

POLITECNICO DI TORINO

Collegio di Ingegneria Chimica e dei Materiali

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Tesi di Laurea Magistrale

**Simulations of Tri-reforming of Methane
Using Solar Energy**



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Extended Abstract in Italian

I.I Prefazione

L'attuale problema energetico è la combustione di combustibili fossili che porta alle emissioni di gas serra ed è noto per contribuire al riscaldamento globale. Si ritiene generalmente che l'aumento della temperatura della terra sia collegato all'aumento delle emissioni di gas serra (principalmente CO₂) nell'atmosfera. La CO₂ è un gas serra principale rilasciato da combustibili contenenti idrocarburi, come il metano, quando vengono bruciati. La maggior parte del fabbisogno energetico mondiale è attualmente supportato dalla combustione di combustibili fossili. L'uso di energia rinnovabile può fornire una soluzione al problema del riscaldamento globale.

Di conseguenza, l'idrogeno diventa un importante carburante alternativo. Ci si aspetta che sostituisca i combustibili fossili perché è una fonte di energia pulita ed ecologica. La reazione dell'idrogeno con l'ossigeno può rilasciare energia in modo esplosivo nei motori a combustione che producono acqua come unico prodotto di reazione. Attualmente, l'idrogeno è comunemente usato come reagente nell'industria chimica. L'idrogeno viene prodotto localmente, utilizzato immediatamente, poiché lo stoccaggio e il trasporto sono costosi. Inoltre, le celle a combustibile a idrogeno hanno i seguenti di zero emissioni, alta efficienza di conversione energetica, bassa rumorosità, ecc. Diventerà un combustibile promettente nel prossimo futuro.

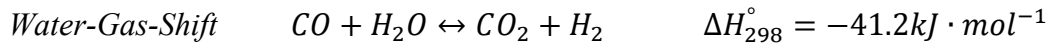
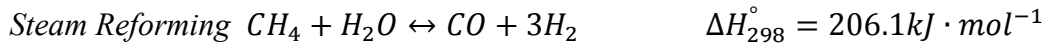
Il processo di reforming è il metodo più economico e ampiamente utilizzato per produrre idrogeno commercialmente in tutto il mondo. Il reforming è la conversione da idrocarburi in syngas (SG). Syngas è una miscela di monossido di carbonio e idrogeno, seguita dalla separazione dell'idrogeno dalla miscela^[4]. SG costituisce la materia prima nelle industrie chimiche e petrolchimiche, per la produzione di metanolo, benzina, MTBE o combustibili liquidi sintetici. Inoltre, il gas di sintesi può essere prodotto da varie materie prime come gas naturale, gas liquido, nafta, coke di petrolio, carbone e alcuni altri idrocarburi^[4,8].

I.II Reazione Di Reforming

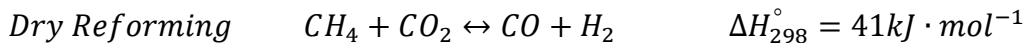
Il metano è il componente principale del gas naturale, ampiamente utilizzato per la produzione di idrogeno grazie al suo alto contenuto di idrogeno (4: 1 rispetto al contenuto di carbonio) e al basso costo. Attualmente, l'avanzamento della fratturazione idraulica e orizzontale ha reso il gas di scisto ben più redditizio, il gas naturale sta notevolmente espandendo l'offerta mondiale di energia^[4]. Il reforming del gas naturale può essere ottenuto mediante una reazione esotermica o endotermica che dipende dal processo chimico scelto^[7].

Lo steam reforming produce syngas con il più alto rapporto H₂: CO, che è considerato per ottenere un'alta concentrazione idrogeno puro. Le reazioni di steam reforming (SMR) sono altamente endotermiche, l'alta temperatura è favorita termodinamicamente (temperature nell'800-1000 °C sono utilizzate nell'industria). Inoltre, con l'espansione del volume, sono favorite anche le basse pressioni, ma i riformatori industriali devono operare a pressioni elevate da 2 a 30 bar. Per ridurre l'enorme quantità di monossido di carbonio prodotta dall'SMR, è necessaria la reazione di spostamento del water-gas-shift (WGS), che è più favorevole a temperature più basse

(tipicamente a 200 -400 °C). Entrambe le reazioni sono reversibili e di solito raggiungono l'equilibrio rispetto al catalizzatore attivo. Inoltre, il rapporto tra vapore e carbonio (S/C) influisce sulla conversione del metano durante l'intero processo, che viene normalmente utilizzato con 3 (S/C).

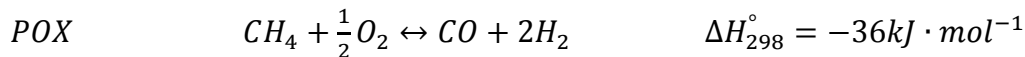


Con l'anidride carbonica disponibile in grandi quantità e a basso costo, la CO₂ può essere utilizzata per la riforma del metano, che si chiama Dry Reforming of Methane (DMR) e per essere una tecnologia promettente per la produzione di syngas.



Tuttavia, il coke, che è la deposizione significativa di carbonio sulla superficie del catalizzatore, contribuisce alla riduzione della sua vita utile e dell'attività di reazione, considerato il principale svantaggio del reforming a secco del metano. La formazione di coke è dovuta alla presenza di anidride carbonica come reagente. Rispetto al reforming a vapore, c'è una possibilità di formazione di la formazione di coke causa del basso rapporto tra vapore e carbonio.

Un'alternativa alla riformazione è l'ossidazione parziale (POX) la stessa di altre, per produrre syngas ricchi di idrogeno, che è una reazione esotermica e considerata più economica della formazione di vapore e di reforming a secco per il fabbisogno di una piccola quantità di energia termica.



I metodi di steam reforming, ossidazione parziale e dry reforming sono combinati in due o tre per dare un nuovo processo per produrre syngas.

Il reforming auto-termico combina la reazione di ossidazione parziale esotermica e la reazione di steam reforming endotermico alimentando insieme metano, acqua e aria. L'energia termica richiesta per il processo di steam reforming è generata dall'ossidazione parziale per risparmiare una quantità significativa di energia. È il nome auto-termico poiché il syngas prodotto consuma l'energia termica generata. Il rapporto H₂: CO è una funzione dell'ingresso di frazioni di reagenti gassosi, che va da 1 a 2.

La combinazione di steam reforming e dry reforming di metano (si chiama bi-reforming) ha suscitato interesse sia dal punto di vista ambientale che industriale. Da un punto di vista ambientale, questi due reagenti contenenti gas ad effetto serra (metano e anidride carbonica), possono essere convertiti in prodotti chimici utili, che rappresentano un'area importante della recente ricerca catalitica. Dall'altro lato, da un punto di vista industriale, la reazione produce syngas con lo specifico rapporto H₂: CO₂ (suggerito per essere chiamato "met-gas"), che è la preparazione perfetta del metanolo senza alcun pericolo di esplosione, confrontandolo con il parziale reazione di ossidazione.

Bi-reforming per produrre met-gas ha un grande potenziale per la materia prima potrebbe essere variato fonti di gas naturale anche contenenti una quantità significativa di CO₂. Inoltre, può anche essere utilizzato per riciclare le emissioni di CO₂ dallo scarico, ad esempio dal combustibile fossile (carbone, petrolio), dalla centrale elettrica di combustione o dalle fabbriche di cemento.

Il nuovo processo produce gas di sintesi con un rapporto H₂: CO auspicabile che utilizza gas di scarico da combustibili fossili o gas di gassificazione della biomassa senza pre-separazione di CO₂. Questa è la cosiddetta reazione tri-reforming, cioè le combinazioni di steam reforming, dry reforming e le reazioni di ossidazione parziale.

Tri-reforming racchiude caratteristiche particolari. L'integrazione dello steam reforming e l'ossidazione parziale con reforming a secco può ridurre o eliminare notevolmente la formazione di carbonio sulla superficie del catalizzatore che è significativa per il reforming a secco, aumentando così la vita del catalizzatore e l'efficienza del processo. Inoltre, l'incorporazione di ossigeno genera calore in situ che potrebbe essere utilizzato per aumentare l'efficienza energetica e l'ossigeno anche ridurre o eliminare la formazione di carbonio sulla superficie del catalizzatore^[16].

Steam reforming è il principale processo di reforming del metano utilizzato per produrre idrogeno che viene prevalentemente utilizzato perché ha il massimo valore per il rapporto H₂: CO, tuttavia, poiché il processo di steam reforming è considerato troppo costoso a causa dell'enorme quantità di calore essendo un processo endotermico. L'ossidazione parziale e il bi-reforming sono buone scelte per produrre syngas quando il valore del rapporto H₂: CO è adeguato per il prodotto a valle mentre il reforming e il tri reforming possono essere usati per ridurre il consumo di energia termica, che è un fattore importante. In breve, si può affermare che la scelta del tipo di reforming catalitico del metano dipende dal tipo di applicazione del syngas prodotto e dalla fattibilità economica del processo correlato alla destinazione.

I.III Collettore Solare

La radiazione solare è un'abbondante fonte di energia, tuttavia è difficile da catturare e utilizzare in modo efficiente. Ad esempio, l'energia solare potrebbe essere utilizzata per la generazione elettrica diretta con celle fotovoltaiche, che attualmente supera i 100 GW di capacità installata globale con un mercato in continua crescita. Tuttavia, le limitate efficienze di conversione energetica (in genere meno del 20%) e il costo relativamente elevato di questa tecnologia ne limitano la crescita, a meno che non venga fornita una grande quantità di sussidi. La conversione dell'energia termica solare, in cui l'energia solare radiante è concentrata e assorbita da un ricevitore trasferito poi come energia termica a un fluido, è un'opzione alternativa di installazioni commerciali con diversi GW a livello globale^[14].

Il processo industriale convenzionale si basa sull'idrocarburo per la produzione di combustibile come syngas (o idrogeno) e materie prime come i metalli. Questi processi industriali sono seriamente energetici e ad alta intensità di carbonio. I problemi legati all'esaurimento dei combustibili fossili e ai cambiamenti climatici aumentano ovviamente, il che si traduce nello sviluppo di soluzioni per processi industriali solari. La tecnologia solare concentrata offre la conversione dall'energia solare in forme termiche, elettriche e chimiche. Mentre l'energia solare convenzionalmente concentrata è stata utilizzata per il calore di processo e le applicazioni di generazione di energia, e si prevede che guidi reazioni chimiche. I processi che utilizzano l'energia solare per fornire calore a reazioni chimiche endotermiche ad alta temperatura sono noti come processi termochimici solari.

La tecnologia convenzionale a energia solare concentrata (CSP) consiste nel focalizzare la luce del sole con una superficie riflettente (uno specchio) per riscaldare un fluido che scorre attraverso un collettore. Recentemente, c'è stato un crescente interesse nell'applicazione della

tecnologia CSP per la sintesi termochimica solare. In un processo termochimico solare CSP, la radiazione solare concentrata viene utilizzata come fonte di calore per generare reazioni altamente endotermiche. Il prodotto di tale processo generalmente appartiene a un "combustibile solare", contenente una frazione di energia chimica generata dall'energia solare. Esistono diversi percorsi termochimici solari, tra cui la divisione dell'acqua, la gassificazione o il cracking di combustibili fossili (carbone, petrolio o gas naturale) e il reforming del gas naturale. Tra questi, il solare termico di reforming del gas naturale ha un grande potenziale a causa delle grandi risorse di gas naturale e dei combustibili solari prodotti, che è principalmente idrogeno o syngas, da utilizzare come materia prima chimica per il prodotto a valle o come combustibile per l'elettricità generazione con turbine a gas^[14].

I fluidi come vapore o olio termico sintetico non possono essere utilizzati, richiedendo invece gas caldo compresso (solitamente con aria). I sali fusi, la maggior parte dei quali sono stabili solo sotto i 550 °C, possono essere utilizzati principalmente per applicazioni di reforming con metano con vapore a bassa temperatura. Il sodio liquido è una scelta adatta per il processo con le sue eccellenti proprietà termodinamiche, tuttavia, è limitato dalla reattività chimica, che richiede precauzioni speciali per prevenire e sopprimere il fuoco e l'esplosione quando a contatto con l'aria.

In generale, non è necessario per il reforming solare termico dei sistemi a metano basato su un approccio indiretto per richiedere un particolare design del reattore. L'unica differenza essenziale rispetto al tradizionale reforming del metano è la fonte di calore, che viene generata dal sole. Pertanto, la geometria tubolare, la stessa di quella dei reattori industriali, può essere utilizzata nel reforming solare termico indiretto dei sistemi a metano. D'altra parte, l'approccio diretto implica molti requisiti speciali per il progetto del reformer che dovrebbe integrare efficacemente il ricevitore solare con l'elemento catalitico. Tali reformers devono soddisfare i requisiti del ricevitore solare / assorbitore (bassa riflettività, bassa emissività e alta resistenza agli shock termici), nonché i requisiti del letto catalitico (alta attività e stabilità contro coking e sinterizzazione).

L'obiettivo del presente lavoro è simulare l'intero processo di produzione dell'idrogeno con fonti di energia rinnovabile. Per raggiungere questo obiettivo, il processo è progettato utilizzando il sistema a energia solare concentrata (CSP) come fonte di energia rinnovabile per fornire energia ai reattori di reforming del metano per produrre idrogeno. Come simulazione di processo, potrebbe anche essere considerato come un dato sperimentale come parte del progetto " a hybrid process to transform municipal waste into energy (SOL-CARE)", che è implementato da molti operatori nelle aree europee.

II. Simulazione

Aspen Plus 7.3 è stato utilizzato per questa simulazione. Le composizioni di equilibrio sono calcolate per la condizione operativa specificata e il bilancio di massa ed energia sono risolti in moduli sequenziali di ciascuna unità.

Il reattore RGibbs è selezionato per le tri-trforming reazioni mentre il reattore REquil è utilizzato per Water-Gas-Shift. Per il reattore RGibbs, le composizioni di equilibrio vengono calcolate riducendo al minimo l'energia totale libera di Gibbs che è la somma su tutte le specie delle potenziali reazioni. Il reattore RGibbs è una scelta adatta per valutare la reazione triforme

poiché mancano i dati cinetici. Per il reattore Reattivo, le composizioni del prodotto derivano dalla situazione in cui tutte le reazioni raggiungono l'equilibrio chimico.

L'equazione di stato di Peng-Robinson è il metodo termico adottato per la simulazione del processo. Inoltre, Peng-Robinson-Boston-Mathias (PR-BM) viene anche testata nel processo, ma non ci sono differenze apprezzabili.

La simulazione del sistema CSP è difficile da fare perché l'ubicazione dell'impianto influenza in modo significativo la capacità e l'efficienza. Inoltre, la simulazione di un impianto CSP non fa alcun uso per la simulazione del triplo reforming delle reazioni del metano. In questo studio, l'impianto CSP è considerato come la risorsa di calore per riscaldare il sodio liquido fino ad una temperatura elevata che viene utilizzata per fornire calore per far arrivare la miscela di gas alla temperatura di reazione.

La prima simulazione è lo steam reforming di metano, al fine di scoprire le condizioni ottimali della corrente di alimentazione e dei reattori. La **Figure 1** mostra che il gas combustibile è metano puro con flusso di massa 100 kg / ha 25 °C. Il combustibile viene miscelato con acqua preriscaldata da un calore recuperato dal WGS e dal dispositivo di raffreddamento. La miscela (combustibile+vapore) viene riscaldata fino alla temperatura di funzionamento del reattore di reforming, variando da 600 a 800 °C. Poiché la temperatura massima potrebbe essere riscaldata dal sodio liquido è 850 °C. L'acqua esce dal serbatoio dell'acqua a 25 °C e la portata dipende dal rapporto vapore / carbonio, che varia da 1 a 5. La pressione delle reazioni di reforming del vapore avviene nel reattore varia da 1 a 5 bar. I syngas fuori dal reattore sono mescolati con un'altra corrente d'acqua per ridurre la frazione molare di CO all'1% all'uscita di WGS. I gas miscelati vengono raffreddati a 330 °C e vanno nel WGS per reagire a 300 °C.

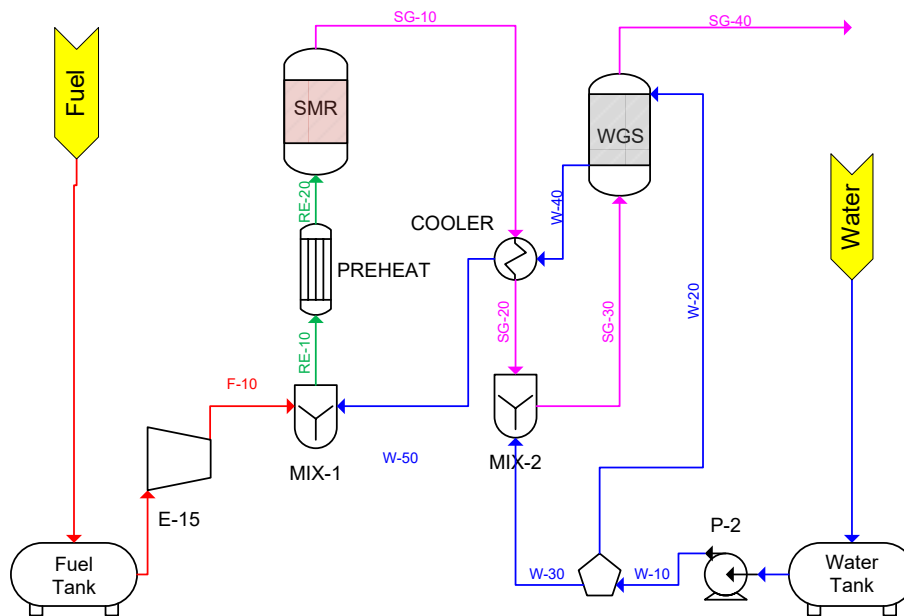


Figura 1 Diagramma di processo dello steam reforming di metano

L'aumento del vapore al carbonio il rapporto da 1 a 5 porta all'aumento della conversione di metano, alla portata totale dell'acqua e al calore richiesto, tuttavia le loro tende tendono a variare.

La conversione del metano aumenta drasticamente quando il rapporto tra vapore e carbonio varia da 1 a 3, ma quando la corrente a razione di carbonio supera 3, la conversione del metano è una funzione debole di quel rapporto. Lo stesso vale per il rapporto di massa tra l'idrogeno prodotto e il metano alimentato, la verifica del consumo di metano è la principale fonte di produzione dell'idrogeno. Pertanto, il trend di conversione del metano viene anche utilizzato per rappresentare la variazione della produzione di idrogeno. Al contrario, la portata totale dell'acqua aumenta lentamente quando il rapporto vapore/carbonio(S/C) cambia da 1 a 3, e aumenta bruscamente quando il rapporto è uguale a 4 e 5, perché c'è abbastanza acqua per ridurre la concentrazione di CO senza il secondo flusso d'acqua quando il rapporto è più di 3. Il calore richiesto continua a crescere con il rapporto tra il flusso e il carbonio, il che significa una relazione diretta tra loro.

