrogen generation step in blue and anode regeneration in red

The E-TAC water-splitting process replaces the conventional water oxidation reaction in alkaline electrolysis with a twostep cycle in which the anode is first charged (electrochemically) and then regenerated (chemically). The hydrogen evolution reaction (HER) in the first step of the process remains the same as in alkaline electrolysis, except that it occurs at ambient temperature instead of elevated temperature (typically 50–80 °C). Therefore, the same cathode materials used in alkaline electrolysis, such as Raney nickel or other HER catalysts, can be used. [4]

On the other hand, the anode, which functions in a completely different manner from conventional alkaline electrolysis, requires careful material selection as it must guarantee stability in alkaline solutions.

#### 1.4.2 When storing hydrogen

As previously reviewed a major challenge in the adoption of hydrogen for (long term and largescale) energy storage is the lack of economical, efficient and safe storage as well as delivery infrastructure and transportation. Hydrogen is either stored in a pressurized gaseous state up to 700 bars or in a liquid state at temperatures below -253°C.Both systems safety-critical, technologically complex and expensive for establishing a large-scale distribution infrastructure.

It is under these premises that a promising alternative is the chemical storage of hydrogen using organic molecules suitable for hydrogenation, from now on Liquid Organic Hydrogen Carriers (LOHC). LOHC are organic molecules which can switch between hydrogen-rich and hydrogenlean states by hydrogenation and dehydrogenation processes respectively and allow safe and long-term storage with high energy density for long time periods.

Most LOCH are liquid at ambient conditions and have physical properties similar to diesel meaning that are easy to handle, safe and could use the existing fuel distribution structure. Is that if we want a transition to hydrogen-based energy system we have to take advantage of our already installed capacity.

Liquid organic hydrogen carriers have proved to be an efficient hydrogen storage technique for energy surpluses in the Renewables-to- $H_2$  optic. Comparison between all the techniques mentioned is presented in Table 3.

Parameters	Compressed Storage (CGH <sub>2</sub> )	Liquid Storage (LH2)	Chemical Storage (LOHC)
Temperature (K)	273	21.5	373-573
Pressure (bar)	700	1	1
Gravimetric Capacity (wt.%)	13	Variable	<18
Volumetric Capacity (kg/m <sup>3</sup> )	<40	70.8	150
Advantages	Highly beneficial for fuel purposes, lightweight, energy effective, occupy smaller space.	Long term, volumetrically and gravimetrically efficient.	Low reactivity, short storage time, high storage density.
Limitations	Requires high pressure cylinders, inefficient volumetrically and gravimetrically.	Boil-off and liquefaction processes are energy expensive.	Slow kinetics for dehydrogenation.

# Table 1: Comparison of various hydrogen storage techniques.

A complete LOHC system consists of reversible cycle dehydrogenation and hydrogenation for release and storage of hydrogen respectively. (Figure 1.3) Though hydrogenation system efficiency is high (98-99%), still dehydrogenation system's efficiency is dependent on various operational parameters. Various LOHC's have been used for the transportation and storage of hydrogen like benzene-cyclohexane, MCH-Toluene, Naphthalene-Decalin, and DBT-PBT systems.



Figure 1.3 LOHC system. LOHC complete cycle for electrolytic grade hydrogen

One of the mostly studied and developed LOHC systems is the Methylcyclohexane-Toluene couple also known as MTH system (Methylcyclohexane-Toluene-Hydrogen) as it has been proved to be safer and less energy exigent than the others. In addition, the boiling points of Toluene and MCH are 111°C and 101°C respectively which is advantageous from an operational point of view.[16]

So as is stated in the title of this work, the combination of these last two innovative processes will be studied to assess if they could mean an improvement in operation with variable energy inputs. By making use of renewable electricity, decoupled water splitting will be run, and the produced hydrogen will be stored by converting Toluene to Methylcyclohexane. Then from hydrogenation plant, transportation of rich LOHC to supply third users as energy application, chemical industrial process or even a fuel filling station for loading onto a vehicle. Finally dehydrogenate methylcyclohexane to produce on-site hydrogen that could even be onboard for a mobility application.

# 1.5 Goals and scope of this thesis.

The goals of this work are focused on the modelling and analysis of synergies of two innovative processes in the supply chain of hydrogen and how the overall efficiency is influenced. The scope is to evaluate the feasibility of this arrangement and to compare it to an already established technology in order to oppose advantages, benefits, weaknesses and disadvantages.

# 1.6 Methods

Simulations are carried out principally using Aspen Plus V.10. Thanks to its great potential for physical properties and engineering modelling it was possible to emulate close-to-real behavior of the processes discussed before.

However, as electrolysis is not supported on the Aspen Plus interface by taking advantage of the software integration with Windows Office Excel it is possible to define mathematically models that recreate real operation of the water splinting units and integrate them within an Aspen Plus process diagram in order to evaluate a whole process than also depends on other devices and apparatuses. (3.Simulation and Modelling).

As it was stated before the scope is to confront two different hydrogen supply change from production to delivery so as to evaluate overall efficiencies and benefits.

Firstly, a conventional water splitting process with a commercial Alkaline Water Electrolyzer (AWE) that store compressed hydrogen (CGH<sub>2</sub>) for up-to-700 bar filling service and liquid hydrogen (LH<sub>2</sub>) in insulated tanks for further delivery.

Then, a combination of the two innovative process discussed before: A decoupled water splitting with two step electrochemical-chemical cycle (ETAC) to produce hydrogen from electricity and a following hydrogenation reaction of an organic liquid compound (LOHC) to chemically store the hydrogen produce before.

Both alternatives are supposed to run by renewable electricity inputs and further qualitative analysis will be done to assess feasibility and adaptability as pros and cons. The whole work searches to provide with ideas on which to work, as well as offer schemes, which can be a starting point for enhanced solutions.

Validation of the simulations will be made over experimental data of the publications on which the processes are based, and certain improvements and modification will be implement using Aspen Plus sensitivity and optimization tools.

Finally, energetic and economics analysis are executed to evaluate heat load requirements and estimate operational and capital incurrences. Sustainability will be also taken into exam as is crucial key in the adoption of new technologies.

# 2. Review: What's behind the innovation?

This section will review both innovative processes in detail to present what are the assets behind these two technologies and discuss advantages, disadvantages and future prospects.

# 2.1 Electrochemical – Thermally Activated Chemical Process (ETAC).

As mentioned before the electrolysis in ETAC is decoupled by a solid-state Redox Mediator (RM) nickel (oxy)hydroxide being the anode during hydrogen generation step. The standard potential of the Ni(OH)<sub>2</sub> /NiOOH redox reaction is higher than that of the OER. Therefore, its oxidized form, NiOOH, can oxidize water and produce oxygen, in a chemical reaction that reduces the NiOOH to Ni(OH)<sub>2</sub>.

NiOOH + H<sub>2</sub>O +  $e^- \rightarrow Ni(OH)_2 + \frac{1}{4}O_2$  (E°= 0,19 V<sub>RHE</sub>)

(Reaction 1: Anode's Regeneration Reaction)

This usually happen in nickel based alkaline batteries such as Ni-MH (Nickel Metal Hydride) or Ni-H<sub>2</sub> (Nickel Hydrogen) as a spontaneous undesired event that causes self-discharge of the battery. The reaction is driven by the difference of the electrochemical potential of OER (1,23 V) and the oxidized nickel oxyhydroxide anode (1,42 V) but at ambient temperature is kinetically impeded allowing batteries to operate without oxygen evolution under many charging-discharging cycles. However, at slightly higher temperatures, the electrode's self-discharge reaction is much more accelerated causing swelling and ultimately battery failure.

Despite that the Ni(OH)<sub>2</sub> /NiOOH redox potential is higher than OER potential, it is still suitable for scissoring conventional water splitting as overpotentials are very low in comparison to the four-electron transfer activation overpotential for OER at coupled electrolysis. Under this scheme, Ni(OH)<sub>2</sub> behaves as an electron coupled proton buffer (ECPB) that goes firstly through oxidation (i.e. charging ) while hydrogen is produce at the cathode. Then a spontaneous chemical reaction to regenerate the original anode while producing oxygen.

This methodology was first reported by Dotan et al.[11] to decouple alkaline water electrolysis using a cobalt-doped Ni(OH)<sub>2</sub> electrode as primary anode and a typical platinized nickel-coated stainless-steel cathode for hydrogen evolution reaction. Process was carried out using a 5 M KOH solution at ambient temperature(25°C) for 100s at constant current density of 50 mA/cm<sup>2</sup>. The following reactions :

 $\begin{array}{c} H_2O + e^{\text{-}} \rightarrow \frac{1}{2} H_2 + OH^{\text{-}} \left(E^{\circ} = 0 \ V_{RHE}\right) \\ (\text{Reaction 2: HER}) \end{array}$ 

$$\begin{array}{c} Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^- (E^\circ = 1,42 \ V_{RHE}) \\ (Reaction 3: Ni(OH)_2 \text{ oxidation}) \end{array}$$

Then with a hold-up charge of 5 C cm<sup>2</sup>, power was switched off and the anode exposed to a  $95^{\circ}$ C hot 5M KOH aqueous solution for another 100s, regenerating anode to its initial state while generating oxygen according to the Reaction 1.

In their work they performed a cycle voltammogram at the same exact previous condition for first step, measuring a displaying redox wave centered around 1.4 VRHE. Then measured the steady-state current – potential plots for the same electrode, in the same electrolyte, measured at ambient

temperature and at 95°C. Results were then overlaid by Landman et al.[1] in a unique graph obtaining:



**Figure 2.1** Cyclic voltammograms. Cyclic voltammogram measured at ambient temperature in 5M KOH aqueous electrolyte with a cobalt-doped Ni(OH)2 working electrode (green line), alongside steady-state current – potential plots for the same electrode in the same electrolyte measured at ambient temperature (blue triangles) and at  $95^{\circ}$ C (red circles). The dashed lines are extrapolated exponential curves. The inset shows the Tafel plots for the steady state polarization at ambient temperature and  $95^{\circ}$ C (same color coding). Plot by Landman et al [1].

At ambient temperature, the steady-state OER current density is less than  $1 \text{ mA/cm}^2$  near the electrode's redox potential (1.4 VRHE). Then the chemical reduction is a spontaneous but occurs at a very slow rate at ambient temperature. However, the reaction rate is significantly enhanced when the temperature increases to 95°C and oxygen evolves completing the water splitting reaction.

Basic steps schemes and an illustration of the full ETAC as batch-mode operation are presented in **figure 2.2.** Electrodes are stationary while electrolyte is pumped to the cell at the required temperature for each step.



Figure 2.2 Schematic illustration of the ETAC cycle. (1) Illustration of the basic steps . The electrochemical hydrogen generation step (Step I, left), is carried out with cold alkaline electrolyte. At this step, the  $Ni(OH)_2$  anode gets oxidized while hydrogen evolves at the cathode. Next, the chemical anode regeneration step (Step II, right), is carried out in a hot (95°C) alkaline solution at open circuit. Oxygen evolves while the oxidized NiOOH anode is spontaneously reduced back to its initial state ( $Ni(OH)_2$  (II) Illustration

of a batch-mode operation and circulation of the cold and hot electrolytes. O Cold electrolyte is circulated though the cell and the anode and cathode are connected to a power source. Then, in O the power is switched off and a hot electrolyte is circulated through the cell.

The poof-of-concept experiments by Dotan et al. [11,12] were performed measuring hydrogen and oxygen evolution during charging step and oxygen during regeneration step for equal time duration (100s). Hydrogen was evolved for 10 cycles without oxygen generation at a constant current density of 50 mA/cm<sup>2</sup> at a near thermoneutral voltage  $V_{th}$  (1,48  $V_{RHE}$ ).

