Thermochemical Power Group

Sustainable Energy

Mod.1: Fuel Cells & Distributed Generation Systems

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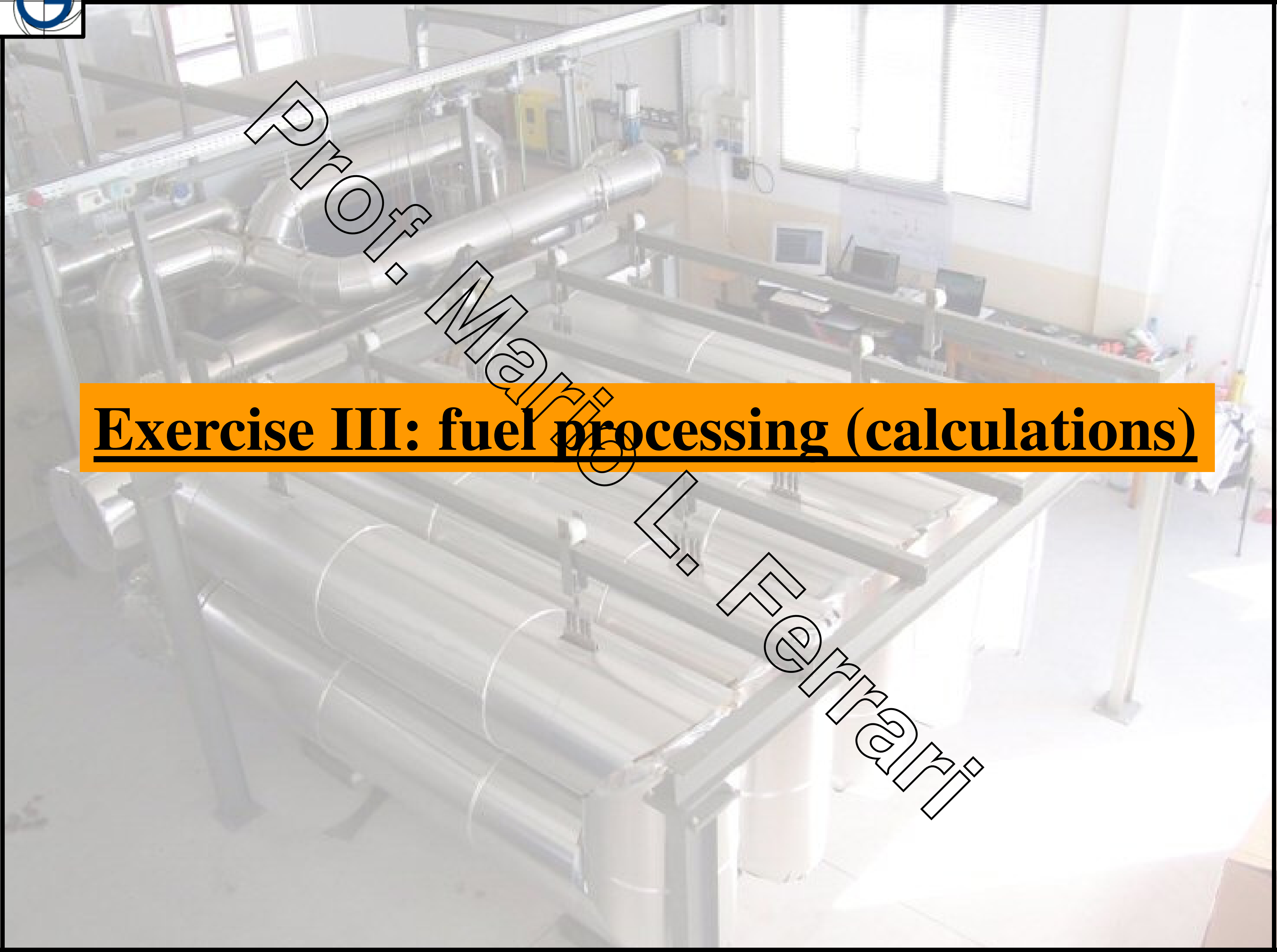

Exercise III: fuel processing (calculations)

Exercise 1: Given a steam reformer operating at 1400ºF, 3 atm, pure methane feed stock, and a steam to carbon ratio of 2 (2 lb mol H_2O to 1 lb mol CH_4), (a) List the relevant reactions; (b) Determine the concentration assuming the effluent exits the reactor in equilibrium at 1400ºF; (c) Determine the heats of reaction for the reformer reactions; (d) Determine the reformer heat requirement assuming the feed stocks are preheated to 1400ºF; (e) Considering LeChâtelier's Principle, indicate whether the reforming reaction will be enhanced or hindered by an elevated operating temperature; (f) Considering LeChâtelier's Principle, indicate whether increased pressure will tend to promote or prevent the reforming reaction.