Le regole per determinare le condizioni ottimali sono la massima conversione del metano con la portata minima dell'acqua e il consumo minimo di energia. In questo caso, viene selezionato il rapporto vapore/carbonio (S/C) 3 per ulteriori simulazioni.

Poiché il reforming con metano di vapore è una reazione fortemente endotermica, la conversione del metano continua a crescere mentre la temperatura di reazione continua a salire. La conversione del metano aumenta rapidamente quando la temperatura sale da 600 a 700 °C, ma sale leggermente dopo che la temperatura raggiunge più di 700 °C. D'altra parte, la conversione del metano è troppo bassa per richiedere la seconda corrente d'acqua per diminuire la concentrazione di CO al WGS quando la temperatura è inferiore a 700 °C, il che si traduce in un basso fabbisogno di calore. Poiché la temperatura supera i 700 °C, il calore richiesto aumenta drasticamente.

La temperatura di reazione ottimale è selezionata a 750 °C, così da ridurre al minimo il consumo di energia la conversione del matano mantenendo alta.

L'aumento della pressione da 1 a 5 bar porta alla diminuzione della conversione di metano dal 97% al 75%, poiché questa reazione è una reazione di aumento della pressione che è favorita a bassa pressione. Il calore richiesto a bassa pressione è quello per riscaldare il secondo flusso d'acqua che è quello di diminuire la concentrazione di CO, ma al contrario, non è necessario per quel flusso a causa della bassa conversione di metano.

Pertanto, la pressione operativa viene selezionata a 2 bar per la conversione più alta del metano e il consumo di calore inferiore, e anche il processo in background industriale è una condizione di considerazione.

Le condizioni di reazione sono ottimali, il rapporto tra vapore e carbonio è uguale a 3, la pressione operativa è a 2 bar e la temperatura di reazione è a 750 °C.

Con la condizione ottimale del reforming del vapore, che è la base del progetto, il processo di troncatura del metano (**Figura 2**) è realizzato con queste condizioni. È considerato come caso di studio I. L'alimentazione del processo consiste in tre flussi, il flusso di carburante è metano con portata (F-10) 100 kg / ha 25 °C, il flusso d'acqua (W-10) proviene dal serbatoio dell'acqua a 25 °C, e viene preriscaldato da una serie di blocchi con il calore recuperato. La portata viene regolata per adattarsi al rapporto ottimale tra vapore e carbonio nel reattore, e il flusso d'aria (A-20) viene alimentato a 25 °C, e deve essere sufficiente per produrre metano reazioni di ossidazione / ossidazione parziale di reforming per fornire calore per le altre reazioni endotermiche. I gas di alimentazione si miscelano con il gas riciclato attraverso un miscelatore e

raffreddano e vengono riscaldati dal sodio liquido che viene riscaldato dal sistema CSP per raggiungere la temperatura di reazione. Il reattore funziona alla condizione ottimale con il fabbisogno netto di energy pari a zero. Il syngas (SG-40) viene raffreddato e inviato al WGS per ridurre la concentrazione di CO (non esiste un altro flusso d'acqua perché la frazione molare di CO è già inferiore all'1%). Quindi viene miscelato con un'altra corrente d'aria che è di 25 kg / ha 25 °C per fornire ossigeno per un'ulteriore reazione. Il syngas miscelato (SG-40) viene raffreddato a 150 °C e inviato al PROX per portare le reazioni di ossidazione del CO con conversione di CO al 99,9%. I gas fuori del PROX sono raffreddati a 130 °C . Quindi il syngas (SG-70) viene raffreddato a 60 °C nel separatore, la fase liquida è l'acqua che viene recuperata nel serbatoio dell'acqua e la fase vapore attraverso la membrana a idrogeno selettivo per separare l'idrogeno come prodotto per ulteriori processi. Lo scarico è diviso in due flussi, il ricircolo (RY-20) che va al blocco MIX-1e lo spurgo (PURGE). Il rapporto del riciclo varia da 0.1 a 0.9. L'intero processo è gestito a una pressione di 2 bar.

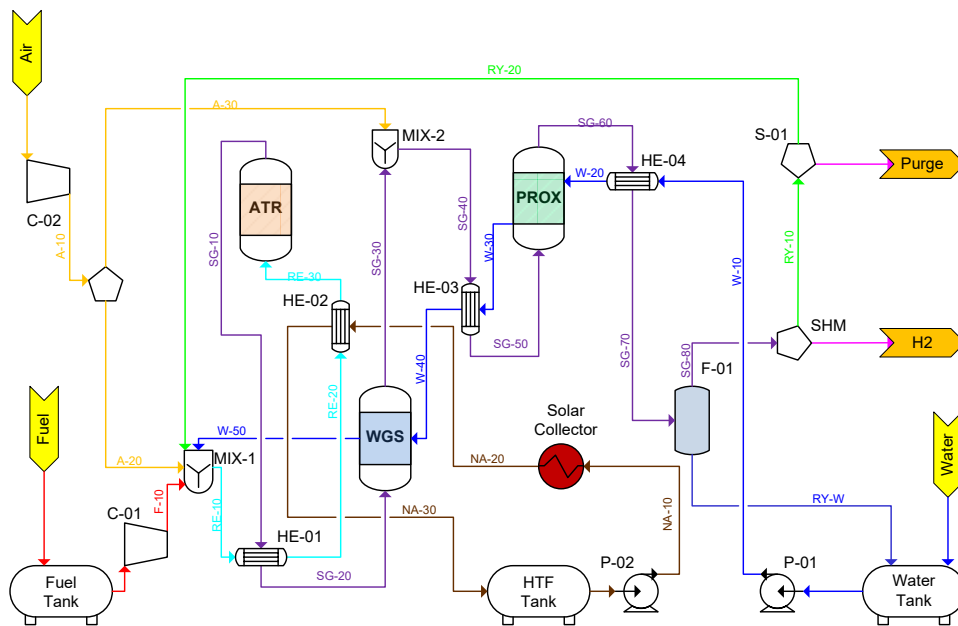


Figura 2 Diagramma di processo del tri-reforming del metano con energia solare nel case-study I

L'effetto del riciclo sulla portata di idrogeno prodotta, il flusso di alimentazione di metano e aria, il bilancio idrico, la concentrazione di CO fuori dal PROX e lo spurgo, il flusso di calore di sodio e liquido richiesto e l'efficienza lorda alle condizioni ottimali di ciascun blocco sono stati analizzati.

L'aumento della divisione del riciclo da 0,1 a 0,9 nell'aumento della portata di idrogeno prodotto con il flusso di alimentazione del metano rimane a 100 kg/h e il flusso d'aria richiesto diminuisce leggermente, da 381 a 379 kg/h. Allo stesso tempo, il flusso d'acqua sale lentamente quando il rapporto di riciclo sale da 0.1 a 0.7, ma sale drasticamente per adattarsi alle crescenti componenti del carbonio di riciclo per rimanere il rapporto vapore/carbonio (S/C) uguale a 3. Inoltre, l'acqua recuperata dal separatore aumenta, di conseguenza, l'acqua netta necessaria per la reazione tririforma diminuisce lungo l'aumento del rapporto di ripartizione del riciclo. Il rapporto

molare di CO, sia dell'uscita PROX sia della corrente di spurgo, diminuisce con l'aumento del rapporto di ripartizione del riciclo.

L'energia richiesta dall'impianto CSP per riscaldare i gas di reazione a 750 °C aumenta con il rapporto di ripartizione ripartito, perché più energia termica viene utilizzata per riscaldare l'aumento del flusso dell'acqua in ingresso. Pertanto, il flusso di sodio liquido caldo richiesto sale dal 1981 al 20939 kg/h. Poiché la temperatura di ingresso del sodio liquido caldo è di 760 °C (per aumentare l'efficienza dello scambio termico) e la temperatura di uscita del sodio liquido caldo è di 460 °C.

Il rapporto ottimale di ripartizione del riciclo dovrebbe essere selezionato a 0.9, in quanto il processo consentirà la massima produzione di idrogeno, la massima efficienza dell'erba con l'acqua minima richiesta e la concentrazione minima di CO della corrente di spurgo. Tuttavia, allo stesso tempo, il calore richiesto per le reazioni è il valore massimo, a 2375 kW; richiede 20939 kg/h di flusso di sodio caldo, è troppo grande per una pianta come condizione limite.

Il processo è migliorato rispetto al case-study I e tutto il processo è lo stesso del caso I prima del blocco PROX. L'uscita di syngas di PROX (SG-60), nel case-study II (**Figura 3**), viene raffreddato a 130 °C, e attraverso la membrana di idrogeno selettivo separa l'idro come prodotto per primo, quindi lo scarico (RY-10) è diviso in due flussi, uno (RY-20) è quello di riciclare, l'altro (RY-30) è quello di eliminare, con il rapporto di ripartizione del riciclo varia da 0.1 a 0.9. Il flusso di riciclo (RY-20) viene inviato al blocco MIX-1, l'altro viene raffreddato a 60 °C in un separatore, la fase liquida è l'acqua da recuperare nel serbatoio dell'acqua e la fase vapore deve essere eliminata. Questo processo funziona anche alla pressione ottimale.

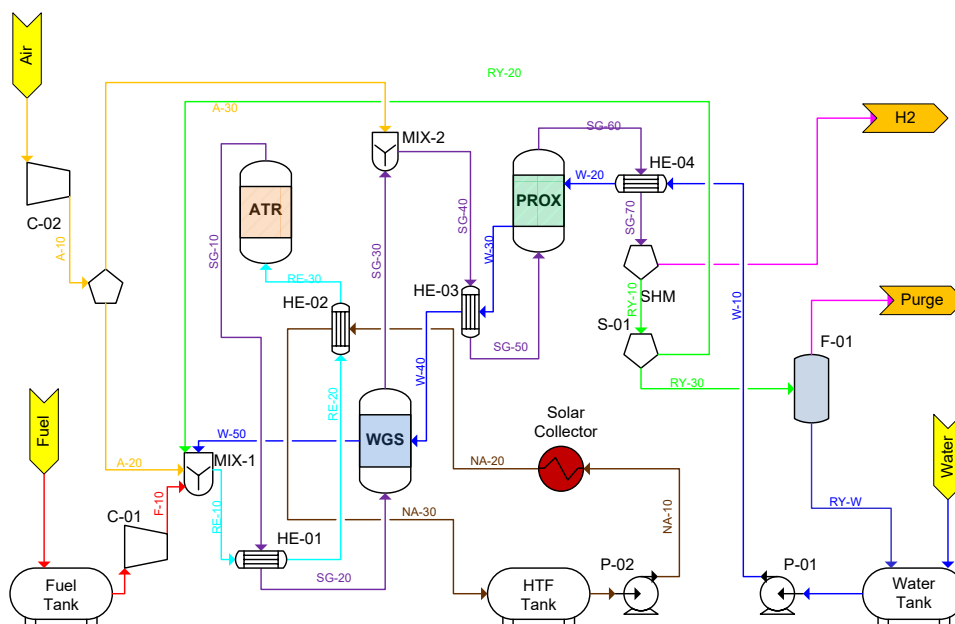


Figura 3 Diagramma di processo del tri-reforming del metano con energia solare nel case-study II

Lo stesso del case-study I, L'effetto del riciclo sulla portata di idrogeno prodotta, il flusso di alimentazione di metano e aria, il bilancio idrico, la concentrazione di CO fuori dal PROX e lo spurgo, il flusso di calore richiesto e il flusso di sodio liquido, e l'efficienza lorda alle condizioni ottimali di ciascun blocco sono stati valutati.

Le tendenze delle variabili sono le stesse del case-study I. Tuttavia, nel case-study II, è impossibile aumentare il rapporto di ripartizione del riciclo fino a 0.8 o 0.9, perché quando il rapporto è troppo alto, il calore trasportato dal flusso di riciclo è così enorme che l'acqua di preriscaldamento sarà surriscaldata, il che significa che la temperatura esterna dell'acqua sarà superiore alla temperatura di ingresso del flusso caldo.

L'aumento della frazione del riciclo porta all'aumento della portata di idrogeno prodotto mentre il flusso d'aria richiesto diminuisce leggermente. Inoltre, l'acqua in ingresso a viene recuperata e aumenta poco, l'acqua richiesta dalla rete diminuisce. Il rapporto molare di CO, sia dell'uscita PROX sia della corrente di spurgo, diminuisce con l'aumento del rapporto di ripartizione del riciclo. Inoltre, quando il rapporto di divisione del riciclo è uguale a 0.1, il rapporto molare di CO nella corrente di spurgo è di 11 ppm (più di 10 ppm), che è vietato spurgare direttamente nell'ambiente.

Inoltre, l'energia termica richiesta aumenta con il rapporto di riciclo ripartito da 0,1 a 0,7, di conseguenza, la portata di sodio liquido calda richiesta sale da 1829 a 2312 kg/h, come il calo di temperatura tra l'ingresso di sodio liquido caldo e l'uscita è di 300 °C. Anche l'efficienza lorda aumenta mentre aumenta il rapporto di ripartizione del riciclaggio.

Nel case-study II, il rapporto ottimale di ripartizione del riciclo è pari a 0,7, che massimizza la produzione di idrogeno, l'efficienza lorda e riduce al minimo il flusso d'aria in entrata e il flusso d'acqua necessario con la concentrazione minima di CO da spurgare. Il calore richiesto per il sistema CSP è di 262 kW, ovvero 2312 kg/h di 760 °C per fornire il calore, che è una quantità molto minore nel processo industriale.

Il flusso SG-70 viene raffreddato a 60 °C al separatore per recuperare l'acqua nel serbatoio dell'acqua. L'enorme quantità di calore è difficile da gestire, perché surriscalda l'acqua quando il rapporto di ripartizione del riciclo è elevato. Il modo di affrontare il calore viene utilizzato da un altro flusso d'acqua per assorbirlo con una temperatura che aumenta da 25 a 35 °C, con il flusso d'acqua di 16085 kg/h alla pressione atmosferica e spurgare l'acqua direttamente nell'ambiente.

PROX, come acronimo per l'ossidazione preferenziale, si riferisce all'ossidazione preferenziale del gas su un catalizzatore. In questo processo, il catalizzatore ossida preferenzialmente il monossido di carbonio (CO) usando un catalizzatore eterogeneo posto su un supporto ceramico [27].

La capacità di PROX, ovvero la conversione di CO nella reazione di ossidazione.



Per spurgare lo scarico direttamente nell'ambiente, la conversione di CO nella reazione PROX deve essere superiore al 99.7% (per garantire la concentrazione di CO inferiore a 10 ppm). Se la capacità non è così elevata da ridurre il rapporto molare di CO inferiore alla concentrazione critica (10 ppm), è richiesto un serbatoio per immagazzinare lo scarico o utilizzare un altro PROX con catalizzatore più efficace per gestire lo scarico.

La **Tabella 1** mostra il risultato della reazione di tripodulazione del metano nel cas-study I e II, entrambi i casi si trovano in condizioni operative ottimali.

Tabella 1 Confronto tra reazione tri-trforming del metano nel case-study I e II

variable		Unit	I	II
operation pressure		bar	2	2
tri-forming reaction	temperature	°C	750	750
WGS reaction	temperature	°C	300	300
recycle split			0.9	0.7
H ₂ OUT	flow rate	kg/h	39.13732	39.10353
H ₂ O OUT	flow rate	kg/h	2914.888	269.6418
H ₂ O IN	flow rate	kg/h	3073	425.0263
	P-01 pressure change	bar	1 to 2	1 to 2
	P-01 motor efficiency		0.9	0.9
	p-01 power	kW	0.09542232	0.01187581
H ₂ O net required	flow rate	kg/h	158.112	155.3845
CH ₄ IN	flow rate	kg/h	100	100
	C-01 pressure change	bar	1 to 2	1 to 2
	C-01 motor efficiency		0.75	0.75
	C-01 power	kW	3.57436701	3.57436701
AIR IN	flow rate	kg/h	379.1081	379.9234
	P-01 pressure change	bar	1 to 2	1 to 2
	P-01 motor efficiency		0.75	0.75
	p-01 power	kW	7.70161131	7.71836558
required liquid sodium	flow rate	kg/h	20939.52935	2312.346242
heat duty	HE-01	kW	1634.73803	564.356601
	HE-02	kW	2374.89162	262.258603
	HE-03	kW	532.20403	185.30324
	HE-04	kW	104.0428	36.537904
	H-WGS	kW	149.3143	75.047735
	H-PROX	kW	13.07475	14.070894
minimum PROX capacity	CO conversion	%	99.5	99.7
CO mole fraction	OUT WGS	ppm	455.256	1378.79
	OUT PROX	ppm	0.45428	1.37058
	PURGE	ppm	0.900282	2.92245
Gross Efficiency		%	93.89952015	93.86461132

La pressione operativa, le temperature dei reattori e la portata del metano di alimentazione sono le stesse. Ci sono poche differenze sull'idrogeno prodotto, sulla portata d'aria in entrata, sull'acqua netta necessaria, sulle potenze elettriche della pompa e dei compressori, sulla capacità minima PROX, sulla concentrazione di CO dello scarico di spurgo e sull'efficienza lorda tra il case-study e II. Tuttavia, i compiti di riscaldamento dello scambiatore di calore nel caso in cui io

sono molto più che nel caso II, che richiede una serie di scambiatori di calore di qualità superiore e un maggiore consumo di energia. Quindi il tridimensionamento del metano nel caso-study II viene selezionato per essere il processo finale del progetto.

Il processo finale del tri-reforming della reazione è progettato come, il rapporto vapore/carbonio (S/C) è uguale a 3, la pressione operativa è a 2 bar, la temperatura di reazione è a 750 °C, la temperatura di reazione WGS è a 300 °C, la capacità PROX è con la conversione di CO del 99.9% e il rapporto di ripartizione del riciclo è pari a 0,3. La conversione del metano al 99.8%, l'idrogeno prodotto 39.1 kg/h, la concentrazione di CO nello scarico di spurgo a 3 ppm e la portata di sodio liquido calda richiesta a 2312 kg / h, l'efficienza lorda al 93.9%.

III Conclusioni

In conclusione, la simulazione della produzione di idrogeno da tri-reforming del metano (carburante+aria+CO₂+vapore) con energia solare è stata effettuata utilizzando Aspen Plus alle condizioni operative dell'unità di ottimizzazione del ritrovamento per la massima velocità di produzione con il minimo costo energetico. Il seguente risultato potrebbe essere raggiunto con questa serie di simulazioni:

-Nel case-study II, per mettere il separatore d'acqua dopo la scissione del riciclo, potrebbe avere un maggiore recupero d'acqua con un minor consumo di energia, rispetto a quello di mettere il separatore d'acqua dopo il PROX (case-study I). Tuttavia, lo svantaggio è che il rapporto di ripartizione del riciclo non può essere consentito troppo alto perché l'acqua di preriscaldamento sarebbe surriscaldata.