After each hydrogen generation steps, the charged anode was taken out of the cold cell and placed in a hot (95 °C) electrolyte (5M KOH) for another 100 s to accelerate spontaneous oxygen release and regeneration of its initial state. Bubbles (O<sub>2</sub>) formation was observed during the anode regeneration step, whereas during the hydrogen generation step, bubbles (H2) were formed only on the cathode.

Anode and cell potential were also recorded during hydrogen generation step showing an increasing nature as Ni(OH)<sub>2</sub> is getting oxidized i.e. as State of Charge (SOC) increases. However, a very little shifting from cycle to cycle demonstrating the cyclability and no degradation of the electrodes under operation with an average anode ( $V_{Anode}$ ) and cell voltage ( $V_{Cell}$ ) of 1,42 V and 1,5 V respectively. Then the ETAC voltage efficiency,  $V_{th}/V_{Cell}$ , is 98,7% (1,48/1,5).

Graphs extracted from Dotan et al. regarding the proof-of-concept experiments are available in Appendix I.

As hydrogen is the desired product, the duration of other steps should be minimized so as to maximize hydrogen production. While the rate of hydrogen is fully linked to the applied current and can be controlled through that, oxygen evolves spontaneously, and temperature must be controlled to inhibit OER in first step as to accelerate regeneration in second step and cut times.

In addition to the proof-of-concept experiments reviewed before, Dotan et al.[12] also executed some complementary test that show important advantages of ETAC process that are crucial for future implementation.

In first place, they have been able to prove that charging and chemically regenerating the  $Ni(OH)_2$  electrodes replacing the electrochemical OER reduces a lot the overpotential which typically contributes the largest energy loss in alkaline and PEM electrolyzers. This was demonstrated from cyclic voltammograms (figure 2.3) of the  $Ni(OH)_2$  vs a state-of-the-art NiFe double-layer hydroxide (LDH) electrode for alkaline electrolysis where it can be seen that the charging of the cobalt-doped nickel (oxy)hydroxide (blue) precedes ,i.e. has lower voltage, the oxygen evolution at the NiFe LDH (red).



*Figure 2.3 Cyclic voltammograms measured at a scan rate of 50 mV/s and ambient temperature in 5M KOH aqueous electrolyte with a cobalt-doped nickel (oxy)hydroxide anode (blue) and a NiFe layered double hydroxide (LDH) anode (red).* 

Subsequently, they carried out water splitting in carbonate-buffers solution to bypass the high pH issues of concentrated alkaline solutions, that sometimes are not suitable for some applications. Using carbonate-bicarbonate 10,6 pH buffer solution, they carried out several cycles of ETAC at a nominal current density of 25 mA/cm<sup>2</sup> obtaining an anode potential ranging between 1,43  $V_{RHE}$  and 1,5  $V_{RHE}$ . This proved the ETAC process to be versatile with electrolyte conditions meaning a less hazardous operation which would involve higher costs and also setting the possibility of using low purity water sources.

In addition, ETAC process present other key advantages that make it a new technology with big prospects of future application. In terms of high-pressure hydrogen and gas purity, decoupled membraneless operation could pave the way to high-pressure production, avoiding gas crossover through the separator at high pressures that currently limits operation pressures in conventional alkaline electrolyzers.

Also, the process could principally be operated without precious metal catalysts, since it is carried out in an alkaline solution where stable nickel-based catalysts are available and cost much less than for instance platinum-based PEM catalysts.

The ETAC process is patented and already exists a prototype by a start-up Israeli company  $H_2Pro$  (Appendix I). Schematic operation of a continuous hydrogen production with a multi-cell alternated cycles is presented in figure 2.4. During hydrogen production, a low-temperature electrolyte circulates through cell A, moving the hydrogen bubbles to the hydrogen separator (blue). Simultaneously, a hot electrolyte flows through cell B to regenerate the (previously charged) anode, producing oxygen and moving the oxygen bubbles to the oxygen separator (red).



**Figure 2.4** Electrolyte flow in the process. Cold electrolyte (blue) circulating in cell A during anode charging stripping generated  $H_2$  gas that is separated in a flash unit. Hot electrolyte (red) regenerating a fully(partially) charged electrode, taking away generated oxygen to the separator unit. Intermediate fluid is recirculated through a bypass most of the time and being sent to all cells in between steps. A schematic cell (right) shows state of electric circuit during hydrogen generation step (closed) and anode regeneration step (open). Illustration was taken from Dotan et al. [11]

In addition to the hot and cold electrolytes, an intermediate temperature (grey) fluid will be used to displace the cold (hot) electrolyte within each cell into the proper separation tank to avoid mixing of the hydrogensaturated (oxygen-saturated) electrolyte with the hot (cold) electrolyte during the switch between cycle steps.
# 2.2 Liquid Organic Hydrogen Carriers (LOHC)

As we have previously reviewed a major challenge in the adoption of hydrogen for (long term and large-scale) energy storage is the lack of economical, efficient and safe storage as well as delivery infrastructure and transportation. Hydrogen is either stored in a pressurized gaseous state up to 700 bars or in a liquid state at temperatures below -253°C. However, their volumetric density remains still at lowest values among the storage technologies available today.

In order to achieve higher densities, bond-formation storage was introduced in the past years as a method to fix hydrogen on materials or chemicals. The strong bonding allows hydrogen to be kept at high density even at ambient conditions. Notwithstanding more energy is required to release chemically bonded hydrogen, result a much more convenient approaches as economical cost derived from high pressures and low temperatures are avoided. In addition, turns to be much safer.

These technologies due to the vast multitude of possibilities are classified into categories, being the two main families the metal hydrides and the chemical hydrides. The difference between both is evidently the metallic and non-metallic nature of atom o group of atoms which hydrogen gets bonded. Among the chemical hydrides, we found also bulk chemicals as ammonia, methanol or formic acid , which play an important role in the chemical industry besides hydrogen storage.



*Figure 2.5 Volumetric and gravimetric hydrogen storage densities*. Volumetric (blue, kg/m<sup>3</sup>) and gravimetric (yellow, wt%.10) storage densities of technologies available.

With this background, Liquid Organic Hydrogen Carriers were introduced as a hydrogen stored due to their suitability for reversible dehydrogenation and hydrogenation maintaining a liquid state in both dehydrogenated and hydrogenated form. It is important to note that ammonia or methanol are liquid, but their dehydrogenation products are gaseous, not being advantageous as  $CO_2$  capture or  $N_2$  separation has to be performed if pure hydrogen is required.

LOHC achieved reversibility by saturation and unsaturation of carbon-carbon bonds. The suitability for hydrogen storage depends on stability and density of these bonds, the long-term

stability of the compounds when alternating between hydrogen-rich and hydrogen-lean forms, the cost of synthesis and the toxicity [16]. In addition, it is quite convenient to work with high boiling point and low frizzing points compounds. The former allows for an easier separation from produced hydrogen, while the latter prevents clogging of equipment and maintains pumpability at low temperatures.

One of the most studied LOHCs is methylcyclohexane and toluene which accounts a gravimetric density of 6.1% wt. and a volumetric density of 47 kg/m<sup>3</sup>. Its dehydrogenation reaction is a well-stablish procedure, especially in petroleum industry. Supported catalyst based on platinum (Pt), palladium (Pd) and rhodium (Rh) are commonly used for dehydrogenation reaction and in the last years nickel-based formulations are being developed so as to replace the previous ones.

MCH is quite stable and for dehydrogenation requires at least 68 kJ/mol (endothermic) with temperatures as high as 350°C. Nonetheless, reaction is quite dependent on catalyst properties like activity, selectivity and stability. In addition, deactivation and coking must be taken into account due to high temperatures at the reactor.

Like dehydrogenation, hydrogenation of toluene usually involves noble metal catalyst, in this case supported ruthenium (Ru) is commonly chosen but same catalyst for dehydrogenation are still suitable to saturate toluene molecules varying reacting condition (temperature and pressure). This set an advantageous opportunity for a more straightforward way to store and reuse hydrogen. In addition, hydrogenation is exothermic, and temperatures typically applied range from 130-250°C. Pressures tend to be higher than in dehydrogenation, in the range of 10-50 bar.

In terms of energy demand, including the costs of heat and electricity supply during both the storage and release of hydrogen, MTH is capable of achieving volumetric densities as much as liquid hydrogen with an operating cost much lower given that the expenses of heat supplied are below those of electricity. Is important that it does not require any considerable input of electricity for hydrogen to be released since the purpose is to reduce the cost of hydrogen produced through water splitting based on renewables.

Anyway, high temperature heat must be generated in order to released hydrogen and if large amounts of it are required in short time period, this heat must be transferred efficiently and quickly. There are few possible sources such as the combustion of material storage, hydrogen or even an external fuel. Also, it can be seized from environment due to heat integration with another process. SOEC fuel cell may be able to provide enough excess high temperature heat to release hydrogen from MCH.

Combustion of the LOHC itself would also produce  $CO_2$  and other molecules that can be toxic. Burning a part of the released hydrogen it is not ideal from the efficiency's viewpoint as more hydrogen must be produced and stored to deliver the same net amount. However, it might be the most practical and applicable method to provide intermittent high-temperature heat in a fast way. Minimum percentage can be calculated with the following equations[16].

$$X_{Hyd} = \frac{\Delta h_{r,Hyd}}{\Delta h_{r,Hyd} + LHV_{Hyd} / (\eta_{burner} \cdot \eta_{HEX})} [\%] \quad (1)$$

$$X_{H2} = \frac{\Delta h_{r,H2}}{\Delta h_{r,H2} + LHV_{H2} / (\eta_{burner} \cdot \eta_{HEX})} [\%]$$
(2)

Hydrogen combustion will be clean but cold start might not be easy to reach. Thus, a small reserve or some other fuel could be used until reaction reaches its proper temperature. An example of this is presented on figure 2.5 that illustrates a prototype of hydrogen vehicle filling station based on LOHC.



Figure 2.6. Concept of hydrogen fueling station from LOHC supply.

Toluene and methylcyclohexane are easily transported in trucks and ships because of their properties at ambient conditions. However, they are flammable and quite toxic so safety assets must be taken into consideration during operations. Regarding to capacity, a 40-ton tanker truck can carry around 1500–2000 kg of hydrogen stored on LOHC. Currently a large-scale MTH system is operating in the Pacific Ocean. Japanese company Chiyoda Corp. has been successfully hydrogenating toluene from natural gas steam reforming in Brunei and transporting MCH back to Japan. Fig



**Figure 2.7 Spera Hydrogen by Chiyoda Corporation.** International supply chain of hydrogen stored with the Toluene-MCH system by Chiyoda Corporation in Japan. Production of "blue" hydrogen is located in Brunei and will be further open to green hydrogen.

Spera Hydrogen® [4] Project has proven in a 10.000 h of operation a great performance achieving yield of dehydrogenation and hydrogenation of 99% and 98% respectively. For both reaction, they have been able to develop a unique catalyst of dispersed Platinum-Sulphur nanoparticles supported on  $\gamma$ -Alumina In addition, their proof-of-concept have demonstrated a hydrogen storage and generation capacity of 50 Nm<sup>3</sup>/h.

Germany-based company Hydrogenous [14] have already commercially available LOHC storage units based on DBT/PDBT system and lately has confirmed the construction of the "world's largest plant for the storage of green hydrogen in Liquid Organic Hydrogen Carriers (LOHC) on an industrial scale".

