

Solar Thermal Reforming of Methane

Michael EPSTEIN

The Weizmann Institute of Science





A picture is worth a thousand words The Mexican Gulf disaster (April 2010)







Oil prices, demand and supply in 2010









Global Crude Oil and Liquid Fuels Consumption

World crude oil and liquid fuels consumption grew by an estimated 2.4 million bbl/d in 2010, to 86.7 million bbl/d, the second largest annual increase in at least 30 years. This growth more than offset the losses of the previous two years and surpassed the 2007 level of 86.3 million bbl/d reached prior to the economic downturn. IEA expects that world liquid fuels consumption will grow by 1.5 million bbl/d in 2011 and by an additional 1.6 million bbl/d in 2012. Non-OECD countries make up almost all of the growth in consumption over the next 2 years, with the largest contributions coming from China, Brazil, and the Middle East.

Why Reforming?

The common well-known process to produce hydrogen and syngas (mixture of H2 and CO) from natural gas, biogas, landfill gas. This is a highly endothermic process and requires high temperatures.

(there are additional ways to produce syngas; e.g. from biomass processing, coal gasification, other hydrocarbons, etc)

Why Hydrogen and Syngas?

These are the basic raw materials to produce synthetic liquid fuels (SLF) and chemicals in Industrially available processes. For ecological, economical and geo-political arguments it is appropriate time to shift from fossil to synthetic liquid fuels

Why Solar Reforming?

There are so many good reasons that the space on this slide is too short to hold but SLF and CO2 fixation are the next challenges for the concentrated solar community









Fig. 5. Fuels and chemicals from synthesis gas.







Conventions of fuel names and composition Table 1:

Name	Synonyms	Components
Fuel gas		C ₁ - C ₂
LPG		C3 - C4
Gasoline		C ₅ - C ₁₂
Naphtha		C8-C12
Kerosene	Jet fuel	C ₁₁ -C ₁₃
Diesel	Fuel oil	C ₁₃ -C ₁₇
Middle distillates	Light gas oil	C ₁₀ -C ₂₀
Soft wax		C ₁₉ - C ₂₃
Medium wax		C ₂₄ - C ₃₅
Hard wax		C ₃₅₊



The reaction of the reactions in the resence proposed syndroms.					
Main reactions					
1. Paraffins	$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$				
2. Olefins	$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O$				
3. Water gas shift reaction	$CO + H_2O \rightleftharpoons CO_2 + H_2$				
Side reactions					
4. Alcohols	$2nH_2 + nCO \rightarrow C_nH_{2n+2}O + (n-1)H_2O$				
5. Boudouard reaction	$2CO \rightarrow C + CO_2$				
Catalyst modifications (M=Fe,	Co, Ni, Ru)				
6. Catalyst oxidation/reduction	a. $M_x O_y + y H_2 \rightleftharpoons y H_2 O + x M$				
	b. $M_x O_y + yCO \rightleftharpoons yCO_2 + xM$				
7. Bulk carbide formation	$yC + xM \rightleftharpoons M_xC_y$				

Table 1.2 Major overall reactions in the Fischer-Tropsch synthesis.





Fig. 18. Plot of $\Delta G^{\circ}/n$ versus carbon number and temperature (adapted from Stull et al., 1969; Janaf, 1971).



Fig. 20. Plots of calculated selectivities (percent carbon atom basis) of carbon number product cuts as a function of the probability of chain growth.

Table 16 Product distributions from Sasol (FT) and Mobil (MTG) processes

	ARGE (fixed bed) FT	Synthol (fluid bed) FT	Mobil (fixed bed) MTG
Temperature/K	490-520	633685	63-685
Pressure/atm	26	22	14-24
Feed	1.7H2:1CO	3H2:1CO	CH OH
Product distribution			-
Light gas C1-C2	11.0	20.1	1.3
LPG C ₃ -C ₄	11.0	23.0	17.8
Gasoline C5-C12	25.4	39.0	80.9
C ₁₃ -C ₁₉	14.0	5.0	0
Heavy oil, C19+	37.0	6.0	0
Oxygenated compounds	2.3	7.0	0
Aromatics, % of gasoline	0	5	38.6





Fluidized bed <u>biomass gasification</u> with FT pilot plant in Austria



Ras Laffan, Qatar 140000 b/d

converting natural gas to <u>petroleum liquids</u> at a rate of 140,000 barrels/day, with additional production of 120,000 barrels of oil equivalent in <u>natural gas liquids</u> and <u>ethane</u>.