-Per entrambi i processi, le condizioni di ottimizzazione sono alimentate con rapporto S/C (vapore/carbonio) a 3, pressione operativa a 2 bar, temperatura del reattore di reforming a 750 °C, reattore Water-Gas-Shift a 300 °C.

-Per entrambi i processi, con la diminuzione del rapporto di divisione del riciclo, il calore richiesto dal collettore solare diminuisce, ma anche la portata della produzione di idrogeno scende, la concentrazione di spurgo del CO aumenta al contrario.

-Il processo di risparmio energetico è considerato il progetto finale. Con il rapporto di riciclo 0.7, alimentato con metano a 100 kg/h, è possibile produrre idrogeno da 39.1 kg/h con conversione di metano al 99.8% e con 2312 kg/h di sodio liquido (da trasferire con fluido termovettore) per fornire calore al reattore per reazioni di reforming (è riportato in **Tabella 1**).

-Sulla base dell'LHV dell'idrogeno e del metano, la massima efficienza totale (da idrogeno a metano) potrebbe raggiungere il 93.9%.

-Viene testata anche la capacità di PROX. La conversione di CO attraverso il PROX deve essere non inferiore al 99.7%, con una concentrazione di CO di spurgo inferiore a 10 ppm (8.8 ppm), per spugarla direttamente nell'ambiente.

-Il tasso di recupero dell'acqua è del 63.4%.

L'intera simulazione potrebbe essere considerata come un tentativo incluso nel progetto energetico europeo "a hybrid process to transform municipal waste into energy (SOL-CARE)". Offre i dati teorici di base che potrebbero essere applicati quando il gas combustibile di alimentazione viene sostituito dal metano al gas di gassificazione nel piano di progetto reale.

Inoltre, l'idrogeno prodotto potrebbe essere utilizzato per ulteriori ricerche, ad esempio, da utilizzare nelle celle a combustibile a membrana a scambio protonico alimentate a idrogeno.

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List of Abbreviations

EU	European Union
CSP	Concentrated Solar Power
SG	Syngas
NG	Natural Gas
DME	Dimethyl Ether
PEMFC	Proton Exchange Membrane Fuel Cell
SMR	Steam Methane Reforming
DMR	Dry Methane Reforming
ATR	Auto-thermal Reforming
CMR	Combined Methane Reforming
POX	Partial Oxidation
CPOX	Catalytic Partial Oxidation
F-T	Fischer-Tropsch
WGS	Water Gas Shift
S/C	Steam / Carbon
HTF	Heat Transfer Fluid
PT	Parabolic Troughs
FR	Fresnel Reflectors
ST	Solar Tower
SD	Solar Dish
PR-BM	Peng-Robinsson-Boston-Mathias
PROX	Preferential Oxidation

Chapter I Introduction

1.1 Background

In the beginning of 18th century, an industrial revolution highlights the supply the energy. That is the fossil fuels, in form of coal and oil (including natural gas), have powered the technology and transportation network, which causes enormous strains to the environment.

The current energetic issue is the burning of fossil fuels which leads to the emissions of greenhouse gases and is known to contribute to the global warming. It is generally believed that the increase in the temperature of the earth is linked to the increase emission in greenhouse gases (mostly CO₂) into the atmosphere. CO₂ is a main greenhouse gas released by fuels containing hydrocarbon, such as methane, when they are burned. Most of the world's energy needs are currently supported by combustion of fossil fuels. The use of renewable energy is an alternative which is possible to provide a favorable solution to the problem of global warming^[1-4].

In 2009, European Union(EU) Head of state and Government set a series of engaging climate and energy targets to be met by 2020 in 2009^[5].

1. A greenhouse gas reduction of 20% in EU below 1990 levels
2. A reduction of 20% in primary energy compared with projected levels.
3. 20% energy consumption from renewable sources.

What's more, On 23 October 2014, EU leaders agreed to reach by 2030 respectively:

1. A greenhouse gas reduction of 40% respect to 1990.
2. 27%of in primary energy compared with projected levels.
3. 27% energy consumption from renewable sources.

As a result, hydrogen becomes an important alternative fuel. That is expected to replace fossil fuels because it is a clean and environmentally friendly energy source. The reaction of hydrogen with oxygen can release energy explosively in heat engines producing water as the production. Currently, hydrogen is commonly used as a reactant in chemical industry. Produced locally, used immediately, as the storage and transport of hydrogen is expensive. In addition, hydrogen-based fuel cells have the advantages of zero emission, high energy conversion efficiency, low noise, etc. It will become a significant fuel in the near future^[2-4].

In fact, hydrogen can be produced with renewable energy sources and it can be converted into fuel cells, producing electrical energy without emission of polluting substances. Recently, the fuel cells have been remarkable growth in their technology along with potential application, stationary and portable power generation. Moreover, the deteriorating quality of crude oil, more stringent petroleum production specifications and environmental problems will all result of an increased need of hydrogen to be used in hydro-processing^[6-8].

1.2 Objectives of the research

The aim of present work is to simulate the whole process of producing hydrogen with renewable energy sources. To achieve this goal, the process is designed by using concentrated solar power (CSP) system as the renewable energy source to provide energy for methane reforming reactors to produce hydrogen. As a process simulation, it also could be considered as an experiment data as a part of project “a hybrid process to transform municipal waste into energy (SOL-CARE)”, which is implemented by many cooperators in European areas.

1.3 Reforming methods

1.3.1 Introduction

The reforming process, which is being the oldest, the most economic and widely used method to produce hydrogen commercially worldwide, means the conversion from hydrocarbon into syngas (SG). Syngas is a mixture of carbon monoxide and hydrogen, followed by separation of hydrogen by the mixture^[4]. SG forms the feedstock in the chemical and petrochemical industries, for producing methanol, gasoline, MTBE, or synthetic liquid fuels. Moreover, syngas can be produced from various primary material so as natural gas, liquid gas, naphtha, petroleum coke, coal and some other hydrocarbons^[4,8].

Dimethyl ether (DME) is a wonderful resource for hydrogen production with its high H/C ratio and high energy volume density. Luo and Li have studied a simulation of steam reforming of DME for a proton exchange membrane fuel cell (PEMFC), the result shows that both the yield of hydrogen and the energy efficiency increase at the same time as the increase of mass ratio between the DME and steam from 0.3:0.7 to 0.4:0.6. They also find that the system using a reactor as heat resource has a better efficiency of hydrogen production than the one using the engine exhaust^[1].

Methanol is another choice used to produce hydrogen with steam reforming reaction. Real and Dumanyan have achieved that reforming methanol to hydrogen with non-concentrating solar collector as the source of heat. The temperature can reach as high as 260 °C, which is sufficient for the complete methanol steam reforming reactions. The highest total efficiency (sunlight and methanol to hydrogen) of 43% surpasses the efficiency of concentrating solar process, which also could be improved by optimizing the catalyst loading and reducing the radiation heat losses from the collector^[6].

Methane is the primary component of natural gas, which is widely used for hydrogen production due to its high hydrogen content(4:1 respect to carbon content) and low cost. Currently, the advance of hydraulic fracturing and horizontal have made the shale gas well more profitable, the nature gas is greatly expanding worldwide energy supply^[4]. Nature gas reforming can be achieved by means of an exothermic or endothermic reaction which depends on the chemical process which is chosen to perform catalytic reforming of methane^[7]. These available processes are:

- 1) Steam Reforming (SMR),
- 2) Partial Oxidation (POX),
- 3) Dry Reforming (DMR),
- 4) Auto Thermal Reforming (ATR),

- 5) Combined Reforming[also called Bi-reforming] (CMR),
- 6) Reforming with Membrane,
- 7) Tri-reforming (TMR).

Moreover, the variable composition of syngas is also decided by the reforming technology for methane, called the H₂: CO ratio, which is the basis of Fischer-Tropsch (F-T) chemistry. Steam reforming produces a syn-gas mixture with a H₂:CO ratio close to 3, which is the maximum ratio, while the minimum ratio close to 1, which produced syngas by carbon dioxide reforming of methane, called dry reforming. Additional steps are requested to adjust the H₂:CO ratio in order to be used in the synthesis. For example, the production of methanol are required the syngas of H₂:CO ratio about 2 (eq 1), the combination of steam reforming and dry reforming as reported to produce the specific ratio. Partial oxidation of methane can also produce the proper ratio of syngas, but it is difficult to control resulting in local hot spots and associated danger of explosion^[9].

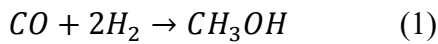


Fig 1 shows the methods differ in the composition of syngas produced H₂:CO ratio ^[7].

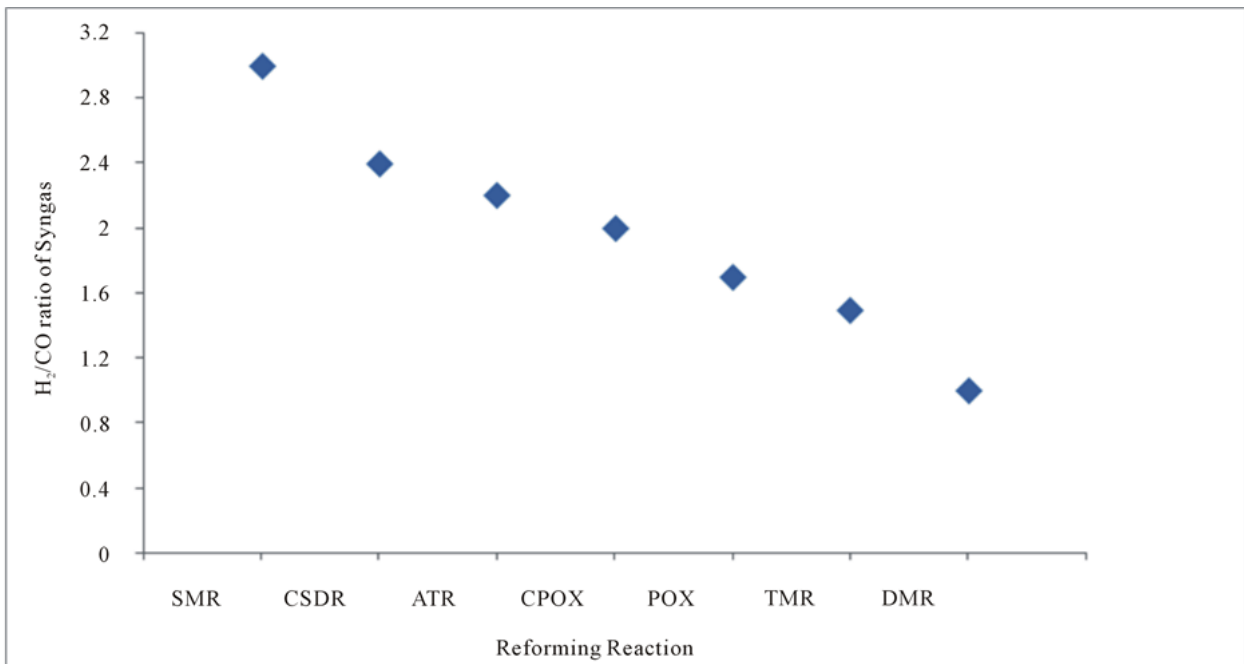
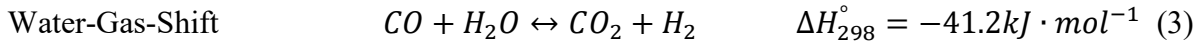
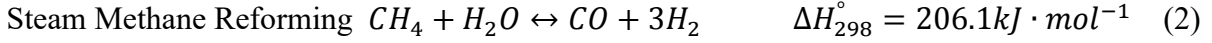


Fig 1 H₂: CO ratio of syngas from various processes^[7].

1.3.2 Steam Reforming and dry reforming

As shown above, steam reforming of methane produces syngas with the highest H₂:CO ratio, which is considered to obtain high composition of pure hydrogen. The overall process of steam reforming can be described as two steps (eq 2 and eq 3):



Both reactions are reversible and usually reach equilibrium over the active catalyst. The steam reforming reactions (SMR) is highly endothermic, high temperature is favored thermodynamically (temperatures of 800—1000 °C are used in industry). In addition, with the expansion of volume, low pressure are favored as well, but industrial reformers have to be operated at elevated pressures from 2 to 30 bar. To reduce the huge amount of carbon monoxide produced through SMR, the water-gas-shift (WGS) reaction is required, which is more favorable at lower temperature (typically at 200—400 °C). Furthermore, the ratio of steam to carbon (S/C) makes influence on the methane conversion during the whole process as well, which is normally used with 3 (S/C). **Fig 2** shows a typical graph made by F. Joesen that the equilibrium conversion of methane varies against temperature, pressure and steam to carbon ratio, which is observed clearly that operating the process at high temperature, low pressure, and relatively high steam to carbon ratio could maintain a high methane conversion^[13].

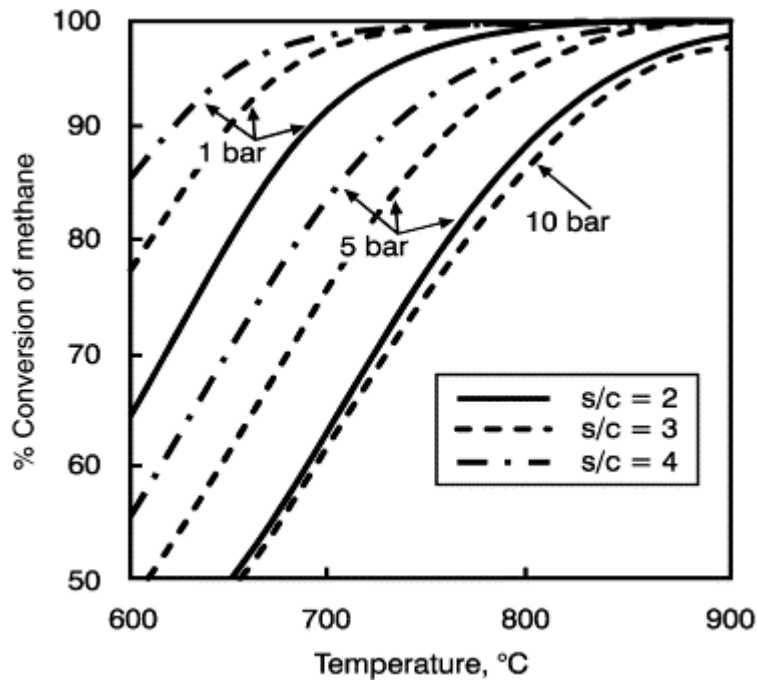
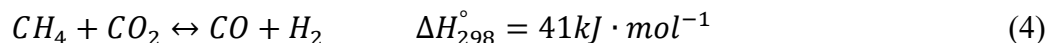


Fig 2 Equilibrium conversion of SMR against temperature, pressure and steam to carbon ratio^[13].

With carbon dioxide available in large quantities and low cost, CO_2 can be used in reforming of methane, which is called Dry Reforming of Methane (DMR) and to be a promising technology for the production of syngas. DMR is a process that produces syngas from natural gas with waste carbon dioxide (eq 4)



The dry reforming of methane is receiving the special attention in this few years due to two main reasons: first, the produced syngas is suitable for produce some liquid s including F-T fuels and DME. Second, there is a consumption of two types of greenhouse gases, carbon dioxide and methane, in this reaction^[7].

However, coke, which is the significant deposition of carbon on the surface of the catalyst, contribute to the reduction of its useful life and the activity of reaction , considered the main disadvantage of dry reforming of methane. Coke formation is due to presence of carbon dioxide as a reagent. Compared to steam reforming, there is a chance of cook formation due to the low steam to carbon ratio. As is shown in Fig 3, the carbon formation conditions for a steam-methane system is on the left side, while for a steam-methane-carbon dioxide system is on the right side. Both of the shaded areas refer to the carbon formation zone at 30 atm, and limiting curves at different pressure (left side) and at different $y_{CO_2}/(y_{CO_2}+y_{CH_4})$ (right side) are also reported^[14].

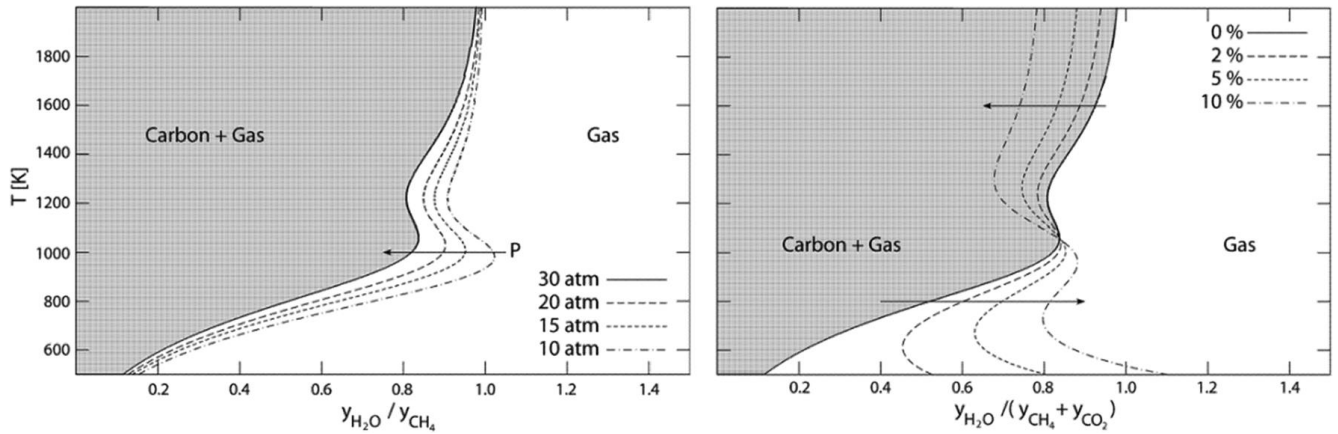
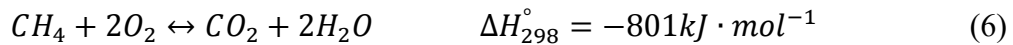
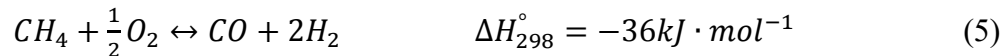


Fig 3 Carbon formation conditions at 30 atm^[14].

1.3.3 Partial Oxidation Reforming (POX)

An alternative to reforming is partial oxidation (eq 5), the same as others, to produce hydrogen rich syngas, which is an exothermic reaction and considered more economic one than steam forming and dry reforming for the requirement of a small amount of thermal energy:



The reactor design of Partial Oxidation (POX) and Catalytic Partial Oxidation (CPOX) is shown in **Fig 4**^[7].

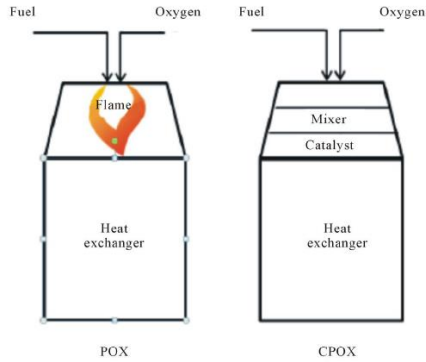


Fig 4 Reactor design for POX and CPOX^[7].