LOHCs are a technology that are being encouraged from the perspective of density as they could outmatch hydrogen liquefaction in terms of electricity. The choice of a large-scale hydrogen storage based on LOHC will impact on the further developments of infrastructure and applications. For instance, we could see sooner the use of LOHC for mobile applications. If 5 kg of onboard hydrogen are required to allow cursing for at least 500 km, with approximate 100-L tank of N-ethyl carbazole the demand will be matched.[16]



*Figure 2.8. Scheme LOHC passenger car.* Vision of a vehicle powered by LOHC. Dehydrogenation occurs on board; the exhaust gases provide the heat for the reaction and lean LOHC returns to the storage to be exchanged at the fuel station.

The dehydrogenation will be carried out on board and the dehydrogenated carrier will be store back in the vehicle until its return to the filling station in exchange for freshly hydrogenated carrier. Different approaches for separated dual chamber or inflatable bags have already been proposed for charging and discharging LOHC at the fuel station.

# 3. Modelling and simulation

Simulations have been carried out using Aspen Plus V.10 and Windows Office Excel 2015. Aspen Plus has several blocks and options where specific routines can be designed and modeled through Excel . Then it gives the software the directives to perform the calculation that is needed depending on the function we are trying to simulate.

# 3.1 Commercial Alkaline Electrolyzer



*Figure 3.1.1 Alkaline Electrolyzer Plant:* Process Flow Diagram of the Alkaline Water Electrolysis (AWE) Plant. AWE stack is carried out using a reactor unit and 2 separators to simulate the diaphragm.

Using a R-Stoic Reactor block it is possible to set the water splitting reaction at a given conversion. Then by sending the outlet to a series of separators it is possible to simulate cathode and anode production with their specific gas crossing due to diffusion in the cell.

Calculator is Flowsheeting Option that will perform a user defined routine to do a specific calculation that is not available in Aspen Plus. Aspen Inputs and outputs are specify in the Define Tab, then calculations are performed in an excel file (Calculate Tab) that contains the electrolyser mathematical model and other variables that cannot be expressed in Aspen such as current density, electrode area or number of cells present in the stack. Calculation is performed following a user define sequence to avoid convergence issues

<b>⊘</b> Define	⊘Calculate	Sequence 🎯	Tears	Stream Flash	Comments						
\land Sample	Sampled variables (drag and drop variables from form to the grid below)										
	Variable	Informat	tion flow	Definition					<b>A</b>		
TEMP         Import variable         Block-Var Block=STACK Variable=TEMP Sentence=PARAM Units=C								<b>•</b>			
	lew	Delete		Сору	Paste		Move Up	Move Dow	View Variables		
<ul> <li>Edit sel</li> </ul>	Edit selected variable										
Variable	<b>© TEMP</b>	•	Refere	nce			Informat	tion flow			
- Category -			Туре	Block	-Var	-	Impo	rt variable			
© All			Block:	STAC	(	-	🔘 Ехро	rt variable			
Blocks			Variable	e: TEMP		- 28	🔘 Tear v	/ariable			
Stream:	s		Senten	ce: PARAM	N						
Model	Utility		Units:	С		•					
O Propert	y Parameters										
🔘 Reactio	ns										

Figure 3.1.0.2. Defined Tab Calculator.

The modeling of the stack was based on previous research of M Sanchez et al,[23,24] that provides the base equations for the polarization curve of cell potential as a function of temperature, pressure and current density, a linked hydrogen rate to the Faradic efficiency and a two parameter dependence Hydrogen to Oxygen ratio to simulate the minor losses due to gas crossover. Therefore, mass and energy balances are stablished in the Aspen Blocks by given them the specific inputs such as reaction conversion to the R-stoic or gas split fraction to the separator in order to approach the stack unit.



Figure 3.1.0.3. Scheme of the stack modelling. Inputs for the Calculator are either given in the Aspen Interface as in Excel.

And ulterior validation of the simulation was done against Sanchez M. et Al [23,24] experimental data and simulated results, obtaining the following parity chart graphs (Fig. ) in order to analyze reliability of the AWE model we have performed. The results show excellent correlation between experimental and modeled data demonstrating accuracy of the simulation under different conditions of temperature, pressure, power load or applied current density.



*Figure 3.1.4. Parity charts diagrams of simulated data vs experimental data.* Parity charts of simulated data from AWE model and experimental data from test beach performed by M. Sanchez et al. (a) Stack voltage. (b) Stack Power. (c) Cell overpotential.

Additionally, validation through a market research of electrolyzers in the range of the production rate was done to compare real characteristics of a stack unit to the simulated one. The performance of our simulated alkaline stack of 12 cells behaves very much like an on-site manufacturing hydrogen unit. The Piel electrolyser Series M fabricated by Mcphy Group can provide a  $H_2$  rate ranging between 2,4 and 4,4  $Nm^3/h$  with a power consumption of 14-26 kW.

Series	Pressure (barg)	H <sub>2</sub> flow range (Nm³/h)	O <sub>2</sub> flow range (Nm³/h)	Electrical power range at nominal rate (kW)
Baby	1	0.4	0.2	3
Р	1-2.5	1 - 1.6	0.5 - 0.8	6 - 9
М	1-2.5	2.4 - 4.4	1.2 - 2.2	14 - 26
н	4 - 8	3 - 10	1.5 - 5	18 - 60

Figure 3.1.5 Fig. Commercial electrolyzers Piel by Mcphy.

# 3.2 Compressed and cryogenic storage

Compress Hydrogen (CGH<sub>2</sub>) and Liquid Hydrogen (LH<sub>2</sub>) methods have been simulated simultaneously like different alternatives, but they could easily be an integrated system able to provide both compressed and liquid hydrogen given that are very closed related in operation and design.

Mainly applications for  $CGH_2$  require pressure vessels with service pressures of 350 bar. Others, like some vehicles instead can hold up to 700 bar pressures. According to the Department of Energy (DOE) of USA, the theoretical energy to compress hydrogen isothermally from 20 bar to 350 bar is 1.05 kWh/kg H2 and only 1.36 kWh/kg H<sub>2</sub> for 700 bar.[7]

Due to compression heating, overpressures are required to achieve a complete fill when rapidly refueling with high pressure  $H_2$  gas. A 350-bar system can require an overpressure as high as 440 bar and the maximum vessel temperature must be limited to 85° C while 700-bar fast fill systems can require an overpressure as high as 880 bar with pre-cooling as low as -40°C.

On the other hand, for liquid hydrogen, liquefaction energy requirements are substantially higher, typically 10-13 kWh/kg LH<sub>2</sub>, depending on the size of the liquefaction operation. Usually it consumes between a 30-40% range of  $H_2$  LHV [7].

Simulation was carried out then using a two-stage cascade compressor arrangement to provide hydrogen at 440 bar and 60°C ; and also hydrogen for mobility at 880 bar and -40°C. The LH<sub>2</sub> system was not entirely simulated as it meant an extensive work of simulation and calculations that are not the scope of this thesis. Instead validated literature data [13] was used as input for heater (Heat Duty).



Figure 3.2.1. Cascade mechanical compression system and cryogenic hydrogen production

Liquid hydrogen is nowadays produced through a series of compression/refrigeration cycles resulting in an average overall 12 to 15 kWh/kg H2 energy consume. Discoveries as magnetic regenerative liquefaction method will reduce substantially these expenses to a third in the future.

As compression is already widely developed and solid technology, was not the key of the simulation to improve efficiencies of the overall process if not to recreate operational conditions to evaluate energy efficiencies when integrated with an Alkaline Water Electrolysis plant. The state of art hydrogen compression is lately achieving up to 10 times the evaluated pressures (~ 5000 bars) [20] with less consume of energy per H<sub>2</sub> kg by using diaphragm compressors.

# 3.3 Electrochemical-Thermal Activated Chemical Process (ETAC)



Figure 3.3 1 Flowsheet E-TAC process

As E-TAC process it is a two-step electrochemical-chemical cycle, simulation was approached by setting the stepwise units where the reactions of Hydrogen Evolution (HER) and Oxygen Evolution (OER) take place. They are simulated as simultaneous processes, but they work as a thermo regenerative electrochemical cycle (TREC) [5]. The charging is performed at ambient temperature while regeneration is over 90°C which means an energetic expense.

Both steps are linked by the anode's state of charge. During HER at the cathode, the  $Ni(OH)_2$  anode is oxidized to NiOOH:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{1}$$

$$2Ni(OH)_2 + 2OH^- \rightarrow 2NiOOH + 2H_2O + 2e^-$$
(2)

Charging the anode can be seen as the charge process of a RC electrical circuit where the anode behaves as a capacitor and the electrolyte as the ohmic resistance. An additional resistance represents the constant HER overpotential at the cathode. Then the applied potential ( $V_b$ ) can be seen as the sum reversible voltage i.e. minimum voltage for the reaction to occur and a series of resistances (Fig.). Activation overpotential is determined from Tafel Equation.



*Figure 3.3 2 Circuit diagram of the cell.* Anode is behaving as a capacitor, cumulating charge as the current flows. The sum of overpotentials come represented as a resistance. Ohmic resistance derives from electrolyte conductivity.

As the charge is transferred to the anode in a stable operation, the number of moles of  $Ni(OH)_2$  that have been oxidized can be calculated from the amount of electrical charge Q(t) according to Faraday's law:

 $nNi(OH)_2 = \frac{Q(t)}{Fz}$  Equation A

F: Faraday Constant z: number of electrons in (2) per moles of Ni(OH)<sub>2</sub>

Regenerative step occurs spontaneously at high temperature according the following equations:

$$4OH^{-} \rightarrow O_2 + 2H_2O + 4e^{-}$$
(3)

$$4\text{NiOOH} + 4\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{Ni(OH)}_2 + 4\text{OH}^-$$
(4)

To avoid gas crossover in the E-TAC water splitting, it is essential that anode charging potential stays below the OER potential. This set an upper limit for the applied constant current, which implies a certain applied cell voltage as oxygen will evolve at the anode if it reaches OER. Then the cell behaves as regular coupled electrolysis and huge amounts of oxygen will mix with hydrogen setting a rather dangerous level of gas contamination that could cause an explosion. Energy flow diagrams of the reactions in electrolytic and ETAC are presented in figure.



**Figure 3.3 3.** Energy diagram of the reactions taking place in alkaline water electrolysis (a) and the E-TAC water splitting process with conventional Ni(OH)<sub>2</sub> (b). The potential values are shown under ambient conditions. The arrows are color-coded as explained in the legend on the right. The orange and yellow arrows represent the reversible and thermoneutral voltages. They apply equally to both cases. The light blue arrows represent the cell voltage, Vcell, that is applied during the electrochemical process in both cases at ambient conditions. Vcell was calculated by  $Erev(a) + \eta OER + \eta HER$  (typical overpotential values) for (a), and by  $Erev(b) + \eta OX + \eta HER$  for the E-TAC case (b).

However, while anode is getting charged at the first step, some oxygen evolves spontaneously at it steady-state rate throughout the entire charging process at HER operational temperature. Because of this phenomenon, a part of the anode's charge is lost, decreasing the faradic efficiency of anode charging and consequently hydrogen production.

This lost charged  $Q_{OER}^{1}$  can be calculated as the steady-state OER current i.e. the current when the anode is fully charged times the charging cycle time. This OER current as mention before, it is considered to be constant during the charging process and it has been experimentally proved to be equal to the current measure at the end of a chronoamperometric test. (Fig 3.3.4)



*Figure 3.3 4* Chronoamperomegram of an initially discharged  $Ni(OH)_2$  anode charged at a constant potential of 1.48 V<sub>RHE</sub> for 2300 s in 5M KOH solution.