Fischer-Tropsch Bintulu (Shell, Malaysia) Natural gas to <u>low-sulfur diesel fuel</u> and <u>food-grade wax</u>. The scale is 12,000 barrels per day.



Solar Reforming

METHANE REFORMING REACTIONS

$\mathbf{CH}_{4} + \mathbf{H}_{2}\mathbf{O} \leftrightarrow \mathbf{CO} + \mathbf{3H}_{2}$	∆H= 205 kJ/mol	(SR)

 $CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad \triangle H= 247 \text{ kJ/mol}$ (DR)

 $CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta H=-41 \text{ kJ/mol}$ (WGS)

 $CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$

and side reactions leading to carbon formation

$$CH_4 \leftrightarrow C + 2H_2$$
 (MC)

$$2CO \leftrightarrow C + CO_2 \tag{B}$$

$$CO + H_2 \leftrightarrow C + H_2O$$
 (RG)



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Carbon formation conditions on the triangular diagram. The shaded area is the carbon formation zone at 800K. Limiting curves at 1000K and 1500K are also shown (P=15 atm)



Carbon formation conditions for a steam–methane system. The shaded area is the carbon formation zone at 30 atm. Limiting curves at different pressures are also shown.



Carbon formation conditions for a steam-methane-carbon dioxide system at 30 atm. The shaded area is the carbon formation zone when no carbon dioxide is present. Limiting curves at different $yCO_2/(yCO_2+yCH_4)$ are also reported.

Steam reforming mechanism and kinetics with Ni/MgAl2O4 catalyst

Xu, J. and G.F. Froment, "Methane steam reforming, methanation and water-gas shift: I. Intrinsic kinetics." *AIChE Journal*, 1989. **35**(1): p. 88-96.

s ₂ :	$H_2O + S = OS + H_2$	
\$3:	COS = CO + S	
S4:	$CO_2 S = CO_2 + S$	
s5:	$\mathbf{H} \cdot \mathbf{S} + \mathbf{H} \cdot \mathbf{S} = \mathbf{H}_2 \cdot \mathbf{S} + \mathbf{S}$	S-excited site on the
s ₆ :	$\mathbf{H}_2 \mathbf{S} = \mathbf{H}_2 + \mathbf{S}$	surface of the catalyst
s ₇ :	$CH_4S + S = CH_3S + HS$	
S8:	$CH_3S + S = CH_2S + HS$	
Sg:	$CH_2S + OS = CH_2OS + S$	
s ₁₀ :	$CH_2OS + S = CHOS + HS$	
s ₁₁ :	CHOS + S = COS + HS	(rate determining step)
s_{12} :	$CHOS + OS = CO_2S + HS$	(rate determining step)
s ₁₃ :	$COS + OS = CO_2S + S$	(rate determining step)
	$r_{1} = \frac{k_{1}}{p_{H_{2}}^{2.5}} \left(p_{CH_{4}} p_{H_{2}O} - \frac{p_{H_{2}}^{3} p_{CO}}{K_{1}} \right) / (D$ for CO + H ₂ O = H ₂ + CO ₂	$EN)^2$
	$r_2 = \frac{k_2}{p_{H_2}} \left(p_{CO} p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_2} \right) / (D_2 p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_2})$	$(DEN)^2$
	for $CH_4 + 2H_2O = 4H_2 + CO_2$	
	$r_3 = \frac{k_3}{p_{H_2}^{3.5}} \left(p_{CH_4} p^2_{H_2O} - \frac{p_{H_2}^4 p_{CO_2}}{K_3} \right) / ($	$(DEN)^2$
	$DEN = 1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH}$	$K_{H_4}P_{CH_4} + K_{H_2O}P_{H_2O} / P_{H_2}$

Steam Reforming

Production of hydrogen by combining steam and hydrocarbons $C_nH_m + nH_2O \leftrightarrow nCO + (m/2 + n)H_2$ can be done in three types of processes:

- > Steam Reforming: $CH_4 + H_2O \leftrightarrow CO + 3H_2$ (endothermal) Carbon Monoxide Conversion (CO-Shift) CO + H₂O → CO₂ + H₂ (exothermal)
 - Tubular; membrane reactors

> Partial Oxidation: $C_nH_m + n/2 O_2 \rightarrow nCO + m/2 H_2$ (exothermal) $CH_4 + 1/2 O_2 \rightarrow CO + 2H_2$

- (Non catalytic) Partial Oxidation (POX)
- Catalytic Partial Oxidation (CPO)
- > Auto-thermal Reforming: $CH_4 + 3/2 O_2 \rightarrow CO + 2H_2O$ H_2 Oxidation: $2 H_2 + O_2 \rightarrow 2 H_2O$ (exothermal) $2CH_4 + O2 + CO_2 \rightarrow 3H_2 + 3CO + H_2O + Heat$ $4CH_4 + O_2 + 2H_2O \rightarrow 10H_2 + 4CO$

Typical Industrial Reformers



Maintaining a tube-wall temperature that is hot enough for the reforming reaction but not overheating the tube surface is a critical factor in reformer heater design



A typical side-fired has over 350 burners. Tubes are 125mm ID; 13mm thick; 12m long made of Cr25%Ni20% alloys The tubes are spaced to allow the down flames to fire between them. The radiant gases leave the box horizontally at the bottom and used to generate the process steam.