POX reactor simply is consisted of two zones, the flame part where hydrocarbons, oxygen, or possibly low amount of steam react together and the heat exchanger which recovers the excess heat of the reaction. The production of syngas depends on the air to fuel ratio at the high temperature of 1200-1500 °C without the catalyst. On the other hand, the use of catalyst lowers the required temperature of the reaction to around 800-900 °C. In CPOX reaction, methane is covered with air (or pure oxygen) over metal (Rh, Pt, Pd) and non-noble metal catalyst to syngas in the single step. Moreover, there is a limitation for CPOX is that the sulfur content of natural gas ought to be below 50 ppm, above which would poison the catalyst. In that case, non-catalyst POX could be used for such fuels^[7].

In the past decade, CPOX has been studied extensively, and this process is likely to become more important in the future of methane reforming due to the thermodynamic advantages which are shown at below:

First, the partial oxidation is a mildly exothermic reaction compared to steam reforming, which is highly endothermic. In addition, it could be combined with endothermic reactions, to become auto-thermal reaction or tri-reforming, which would be shown later, to achieve a more energy efficiency. Second, the H₂: CO ratio produced in stoichiometric partial oxidation is around 2, which is ideal for downstream processes, in particular methanol synthesis, Although, hot-spot might occur in the catalyst bed. Third, there is a low content of carbon dioxide in the produced gases from methane partial oxidation, which has to be moved before synthesis gas used in downstream. Last but not least, partial oxidation technology avoids the requirement of large amount of expensive superheated steam, and there is great economic potential in this process^[8].

1.3.4 Auto-thermal Reforming, Bi-reforming and Tri-reforming

Steam reforming, partial oxidation and dry reforming methods are combined in two or three to give a new process to produce syngas.

Auto-thermal reforming combines the exothermic partial oxidation reaction and endothermic steam reforming reaction by feeding methane, water and air together. The thermal energy required for steam reforming process is generated from partial oxidation to save a significant amount of energy. It is name auto-thermal since the produced syngas consumes the thermal

energy it generated. The H₂: CO ratio is a function of the gaseous reactant fractions input, ranging from 1 to 2.

A schematic with flow streamlines of the auto-thermal reformer (ATR) is pictured below (**Fig 5**). An ATR reactor contains a combustion zone at the top and a catalyst filled bed at the bottom. The fuel gas is mixed with a sub-stoichiometric amount of oxidant and burned in the combustion zone, connecting with intermediate conical recirculation section where the hot gases continue to react, but are far from equilibrium. Then the gases pass through the catalyst in the bottom section to achieve as close to an equilibrium mixture as possible. ATRs have limited commercial experience, so there are only a handful of sites that use this technology. For examples, SASOL in South Africa, uses ATRs licensed by Lurgi out of Germany, and KBR-designed ATRs are installed in ammonia plants in Kitimat, Canada and Liaohe, China^[15].

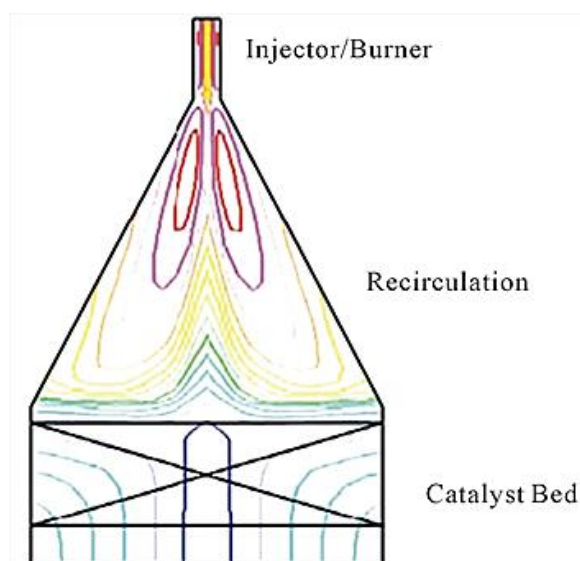
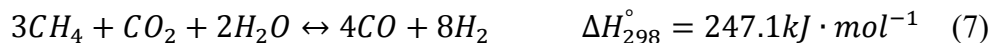


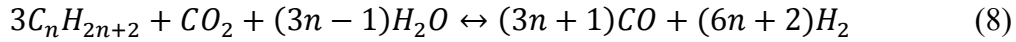
Fig 5 Schematic cross section of an ATR reactor vessel^[15]

The combined dry reforming and steam reforming of methane, which is called bi-reforming (eq 7), has attracted interest from both environment and industrial perspectives. For one side, from an environment point of view, these two reactants containing greenhouse gases, methane and carbon dioxide, could be converted into useful chemical products, which is an important area of recent catalytic research. On the other side, from an industrial perspective, the reaction produces syngas with the specific H₂: CO ratio 2 (suggested to be called “met-gas”), which is the perfect preparation of methanol without any danger of explosion, comparing with partial oxidation reaction.



Bi-reforming to produce met-gas has a great potential for the feedstock could be varied natural gas sources even containing significant amount of CO₂. In addition, it can also be used to recycle CO₂ emissions from the exhaust, such as from the fossil fuel (coal, petroleum), burning power plant or the cement factories.

Moreover, bi-reforming to met-gas is adaptable for reforming shale gas as well. The dry shale gas is essentially methane, while the wet shale gas is also containing ethane, propane, or some higher hydrocarbon homologues^[9]. (with the reaction eq 8).



The new process produces synthesis gas with desirable H₂: CO ratio using flue gas from fossil fuel or the gasification gas of the biomass without pre-separation of CO₂. That is so called tri-reforming reaction, meaning the combinations of steam reforming, dry reforming and the partial oxidation reactions. The tri-reforming concept as the new approach is illustrated in the following process diagram^[16]. (Fig 6)

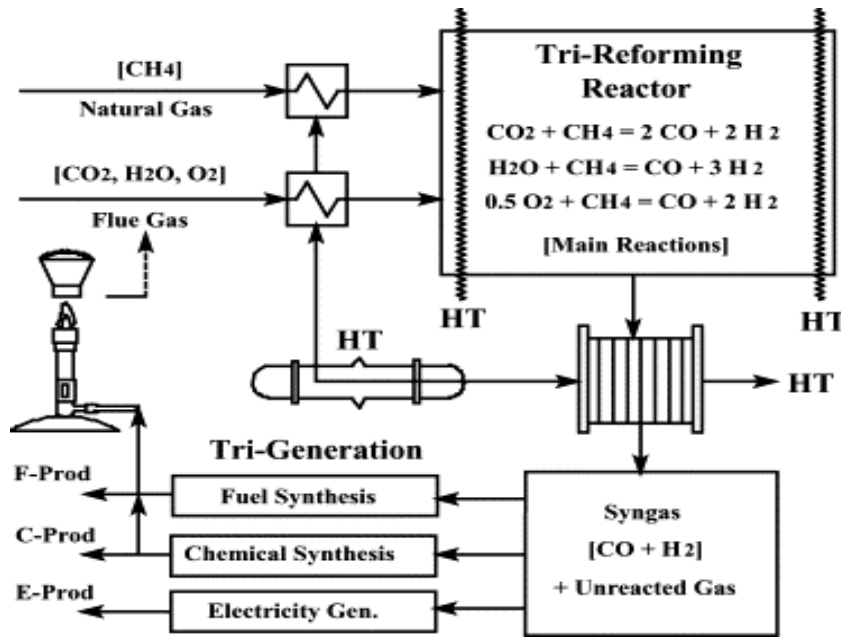


Fig 6 Process concept for tri-reforming of nature gas^[16].

Tri-reforming encompasses its unique features. Integrating steam reforming and partial oxidation with dry reforming can dramatically reduce or eliminate carbon formation on the catalyst surface which is significant for dry reforming, thus, to increase the catalyst life and process efficiency. Furthermore, the incorporation of oxygen generates heat in situ which could be used to increase energy efficiency and oxygen also reduce or eliminates the carbon formation on catalyst surface^[16].

1.3.4 Comparison of different method of methane reforming

Steam reforming is the main used methane reforming process to produce hydrogen that is predominantly utilized because it has the greatest value for H₂: CO ratio, however, as the process of steam reforming is considered too expensive. Partial oxidation and bi-reforming are good choices to produce syngas when the value of H₂: CO ratio is adequate for downstream product

while auto-thermal reforming and tri-reforming could be used to reduce the consumption of thermal energy, which is an important factor. In short, it can be said that the choice of the type of catalytic methane reforming depends on the type of the produced syngas application and the economic viability of the process related to the destination.

Table 1 illustrates a comparison of syngas production technologies fed with natural gas^[6]

Table 1 comparison of various method of methane reforming

Technology	Advantages	Disadvantages
POX	Feed stock desulfurization not required	Very high process operating temperature Usually requires oxygen plant
SMR	Most extensive industrial experience Oxygen not required, lowest process operating temperature Best H ₂ /CO ratio for production of liquid fuels.	Highest air emissions More costly than POX and auto-thermal reformers Recycling of CO and removal of the excess hydrogen by means of membranes
ATR	Lowest process temperature requirement than POX. Syngas methane content can be tailored by adjusting reformer outlet temperature	Limited commercial experience Usually requires oxygen plant
DMR	Green house gas CO ₂ can be consumed instead of releasing into atmosphere Almost 100% of CO ₂ conversion	Formation of coke on catalyst. Additional heat is required as the reaction takes place at 873 K
CSDR	Best H ₂ /CO ratio for production of liquid fuels Coke deposition drastically reduced.	Separation of un-reacted methane from SMR syngas. Project installation cost.
TMR	Directly using flue gases, rather than pre separated and purified CO ₂ from flue gases. Over 95% of methane and 80% CO ₂ conversion can be achieved	Usually requires oxygen plant. Low H ₂ /CO ratio ratios limit its large-scale application for F-T & MeOH synthesis

1.4 Concentrated Solar Power Technology

1.4.1 Introduction

Solar radiation is an abundant energy source, however, it is difficult to capture and utilize in an efficient way. For example, solar energy could be used for direct electricity generation with photovoltaic cells, which, currently, is exceeding 100 GW of global installed capacity with a continuously growing market. However, the limited energy conversion efficiencies (usually less than 20%) and relatively high cost of this technology confine its growth unless a large amount of subsidies are provided. Solar thermal energy conversion, where the radiant solar energy is concentrated, and absorbed by a receiver then transferred as thermal energy to a fluid, is an alternative option of commercial installations with totally several GWs globally^[14].

Conventional industrial process rely on hydrocarbon for fuel production like syngas (or hydrogen) and commodities like metals. These industrial processes are seriously energy and carbon intensive. The issues of fossil fuel depletion and climate change increase obviously, which result in the development of solar industrial process solutions. Concentrated solar technology offers the conversion from solar energy into thermal, electrical and chemical forms. While conventionally concentrated solar energy has been used for process heat and power generation applications, and it is expected to drive chemical reactions. Processes making use of solar energy to supply heat to high temperature endothermic chemical reactions are known as solar thermochemical processes.

The trend in publications on solar thermochemical processes obtained from Scopus, is shown on **Fig 7**. After the oil crisis in 1973, efforts were directed to change from hydrocarbon to a hydrogen economy, and the research on thermochemical process for hydrogen production was initiated in this context. High oil prices and the policy of oil embargo, which ensured to focus researches on solar thermochemical processes and keeping the momentum for about a decade. Along with the stabilization of the oil market, there were fewer publications for next one and half decade. However, the interest in solar thermochemical processing was again renewed in middle of 20th century with emphasis on climate change^[18-20].

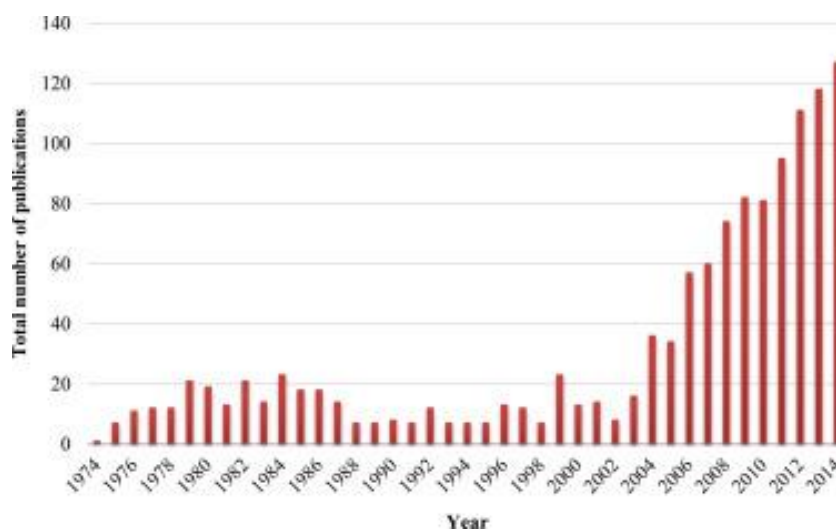


Fig 7 The trend in publications on solar thermochemical processes^[18]

The earth receives about 1.74×10^{14} kW of solar radiation at the top of the atmosphere. **Fig 8** presents that approximately 30% are reflected back to space and another fraction is absorbed by clouds and oceans so that only about 40% reach the surface (this amount is still much higher than the energy consumption rate of the entire planet), and the irradiance available for terrestrial use is on order of magnitude of 1 kW m^{-2} , which can only generate low temperatures, being insufficient for applications involving solar thermochemical conversion. Therefore, it is essential to use optical concentration devices, which supplies special requirements for catalyst and reactor design^[14].

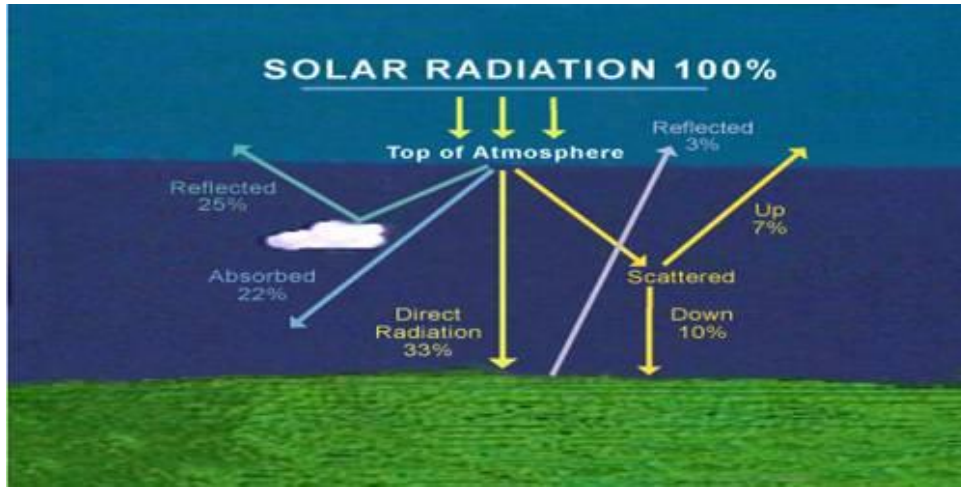


Fig 8 Available Solar radiation

Conventional concentrated solar power (CSP) technology is to focus sunlight with a reflecting surface (like a mirror) to heat a fluid flowing through a collector (**Fig 9**). There are four types of collectors: parabolic troughs (PT), Fresnel reflectors (FR), solar towers (ST) and solar dishes (SD), and the PTs are the most commercially mature technology (with more than 90% of the currently installed CSP capacity). The front three types of collectors are mainly used for centralized electricity generation, while solar dishes are more suitable for distributed generation. The heated fluid (like pressurized steam) can be used to supply heat for downstream applications or to generate electricity through steam turbines. Some other heat transfer fluids, for example, synthetic thermal oils and molten salts, which have higher heat capacities than steam, can be also used for steam generation via heat exchange to generate electricity. An important advantage of the CSP technology is to be integrated into existing fossil fuel based power plants which use gas and steam turbines for electricity generation. In this case, the heat produced by combustion of the fossil fuels can be partially substituted by the heat from the CSP plant, which is originated from solar energy, reducing fossil fuel consumption, greenhouse gas emissions, or other types of pollution. In addition, some large CSP plants can be equipped with heat storage systems to supply heat or electricity during the night^[14, 17].

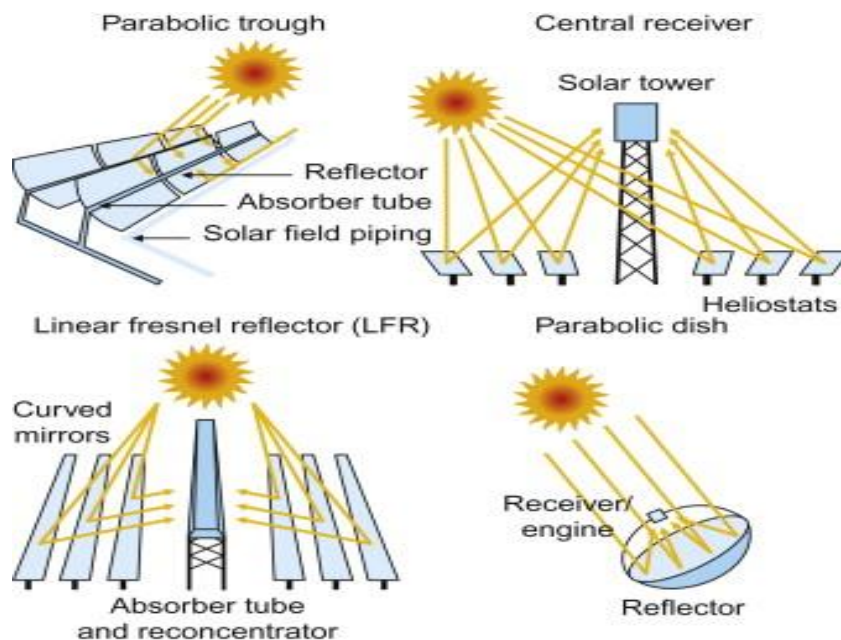


Fig 9 Types of solar collector

Recently, there has been a growing interest in applying CSP technology for solar thermochemical synthesis. In a CSP solar thermochemical process, the concentrated solar radiation is used as a source of heat to drive highly endothermic reactions. The product of such a process generally belongs to as a “solar fuel”, containing a fraction of chemical energy that generated from solar energy. There are several solar thermochemical pathways including splitting of water, gasification or cracking of fossil fuels (coal, oil, or natural gas), and natural gas reforming. Among these, solar thermal reforming of natural gas has a great potential due to large resources of natural gas and the produced solar fuels, which is mainly hydrogen or syngas, to be used as a chemical feedstock for downstream product or as a combustion fuel for electricity generation with gas turbines^[14].