Because of this, the OER current value is approximated using the Cottrell Equation that describes the current response, in time, as a function of a step-in potential.[5] The current measured depends on the rate at which the analyte diffuses at the electrode, which in this step is the proton deintercalation from Ni(OH)<sub>2</sub> (Fig). So, the current is said to be "diffusion controlled." For the halfreaction (2), starting from the concentration profile with linear diffusion for a planar electrode of area A, the current-time response observed during an instantaneous potential step experiment is:

$$i(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$$
 Equation B

where  $D_o$  is the proton diffusion coefficient and  $C_o^*$  is the initial concentration of the reducible ion (OH<sup>-</sup>)



Figure 3.3 5 Schematic illustration of proton release during charging process of the nickel hydroxide anode.

Therefore, the  $nNi(OH)_2^1$  correspond to capacitive charge (Qc, Fig) that remains at the end charging process and can be calculated as:

 $Qc = Qt(t) - Qoer(t)^2$ 

Then Faradaic efficiency of anode charging process is:

$$\eta F = \frac{Qc(t)}{Qt(t)}$$
 Equation C

And the linked H<sub>2</sub> rate:  $nH_2 = \frac{nF.I.N}{z.F}$  [3]; N: number of cells, z=2 n. of electrons reaction (1), F: Faraday Constant. Oxygen rate during charging is equivalent to the Qoer:  $nO_2 = \frac{Qoer.N}{z.F.t}$ ; z=4 n. of electrons reaction (3); t: cycle time.

As mention before, the HER and OER units work as a thermo regenerative cycle system. So once completed the first step with a fully charged anode, second step is regeneration of the anode to start a new cycle. This step is entirely chemical and depends on reactions (3) and (4) kinetics, which occur simultaneously depending on thermodynamic conditions.

From the experimental data apported by Dotan et al.[11], kinetics parameters were obtained. The reaction is first order to the NiOOH (Equation D), and the oxygen rate at the OER unit is couple to the anode regeneration. Kinetic data is available in Appendix IV. Oxygen rate is considered to be constant over cycle time for the simulation calculations as the nO2 is the reaction equivalent to moles of nickel oxyhydroxide that have reacted in  $t_f$  time:

<sup>&</sup>lt;sup>1</sup> Number of moles of nickel hydroxide

<sup>&</sup>lt;sup>2</sup> Qoer(t) =  $\int i(t)dt$ ; i(t) Cottrell equation (Equation B)

Following relations clarify the OER unit calculations:

 $nO_2 = \frac{1}{4} (nNiOOH)_{tf}$  (moles of oxygen evolved from anode's regeneration).

 $(nNiOOH)_0 = (nNiOOH)_{HER}$  (Moles of anode to be regenerated after HER reaction is concluded).

 $(nNiOOH)_{HER} = (nOH^{-})_{HER}$  (Equivalence between moles of oxidized anode and reduced water; reaction (1) & (2)).

Nevertheless, in order to avoid complicated calculations with a solid state material, as the reactions in HER unit are "coupled", the nOH<sup>-</sup> produced in (1) are equivalent to the nNi(OH)<sub>2</sub> oxidized in (2), the charged anode can be represented as an hydroxyl flow from the HER unit to the OER unit(ANODE, Fig). Then in the OER unit, it will represent the number of initial moles of NiOOH giving the input to the regeneration block. Finally, as regeneration is not completed a hypothetical flow (REGANODE, Fig) is set in order to maintain charge and mass balances.

Calculations for both units are carried out by USER2 block which allows to supply input data and additional operating parameters to an Excel model and then retrieve results complying with mass balances (Fig)

HER (User2) × +											
Subroutines 🎯	Subroutines 📀 User Arrays Configured Variables Calculation Options 📀 Stream Flash Streams Reactions Comment										
– User2 subroutine	es	Length of work arra	vs								
Model		Integer	1 🚭								
Report		Real	1 😜								
Excel file name - C:\USERS\ABA	A\DESKTOP\TES	I\ASPEN\ETAC\HER.XLS	;			Browse					
-Additional users	subroutines —										
Subroutine name											

Figure 3.3 6 User2 routine input from excel model.

Parameters for the model can be specify as part of the routine from Aspen interface in order to render the model more adaptative. Real and integer parameters are respectively entire and decimal parameters for the model such as number of cells or current density applied. (Fig.3.3.6). They can also show retrieved information after calculations are done as Power input or cycle time for fully charged anode:

HE	HER (User2) × +											
Subroutines User Arrays Configured Variables Calculation Options Stream Flash Streams Reactions									Comments			
,						-				-	-	
ſ												
	integer 2 Keal 15 Character 15											
-	Values for parameters											
	Integer Real Character									<b>A</b>		
	►	1	12	0,2	NUMBER CE	NUMBER CELLS / CURRENT DENSITY (A/CM2)						
		2		1000	CYCLE TIME	(SEC)	/ ELECTRODE /	ACT	IVE AREA (CM2)			
		3		3	ELECTRODE	тніс	KNESS (MM)					
		4		300	SPECIFIC CH	ARG	E CAPACITY (M/	AH/	G)			=
		5		500	SPECIFIC CA	PACI	TANCE (F/G)					
		6		198,6	OH- LIMITIN	IG CO	ONDICTIVITY ((	СМ2	/MOL*OHM)			
		7		73,52	K+ LIMITIN	G CO	NDICTIVITY (C	M2/	MOL*OHM)			
nula	atio	n		0,018	8 EXCHANGE CURRENT IO (A)							
		9		1,1e-11	1 PROTON DIFFUSION COEFFICIENT (CM2/S)							
		10			H2 PRODUC	H2 PRODUCTION (MOL/SEC)						

Figure 3.3 7. Integer and Real parameter at the USER2 interface.

In order to guarantee the Aspen execution of the calculation routine, the Excel model must maintain a certain structure of variables and parameters. (Figure 3.3.8).

It is essential to assure mass balance due to thermodynamic properties will be estimated from composition at specify temperature and pressure.

The vapor fraction in the outlet stream of each unit is separated using flash separators vessels and the remain electrolyte sent to make-up the feed stream.

The validation of model was carried out following supplementary information of Dotan et al. [12] on which under certain system characteristics and assumptions, few values like heat losses or power consumption are estimated. These empiric and estimated outcomes allowed us to frame our simulation and compare them to our results. Dotan et al. made the following assumptions that we have used to execute the E-TAC simulation.

- Plug flow in the cell
- Hydrogen generation at 25°C and Anode regeneration at 95°C.
- Anode is 3mm thick and 85 vol% porous, 10 vol% Ni(OH)<sub>2</sub> and 5 vol% Ni.

They measured experimentally in 10 consecutive cycles an accumulated volume of 6,4 ml of H<sub>2</sub> (1 atm, 25°C) consuming 20,8 mWh based on 50 mA cm<sup>-2</sup> current achieving

F1	.4 *	1 ×	$\checkmark f_x$	
	А	В	с	D
1	INPUT	1		Concentration
2	H2O	4,3056E-05		0,77569
3	КОН	0		997
4	H2	0		0,000778026
5	02	0		
6	K+	4,1664E-06		5,35509222
7	KOH(S)	0		
8	KOH*W(S)	0		
9	KOH:2(S)	0		
10	OH-	4,1664E-06		
11	TOTFLOW	5,1389E-05		
12	TEMP	298,15		
13	PRES	100000		
14	ENTHALPY	-14175146,5		
15	VAP FRAC	0		
16	LIQ FRAC	1		
17	ENTROPY	-7543,68366		
18	DENSITY	1211,30282		
19	MOLE WT	19,6428969		
20				
21				
22				
22		Acron PEAL	DADANAS	
	• • • •	Aspen_REAL	PARAIVIS	Aspen_INPUT AS

Figure 3.3 8. Excel input parameters arrangement for USER2

an energy consumption of 39,9 kWh/kg H<sub>2</sub>.[3]. (Appendix I. Proof of concept experiments)

In our simulation, under all the previous assumptions and hypothesis our E-TAC process simulation achieved also a low electrical power consumption of 43,41 kWh/kg H<sub>2</sub>.

Also, from experimental data [11] by Dotan el al. the following validations of our two-stage water simulation was performed so as to confirm operation within the awaited values:



*Figure 3.3 9 Parity chart experimental vs simulated data for ETAC:* Cell voltage during hydrogen generation step at different constant current densities for a fully charged anode

# 3.4 Methylcyclohexane-Toluene-Hydrogen System (MTH)

Simulation of the completed cycle was carried out considering a storage step and transport step to estimate expenses. Hydrogenation and dehydrogenation are, of course, spatially separated and integrated with the hydrogen production process as with the hydrogen use at the end unit respectively.

As mentioned before, our LOHC cycle is based on Toluene-Methylcyclohexane hydrogenation/dehydrogenation respectively on platinum-based catalysts which have always present the best features and performance for these reactions.

Both units are catalytic tubular reactors of plug flow. The kinetics are based on experimental research of Usman et al. [25] for 1 wt. % Pt/ $\beta$ -Zeolite and operational conditions are based on simulation study of Hamayun et al. [10] for a similar system.



Figure 3.4 1 Schematic illustration of MTH system

According to Usman et al. [25] both reactions were found to be not clean under the conditions studied and, in each case, contained a large proportion of by-products. Generally, the isomers of dimethylcyclopentane (DMCP), ethylcyclopentane (ECP), and 3-methylhexane (MXN) were among the important ones obtained in each of the reactions. **Table** 

Table 2: H2UP/H2DOWN reactions						
Hydrogenation						
	$TOL + 3H_2 \leftrightarrow MCH$					
	$TOL + 3H_2 \leftrightarrow DMCP$					
	$TOL + 3H_2 \leftrightarrow ECP$					
	$TOL + 3H_2 \leftrightarrow MXP$					
Dehydrogenation						
	$MCH \leftrightarrow TOL + H_2$					
	$\mathrm{MCH} \leftrightarrow \mathrm{DMCP}$					
	$\mathrm{MCH}\leftrightarrow\mathrm{ECP}$					

 $MCH + H_2 \leftrightarrow MXP$ 

TOL: Toluene; MCH: Methylcyclohexane; DMCP: Dimethylcyclopentane; ECP: Ethylcyclopentane; MXP: 3-Methylhexane .

These by-products affect the overall efficiencies of both reactions. However, optimization of the reacting conditions was conducted in order to maximize main product selectivity and reactant conversion based on experimental data and similar models of hydrogenation/dehydrogenation of LOHC. Kinetic data is presented in **Table 3**.

	Hydrogena	tion	Dehydrogenation				
Power La	W						
(-	$(r_{T1}) = k_T \Big( P_T P_H \Big)$	${_{H2}}^3 - \frac{P_A}{K_T}\Big)^{n_T}$	$(r_T) = k_A \left( P_A - \frac{P_T P_{H2}^3}{K_A} \right)^{n_A}$				
$(-r_{T2})$ :	$= k_T \left( P_T P_{H2}^{\frac{16}{6}} - \right)$	$\left(\frac{\left(P_D^3 P_E P_M\right)^{\frac{1}{6}}}{K_T}\right)^{n_T}$	$(r_D) = k_D \left( P_A - \frac{P_D}{K_D} \right)$ $(r_E) = k_E P_A$				
Paramete	ers						
kт	0.5252.10 <sup>-4</sup>	mol s <sup>-1</sup> gcat <sup>-1</sup> bar <sup>-nT</sup>	ka	0.4135.10 <sup>-5</sup>	mol s <sup>-1</sup> gcat <sup>-1</sup> bar <sup>-</sup>		
Eat	129,14	kJ mol <sup>-1</sup>	kd	6.816.10 <sup>-5</sup>	mol s <sup>-1</sup> gcat <sup>-1</sup> bar <sup>-1</sup>		
n <sub>T</sub>	0.3088		k <sub>E</sub>	0.1536.10 <sup>-5</sup>	mol s <sup>-1</sup> gcat <sup>-1</sup> bar <sup>-1</sup>		
			Ea <sub>A</sub>	6,488	kJ mol <sup>-1</sup>		
			Ead	88,111	kJ mol <sup>-1</sup>		
			Ea <sub>E</sub>	110,988	kJ mol <sup>-1</sup>		
			na	-0,0965			

**Table 3: T**:Toluene; **A**: Methylcyclohexane **D**: Dimethylcyclopentane **E**: Ethylcyclopentane **M**: Methylhexane  $(-\mathbf{r}_{T1})$ : rate depletion of toluene to A;  $(-\mathbf{r}_{T2})$ : rate depletion of toluene to by-products;  $(\mathbf{r}_T)$ : rate formation of toluene from A;  $(\mathbf{r}_D)$ : rate formation of D from A;  $(\mathbf{r}_E)$ : rate formation of E from A;  $\mathbf{K}_T$ ,  $\mathbf{K}_A$ ,  $\mathbf{K}_D$  equilibrium constants for the reactions based on their Gibbs free energy of formation of the components involve.  $\mathbf{P}_i$ : partial pressure of i.