Industrial reformers heated by flames



Figure 7. Approximate temperature profiles across a reformer

 a) Reformed gas (average over tube cross section); b) Tube wall inside; c) Tube wall outside; d) Heater wall; e) Local heat flux; f) Flue gas; g) Flame



Figure 2. Equilibrium composition for methane reforming at 500-1000 °C and pressures (in the direction of the arrows) of 0.1, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4 MPa. Molar steam: methane ratio 3.333 corresponding to 5 kg H₂O per kilogram of carbon

Non-"commercial" Reformers

- Membrane Reformers
- Indirectly heated reformers with intermediate HTF

Helium - Nuclear reformers for HTGR

Sodium heat pipe

Air

- Directly heated tubular Solar Reformers
- Directly heated windowed volumetric Solar Reformers

Static catalytic bed

Fluidized particles Solar Reformer





Fig. 2. Schematic illustration of an integrated solar central receiver (SCR)—thermochemical pipe (TCP) system for solar heat conversion, transmission and storage.



Left side: Reformer tube bundle with baffles and Raschig ring bed catalysts

Right side: Reformer tube bundle with concentric tubes ar disk catalysts





Process flow diagram of ASTERIX (100%-load case).

CH₄ conversion

(%)

Test no.	1	2	3	4	5	
Temperature (°C)	702	750	753	802	803	
Pressure (bars)	7.6	7.7	7.7	6.1	7.8	
Water-mass flow (kg/h)	26	32	36	35	39	
Composition of the synthesis gas						
- H ₂ O (mol-%)	33.8	30.9	35.5	31.3	31.3	
- H ₂ (mol-%)	48.6	52.4	44.6	50.7	51.0	
- CO (mol-%)	4.6	6.3	9.4	11.3	10.4	
- CO ₂ (mol-%)	7.4	6.9	7.5	5.4	5.7	
- CH ₄ (mol-%)	5.6	3.5	3.0	1.3	1.6	
Approach (°C)	9	14	3	10	8	

68

79

84

93

91

Table 1. Results of the Steady State ASTERIX Tests ($m_{air} = 525 \text{ kg/hr}$)



Figure 4. Temperature behavior along the ASTERIX reformer tube.

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The ASTERIX reforming (H2O/CH4) project

Joint project DLR-CIEMAT

Indirectly heated reformer with hot air supplied from the GAST solar facility



Figure 5. ASTERIX transient test.

Sodium Heat-Pipe Reformers

Pseudo-Isothermal Reformers





20 kW SANDIA-ISRAEL REFLUX HEAT-PIPE RECEIVER/REACTOR

20 kW Sodium Reflux Solar Reformer Under testing at the Weizmann solar furnace (1983-1984)

Solar tests results

Table 1. Process parameters					
Sodium vapor temperatures, °C	685-825				
Reaction temperatures, °C	650-800				
Inlet pressures, atm	2-6				
Feed flows, SLPH	1000-5700				
Molar ratio, CO ₂ /CH ₄	1-1.2				
CH ₄ conversion, %	50-70				
Energy input, kW	1.5-7.8				
Reactor heat flux range, kW/m2	10-80				

Table 3. Results of reaction experiments CH4 CH4 flow (SLPH) P Tw Distance converted Q1 (kW) Flux T_G Qh (kW) CO₂/CH₄ Run (atm) (°C) (°Č) (cm) (%) (kW/m²) RI 530 2.0 1.09 720 20 576 9.6 0.44 0.86 1.12 0.30 15.8 50 681 30.0 12.3 12.2 0.40 65 685 42.4 0.45 130 700 _ _ _ R2 1100 3.0 1.20 725 20 554 8.7 0.70 0.99 35.4 35 650 22.0 0.88 1.61 32.9 662 672 50 26.5 0.91 1.79 25.6 65 85 33.9 38.8 2.06 2.24 0.93 22.0 0.96 18.8 130 711 6.4 _ R3 2100 5.0 1.17 818 20 551 1.31 1.71 61.2 35 672 20.8 1.68 2.97 60.5 36.3 52.7 68.1 6.2 65 716 1.95 4.33 46.1 797 552 672 115 130 20 35 50 65 85 2.20 5.45 33.0 2.26 1.54 2.14 6.22 1.99 3.58 33.4 R4 2513 5.5 1.20 825 71.2 73.2 19.0 702 713 4.23 4.70 25.8 2.22 60.3 31.6 2.27 50.0 40.9 59.5 5.41 _ 2.39 44.3 115 2.65 2.82 6.92 42.0 130 798 69.1 7.87 41.9