1.4.2 Methods for solar thermal reforming of methane

Solar thermal energy can be applied into a reforming system either indirectly or directly. The indirect application is similar to conventional CSP plants that a Heat Transfer Fluid (HTF) is used to transport solar heat from the receiver to the point of use, but difference is that in solar thermal systems the heat transfer fluid is used to heat the reformer. Since steam reforming or dry reforming of methane requires temperature at close to 800 °C or more to achieve high methane conversions, conventional heat transfer fluids such as steam or synthetic thermal oil cannot be used, requiring compressed hot gas (usually with air) instead. Molten salts, most of which are only stable below 550 °C, can be mainly used for low temperature steam methane reforming applications. Liquid sodium is a suitable choice for the process with its excellent thermodynamic properties, however, it is limited by the chemical reactivity, which requires special precautions to prevent and suppress fire and the explosion when in contact with air. Some conventional HTFs with their properties are presented in **Table 2**^[21].

Table 2 Properties of some possible HTF (source Jähnig 2005)

Medium	Max. temperature [°C]	Heat capacity [J/kg/K]	Heat conductivity [W/m/K]	Vol. spez. heat capacity [kWh/m ³ /K]	Cost
Mineral oil	300	2600	0.12	0.55	+
Synth. oil	400	2300	0.11	0.57	-
Silicon oil	400	2100	0.1	0.525	-
Nitride salt	450	1500	0.5	0.75	○
Nitrate salt	565	1600	0.5	0.8	+
Carbonate salt	850	1800	2.0	1.05	-
Sodium (liquid)	850	1300	71.0	0.3	○

+ low
 ○ moderate
 - high

In directly irradiated reforming systems, solar radiation is focused on the catalytic element, with the meaning that the reformer is an integrated unit that combines the solar receiver and the catalytic bed in one simple system. PT and FR technologies are limited for temperature less than 600 °C, thus, regardless of the reactor type, the required higher temperatures for effectively steam reforming of methane limit the choice of solar concentrator to ST or SD. Since the reformer is directly irradiated with sunlight, there is much better heat efficiency due to the radiative character of heat transfer in contrast to regular conduction and convection, enabling operation at temperatures more than 800 °C.

1.4.3 Reactors for solar thermal reforming of methane

Generally, it is not necessary for solar thermal reforming of methane systems based on indirect approach to require any special reactor design. The only essential difference from the traditional methane reforming is the source of heat, which is now generated from sun. Therefore, tubular geometry, the same as that of industrial reactors, can be used in indirect solar thermal reforming of methane systems. On the other hand, the direct approach implies many special requirements to the reformer design which should effectively integrate the solar receiver with catalytic element. Such reformers have to fulfill requirements of the solar receiver/absorber (low reflectivity, low emissivity and high thermal shock resistance), as well as the requirements of the catalytic bed (high activity and stability against coking and sintering).

1.4.3.1 Indirect methane solar thermal reformer: sodium heat pipe reformer

The sodium (Na) heat pipe has been suggested to transfer the heat from the receiver to the reformer, as shown in Fig 10^[22]. In this case, concentrated sunlight is used to evaporate liquid sodium contained in an evacuated chamber. Then the sodium vapor is condensed on the reformer tubes in the chamber releasing the heat to drive the endothermic reforming reaction, and the

liquid sodium fluids back into the absorber by gravity as a cycle. The approach is in principle indirect, for there is no direct irradiation of the catalyst bed, but the solar receiver and the catalytic reformer are integrated in the same unit. An important advantage of this system is the wonderful heat transfer characteristics of evaporating and condensing sodium, to result in the more uniform temperature distribution throughout the chamber. On the contrary, the flammability of sodium vapors is a safety concern for the system.

The concept was tested first for methane steam reforming in the Na heat pipe reactor with a single reformer tube (20 kW capacity), a commercial 14 wt% Ni/Al₂O₃ catalyst was used which was simulated solar radiation (infrared lamps). The reformer was successfully operated at 600–900 °C for many times of experiments with simulating daily insolation profiles. Near-equilibrium methane conversion was achieved and no observable catalyst deactivation appeared when operating with feed steam to carbon ratio higher than 2.5^[23].

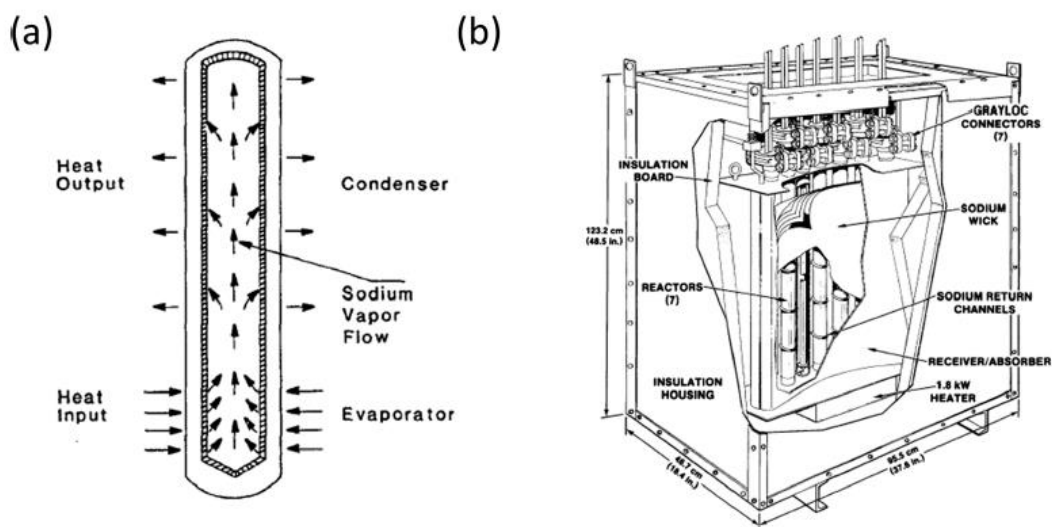


Fig 10 Sodium reflux heat pipe receiver reactor^[22]

1.4.3.2 Indirect methane solar thermal reformer: molten salt tubular reformer

A composite material containing the molten salt of Na₂CO₃ loaded with ceramic particles, which is to increase heat capacity, was used as a heat transfer medium and methane dry reforming was performed in a double-walled tubular reformer (about 1 kW capacity). The commercial catalyst (spherical pellets with a diameter of 3 mm), containing 2 wt% Ru, supported on γ -Al₂O₃, are loaded in the inner tube and the Na₂CO₃/MgO composite molten salt filled in the shell, **Fig 11**. Experiments were operated at atmospheric pressure and at 920 °C, using simulated solar radiation (electric furnace). As a result, nearly complete CH₄ conversion was obtained with CO₂/CH₄ = 3 in the feed and the residence time was 0.3 s. Since the high heat capacity of the heat transfer medium, it was possible to remain CH₄ conversion at a significantly high level for 1 h without heating (simulating cloud passages). There is a future of the tubular double-walled design with a composite molten salt/ceramic, for its simplicity and the high heat capacity of the heat transfer or storage medium. However, it is not clear that whether it is

possible to concentrate sun radiation effectively on such a receiver, and more complex design solutions would be required to integrate the tubular reformer into a real CSP system (PT, FR, ST or SD)^[24].

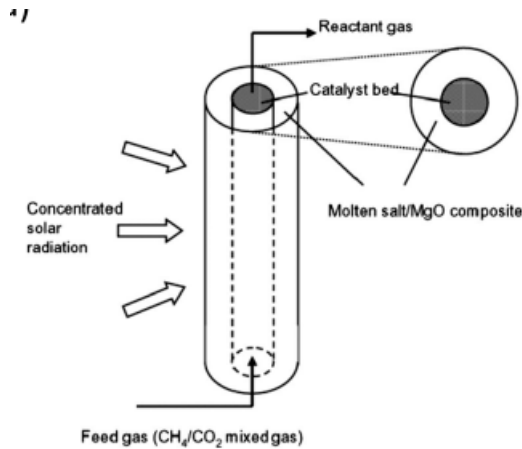


Fig 11 Molten salt tubular reformer^[24]

1.4.3.3 Windowed/Volumetric reformer–receiver

With the nature of the intermittent of the solar radiation, the catalyst of solar thermal reforming reactions should feature high thermal stability and also to be capable of operating under highly dynamic thermal conditions. The catalytic element should be designed in such a way which concentrated solar radiation can be efficiently absorbed without significant losses. As high temperatures are thermodynamically favored for high methane conversions in steam reforming reaction, however, high-temperature operation is disadvantageous for materials selection and catalyst metal. Several types of directly approach of irradiated solar thermal reformers have been demonstrated in solar tests.

Early designs of direct solar thermal reforming systems were based on a tubular geometry. In the direct-irradiated tubular receiver-reformer, the concentrated solar radiation is focused to be absorbed by the exterior metallic wall of the reactor, which transfers the solar heat energy to the catalytic bed inside the tube. More advanced solutions are developed as the volumetric receiver–reformers (also called direct catalytic absorption receiver reactors). Inside the volumetric receiver–reformer (**Fig 12**), concentrated solar radiation irradiates directly on window the catalyst bed through a transparent, which is a ceramic statue (honeycomb, ceramic or metallic foam) coated with the catalyst. Ceramic and metallic foams provide high gas permeability with an effective and uniform absorption of solar radiation preferably over honeycomb monoliths at the same time. In principle, such solar reformers can operate at high temperature (even reach 1000–1100 °C), since the problem of temperature limit of traditional metal tubular reformers is solved and due to the higher heat fluxes generated by direct solar irradiation. High temperature is advantageous at the point view of thermodynamic and kinetic in reforming reactions (high equilibrium conversions and reaction rates), but it implies as well the restrictions related to the thermal stability of the ceramic monolith and the catalyst. Two most effective catalysts used in

direct solar thermal reforming of methane studies are rhodium (Rh) and ruthenium (Ru). Both are highly active with excellent thermal stability, which is of crucial importance for the applications^[14,17].

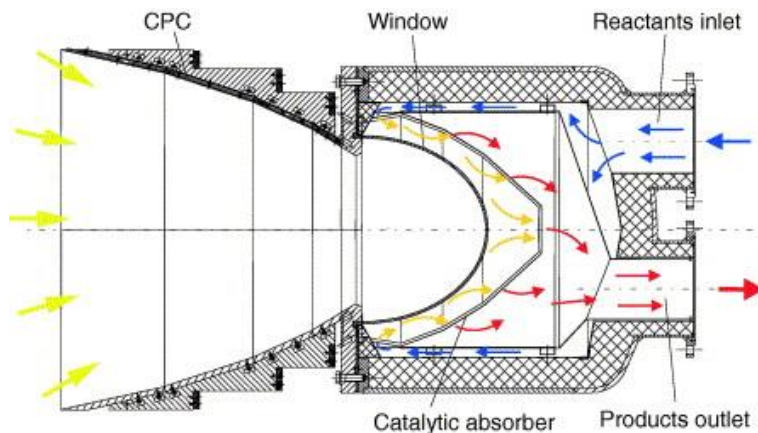


Fig 12 Scheme of a volumetric solar reactor concept^[17]

1.4.3.4 Direct catalytic absorption receiver reactor

Solar dry reforming of methane was successfully demonstrated with a direct absorption receiver-reformer in a 150 kW capacity parabolic solar dish (**Fig 13**). The reformer was integrated with a CSP system containing the directly irradiated catalytic element, which is a porous alumina (92 wt% α -Al₂O₃ and 8 wt% mullite) foam disk coated with Rh catalyst. The foam disk was coated with γ -Al₂O₃ at first to increase the specific surface area (using an order of magnitude) and then with Rh (0.2 wt%) as the active catalyst composition. The absorber temperature ranged from 550 –1100 °C, which depends on the insolation conditions (such as passing clouds). Interestingly, it was indicated that the insolation dropped from 600 W m⁻² to almost zero during the cloud passage, which is the challenge of solar reforming. Though the reformer demonstrated a good performance, by absorbing 100 kW of solar power and driving the methane conversion up to 70%, major issues were encountered with the catalytic element degradation and catalyst deactivation. Numerous surface dislocations, cracks of random length and direction were observed after operation due to the high thermal stresses. In addition, the Rh content with non-uniform performance and significant sintering of the Rh nanocrystallites was observed as well. In the untested catalytic element Rh was dispersed homogeneously at the surface as 2–6 nm nanoparticles, and, in the tested absorber-reformer, the Rh nanoparticles size ranged from 8 to 28 nm on the front surface while 4–14 nm on the back of the absorber. This sintering phenomenon indicated the development of strong temperature gradients across the catalytic element during the process. The significant loss of the active surface, result in the deactivation of Rh catalyst, in addition to the mechanical fracture of the foam disk. Especially, no carbon formation was observed^[25].

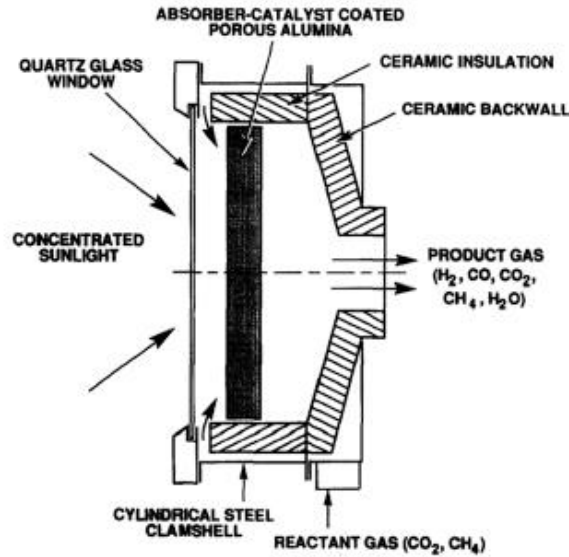


Fig 13 Scheme of a volumetric solar reactor concept^[25]

1.4.2.2. Directly irradiated annular pressurized receiver

A DIAPR system which is driving a steam reforming of methane with a Ru supported on Al_2O_3 catalyst promoted by Mn oxides was studied by Berman. A directly irradiated annular pressurized receiver reactor (Fig 14) was used to be the receiver reactor to be conjuncted with a field of heliostats. The absorber of the receiver consisted of arranged pins in the shape of porcupine which are made of sintered alumina (99.7 wt% Al_2O_3). The catalyst activity and stability was tested for methane reforming conversion at different temperature ranging from 500–1100 °C with fresh catalyst and the catalyst which has been used for 506 hours at 1100 °C. It was achieved that the activity of the catalyst did not change significantly even after prolonged use, which suggested the thermal stabilities of the catalyst. The same tests when compared with the same catalyst but without Mn oxides presented that the activity of the catalyst decreases drastically at a higher temperature^[20,26].

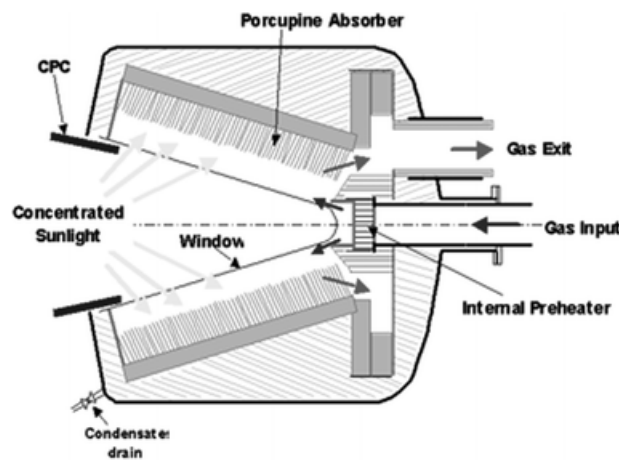


Fig 14 Schematic of DIAPR solar facility^[20]

Chapter II Methodology and Simulations

2.1 Methodology

Aspen Plus 7.3 has been used for this simulation. The equilibrium compositions are calculated for the given operating condition and the mass and energy balance are solved in sequential modules of each unit.

The RGibbs reactor is selected for the tri-reforming reactions while the REquil reactor is used for Water-Gas-Shift. For the RGibbs reactor, the equilibrium compositions are calculated by minimizing the total Gibbs free energy which is the summation over all the species of the potential reactions. The total Gibbs free energy of a system is give by the summation over i species:

$$G^t = \sum_{i=1}^N n_i G_i^0 + R(T + 273.15) \sum_{i=1}^N n_i \ln \frac{f_i}{f_i^0}$$

In the equation, G_i^0 is the Gibbs free energy of the species i under standard conditions; R is the molar gas constant; f_i^0 and f_i are fugacity of species I at standard and operation conditions, respectively. The RGibbs reactor is a suitable choice for evaluating tri-reforming reaction since there is a lack of kinetic data. For the REquil reactor, the compositions of product are derived from the situation which all the reactions reach chemical equilibrium.

Peng-Robinson equation of state is the thermal method adopted for the process simulation. In addition, Peng-Robinson-Boston-Mathias (PR-BM) is also tested in the process but there are no appreciable differences.

The simulation of CSP system is hard to do because the location of the plant makes a significant influence on the capacity and efficiency. Moreover, the simulation of CSP plant makes no use for the simulation of tri-reforming of methane reactions. In this study, the CSP plant is considered as the heat resource to heat the liquid sodium up to a high temperature which is used to supply heat to make the gas mixture arrive the reaction temperature.

2.2 Simulations

2.2.1 Simulation of steam reforming of methane

The first simulation is the steam reforming of methane, in order to find out the optimum condition of the feed stream and the reactors. **Fig 15** shows the fuel gas is pure methane with mass flow 100 kg/h at 25 °C; mixed with water which is pre-heated by a recovered heat from the WGS and the cooler via a mixer, and to be heated to the operation temperature of the reforming reactor, varying from 600 to 800 °C (as the maximum temperature could be heated by liquid sodium is 850 °C), the water comes out from water tank at 25 °C and the flow rate depends on the steam to carbon ratio, which varies from 1 to 5. The pressure of steam reforming reactions taken place in the reactor varies from 1 to 5 bar. The syngas out of the reactor are mixed with another stream of water for decreasing the CO mole fraction to 1% at the outlet of WGS. The mixed gases across a cooler to be cooled down to 330 °C and go into WGS to take reactions at 300 °C.