The rich-LOCH (LOCH+) is a high concentrated mixture of methylcyclohexane and reaction byproducts. It will be storage or delivered to end users who will return the lean-LOCH (LOCH-) after chemically desorbing the hydrogen. The latter according to the percentage of toluene would be directly recycle to hydrogenation or reprocessed up to required conditions for hydrogenation.



Figure 3.4 2 Process Flow Diagram of MTH system. Plug flow reactors of 1 wt. % Pt/8-Zeolite supported catalyst.

As hydrogenation is exothermic, reactor outlet is used to preheat the feed before it is passed to the storage tanks. Analogously, the outgoing dehydrogenated mixture is used to preheat the incoming MCH and afterwards sent to recycling.

The heat required for dehydrogenation reaction is a critical point in the process due to reaction endothermic nature and slow kinetics. Pairing the  $H_2$ Down unit to a process or unit able to provide the enough heat to run the reaction is the optimal approach if method is to become sustainable. While for the contrary, heating expenses must be considered for the on-site generation.

A validation step of both units was carried out to screen simulation reliability. Experimental data was obtained from research by Usman et al. [25] and the following scattered diagrams were realized for different for few different operation conditions such as temperature, pressure or hydrogen ratio.



Figure 3.4 3 Parity scattered diagrams for hydrogenation reaction. Plot A: simulated conversion of Toluene vs experimental conversion at diverse temperature and pressure conditions. Plot B: simulated yield of methylcyclohexane and one of the by-products: dimethyl cyclopentane (DMCP) vs experimental yields. Experimental data extracted from Usman et al.[25].

As well it can be observed that in the dehydrogenation reaction the series of points belong to two different models. (Figure 3.4.4) First one (Model 1) recreates the exact same experimental reactor characteristics i.e. quantity of catalyst per mol of feed, particle density, etc. The second one (Model 2) instead was performed by sensitivity and optimization, adjusting few reactor's parameters in order to bypass intrinsic limitations of Aspen Plus when simulating catalyst real characteristics and mass transfer phenomena, which are very difficult to simulate if accurate information is not available.



**Figure 3.4 4 Parity scattered diagrams for dehydrogenation reaction**. **Plot A:** simulated conversion of MCH of two different models (Model 1=M1;Model 2=M2) vs experimental conversion at diverse temperature and pressure conditions. Plot B: simulated yield of toluene and one of the by-products: dimethyl cyclopentane (DMCP) vs experimental yields for previous conditions. M1= Experimental Conditions; M2= Optimized conditions. Experimental data extracted from Usman et al.[25].

So, the latter shows evidently how closed to real behavior is the modified-conditions model number 2, were the quantity of catalyst is almost double and particle density is lower than the experiment conditions. In addition, number of tubes and length did not cause any effect on Aspen Plus calculations for both reactions and was taken approximately as the number of tubes of diameter 1,02 cm to fulfill a reactor diameter of 1 m pair to 10000 tubes.

# 4.Why hydrogen?

By 2050, Europe aims for a high-renewable scenario with 85% of energy coming from renewable sources as strategy to comply with the Paris Agreement and limit the average global temperature rise to below 2°C. Substantial greenhouse emission reduction in all sector along with a higher renewable power sources penetration and increased energy efficiencies can help society to meet this goal. Hydrogen could thus be the "missing link" and play key role in facilitating these outcomes.

The decarbonization of sectors such as the industrial and the transport are main task in the road to a full renewable dependability. The replacement of natural gas and fossil-fuels with hydrogen have been a challenge from many years due to scares technological advances. However, nowadays the scenario has swap and hydrogen from renewables will be able to "make the transition".

Industrially hydrogen have been used for decades in the production of bulk chemicals and refineries. In the short-term Renewables-to- $H_2$  is expected to prompt these markets as important cost reductions would be possible because of their capacity of generating immediate scale effects. Electrochemical ammonia and green hydrogen hydrocracking are presumed to be "game changer". In addition, cement and iron industries could also shift to high-grade heat from hydrogen and also help to replace some steelmaking processes such as coal coking.

Regarding to transport sector, FCEVs have a remarkable potential in the near term for heavy duty vehicles market and are an opportunity for the medium to large passenger vehicles segment. Fuel cell busses have already been demonstrated and trucks are under development. The short fueling times and the suitability for longer distances or high utilization rate allows FCEVs to outmatch BEVs that remain constrained to a specific market.

In addition to road transport, in the long-term hydrogen could contribute to decarbonizing rail, shipping and aviation. Rail is electrification is actually widespread but in several cases hydrogen powered trains could allow providers to avoid the high capex of building overhead wires. Fuel cell ships are at demonstration stage and due to space availability, they are quite advantageous regarding top hydrogen storage.

As respects for aviation, in the mid-term, it could rely on E-fuels, which are produced from electrolytic hydrogen and a carbon source such as captured  $CO_2$ . The so called "Power-to-Liquids" makes use of renewable electricity to synthetize a sustainable alternative fuel that resembles the conventional jet kerosene with a final zero carbon balance. Main efforts at this approach are to increase energy efficiencies of the processes involved.

Renewables-to- $H_2$  will become a reality as the global system must undergo through a profound transformation to guarantee continuity. Hydrogen has a singular potential in any sector. As an energy carrier will have the key advantage over electricity since its storage is not limited technologically and does not suffer from self-discharge. In addition, hydrogen could generate both electricity and heat just from a domestic fuel cell or replace natural gas for certain households.

### 5.Results

### 5.1 Production plant

Process block diagrams for both processes are presented in the **Figures 5.1** and detailed mass and energy balances are also available in **Appendix**. A 50 Nm<sup>3</sup>/h hydrogen generation capacity was set for each alternative. Energy loads and losses consider the electrical and heat streams involved. Operating conditions for each process are presented in the following table:

$AWE + CGH_2$		<b>ETAC + MTH</b> ( $H_2UP$ )	
Electrolysis		Electrolysis (Stage 1)	
Current density (mA/cm <sup>2</sup> )	420	Current density (mA/cm <sup>2</sup> )	250
Number of Cells (N)	300	Number of Cells (N)	480
Temperature (°C)	80	Temperature (°C)	25
Pressure (bar)	7	Pressure (bar)	1,0123
Water feed/cell (l/hr)	0,17	Cycle time (min)	15
		Water feed/cell (l/hr)	0,25
		Anode Regeneration (Stage 2)	
		Temperature (°C)	95
		Pressure (bar)	1,0123
		Cycle time (min)	16
Power Input (kW)	256		200
	Sto	rage	
Pressure (bar)	880 (max)	Pressure (bar)	8
Temperature (°C)	-40	Hydrogenation temperature (°C)	220
		Catalyst weight (g.s/molTOL)	6,41x10 <sup>4</sup>
		Tube diameter (cm)	1,02
		Reactor Length (m)	1
		Number of tubes (n)	10000

**Table 4:** Operating conditions for compressed hydrogen (CGH<sub>2</sub>) from alkaline water electrolysis (AWE) on the left. On the right, ETAC process and MTH hydrogenation information. Number of cells equal to both processes so as to confront results.

For the balances ,for both alternatives, have been considered up to their capacity to provide hydrogen at "storage condition", which for the conventional process is compressed hydrogen (CGH<sub>2</sub>) while for ETAC+MTH is the methylcyclohexane. For the latter, dehydrogenation and H<sub>2</sub> supply will be analyzed in a following section as it would usually be spatially separated from the Power-to-H<sub>2</sub> facility.



**Figure 5.1.1 Process Block diagram of AWE + CGH2**. Process Block diagram for the conventional alkaline water electrolysis (AWE) for a stack of 300 cells. Produced hydrogen is equally supplied at 440 and 880 bar for 350-bar and 700-bar applications. Detailed mass and energy data from Aspen Plus are available in the Appendix.



**Figure 5.1. 2 Process block diagram for ETAC+MTH.** Detailed flows are for 480 cells that alternates operation between (1) and (2). Step one lasts 13 min while step two 16 min. Water splitting step is constantly feeding hydrogen at 8 bar to the H2UP unit at the m7 flow rate in a 4.34 molar ratio with toluene. Yield of toluene to methylcyclohexane is about 80%.

Feed to the AWE is dependent to applied current density. Then water consumption is linked to the rate since water splits in hydrogen and oxygen contemporaneously. For ETAC instead, water consumption is linked to the regeneration rate at the second step (3.Simulation and modelling. Equation 4). Thus, water consumption of ETAC result to be slightly smaller than AWE accounting for 35 l/h against 42 l/h.

# 5.2 Water Splitting

Being the Hydrogen Evolution Reaction the key step in both alternatives. Plots of polarization curve within the cell and the rate of hydrogen evolving are presented in figure 5.2.1. At very low current densities, polarization at the electrodes depends mainly on their thermodynamic potential, which is lower for conventional electrolysis  $(1.23V_{RHE} \text{ vs } 1.42V_{RHE})$ . Regardless of this, as currents start to increase, the intrinsic overpotentials influence the overall cell voltage as displayed in figure (left). For ETAC process, the one-electron transfer reaction exhibits then a much lower overpotential than AWE, working even without oxygen evolution at high currents.



**Figure 5.2 1 Polarization curve and Hydrogen rate plots of conventional alkaline electrolysis vs hydrogen generating step at ETAC at constant current densities. Left:** Polarization curve of ETAC (blue) tends to be greater up to current densities 220 mA/cm2, then the tendency changes (Voltage values over OER potential). **Right:** Hydrogen flow rates of ETAC and AWE electrolysis step for Ncell = 12. Alkaline water electrolysis exhibits no hydrogen evolution at very low current densities (under OER potential).

ETAC configuration displays a higher volume rates of hydrogen than the AWE fuel cell for low current densities. This is because the activation conditions for the second one do not achieve the minimum energetic levels to make the reaction proceed, while ETAC anode is capable of getting charge allowing water to reduce at the cathode. However, is important to remember that ETAC anode has to work under OER potential conditions in order to avoid oxygen generation, which would recouple the HER rate to the oxygen formation. Power modulation is crucial as should maintain cell potential lower than OER limit. In addition, ETAC cells have no membrane and minimum quantities of oxygen could result in explosive mixtures.

Regarding to the last argument, performance of both processes under different pressures was analyzed so as to observe formation of dangerous mixtures due to gas crossover. As parasitic oxygen evolves at the steady state current during HER, the OTH ratio remains constant for ETAC as potential variations with pressure are negligible. However, for AWE, high pressures cause an increment in the hydrogen permeation through the separating diaphragm limiting the operation pressure as flammability limit could be reached.