Single reactor tube details

Solar Reforming The Weizmann Inst. 480 kW solar tubular reformer/receiver

Directly heated reformer tubes. 8 tubes (2.5 inch, Sch. 80) 4.5 m long. Steam and CO2 reforming, 18 bars, syngas at 800C (1993-1998).

WIS first tubular reformer and system installed on the roof of the tower 1992

Direct heating of the catalyst bed

Transparent windowed solar reformers

The CAESAR Reformer (CO2/CH4) 1987-1990

Tested at the 17-m parabolic dish facility (PAN) at DLR, Lampoldshausen,

Volumetric reformer with porous alumina absorber coated with Rh catalyst

97 kW absorbed, 70% CH4 conversion, 85% thermal efficiency of the receiver

Schematic diagram of the CAESAR reformer/receiver.

Comparison of different novel Ru catalysts for steam/CO₂ reforming of methane developed at WIS for systems at high operation temperatures, high CO_2/C and low H₂O/C ratio

Berman A, Karn R K, Epstein M, (2005) Kinetics of steam reforming of methane on Ru/Al2O3 catalyst promoted with Mn oxides. Applied Catalysis A: General vol. 282/1-2 pp. 73-83

Fig. 9 Steam reforming of biogas on $2\% Ru/(\alpha\text{-}Al_2O_3$ + $MnO_x)$ catalyst.

Fig. 12 Conversion of methane as a function of temperature at P = 1 bar for the fresh sample as well as after testing for 506 h at 1100 °C.

Catalyst development

Novel ceramic pin-fins catalyst bed arrangement

* Catalyst is based on Ru/Al₂O₃ stabilized with oxides of Mn, Ce and La to prevent carbon deposition Ben-Zvi R, Karni J, Simulation of a volumetric solar reformer, J. of Solar Energy Engineering 129 (2007) pp 197-204

CFD modeling of the porcupine catalytic absorber

orcupine 30 W Solar Reformer at W S Solar ower est Station

Front Secondary Concentrator (CPC)

Porcupine Solar Reformer

NOVEL SOLAR ASSISTED FUEL DRIVEN POWER SYSTEM

SOLAS S

01.06.1998 to 30.06.2002

articipants

Deutsches Zentrum für Luft- und Raumfahrt e.V., Institut für Technische Thermodynamik, DLR.ITT (Coordinator)

ORMAT Industries Limited, Research and Development Department, ORMAT.RD

Weizmann Institute of Science – National Council for Research and Development, Solar Research Facilities Unit, INWEIZ.SRF

STORK Product Engineering BV, STORKPE

Netherlands Energy Research Foundation, ECN

Figure 3.3-12: Receiver vessel

vessel Figure 3.3-13: Segment of the internal insulation

Figure 3.3-26: Quartz window attached to inner window flange Fig

Figure 3.3-20:

Pre-assembled main absorber (tolerance check)

Figure 3.2.4: The duel fuel Injector

Figure 3.1-2: Simplified scheme of the SOLASYS test loop

Figure 3.3-2: Heliostat utilization factors

t Solar S S S Reformer on op of t e o er . nder operation

Data Point	date 27.05.20	02, time 12:39						
p _{resc} pressure in reactor	4.9 bar _{abs}	4.9 bar _{shs}						
T ₀	450°C	450°C						
T _{reac,out}	716°C							
Mass flow steam	100 kg/h	$m_0 = 133 \text{ kg/b}$	1					
Mass flow LPG	33 kg/h	33 kg/h						
	Feed	gas						
	based on m	easurements						
	mole-%	h _{i,ie} in mole/h						
CH4	22.7	1694						
CO3	7.6	568						
co	0.0	3.0						
H ₂ O	59.3	4417						
H ₂	10.3	771						
	$h_{in} = 743$	i3 mole/h						
	RESU	JLTS						
	Product ga: based on m	composition ensurements	Product gas equilibrium	composition composition				
	mole-%	ή _{i,out} in mole/h	mole-%	h _{l.ou} in mole/h				
CH4	4.7	475	4.6	454				
CO1	7.8	788	8.8	\$71				
co	10.0	1003	9.5	940				
H ₂ O	29.6	2977	28.9	2876				
H ₂	47.9	4825	48.3	4798				
n _{est} in mole/h		10067		9939				
	mea	sured	calcu	lated				
CH ₄ Conversion	72	0%	73.	2.%				
VRR total power	101	kW	100 kW					
D	2	2.4	22.2					
Power increase	-							