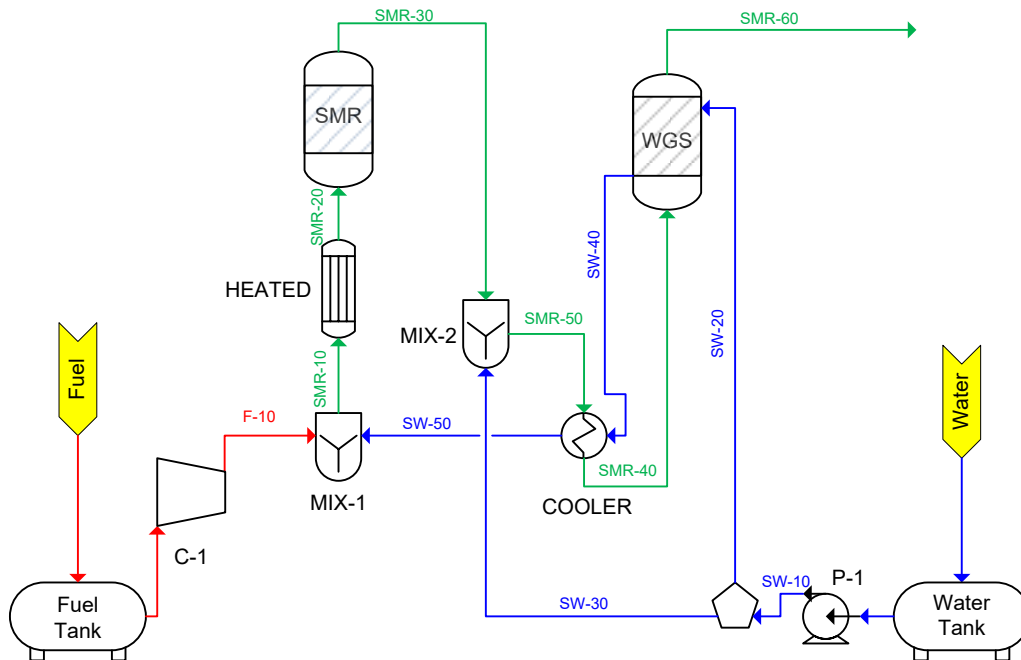
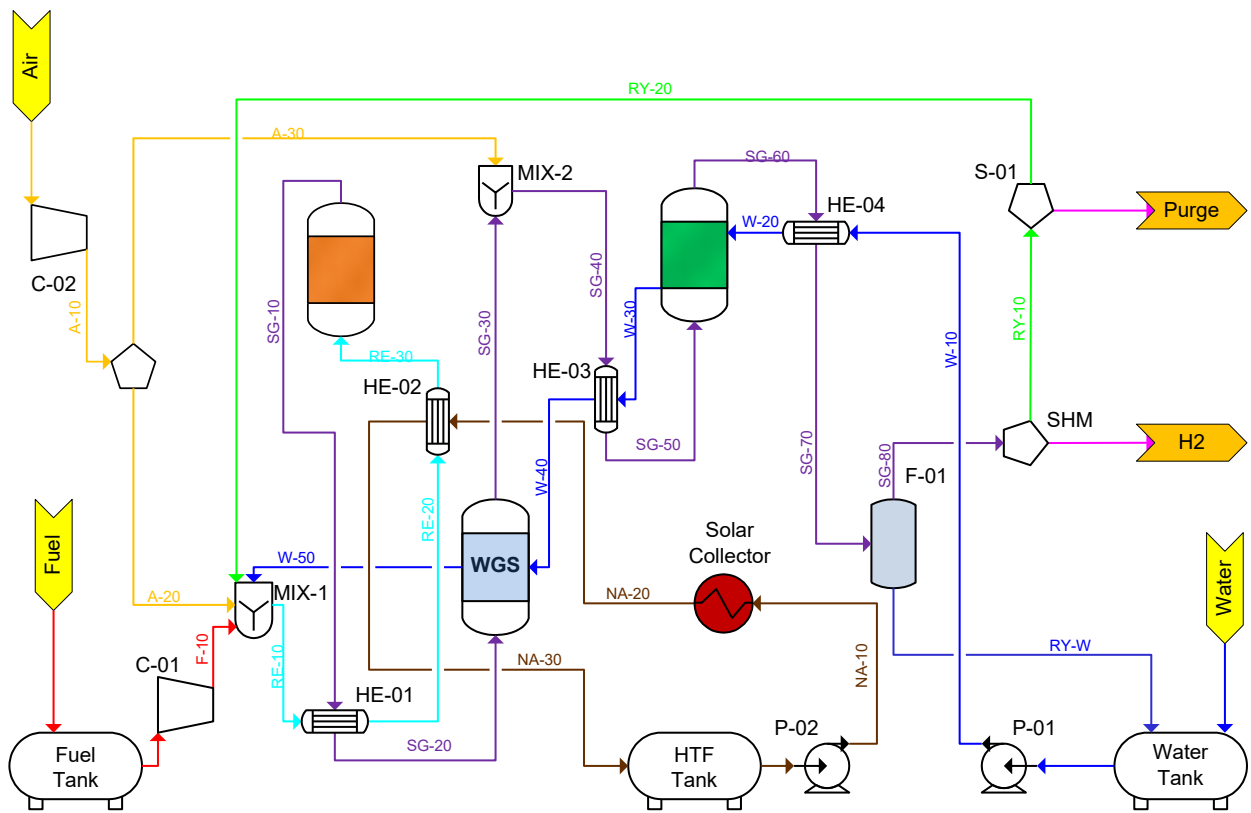


Fig 15 Process diagram of methane steam reforming

2.2.2 Simulation of tri-reforming of methane in case-study I

After determining the optimum conditions of the steam reforming, which is the base of the project, the tri-reforming of methane process (**Fig 16**) is made with these conditions. The feed of the process consist of three stream, the fuel flow is methane (F-10) 100 kg/h at 25 °C, the water flow (W-10) comes from the water tank at 25 °C , and is preheated by a serious of blocks with

the recovered heat, the flow rate is adjusted to suit the optimum steam to carbon ratio in the reactor, and the air flow (A-20) is fed at 25 °C, and it must be enough to make methane oxidation/partial oxidation reforming reactions and supply the heat for the other endothermic reactions. The feed gases mixed with the recycled gas via a mixer and cool down the syngas outlet of the reactor, and then heated by the liquid sodium that is heated by the CSP system to reach the reaction temperature. The reactor operates at the optimum condition with net heat duty equal to zero. The syngas (SG-10) is cooled down and sent to the WGS to reduce the concentration of CO (there is no another stream of water because the mole fraction of CO is already below 1%). Then it is mixed with another stream of air (A-30) which is 25 kg/h at 25 °C to supply oxygen for further reaction. The mixed syngas (SG-70) is cooled down to 150 °C and sent to the PROX to take the CO oxidation reactions with conversion of CO at 99.9%. The gases outlet of the PROX is cooled down to 130 °C (to recover heat and the water boiling point at operation pressure is close to 121 °C). Then the syngas is cooled down to 60 °C in the separator, the liquid phase is water which is recovered to the water tank and the vapor phase across the selective-hydrogen membrane to separate hydro as the product for further research, the exhaust is divided into two streams, one (RY-20) is to recycle to the block MIX-1, the other (PURGE) is to purge, with the split ratio of recycle varies from 0.1 to 0.9. The whole process is operated at the



optimum pressure.

Fig 16 Process diagram of tri-reforming of methane with solar energy in case-study I

2.2.3 Simulation of tri-reforming of methane in case-study II

The process is improved compared to case-study I, and all the process are the same as case I before the block PROX. The syngas outlet of PROX (SG-60), in case II (**Fig 17**), is cooled down to 130 °C, and across the selective-hydrogen membrane to separate hydro as the product for first, Then the exhaust (RY-10) is divided into two streams, one (RY-20) is to recycle, the other (RY-30) is to purge, with the split ratio of recycle varies from 0.1 to 0.9. The recycle stream (RY-20) is sent to the block MIX-1, the other one is cooled down to 60 °C in a separator, the liquid phase is water to recover to the water tank and the vapor phase is to purge. This process is operated at the optimum pressure as well.

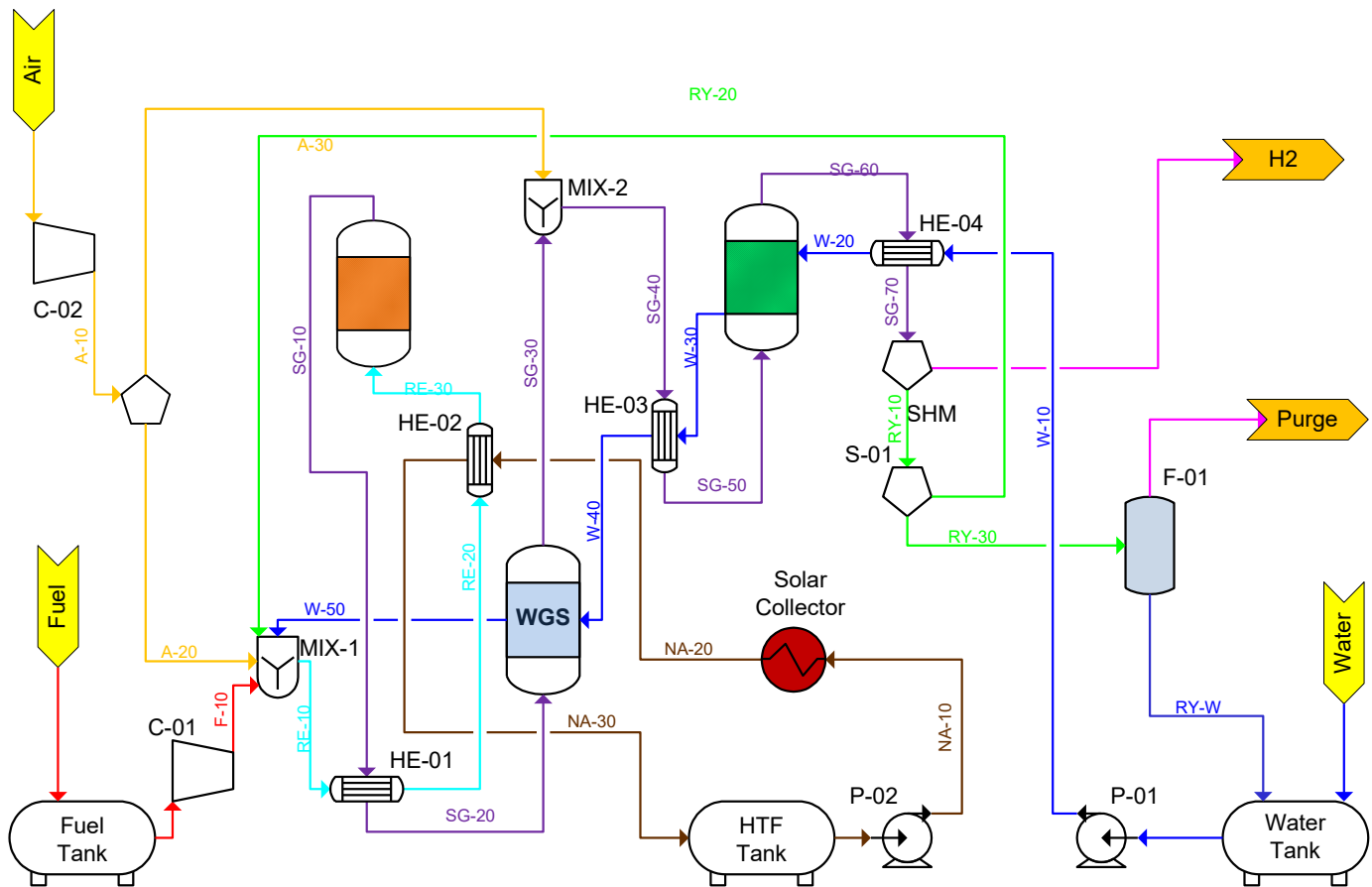


Fig 17 Process diagram of tri-reforming of methane with solar energy in case-study II

Chapter III Results and Discussion

3.1 results of steam reforming

3.1.1 Effect of steam to carbon (S/C) ratio

The ratio of steam to carbon (S/C) plays the most important role in the steam reforming reaction, especially for the production of coke, which is the most disadvantage of methane reforming (see Chapter 1.3.2). The effects of steam to carbon ratio on the conversion of methane, the mass ratio between produced hydrogen and fed methane, the required heat for the block HEATED, and the water flow in the reaction are shown in **Fig 18**.

The increase of S/C ratio from 1 to 5 leads to the increase of conversion of methane, the total water flow rate and the required heat, however, their trends go differently. The conversion of methane increase drastically when the steam to carbon ration varies from 1 to 3, but when the stream to carbon ration exceeds 3, methane conversion is a weak function of that ratio(**Fig 18-a**). The same tend with the mass ratio between produced hydrogen and fed methane (**Fig 18-b**), verifying the consumption of methane is the main source of the production of hydrogen, which is also known in eq 1. Therefore, the methane conversion trend is also used to represent the change of hydrogen production. On the contrary, the total water flow rate increases slowly when the steam to carbon ratio changes from 1 to 3, and increases sharply when the ratio equals 4 and 5, because there is enough water for reduce the CO concentration without the second water stream when the ratio is more than 3(**Fig 18-c**). The required heat keeps growing with the stream to carbon ratio going up which means a straightforward relationship between them (**Fig 18-d**).

The rules of finding out the optimum conditions are the maximum methane conversion with the minimum water flow rate and the minimum energy consumption. In this case, steam to carbon ratio 3 is selected for further simulation.

3.1.2 Effect of reaction temperature

The methane conversion and the required heat from the CSP plant as functions of reaction temperature, with steam to carbon ratio equal to 3 and a pressure at 2 bar can be seen in **Fig 19**.

Since steam methane reforming is a strongly endothermic reaction, the methane conversion keeps raising while the reaction temperature keeps going up. The methane conversion increases fast as the temperature raises from 600 to 700 °C but it rises up mildly after the temperature achieves higher than 700 °C(**Fig 19-a**). On the other hand, the methane conversion is too low to need the second water stream to decrease the CO concentration at the WGS when the temperature below 700 °C, which result in the low requirement of heat. As the temperature exceeds 700 °C, the requested heat increases drastically (**Fig 19-b**).

The optimum reaction temperature is selected to at 750 °C to minimize the energy consumption with a higher methane conversion.

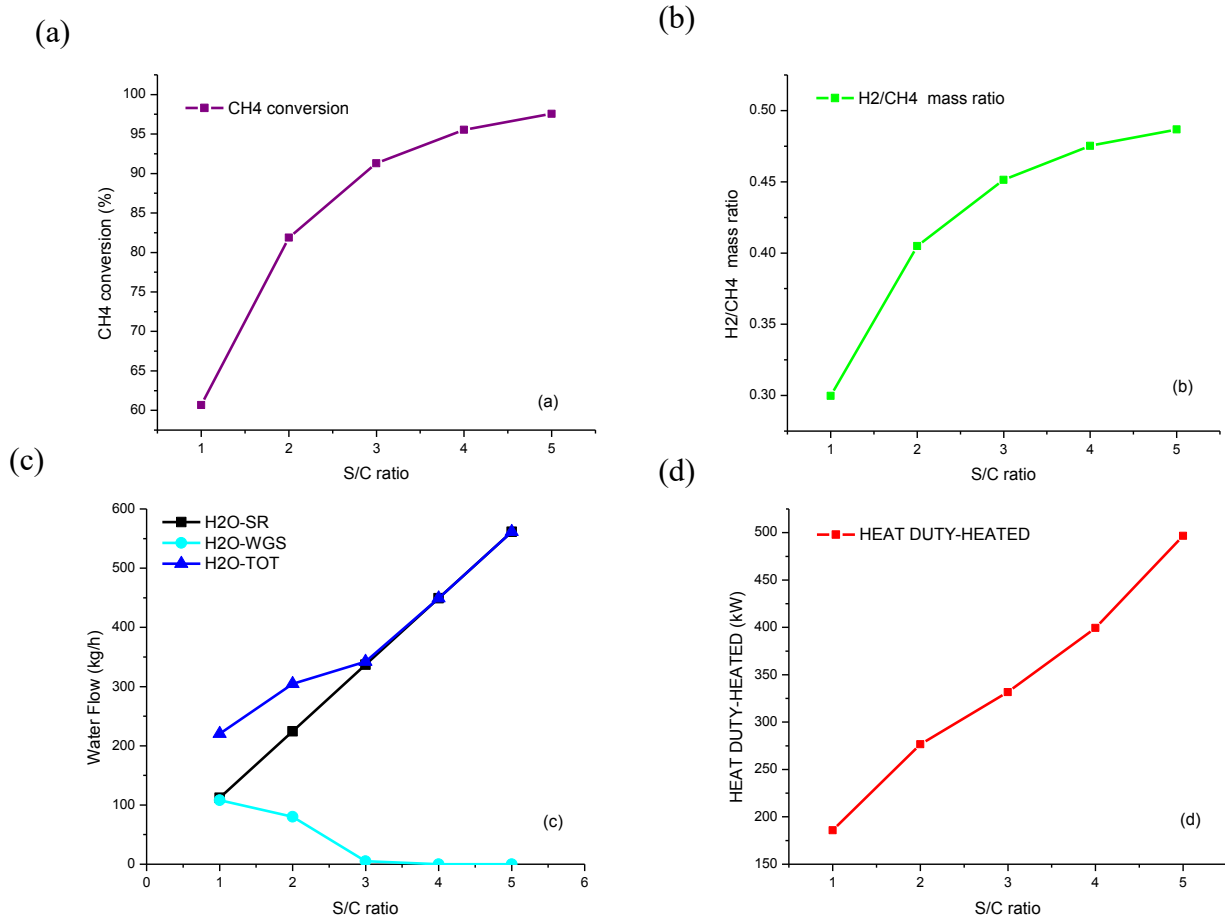


Fig 18 Effect of steam to carbon ratio on equilibrium (a) methane conversion, (b) mass ratio between produced hydrogen and fed methane, (c) water flow rate, (d) required heat duty

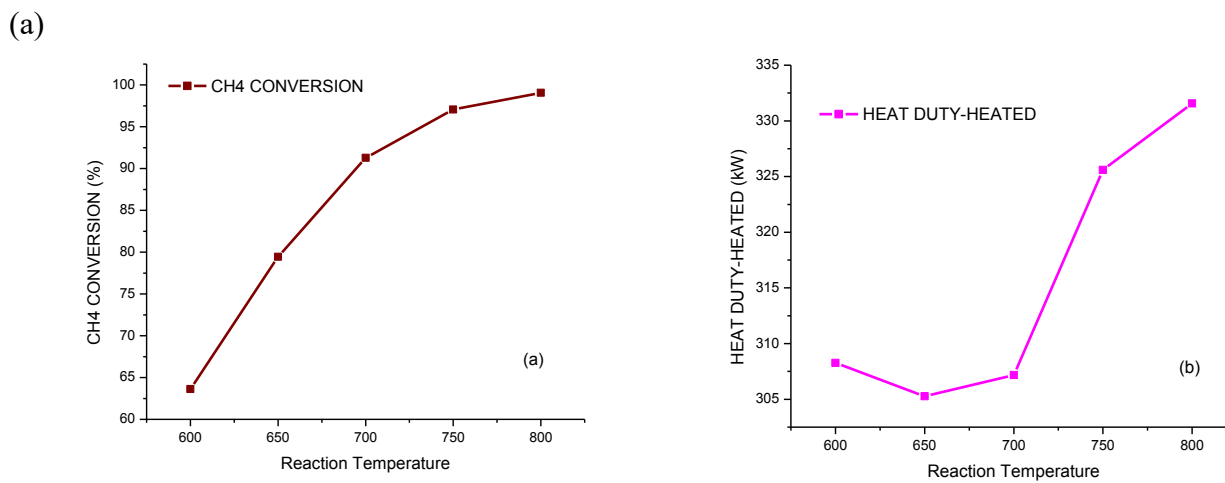


Fig 19 Effect of reaction temperature on equilibrium (a) methane conversion, (b) required heat duty

3.1.3 Effect of reaction pressure

The effect of steam reforming reaction pressure on methane conversion and the required heat from the CSP plant with steam to carbon ratio equal to 3 and reaction temperature is 700 °C is presented in Fig 20.