**Figure 5.2 2 Hydrogen and oxygen mixtures during water splitting steps.** Hydrogen to Oxygen (HTO) for alkaline water electrolysis and Oxygen to Hydrogen ratio for ETAC cycle. HTO increases with pressure due to higher permeation of hydrogen to the OER compartment. OTH in ETAC remains constant at 0,016% as both evolution rates are proportional to the cell potential.

### 5.3 Hydrogenation

Toluene hydrogenation is conducted at 220°C and 8 bar (Figure H<sub>2</sub>UP unit) with a hydrogen/toluene ratio of 4.34 that result to increase rate of reaction as product selectivity. The hydrogen storage rate is 0.7 mol per mol of hydrogen at the feed with a methylcyclohexane's yield of 80.6%. Thus, excess hydrogen is recycled to achieve the feed ratio at make-up allowing for a stochiometric reactant feed. Table Toluene's conversion is complete (traces of TOL less than 4e-5% wt.).

Compound	Unit	FEED	PRODUCTS
МСН	kmol/hr	0	0,4141
TOL	kmol/hr	0,5133	1,7686E-05
H2	kmol/hr	2,2319	0,6720
DMCP	kmol/hr	0	0,0595
ECP	kmol/hr	0	0,0198
MXN	kmol/hr	0	0,0198

Table 4: Hydrogenation results at H<sub>2</sub>UP unit (220°C ,8 bar).

Despite of the fact that the by-products' yield is almost 20% wt., a separation step to obtain a higher purity methylcyclohexane is not considered yet as some of the present by-products are still suitable for dehydrogenation or/and reconversion to MCH in the following step, increasing the hydrogen releasing capacity within the LOCH cycle.

As mentioned, hydrogenation of Toluene is an exothermic reaction which generates about 2,04 MJ/kg LOHC (9,08 kWh/kg H<sub>2</sub>). This heat could be integrated with the anode regeneration step that 2,04 kWh/kg H<sub>2</sub> at ETAC or used in another application.

Finally, methylcyclohexane is laid up in tanks in 20 Nm<sup>3</sup> which account approximately for 10000 Nm<sup>3</sup> of hydrogen to be released.



Figure 5.3 1 Spera Hydrogen ® by Chiyoda Corporation

# 5.4 Dehydrogenation

The dehydrogenation of saturated LOHC is performed at 360°C and atmospheric pressure. As the reaction is endothermic, it is favored by high temperatures, but not by high pressures due to reaction intermediates and adsorption equilibrium.



Figure 5.4.1 Process block diagram for dehydrogenation step at MTH. Hydrogen is recycled up to 5:1 molar ratio with MCH.

The presence of hydrogen in the feed has proven to have a positive effect increasing the rate of reaction and the selectivity of MCH towards Toluene. So, hydrogen is partially recycled up to 5:1 molar ratio to the MCH fed achieving an overall MCH conversion of 88,3%.

Compound	Unit	FEED	PRODUCTS	NET $H_2$
МСН	kmol/hr	0,4141	0,0485	0
TOL	kmol/hr	1,7686E-05	0,3762	0
H2	kmol/hr	2,0705	3,1992	1,1287
DMCP	kmol/hr	0,0595	0,0377	0
ECP	kmol/hr	0,0198	0,0310	0
MXN	kmol/hr	0,0198	0,0198	0

Table 5: Dehydrogenation results at H<sub>2</sub>Down unit. Mole flow for any component at feed and outlet stream at dehydrogenation unit. Operation at 360°C and 1 atm.

The net hydrogen flow is about 27 Nm<sup>3</sup>/. If yield of toluene was calculated from **table** data, it would be slightly higher than 1. This is because, at reacting conditions by-products can isomerize towards methylcyclohexane and subsequently release hydrogen, increasing the percentage of Toluene's recovery over by-product concentration at end.

Considering then the results for both processes, the system release/store capacity is around 27  $Nm^3/h$  per 33  $Nm^3/h$  respectively, that is a capacity factor of 81%.

Regarding to heat demand for dehydrogenation process, heat must be supply at a rate of 28,25 kJ/sec, which means a heat generating system must be installed to the demand. Gravimetrically, it represents 2,01 MJ/kg LOHC fed, being slightly lower than the one generated at hydrogenation step. This set an opportunity if some heat storage technology could be implemented when both units are located together for energy storage means, absorbing and releasing heat depending on electricity demand.

Re-electrification using a SOFC fuel cell allows for heat integration, the efficiency increases for LOHC as storage technology because high temperature excess heat is produced during operation and can be directly provided. Solid oxide fuel cells work in the range of 700-1000°C. Benefits from this arrangement will be evaluated in the next section.

#### **6.Energy Analysis**

An energy analysis with the scope to value energy efficiencies within the processes were carried out. Electrical efficiency is the ratio between the produced energy for mass unit i.e. HHV<sup>3</sup> of the fuel and the direct energy used in the process of generation, in this case the amount of electricity. So, for an electrolysis process:

$$Energy \ Efficency = \frac{HHV \ of \ produced \ hydrogen}{Electricity \ used + Heat \ Supply}$$
(1)

In addition, electrolysers come also characterized by the voltage efficiency that measures the loss of voltage due to cell polarization. Voltage is intrinsically linked to the amount of electric energy used on the process, and consequently to the overall efficiency. A 100% voltage efficiency corresponds to a water splitting process at a thermoneutral voltage:

$$Voltage \ Efficency = \frac{Thermoneutral \ Voltage \ (V_{th})}{Cell \ Voltage \ (V_{cell})}$$
(2)

Either AWE or ETAC are operating at near ambient conditions, so no heat is supplied for the hydrogen generation step and neither considered in the efficiencies above. Instead cooling is required to guarantee operability in both cases. For the anode regeneration step, on the other hand, efficiencies have been determined either by considering an external heat supply or thermal integration with the hydrogenation process. Variation of energy efficiencies along the line come presented in the following tables:

UNIT	POWER		POWER/KG H2		SYSTEM EFFICIENCY	NOTES
STACK	251	kW	52.87	1/W/b/l/g	72 160/	
PUMP	0,052	kW	55,67	K W II/Kg	/3,1070	
C-101	16,681	kW	3,579	kWh/kg	68,61%	350 bar
C-102	1,688	kW	0,724	kWh/kg	68,18%	700 bar

 $AWE + CGH_2$ 

**Table 6: Electrical efficiencies for AWE + CHG2.** Electrical efficiencies based on equation n. along the process. Efficiencies values are showed in sequences since every step (black line) has a new electrical consume. C-101 and C-102 represent the compressors at the compression step.

<sup>&</sup>lt;sup>3</sup> HHV usually for electrolysers in Europe, while in North America efficiencies are related to LHV.

#### ETAC + MTH

UNIT	POWER		POWER/ KG H2		HEAT		SYSTEM EFFICIENCY	NOTES
S-1	200	kW			-13	kW	84,51%	
S-2 PUMP	3e-4	kW	44,59	kWh /kg	9,2	kW	(88,39%)*	
H2UP PUMP C-201	0,13 0,30	kW kW	0,138	kWh /kg	-28,53	kW	84,26% (88,12%)*	Toluene H <sub>2</sub>
H2DOWN PUMP	0,014	kW	0,007	kWh /kg	28,25	kW	84,15% (87,98%)*	Heat produce by burning part of hydrogen produced
* values for	haat fan S. 2 fm		1					

\* values for heat for S-2 from  $H_2UP$ 

**Table 7: Electrical efficiencies for ETAC + MTH.** Electrical efficiencies based on equation n. along the process. Efficiencies values are showed in sequences since every step (black line) has a new electrical consume. S-1 and S-2 are the steps of ETAC while the pumping is for both. Hydrogenation and dehydrogenation have also electrical consumes due to pump and compressors involved. For all steps heat duties have been also specified.

Instead, if the H<sub>2</sub>DOWN unit was thermally integrated with a SOFC for energy purposes, supposing an average 75% energy efficiency ( $\eta_{SOFC}$ ) for high-temperature operation and pure hydrogen, the overall efficiency from ETAC going through MTH and finally re-electrifying would be:

$$\eta = \frac{(HHV \text{ of } H_{2_{deh}}) \bullet \eta_{SOFC}}{Electricity \text{ used}}$$

Where  $H_{2deh}$  is produced hydrogen at dehydrogenation and the "Electricity used" are the quantities specified in **table 7** the overall efficiency obtain is approximately :

On the other hand, voltage efficiency for the water splitting steps for each process according to equation (2):

$$\eta V_{AWE} = \frac{1.48 V}{1.99 V} \% = 74,37 \%$$
  $\eta V_{ETAC} = \frac{1.48 V}{1.66 V} \% = 89,15 \%$ 

ETAC+MTH are much more efficient when coupled as hydrogenation excess heat is a source for the anode regeneration step. With both powered by renewables, ETAC will be able to transform much more energy into hydrogen from low power inputs avoiding intermittency while a regular hydrogen feed to MTH hydrogenation step will optimize storage operability and allow constant heat supply from  $H_2UP$  unit to the heat exchanger for anode regeneration step hot alkaline solution.

### 7. Economic Analysis

Economic evaluation is divided in the three steps of hydrogen supply chain for both alternatives. Production, storage and transport cost are presented in **tables 8 to 12.** and related to their specific units of time, weight or distance. Cost and economic calculation were all performed in Euro ( $\in$ ). For compressed hydrogen from AWE, certain information is taken directly from manufacturers since costs are widely available. For ETAC stack cost is based on Dotan et al. information data [12]. Few things have been supposed and others neglected as the intention of this analysis is to provide a general idea of both alternatives.

Regarding to storage and transport approximate costs for tanks and trunks are included. For LOHC they have been taken from steel units used for liquid fuels such as diesel. It also includes additional expenditures. Location of the systems for calculations is preinstalled wind farm in Abruzzo, Italy with a wind output power of 10 MW from 5 wind turbines. Operation time is 5000 h per year. According to IRENA (International Renewable Energy Agency) onshore wind electricity price in 2019 is at an average price of 0,045€/kWh.

#### $AWE + CGH_2$

Electrolyser stack , compressor and storage tanks capital expenses (CAPEX) are estimated from equations provided by Gutiérrez-Martín et al. for PEM electrolyzers [10] and data from IRENA about hydrogen production through electrolysis [15]. Cost have been obtained by curve fitting of specific costs of manufacturers as a function of the capacity and current densities and includes all auxiliary systems such as water and purification and stack exchange. For compression stage, the Aspen plus results for 50 Nm<sup>3</sup>/h hydrogen flow were used. Compressed hydrogen storage tanks have been supposed for 2 ton of hydrogen. An alkaline water electrolyser capital cost is approximately 65% of a PEM electrolyser in Europe.

$$E_{CAPEX}(\pounds) = 1.9136x10^4 * \left(capacity\left(\frac{Nm^3}{h}\right)\right)^{0.79} * \left(current \ density\left(\frac{kA}{m^2}\right)\right)^{-0.32}$$
(1)

$$C_{CAPEX}(\pounds) = 1.3979 \times 10^4 * (motor power(kW))^{0.52}$$
 (2)

$$S_{CAPEX}(\pounds) = 9.158 \times 10^3 * \left( tank \ capacity(ton_{H_2}) \right)^{0.66}$$
(3)

Operational expenses (OPEX) ,excluding electricity use, range from 2-3% of CAPEX. Electricity price is parameter which reflects hydrogen cost. Costs for AWE + CGH<sub>2</sub> are thus the electrical consumes involved in the previous units and the auxiliary systems. A 4% annual of the CAPEX have been supposed for O&M cost.

$$U_{OPEX}(\notin/kg) = Electricity Price \left(\frac{\notin}{kWh_{el}}\right) * P_{el} (kWh/kg H_2)$$
(4)

U stands for Unit which is applicable for electrolyser and compressor

### ETAC + MTH

ETAC cells are membraneless electrolysers and cost of assembly decrease due to simplicity of construction and less need for expensive components. In the overall price, anode materials represent almost a 5% of the total cost for a PEM electrolyser, while membrane and bipolar plates are about the 40% of it.