he DLR Solar Reformer

Figure 2.1. Side views and oblique view renderings of the ceramic foam microstructure within a representative volume (RV). Gas flow is in the direction paralle with the longer dimension of the geometry shown.

Figure 4.2 Average temperature in the gas mixture and absorber matrix in the preliminary simulation of CO₂ reforming of methane over Rhodium catalyst

Solar Reforming

SFERA Winter School Solar Fuels & Materials 2.3 Absorptivity

Table 2: Absorptivity data for some catalyst coated SiC foams

	Samples	Absorptivity %	
		Reduced in 5% H ₂ /N ₂ at 500°C for 4 hours	Reduced in 5% H_2/N_2 at 1000°C for 10 hours
1	C 795-145	96	94
2	C 795-145	95	95
3	C 795-143B	96	95
4	C 795-143B*	96	94
5	C 795-144B	96	95
6	C 795-144B*	96	95
7	C924-1	95	96
8	C924-1	95	96
9	APTL	93 ^{a)}	96
10	DLR	95 ^{a)}	94

*Sample had closed pores; a) Sample was reduced at 550 °C for 1h and at 750 °C for 2 h

Figure 5: Activity results for SiC foam coated with a 20 % Ni catalyst, FODLS006 (APTL)

Figure 4: Activity results for SiC foam coated with a 2% Rh catalyst (C795-145, JM)

SiC foams.

CO₂ Fixation

he CO₂ reforming of methane is an important technology for use with

- biogas,
- landfill gas,
- CO₂ reach natural gas,
- inorganic CO₂ from e.g. limestone calcination,
- recycling CO₂ from flue gases for the synthesis of li uid fuels

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Major Components of Flue Gases

C un an Son C emical nno ation _

	Coal-Fired Boilers	Gas-Fired Boilers
CO ₂	12-14	-10
H ₂ O	-10	1 -20
O ₂	3-	2-3
2	72-77	7-72

ndu trial c emical proce e re uire continuou upply of ydro en

or

Stora e of olar ener y in c emical form

Metal- Metal oxide Redox cycle

emperatures can be substantially lowered using e.g. CH₄ as a reducing agent

 ΔG^0 vs. emperatures for the general reaction M_xO_y yCH₄ xM y(2H₂ CO)

e Sn C Sy tem C S R and R C

SnO ₂	2C	Sn(l)	2CO(g) 🛆	H _{0C}	37.	J	(1)
SnO ₂	C the by	Sn(l) drolvsi	CO ₂	^	₩ _{oc}	177	J	(2)
Sn		a) Sn	$\sim 3 \text{ step is}$, (α) γ	н	- 7	Л	(3)
011	21120(9) On	\mathbf{v}_2 \mathbf{z}_2	(9)	00 C		•	(0)

he reduction of SnO2 can be also performed with methane according to SnO₂ $2CH_4$ Sn(I) 2CO $4H_2$ ΔH_{0C} 34 J (4)

he advantages of the SnO₂/Sn compared to the ZnO/Zn system are

he oxide reducing temperatures are lower by 200-300 C (0-900 C for the SnO₂/Sn system compared to 1100-1200 C for the ZnO/Zn).

• the Sn remains in the reactor and can be separated directly from there or can be hydrolyzed in situ at the end of the day.

Reaction	ΔH [kJ/mole]	ΔH [kJ/kg]	H ₂ [liters]	H ₂ total [liters]	Solar Contributio n
$SnO_2+2C \rightarrow Sn(l)+2CO$	357 (650°C)	2369/kg SnO ₂			
$Sn+H_2O\rightarrow SnO_2+2H_2$	-92.6 (450°C)	-780 kJ/kg Sn	0.38/gr Sn	0.59/gr SnO ₂	36%
ZnO+C→Zn+CO	241.6 (950°C)	2968 kJ/kg ZnO			
$Zn+H_2O\rightarrow ZnO+H_2$	110.8 (450°C)	-1694.2 kJ/kg Zn	0.34/gr Zn	0.55/gr ZnO	48%