The increase of pressure from 1 to 5 bar leads to the decrease of methane conversion from 97% to 75%, because this reaction is pressure increasing reaction which is favored at low pressure (Fig 20-a). The more requested heat in low pressure is to heat the second stream of water which is to decrease the concentration of CO, but on the contrary, it is not necessary for that stream because of the low methane conversion (Fig 20-b).

Therefore, the operation pressure is selected at 2 bar for the higher methane conversion and lower heat consumption, and the process under industrial background is a consideration condition as well.

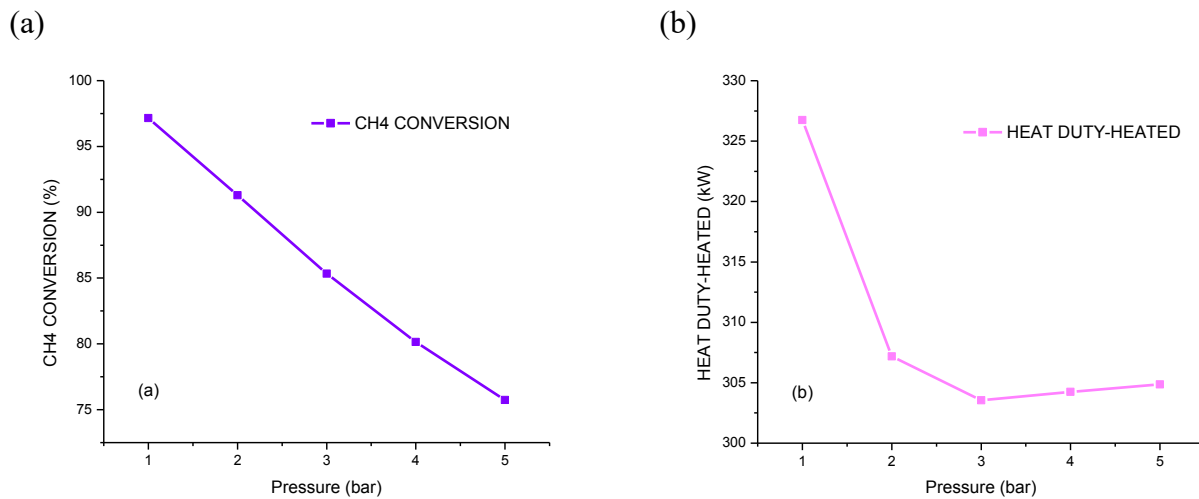


Fig 20 Effect of reaction pressure on equilibrium (a) methane conversion (b) required heat duty

3.1.3 Result of steam reforming process under optimum conditions

After determining optimum reaction conditions, the steam to carbon ratio equal to 3, the operation pressure is at 2 bar and the reaction temperature is at 750 °C, the simulation results for steam reforming process is presented in Table 3. It is seen that the conversion of methane reaches at 91.3%, and the syngas with CO mole ratio at 1% is used for further design which is based on the steam reforming process.

Table 3 Simulation results for steam methane reforming process under optimum conditions

	F-10	SMR-10	SMR-20	SMR-30	SMR-40	SRM-50
Temperature C	25	90.00264	700	700	684.5617	330
Pressure bar	2	2	2	2	2	2
Vapor Frac	1	0.694476	1	1	1	1
Mass Flow kg/hr						
CH4	100	100	100	8.715664	8.715664	8.715664
H2O	0	336.8862	336.8862	187.1679	192.3105	192.3105
CO	0	0	0	85.97805	85.97805	85.97805
CO2	0	0	0	115.3303	115.3303	115.3303
H2	0	0	0	39.69419	39.69419	39.69419
Mole Frac						
CH4	1	0.25	0.25	0.014961	0.014844	0.014844
H2O	0	0.75	0.75	0.286103	0.291671	0.291671
CO	0	0	0	0.084528	0.083869	0.083869
CO2	0	0	0	0.072165	0.071602	0.071602
H2	0	0	0	0.542243	0.538014	0.538014
	SRM-60	SW-10	SW-20	SW-30	SW-40	SW-50
Temperature C	300	25	25	25	117.3595	121.7556
Pressure bar	2	2	2	2	2	2
Vapor Frac	1	0	0	0	0	0.571372
Mass Flow kg/hr						
CH4	8.715664	0	0	0	0	0
H2O	143.6058	342.0287	336.8862	5.142532	336.8862	336.8862
CO	10.25137	0	0	0	0	0
CO2	234.3117	0	0	0	0	0
H2	45.14417	0	0	0	0	0
Mole Frac						
CH4	0.014844	0	0	0	0	0
H2O	0.217802	1	1	1	1	1
CO	0.01	0	0	0	0	0
CO2	0.145471	0	0	0	0	0
H2	0.611883	0	0	0	0	0

3.2 Results of tri-reforming of methane in case-study I

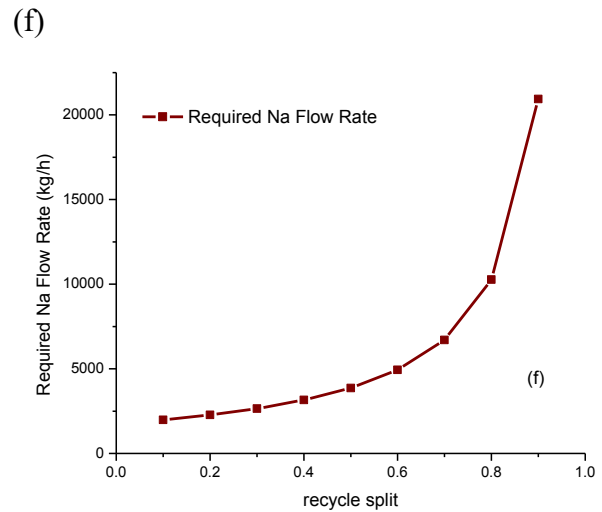
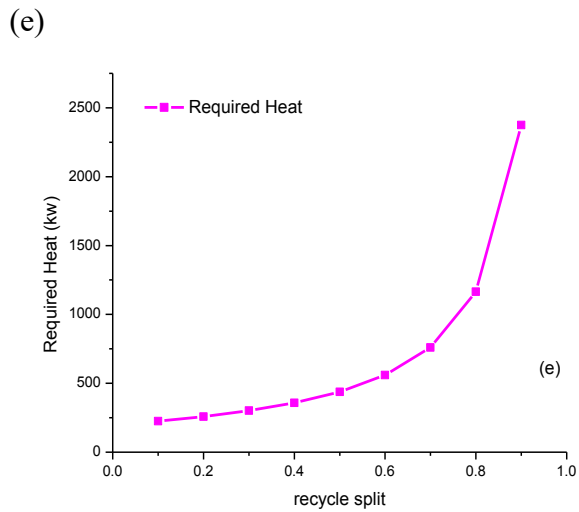
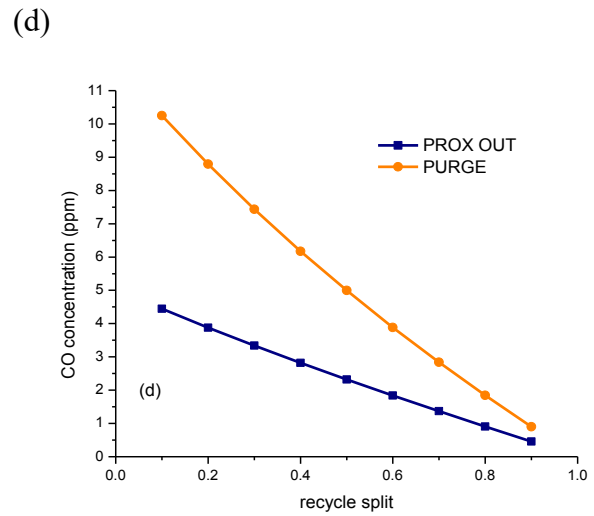
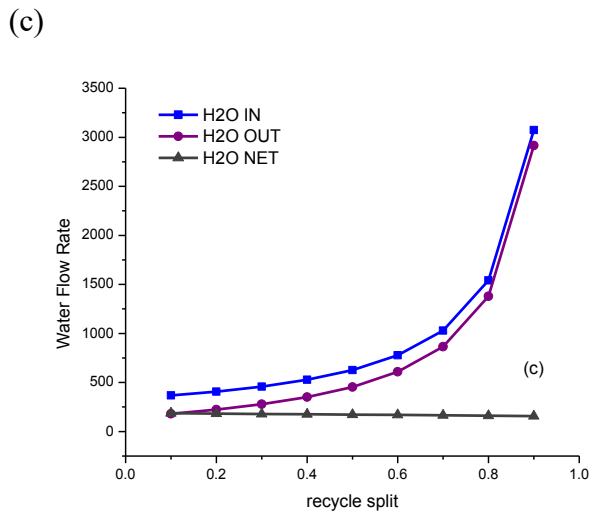
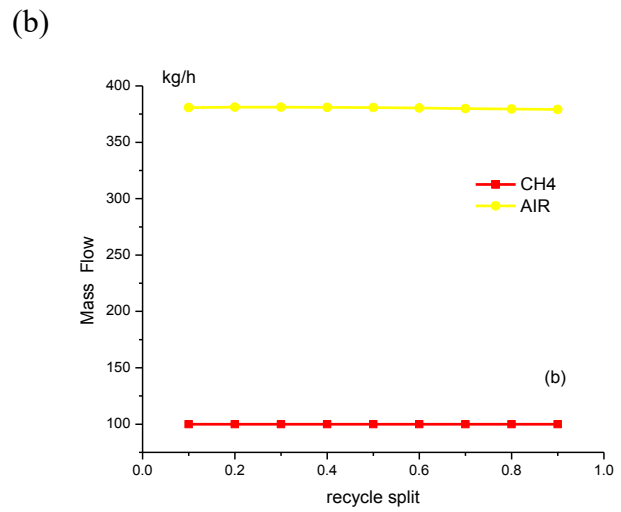
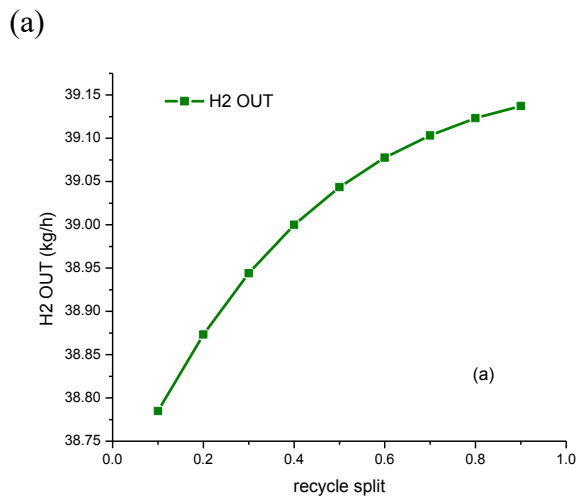
The effect of recycle on the produced hydrogen flow rate, the feed flow of methane and air, the water balance, the CO concentration out of the PROX and purge, the required heat and liquid sodium flow rate, and the gross efficiency at the optimum conditions of each block is shown in **Fig 21**.

The increase of recycle split from 0.1 to 0.9 results in the produced hydrogen flow rate (**Fig 21-a**) increase with the feed flow of methane remain at 100 kg/h and the required air flow decrease a little, from 381 to 379 kg/h (**Fig 21-b**). At the same time, the water flow goes up slowly when the recycle split raise from 0.1 to 0.7, but it rise up drastically to suit the increasing recycle carbon components to remain the steam to carbon ratio equal to 3. In addition, the recovered water which comes from the separator increase as well, as a result, the net required water for the tri-reforming reaction decreases along the increase of the recycle split ratio (**Fig 21-c**). The mole ratio of CO, both of outlet PROX and of the purge stream, decreases with the rising up of recycle split ratio (**Fig 21-d**)

The requested energy (**Fig 21-e**) from the CSP plant to heat the reaction gases to 750 °C increase with the recycle split ratio goes up, because the more thermal energy is used to heat the increasing inlet water flow. Thus, the required hot liquid sodium flow rate rises up from 1981 to 20939 kg/h (**Fig 21-f**), as the hot liquid sodium inlet temperature is 760 °C (to increase the efficiency of heat exchange) and the hot liquid sodium outlet temperature is 460 °C. The gross efficiency (eq 9) also keeps raising when the recycle split ratio keeps increasing (**Fig 21-h**).

$$\eta_{gross} = \frac{P_{H_2}}{P_{CH_4}} = \frac{W_{H_2} \times LHV_{H_2}}{W_{CH_4} \times LHV_{CH_4}} \quad (9)$$

The optimum recycle split ratio should be selected to 0.9, because the process will achieve the maximum hydrogen production, the maximum gross efficiency with the minimum net requested water and the minimum CO concentration of purge stream. However, at the same time, the requested heat for the reactions is maximum value, at 2375 kW; it requires 20939 kg/h of the hot sodium stream, is too large for a plant as the limit condition.



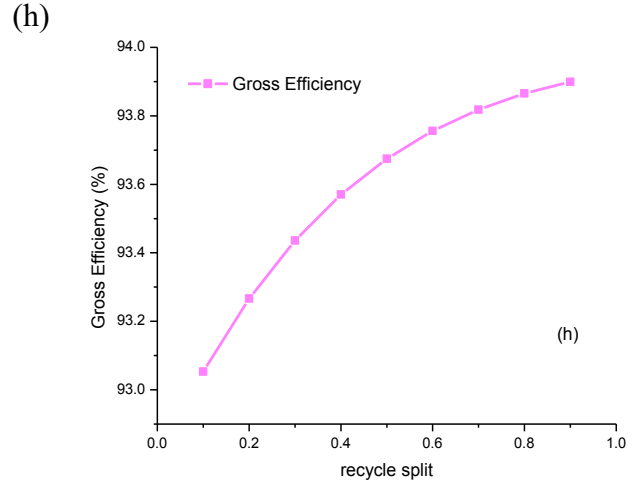
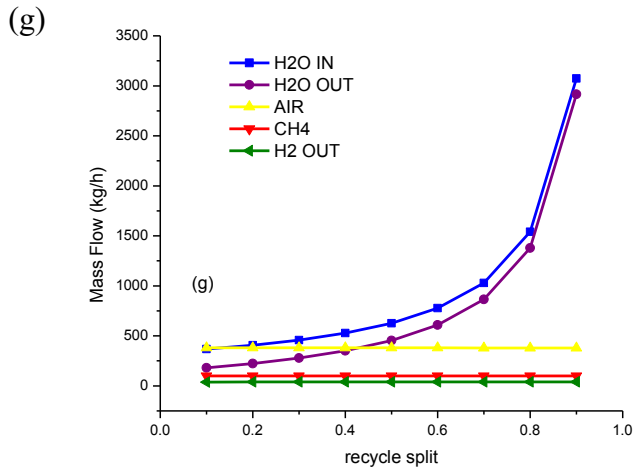
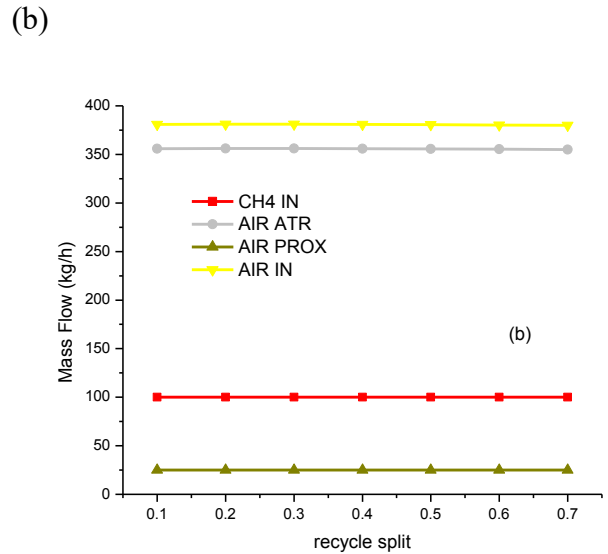
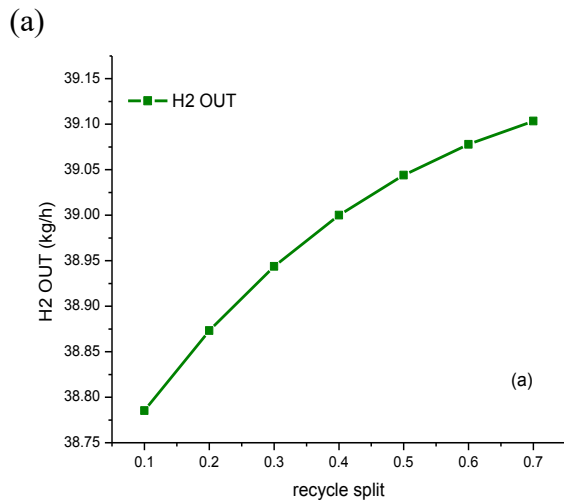


Fig 21 Effect of recycle split ratio on equilibrium (a) hydrogen production, (b) inlet air and methane, (c) water balance (d) CO concentration, (e) required heat, (f) required hot sodium flow rate, (g) mass balance, (h) gross efficiency in case-study I

3.3 results of tri-reforming of methane in case-study II

3.3.1 Effect of recycle split ratio

The same as in case-study I, The effect of recycle on the produced hydrogen flow rate (Fig 22-a), the feed flow of methane and air (Fig 22-b), the water balance (Fig 22-c), the CO concentration out of the PROX and purge (Fig 22-d), the required heat (Fig 22-e), and liquid sodium flow rate (Fig 22-f), and the gross efficiency (Fig 22-h), at the optimum conditions of each block is shown in Fig 22.