According to Dotan et al. their ETAC cell does not require them as it is a membraneless component. The manufacturing of these parts occur in large portion of the global cost as is a highly strict operation and very challenging [11]. In addition, electrode materials are less expensive for ETAC as both anode and cathode are nickel-hydroxide and nickel based. ETAC stack cost is then estimated as:

$$E_{CAPEX}(\pounds) = 1,7664x10^4 * \left(capacity\left(\frac{Nm^3}{h}\right)\right)^{0.79} * \left(current \ density\left(\frac{kA}{m^2}\right)\right)^{-0.32}$$
(5)

Capital expenses for pumps and piping have been neglected since the main point is to compare techno-economic feasibility of both alternative. The anode regeneration heat is provided from the previous step via heat integration because of heat excess surplus at step 1. It is important to remember the crucial role of temperature during charging and regeneration.

Produced hydrogen is up to 8 bar of pressure for hydrogenation of toluene in the following step. Cost of compressor is then estimated with same equation used previously (2) and OPEX for pumps and compressors with equation (4).

The investment for hydrogenation and dehydrogenation reactors is highly uncertain due to technologies immaturity. Different authors have made cost estimations and certain assumption in order to approximate to real cost. However, significant inconsistency regarding to expenses is found between them. For this analysis, estimations from Eypash et al. [19] were used since they worked on specific cost of small-scale LOHC systems. For a 1  $MW_{H2,LHV}^4$  (30kgH<sub>2</sub>/h) specific costs are respectively €252 and €368 /kW<sub>H2,LHV</sub> for hydrogenation and dehydrogenation.

For hydrogenation, toluene is a feedstock and can be purchased in Europe in bulk amount at  $0,3 \in /kg$ . Storage for Toluene and MCH is done into steel tanks used for oil or diesel of approximately 2,5 Nm<sup>3</sup> per each component with a capital expenditure of  $\in 600/m^3$  including additional expenses like installation and insulation [19]. 500 Nm<sup>3</sup> of hydrogen per Nm<sup>3</sup> can released from MCH.

Transport instead depends on the state of aggregation of end product. Cost are related to a distance of 100 km. For CGH<sub>2</sub> transport by tube trailers is approximately at  $\in 0,60/\text{kg H}_2$  while for a diesel road tanker, suitable for transporting LOHC, cost is around  $\notin 0,12/\text{L}$ . According to Hydrogen Europe[20], single tube trailers, depending on pressure and container material, carry approximately 500 kg of hydrogen. On the other hand, tank trucks capacity ranges from 20000 to 44000 L.

 $<sup>^{4}</sup>$  1 MW<sub>LHV,H2</sub> = 3600 MJ/h = 30 kg H<sub>2</sub>/h . 120 MJ/kg H<sub>2</sub> (LHV)

### **Table 8: Hydrogen Production**

	AWE	ETAC
Stack CAPEX (€)	265826,14 (300 cells)	289690,7 (480 cells)
Total CAPEX (€)	265826,14	296471,03
OPEX (€/kg H2)		
-Stack	2,42	2,09
-KOH Electrolyte	0,007	0,007
Total OPEX	2,43	2,10
Annual OPEX (€/y)	47276,77	56647,52
O&M (€/y)	10633,04	11858,84
Annual Capacity (ton H <sub>2</sub> /y)	23,3	22,45
Cost Production (€/kgH <sub>2</sub> )	2,88	2,66

### Table 9: Hydrogen Storage

	CGH <sub>2</sub>	MTH
CAPEX (€)		
-Tanks	14470,39	6000
-Compressors	87962,18 <sup>1</sup>	6780,33
-Reactors <sup>2</sup> (hyd)	-	37714,32
Total CAPEX	102432,58	50494,65
OPEX		
-Electricity (€/kg H <sub>2</sub> )	0,16	6,21e-3
Feedstocks(€/kg)		0,3 <sup>3</sup>
Total OPEX (€/y)	3728	3045,66 <sup>4</sup>
O&M (€/y)	4097,30	2739,77
Cost Storage(€/kgH <sub>2</sub> )	0,33	0,25

1-Includes the two compressors for 350 and 700 bar.

2-hyd: hydrogenation reaction for 149,66 kW $_{LHV,H2}$ ; dehyd: dehydrogenation reaction for 149 kW $_{LHV,H2}$ 

3- Fresh toluene price.

4-LOHC is recycle for at least 30 cycles, quantity of fresh toluene is approx. 10 ton/y according to capacity.

### Table 10: Hydrogen Release

	CGH <sub>2</sub>	MTH
CAPEX (€)	-	
-Reactors (dehyd)	-	54832
Total CAPEX (€)	-	54832
OPEX (€)	-	
-Heat (€/kWh) <sup>6</sup>	-	0,0786
Total OPEX (€/y)	-	4853,52
O&M (€/y)	-	2193,28
Cost Release (€/kgH2)	-	<b>0,31 (0,09)</b> <sup>7</sup>

6 – Cost of heat supply

7- Contribution if heat is provided by integration.

### Table 11: Hydrogen Transport

	CGH <sub>2</sub>	МСН
OPEX (€/kg)	0,6	0,09
Cost Transport (€/kgH2)	0,6	5,54e-3

Finally, the depreciation of capital investment (CAPEX) can be calculated with the annuity method to distribute the capital expenditures over equipment lifetime using the following equations for the annuity factor (ANF) and capital depreciation ( $C_{CP}$ ):

$$ANF = \frac{(1+i)^{N} \cdot i}{(1+i)^{N} - 1}$$

$$C_{CP} = (\sum (CAPEX)) \cdot ANF$$
(6)
(7)

Where *i* is interest rate of 8% and N=15 is the lifetime number of periods of the investment (15 years).

$\mathbf{ANF} = 0, 116$	
$C_{CP}(AWE+CGH_2) = \notin 43023, 43/y$	€1,84 /kg H2
C <sub>CP</sub> (ETAC+MTH) = € 46631,73/y	€2,07 /kg H2

Then the resulting cost of hydrogen for both alternatives presented in the following table. Average price of hydrogen globally is 6 USD/kg.

Table 12: Cost of H2	AWE+CGH <sub>2</sub>	ETAC+MTH
Cost of Hydrogen (€/kg)	5,65	5,29 (5,07)

From results it can be seen that capital investments will be greater for ETAC as for an equal production capacity requires a greater number of cells. Nevertheless, OPEX are bigger for AWE+CGH2 due to high electrical consumes for electrolysis and compression. Hydrogen from ETAC+MTH could cheaper than the commercially available technologies in range of 0,3 to 0,6  $\in$ . H<sub>2</sub>PRO, the first company of implement ETAC and patent holders aims for 1USD/kg H<sub>2</sub> for 2050.
## 8.Discussion

Alkaline water electrolysis is a mature technology and it is so far the best alternative for carbon emitting Methane Steam Reforming (MSR) for hydrogen as a feedstock. The technology has demonstrated over the years to be well suited for operations in stationary conditions where compacity and high-power densities are not required. However, for hydrogen as an energy carrier, although AWE is the cheapest way to produce electrolytic grade hydrogen, the lack of flexibility and reactivity to capture multiple and variable revenues from renewable power sources is a disadvantage compared to other emerging water splitting technologies.

PEM electrolyzers are the second most mature technology for water splitting. They have a remarkable flexibility being able to operate easily between zero and very large current densities and under high pressures up to 80 bar. They are rapidly entering commercial deployment but still remain more expensive than AWE and in terms of lifetime, doubled by the latter.

As seen previously, alkaline water electrolysis faces few technological challenges. The required minimum load and limited operation time lead to a high number of startup and shutdown cycles, that could exceed the manufacturer's limit and enhance electrode degradation. Produce high pressure and high purity hydrogen from intermittent renewables and increase energy efficiency to be more competitive are major tasks in development.

ETAC process can address these challenges. Have proved to be 15% more energy efficient and quite flexible in operation. It outmatches AWE for partial loads and is able to work at low current densities from 100 mA/cm<sup>2</sup> allowing for day-long operation without compromising electricity demand.

The scissoring of the water splitting reaction with a thermochemical OER deploys the energy losses associated to the excessive overpotential exhibited even for state-of-art available AWE anodes. Voltage efficiency results also improved, reaching almost 90%. ETAC produces hydrogen with high purity and without

Although the capital expenses for ETAC are lower than conventional AWE cells due to lack of expensive components, investments for ETAC technology would be greater than AWE for equal capacity. Improvements in material and electrode design are still needed to increase reaction rates at low densities and cell potential under OER voltages.

Due to its lower energy demand to run electrolysis, ETAC could be even suitable for home applications as an energy storage system to replace current electric batteries and bypass the physical limitations of these technologies. Paired with low-current devices such as PV panels and with proper heat integration, could provide homes with a method to harvest and save energy for domestic fines.

Efforts have to be done along the chain as well. High density hydrogen storage faces purely technical barriers and the costs associated of the storage technologies are a concern. Transport and delivery to end users must be taken always in consideration in a hydrogen-based economy.

Compressed hydrogen has the lowest volumetric hydrogen storage densities of available technologies and yet is the most used up to date, directly affecting the investments costs since determines the size of storage. Even for a high storage pressure of 700 bar, system shows certain

limitations. CGH<sub>2</sub> rises also in expenses because of the main part of the operating cost is related to electricity use, being generally produced and store during time of low electricity price.

Liquid Organic Hydrogen Carriers reunite several characteristics that make them a very attractive for hydrogen storage. They are liquid both hydrogenated and dehydrogenated form at ambient conditions, have a high gravimetric density and volumetrically almost match liquid hydrogen density without going through an energy-intensive process like liquefaction. However, different to compress hydrogen is a technology that requires an energy input for releasing the hydrogen.

Simulation have revealed the importance of catalyst and reacting conditions in both reactions suggesting the need of a purification step according to the byproducts fraction. Reality instead have showed hydrogenation of Toluene and dehydrogenation of MCH to be highly selective processes over various efficient heterogenous catalyst. In addition, it is the most recognized LOHC system and as a technology it has already passed demonstration stage.[4]

However, the release of hydrogen still sets a drawback in term of energy demand to guarantee full applicability of the MTH system because high-temperature heat must be always provided in any way. Research in the field is aiming for lower dehydrogenation temperatures and constant improvement on selectivity to ensure cyclability and minimize degradation.

# 9.Conclusion

With growing share of intermittent renewable electricity around the world to replace fossil fuels sources, efficient and viable way of transforming this variable inputs will become very important. Hydrogen from electrolytic grade is the "missing link" and not only will encourage the energy sector to move towards its application as energy carrier, it also will prompt the economy and principally privates to come up with "the change".

In this work a description of a combination of two innovative processes is provided. Their performances are simulated and an analysis of their limitations and opportunities is carried out. Results are confronted with a mature and commercially available technologies and main challenges are presented in order to assess feasibility of this cutting-edge arrangement.

ETAC process display the possibility of low voltage and low current water splitting (near thermoneutral conditions) with higher energy efficiency and hydrogen purity. Technologically is less complex than commercially available technologies and require less and cheaper materials with lower assembly costs. In addition, comply with the need of being more flexible and is suitable for part load operation. ETAC process coupled with renewables could provide a better grid balancing due to it potential for hydrogen evolution at low voltages.

However, it a method that still must be refined and there is a lot of improvements to make regarding to electrode design, reaction kinetics and regeneration thermodynamics. Being hydrogen the desired product, duration of the besides steps should be minimized so as to maximize the HER step throughput. Possible advances in the regeneration step will significantly increase efficiency and output rate.