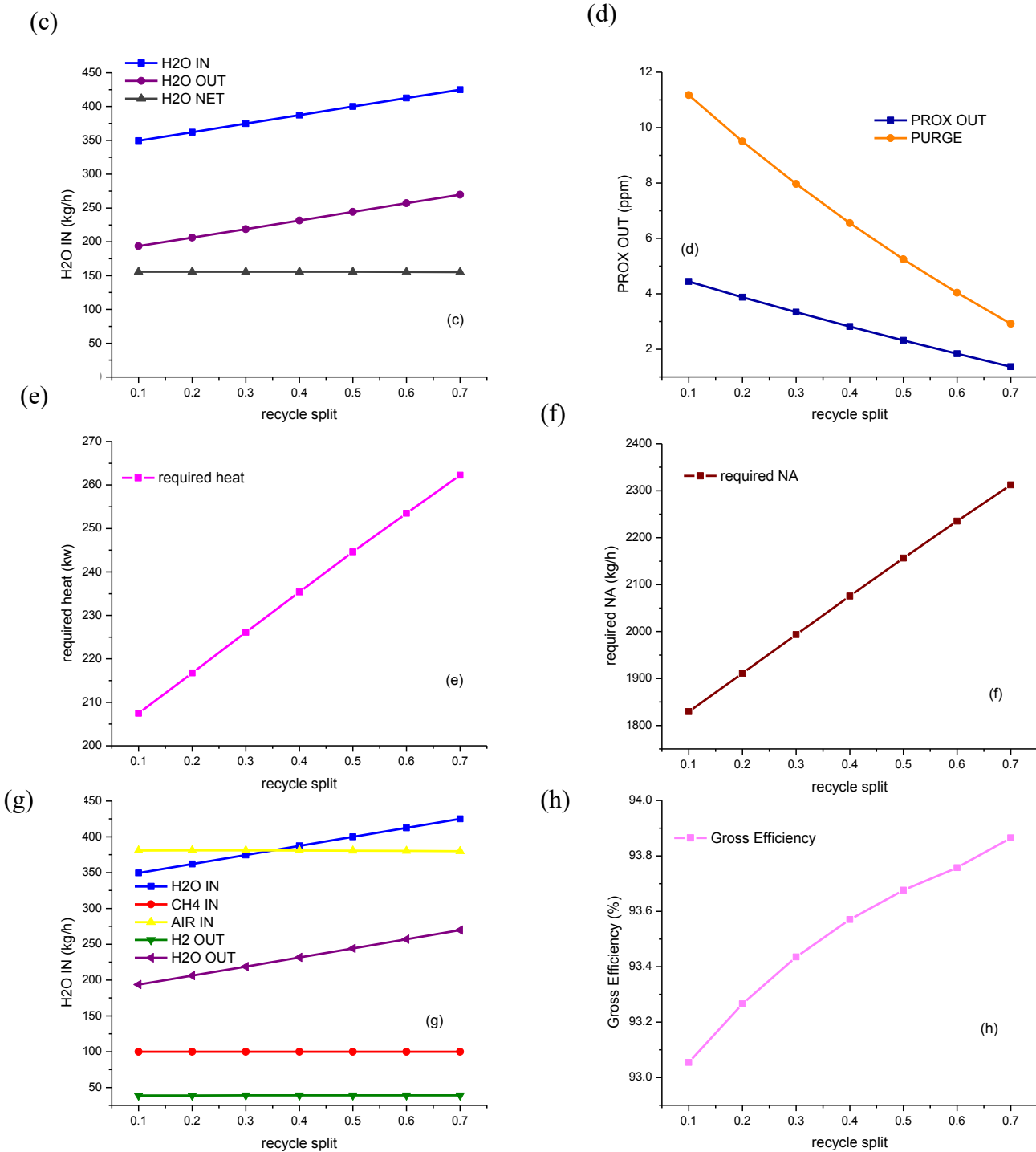


Fig 22 Effect of recycle split ratio on equilibrium (a) hydrogen production, (b) inlet air and methane, (c) water balance (d) CO concentration, (e) required heat, (f) required hot sodium flow rate, (g) mass balance, (h) gross efficiency in case-study II

The trends of variables are the same as case-study I. However, in case-study II, it is impossible to increase the recycle split ratio as high as 0.8 or 0.9, because when the ratio is too high, the heat carrying from the recycle stream is so huge that the preheat water will be over heated, meaning the out temperature of the water will higher than the hot stream inlet temperature.

The increase of recycle split leads to the produced hydrogen flow rate increase while the required air flow decreases a little. Besides, the inlet water flow recovered and goes up slowly, but the net required water for the whole process decreases. The mole ratio of CO, both of outlet PROX and of the purge stream, declines with the rising up of recycle split ratio. In addition, when the recycle split ratio equals to 0.1, the mole ratio of CO in purge stream is 11 ppm (more than 10 ppm), which is forbidden to purge directly into the environment.

Moreover, the required thermal energy increases with the recycle split ratio goes up from 0.1 to 0.7, as a result, the required hot liquid sodium flow rate rises up from 1829 to 2312 kg/h, as the temperature drop between hot liquid sodium inlet and outlet is 300 °C. The gross efficiency also rises up while the recycle split ratio increases.

In case-study II, the optimum recycle split ratio is 0.7, which maximizes the hydrogen production, the gross efficiency and minimizes the inlet air flow and the net required water flow with the minimum CO concentration to purge. The required heat for CSP system is 262 kW, or 2312 kg/h of 760 °C to supply the heat, which is a much less quantity in industry process.

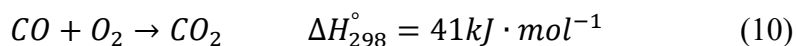
3.3.2 Heat from the separator

As shown in **Fig 17**, the stream SG-70 is cooled down to 60 °C to the separator to recover the water into the water tank. The huge amount of heat is hard to deal with, because it will overheat the water when the recycle split ratio is high. The way to deal with the heat is used another water stream to absorb it with the temperature increasing from 25 to 35 °C, with the water flow 16085 kg/h at atmosphere pressure, and purge the water direct into environment.

3.3.3 Capacity of the PROX

PROX, as an acronym for preferential oxidation, refers to the preferential oxidation of gas on a catalyst. In this process, the catalyst preferentially oxidizes carbon monoxide (CO) using a heterogeneous catalyst placed upon a ceramic support^[27].

The capacity of PROX, meaning the conversion of CO in the oxidation reaction (eq 10), is tested in **Fig 23**.



As shown in **Fig 23**, in order to purge the exhaust directly into the environment, the conversion of CO in the PROX reaction must higher than 99.7% (to ensure the CO concentration below 10 ppm). If the capacity is not so high to decrease the CO mole ratio below the critical concentration (10 ppm), it is requested a tank to store the exhaust or using another PROX with more effective catalyst to deal with the exhaust.

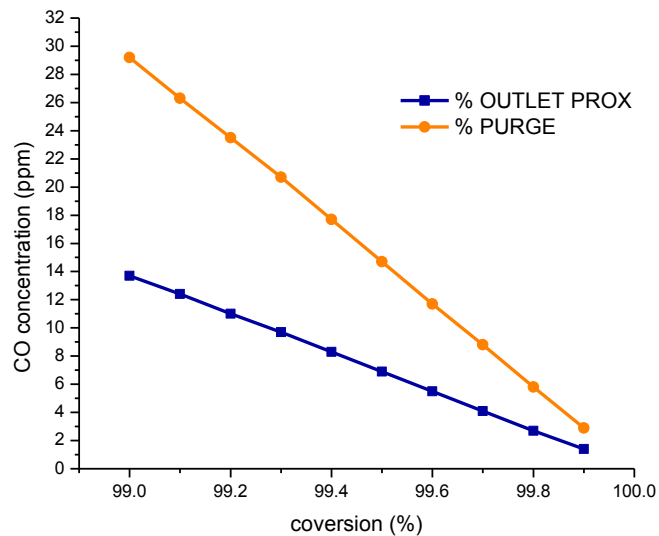


Fig 23 Capacity of PROX

3.3.4 Comparison of optimum operation conditions between case-study I and II

Table 4 demonstrates the result of methane tri-reforming reaction in case-study I and II, both of the cases are under optimum operation conditions.

As shown, the operation pressure, the reactors temperatures and the feed methane flow rate are the same. There are few differences on produced hydrogen, inlet air flow rate, net required water, the electricity powers of the pump and compressors, the minimum PROX capacity, the CO concentration of the purge exhaust, and the gross efficiency between case I and case II. However, the heat duties of the heat-exchanger in case I are much more than in case II, which requires a serious of higher quality heat-exchangers and a larger energy consumption. So the tri-reforming of methane in case II is selected to be the final process in the project.

Table 4 Comparison of methane tri-reforming reaction in case-study I and II

variable		Unit	I	II
operation pressure		bar	2	2
tri-forming reaction	temperature	°C	750	750
WGS reaction	temperature	°C	300	300
recycle split			0.9	0.7
H ₂ OUT	flow rate	kg/h	39.13732	39.10353
H ₂ O OUT	flow rate	kg/h	2914.888	269.6418
H ₂ O IN	flow rate	kg/h	3073	425.0263
	P-01 pressure change	bar	1 to 2	1 to 2
	P-01 motor efficiency		0.9	0.9
	p-01 power	kW	0.09542232	0.01187581
H ₂ O net required	flow rate	kg/h	158.112	155.3845
CH ₄ IN	flow rate	kg/h	100	100
	C-01 pressure change	bar	1 to 2	1 to 2
	C-01 motor efficiency		0.75	0.75
	C-01 power	kW	3.57436701	3.57436701
AIR IN	flow rate	kg/h	379.1081	379.9234
	P-01 pressure change	bar	1 to 2	1 to 2
	P-01 motor efficiency		0.75	0.75
	p-01 power	kW	7.70161131	7.71836558
required liquid sodium	flow rate	kg/h	20939.52935	2312.346242
heat duty	HE-01	kW	1634.73803	564.356601
	HE-02	kW	2374.89162	262.258603
	HE-03	kW	532.20403	185.30324
	HE-04	kW	104.0428	36.537904
	H-WGS	kW	149.3143	75.047735
	H-PROX	kW	13.07475	14.070894
minimum PROX capacity	CO conversion	%	99.5	99.7
CO mole fraction	OUT WGS	ppm	455.256	1378.79
	OUT PROX	ppm	0.45428	1.37058
	PURGE	ppm	0.900282	2.92245
Gross Efficiency		%	93.89952015	93.86461132

3.3.5 Result of tri-reforming of methane process under optimum conditions

The final process of tri-reforming of reaction is designed as, the steam to carbon ratio equal to 3, the operation pressure is at 2 bar , the reaction temperature is at 750 °C, the WGS reaction temperature is at 300 °C , the PROX capacity is with CO conversion 99.9%, and the recycle split ratio is at 0.3. The stream table is presented in **Table 5**, with the conversion of methane at 99.8%, produced hydrogen 39.1kg/h, CO concentration in purge exhaust at 3 ppm and the requested hot liquid sodium flow rate at 2312 kg/h, the gross efficiency at 93.9%.

Table 5 Steam table of tri-reforming of methane

	A-20	A-30	F-10	H2	NA-20	NA-30
Pressure bar	2	2	2	2	1	1
Temperature C	25	25	25	120	760	691.7835
Vapor Frac	1	1	1	1	0	0
Total Flow kg/hr	354.9234	25	100	39.10353	10000	10000
Mass Flow kg/hr						
CH4	0	0	100	0	0	0
CO	0	0	0	0	0	0
CO2	0	0	0	0	0	0
H2	0	0	0	39.10353	0	0
H2O	0	0	0	0	0	0
O2	82.66769	5.822925	0	0	0	0
N2	272.2557	19.17707	0	0	0	0
C	0	0	0	0	0	0
NA	0	0	0	0	10000	10000
Mole Frac						
CH4	0	0	1	0	0	0
CO	0	0	0	0	0	0
CO2	0	0	0	0	0	0
H2	0	0	0	1	0	0
H2O	0	0	0	0	0	0
O2	0.21	0.21	0	0	0	0
N2	0.79	0.79	0	0	0	0
C	0	0	0	0	0	0
NA	0	0	0	0	1	1

	P-10	RE-10	RE-20	RE-30	RE-W	RY-10
Pressure bar	2	2	2	2	2	2
Temperature C	60	102.3038	557.9489	750	60	120
Vapor Frac	1	0.995661	1	1	0	1
Total Flow kg/hr	596.2044	2900.258	2900.258	2900.258	269.6418	2886.154
Mass Flow kg/hr						
CH4	6.06E-03	100.0141	100.0141	100.0141	2.58E-08	0.020192
CO	1.50E-03	3.51E-03	3.51E-03	3.51E-03	6.96E-10	5.01E-03
CO2	274.3002	640.0551	640.0551	640.0551	9.16E-03	914.3644
H2	0.118496	0.27649	0.27649	0.27649	9.53E-08	0.394985
H2O	29.45618	1122.9	1122.9	1122.9	269.6325	996.9623
O2	0.88935	84.74286	84.74286	84.74286	8.26E-06	2.964527
N2	291.4326	952.2655	952.2655	952.2655	1.70E-04	971.4426
C	0	0	0	0	0	0
NA	0	0	0	0	0	0
Mole Frac						

CH4	2.06E-05	0.052001	0.052001	0.052001	1.07E-10	1.13E-05
CO	2.92E-06	1.04E-06	1.04E-06	1.04E-06	1.66E-12	1.61E-06
CO2	0.339508	0.12131	0.12131	0.12131	1.39E-05	0.187033
H2	3.20E-03	1.14E-03	1.14E-03	1.14E-03	3.16E-09	1.76E-03
H2O	0.089065	0.519911	0.519911	0.519911	0.999986	0.49818
O2	1.51E-03	0.02209	0.02209	0.02209	1.72E-08	8.34E-04
N2	0.566688	0.283543	0.283543	0.283543	4.05E-07	0.312176
C	0	0	0	0	0	0
NA	0	0	0	0	0	0
<hr/>						
	RY-20	RY-30	SG-10	SG-20	SG-30	SG-40
Pressure bar	2	2	2	2	2	2
Temperature C	120	120	750	330	300	298.4564
Vapor Frac	1	1	1	1	1	1
Total Flow kg/hr	2020.308	865.8462	2900.258	2900.258	2900.258	2925.258
Mass Flow kg/hr						
CH4	0.014135	6.06E-03	0.020192	0.020192	0.020192	0.020192
CO	3.51E-03	1.50E-03	100.9726	100.9726	5.009252	5.009252
CO2	640.0551	274.3093	755.7246	755.7246	906.5018	906.5018
H2	0.27649	0.118496	32.59213	32.59213	39.49852	39.49852
H2O	697.8736	299.0887	1058.682	1058.682	996.9623	996.9623
O2	2.075169	0.889358	8.00E-16	8.00E-16	8.00E-16	5.822925
N2	680.0098	291.4328	952.2655	952.2655	952.2655	971.4426
C	0	0	1.21E-28	1.21E-28	1.21E-28	1.21E-28
NA	0	0	0	0	0	0
Mole Frac						
CH4	1.13E-05	1.13E-05	9.70E-06	9.70E-06	9.70E-06	9.64E-06
CO	1.61E-06	1.61E-06	0.027793	0.027793	1.38E-03	1.37E-03
CO2	0.187033	0.187033	0.132391	0.132391	0.158805	0.157751
H2	1.76E-03	1.76E-03	0.12465	0.12465	0.151064	0.150062
H2O	0.49818	0.49818	0.453075	0.453075	0.426661	0.423829
O2	8.34E-04	8.34E-04	1.93E-19	1.93E-19	1.93E-19	1.39E-03
N2	0.312176	0.312176	0.262081	0.262081	0.262081	0.265585
C	0	0	7.74E-32	7.74E-32	7.74E-32	7.69E-32
NA	0	0	0	0	0	0
<hr/>						
	SG-50	SG-60	SG-70	W-10	W-20	W-30
Pressure bar	2	2	2	2	2	2
Temperature C	150	150	120	25	93.16047	118.9736
Vapor Frac	1	1	1	0	0	0
Total Flow kg/hr	2925.258	2925.258	2925.258	425.0263	425.0263	425.0263
Mass Flow kg/hr						
CH4	0.020192	0.020192	0.020192	0	0	0
CO	5.009252	5.01E-03	5.01E-03	0	0	0
CO2	906.5018	914.3644	914.3644	0	0	0

H2	39.49852	39.49852	39.49852	0	0	0
H2O	996.9623	996.9623	996.9623	425.0263	425.0263	425.0263
O2	5.822925	2.964527	2.964527	0	0	0
N2	971.4426	971.4426	971.4426	0	0	0
C	1.21E-28	0	0	0	0	0
NA	0	0	0	0	0	0
Mole Frac						
CH4	9.64E-06	9.65E-06	9.65E-06	0	0	0
CO	1.37E-03	1.37E-06	1.37E-06	0	0	0
CO2	0.157751	0.159228	0.159228	0	0	0
H2	0.150062	0.150164	0.150164	0	0	0
H2O	0.423829	0.42412	0.42412	1	1	1
O2	1.39E-03	7.10E-04	7.10E-04	0	0	0
N2	0.265585	0.265767	0.265767	0	0	0
C	7.69E-32	0	0	0	0	0
NA	0	0	0	0	0	0
<hr/>						
	W-40	W-50				
Pressure bar	2	2				
Temperature C	121.7556	121.7556				
Vapor Frac	0.68212	0.960679				
Total Flow kg/hr	425.0263	425.0263				
Mass Flow kg/hr						
CH4	0	0				
CO	0	0				
CO2	0	0				
H2	0	0				
H2O	425.0263	425.0263				
O2	0	0				
N2	0	0				
C	0	0				
NA	0	0				
Mole Frac						
CH4	0	0				
CO	0	0				
CO2	0	0				
H2	0	0				
H2O	1	1				
O2	0	0				
N2	0	0				
C	0	0				
NA	0	0				
<hr/>						

Chapter IV Conclusion

In conclusion, the meticulous simulation of hydrogen production from methane tri-reforming (fuel+air+CO₂+steam) with solar energy was carried out using Aspen Plus to find optimization unit operation conditions for maximum production rate with the minimum energy cost. The following result could be achieved with this series of simulations:

-Two similar processes simulated are compared. In case-study II to put the water separator after the recycle split, could have a higher water recovery with a less energy consumption, compared to the one to put the water separator after the PROX(case-study II). However, the disadvantage is that the split ratio of recycle could not be allowed too high for the preheat water would be over-heated.

-For both case-studies, the optimization conditions are fed with S/C (steam/carbon) ratio at 3, operation pressure at 2 bar, temperature of reforming reactor at 750 °C, Water-Gas-Shift at 300 °C.

-For both case-studies, with the decrease of the split ratio of recycle, the required heat from the solar collector declines, but the flow rate of hydrogen production goes down as well, the CO purge concentration increases on opposite.

-The energy-saving process is considered as the final design. With recycle ratio 0.7, fed with methane at 100 kg/h, it could produce hydrogen 39.1 kg/h with methane conversion at 99.8%, and with 2312 kg/h of liquid sodium (to be Heat Transfer Fluid) to supply heat to the reactor for reforming reactions (reported in **Table 4**).

-Based on the LHV of hydrogen and methane, the highest gross efficiency (hydrogen to methane) could achieve at 93.9%.

-The capacity of PROX is also tested. The conversion of CO through the PROX must be no less than 99.7%, with the concentration of CO to purge is lower than 10 ppm (8.8 ppm), to purge it directly into environment.

-The water recovery rate is at 63.4%.

The whole simulation could be considered as an attempt included in the European energy project 'solar assisted catalytic reforming: an hybrid process to transform municipal waste into energy (SOL-CARE)'. It offers the basic theoretic data that could be applied when the feed fuel gas is replaced from methane to the gasification gas in the real project plan. In addition, the produced hydrogen could be used for further research, for example, to be used in hydrogen-fueled proton exchange membrane fuel cells

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