LOHCs are a very attractive alternative since the current hydrogen storage and transportation solutions are unprofitable and unsafe because of the low densities, the high pressures or the excessive electricity consume. Features that make LOHCs very similar to crude oil set a unique opportunity for use with the existing infrastructure and specially MTH system shows a very high potential for large-scale production and international market.

Results show that hydrogenation of toluene is a very cost-effective way of storing hydrogen when produced from renewables because of little thermodynamic requirements and energy savings from operation with liquid-state flows at reactor pressure. Nonetheless, the percentage of side products suggest that catalyst selection plays a very important (in fact the most important) role in the whole system performance. Activity and selectivity are the desired characteristics.

On the other hand, for dehydrogenation it is possible to conclude that the technology has potential to become much more applicable, even for mobility. The main challenge for making LOHC an established hydrogen storage technology is their energy need for releasing hydrogen at the end-user. Coupling with excess heat from other processes or hydrogen-fueled devices is a strategy that not always will be possible to achieve and will require further developments.

The processes reviewed have a positive synergy and several advantages against the commercially available technologies. They should be even considered at an early stage for its application, from locally to regionally, as they have potential to encourage other actors to move in a similar direction. A Renewables-to-H<sub>2</sub> future will see infinite number of new applications and methods

since humanity will need to channel renewable electricity to different sectors for which decarbonization will be otherwise difficult without the hydrogen.

### 10. References

- [1]. A. Landman, G. Grader, A.Rothschild. (2019). Decoupled Water Splitting: From Basic Science to Application.
- [2]. Alexander G. Wallace. Mark D. Symes. (2018). Decoupling Strategies in Electrochemical Water Splitting and Beyond.
- [3]. Caitian G, Seok Woo L, Yuan Y.(2017). Thermally Regenerative Electrochemical Cycle for Low-Grade Heat Harvesting.
- [4]. Chiyoda Corporation. (2021). Spera Hydrogen® :Chiyoda's Hydrogen Supply Chain Business.< www.chiyodacorp.com>
- [5]. Cottrell equation by Tim Paschkewitz 2019, Pine Research, < https://pineresearch.com>
- [6]. D. Teichmann, W. Arlt, P.Wasserscheidb and R. Freymanna. (2011) .A future energy supply based on Liquid Organic Hydrogen Carriers (LOHC).
- [7]. Department of Energy (DOE), United States. (2009). Energy requirements for hydrogen gas compression and liquefaction as related to vehicle storage needs.
- [8]. G. Sandy. (2004). Hydrogen storage and its limitations. Electrochemical Society Interface.
- [9]. Godula-Jopek, Agata. (2015) Hydrogen Production: by Electrolysis. Fundamentals of Water Electrolysis by Pierre Millet.
- [10]. Gutiérrez-Martin F, Guerrero-Hernández I.(2011). Balancing the grid loads by large scale integration of hydrogen technologies.
- [11]. H. Dotan, A. Landman, S.W. Sheehan et all. (2019). Decoupled hydrogen and oxygen evolution by a two-step electrochemical-chemical cycle for efficient overall water splitting.
- [12]. H. Dotan, A. Landman, S.W. Sheehan et all. (2019). Supplementary information.
- [13]. Hydrogen Europe. (2020). <https://hydrogeneurope.eu/transport>
- [14]. Hydrogenous LOHC Technologies (2021). <www.hydrogenious.net>
- [15]. International Renewable Energy Agency. (2019). Hydrogen from Renewable Power: Technology outlook for the energy transition.
- [16]. J. Andersson, S. Gronkvist. (2019). Large-scale storage of hydrogen
- [17]. J.W.Sheffield, K.B.Martin, R.Folkson. (2014). Alternative Fuels and Advanced Vehicle Technologies for Improved Environmental Performance
- [18]. M. Eypah M. Schimpe et al. (2016). Model-based techno-economic evaluation of an electricity storage system based on Liquid Organic Hydrogen Carriers.
- [19]. M.H. Hamayun, M. Hussain, I. M. Maafa, R. Aslam. (2019). Integration of hydrogenation and dehydrogenation system for hydrogen storage and electricity generation e simulation study.
- [20]. Neuman & Esser Group. (2020) Mobility with Hydrogen Filling Stations. Diaphragm Compressors.
- [21]. P. Chandra Rao.(2020).Potential Liquid-Organic Hydrogen Carrier (LOHC) Systems: A Review on Recent Progress
- [22]. S.A Grigoriev.(2020). Current Status, research trends, and challenges in water electrolysis science and technology.
- [23]. Sánchez M, Amores E, Rodríguez L, Abad D, Clemente-Jul C. (2019). Aspen Plus model of an alkaline electrolysis system for hydrogen production.
- [24]. Sánchez M, Amores E, Rodríguez L, Abad D, Clemente-Jul C. (2019). Semi-empirical model and experimental validation for the performance evaluation of a 15-kW alkaline water electrolysis.
- [25]. Usman MR, Alotaibi FM, Aslam R. (2015). Dehydrogenation/hydrogenation of methylcyclohexane-toluene system on 1.0 wt% Pt/zeolite beta catalyst. Prog React Kinet Mech 2015

#### **Appendix I :**

#### **Proof-of-Concept Experiments**



**E-TAC water splitting in alkaline electrolyte ( 5 M KOH solution).** a, Anode potential and cell voltage during the hydrogen generation steps of ten consecutive cycles at a nominal current density of 50 mA/cm<sup>2</sup>. b, Corresponding average anode potential and range for each cycle. c, Average cell voltage and range in each cycle. d, Cumulative hydrogen production (at 1 atm and 25 °C) as a function of electrical power consumption.

## <u>H₂Pro</u>

www.h2pro.co



Prototype of H<sub>2</sub>Pro ETAC

# Appendix II

## **Mass Balances**

## AWE

		FEED	02	H2	PURGE
Mass Flows	kg/hr	41,09	14,6660159	2,9425693	23,4809493
H2O	kg/hr	26,7108143	0,28719833	0	0,0187527
H2	kg/hr	0	4,45E-08	2,9425693	0,01209103
02	kg/hr	0	9,65E-05	0	23,4501056
КОН	kg/hr	0	0	0	0
H3O+	kg/hr	0	0	0	0
OH-	kg/hr	4,3599924	4,35877225	0	0
K+	kg/hr	10,0227537	10,0199488	0	0

### ETAC : STEP 1

		FEED	H2	ANODE	ELECTROLYTE
Mass	kg/hr	145,36	4,49	-4,43	145,30
Flows					
H2O	kg/hr	111,70	0,00	0,00	111,63
КОН	kg/hr	0,00	0,00	0,00	0,00
H2	kg/hr	0,00	4,49	0,00	0,00
02	kg/hr	0,00	0,00	0,00	0,01
K+	kg/hr	23,46	0,00	0,00	23,46
OH-	kg/hr	10,20	0,00	0,00	10,20
ΔAnode	kg/hr	0,00	0,00	-4,43	0,00

#### ETAC: STEP 2

		FEED	ANODE	02	ELCTROLYTE	<b>REGEN ANODE</b>
		145,36	-4,43	31,59	109,79	3,44
H2O	kg/hr	111,70	0,00	0,00	76,13	0,00
КОН	kg/hr	0,00	0,00	0,00	0,00	0,00
H2	kg/hr	0,00	0,00	0,00	0,00	0,00
02	kg/hr	0,00	0,00	31,59	0,00	0,00
K+	kg/hr	23,46	0,00	0,00	23,46	0,00
OH-	kg/hr	10,20	0,00	0,00	10,20	0,00
ΔAnode	kg/hr	0,00	-4,43	0,00	0,00	3,44

# Appendix III

Types of water electrolyzers	Alkaline	PEM	Solid Oxide
Technology status	mature technology		lab-scale R&D
T range (°C)	ambient - 120		700-1000
Flectrolyte/pH	25-30 wt% (KOH)	perfluorosulfonic acid	$Y_2 \Omega_2 - Zr \Omega_2$ Sca $\Omega_2 - Zr \Omega_2$
hierdolyte, pri	25 56 were (Ronjaq	permaorosanome dela	$MgO - ZrO_2$ , $CaO - ZrO_2$
Charge carrier	OH-	H <sup>+</sup>	0 <sup>2-</sup>
Overall reaction	$H_2O \rightarrow H_2 + 1/2O_2$		
Anode reaction	$2OH^- \rightarrow 1/2O_2 + H_2O + 2e^-$	$H_2O \rightarrow 1/2O_2 + 2e^- + 2H^+$	$O^{2-}-2e^- \rightarrow 1/2O_2$
Cathode reaction	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$2H^+ + 2e^- \rightarrow H_2$	$H_2O + 2e^- \rightarrow H_2 + O^{2-}$
Anode catalyst	Ni <sub>2</sub> CoO <sub>4</sub> , La-Sr-CoO <sub>3</sub> , Co <sub>3</sub> O <sub>4</sub>	Ir/Ru oxide	(La,Sr)MnO <sub>3</sub> , (La,Sr)(Co,Fe)O <sub>3</sub>
Cathode catalyst	nickel foam/Ni- stainless steel	platinum	Ni-YSZ or Ni-GDC Cermet
	Ni-Mo/ZrO <sub>2</sub> -TiO <sub>2</sub>		
Separator	asbestos, polysulfone-bonded	polymer membrane	ceramic
	polyantimonic acid,		
	ZrO2 on polyphenylsulfone, NiO,		
	polysulfone impregnated with		
	Sb <sub>2</sub> O <sub>5</sub> polyoxide		
Sealant	metallic	synthetic rubber/fluoroeleastomer	glass and vitro-ceramics
Current distributor	Ni	titanium	ferritic stainless steel (Crofer APU)
Containment material	nickel plated steel	stainless steel	stainless steel
P range (bar)	1-200	1–350 (700)	1-5
Conventional current	0.2-0.5	0–3 (up to 20)	0-2
density (A/cm²)			
Efficiency (%)	60-80	80	100
(at i A/cm²/Ucell V/T°C)	0.2-0.5/2.0/80	1.0/1.8/65	3.6/1.48/950
Capacity (Nm³/hour)	1-500	1–250	1
Durability (hours)	100,000	10,000-50,000	500-2000
H <sub>2</sub> O specification	liquid	>10 MΩ.cm	steam
Load cycling	medium	good	good
Stop/go cycling	weak	good	weak
T cycling	weak	good	weak

## **Commercially Available Electrolysers**

# Appendix IV

#### **Anode Regeneration Step Kinetics**

Regenerate mAh/cm2	ed Charge			
T (min)	90°C	80°C	70°C	60°C
2	0,35	0,2375	0,15	0,1125
4	0,525	0,45	0,2	0,125
8	0,65	0,525	0,2875	0,175
16	0,95	0,6126	0,425	0,275
32	1,1	0,75	0,55	0,35

- Charge is equivalent to mol of Ni(OH)<sub>2</sub> through Faraday Law.

nNi(OH)₂ (mol)				
T (min)	90°C	80°C	70°C	60°C
2	1,3059E-05	8,86161E-06	5,5968E-06	4,1976E-06
4	1,9589E-05	1,67904E-05	7,4624E-06	4,664E-06
8	2,4253E-05	1,95888E-05	1,0727E-05	6,5296E-06
16	3,5446E-05	2,28574E-05	1,5858E-05	1,0261E-05
32	4,1043E-05	2,7984E-05	2,0522E-05	1,3059E-05



- From the curves above, parameters can be retrieved with the logarithmic method of linearization.
- Kinetics are characterized by the following parameters:

Activation Energy	17,5 kJ/mol
Preexponential Factor	38,82
n	1

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