Solution (1/3):

•The relevant reactions for the steam reformer are:

$$CH_4 + H_2O \Leftrightarrow 3H_2 + CO$$ (Steam Reforming Reaction)

$$CO + H_2O \Leftrightarrow CO_2 + H_2$$ (Water Gas Shift Reaction)

•Composite reaction (reforming+shifting): $CH_4 + 2H_2O \Leftrightarrow 4H_2 + CO_2$

•The determination of the equilibrium concentrations is a difficult problem.

•In Exercise 7 for fuel cells, hydrogen was consumed within the fuel cell, thus driving the reforming reaction to completion.

•Without being able to assume the reforming reaction goes to completion, two independent equilibrium reactions must be solved simultaneously.

•Minimization of Gibbs free energy with ASPEN™ software:

	Inlet Composition (lb mols/hr)	Effluent Composition (lb mols/hr)	Effluent Composition (mol fraction)
CH_4	100	11.7441	2.47
CO	0	64.7756	13.59
CO_2	0	23.4801	4.93
H_2	0	288.2478	60.49
H_2O	200	88.2639	18.52
Total	300	476.5115	100.00

Solution (2/3):

- This problem is rather time-consuming from thermodynamic fundamentals
- From Girdler tables:

$CH_4 + H_2O \Leftrightarrow 3H_2 + CO$	ΔH_r(1800 °F)= 97,741 Btu/lb mol
$CO + H_2O \Leftrightarrow CO_2 + H_2$	ΔH_r(1800 °F)= -13,892 Btu/lb mol

- A positive heat of reaction is endothermic (heat must be added to maintain a constant temperature), while a negative heat of reaction is exothermic (heat is given off).
- Note: 1 Btu = 1.05 kJ (Btu = British thermal unit)
- With knowledge of the equilibrium concentration and the heats of reaction, the heat requirement for the reformer can be approximated.
- Knowing that for each lb mol of CH_4 feed, 88.3% [(100-11.7)/100= 88.3 percent] of the CH_4 is reformed and and 26.6% [23.5/88.3= 26.6%] of the formed carbon monoxide shifts to carbon dioxide,
- .Heat required (ref.) (Btu/lb mol): Q_{ref}=97,741*0.883=86,305 Btu/lb mol
- Heat produced (shift): Q_{shift}=(-13,892)*0.883*0.266=-3,262 Btu/lb mol
- So, the heat requirement for reformer is: Q = 83043 Btu/lb mol
- This approximate value neglects the change in sensible heat in taking the reactants from 1400 °F to the reference temperature of 1800 °F, and then the products from the reference temperature (1800 °F) back to 1400 °F.

Solution (3/3):

•LeChâtelier's Principle states: "*if a stress is applied to a system at equilibrium, then the system readjusts, if possible, to reduce the stress*".

•To facilitate the application of the principle, write the endothermic reforming reaction (which is the dominant heat of reaction) with a heat term on the left side of the equation.

$$CH_4 + H_2O + Heat \Leftrightarrow 3H_2 + CO$$

•Consider that raising the temperature of the system is the applied stress.

•**Reforming reaction is favored by high temperatures.**

•To solve this application of LeChâtelier's Principle, write the reforming reaction in terms of the number of gaseous molecules on the left and right sides.

$$CH_{4(g)} + H_2O_{(g)} \Leftrightarrow 3H_{2(g)} + CO_{(g)}$$

$$2Molecules_{(g)} \Leftrightarrow 4Molecules_{(g)}$$

•Now imagine the reformer at equilibrium, and increase the pressure (the applied stress).

•Because a reduction in the number of molecules will reduce the stress, **elevated pressure will tend to inhibit the reforming reaction**.

•Reformers often operate at moderate pressures (it reduces costs too).

Exercise 2: Given the problem above, (a) List three potential coking (carbon deposition, or sooting) reactions, and (b) Considering LeChâtelier's Principle, indicate whether excess steam will tend to promote or inhibit the coking reactions.

Solution (1/2):

•Three of the most common/important carbon deposition equations are:

$CH_4 \Leftrightarrow C + 2H_2$	(Methane Coking)
$2CO \Leftrightarrow C + CO_2$	(Boudouard Coking)
$CO + H_2 \Leftrightarrow C + H_2O$	(CO Reduction)

•Considering LeChâtelier's Principle, the addition of steam will clearly inhibit the formation of soot from the CO reduction reaction.

•The introduction of excess steam will encourage the reaction to proceed towards the reactants.

•Excess steam does not have a direct effect on Methane coking or Boudouard coking reactions except that the presence of steam will dilute the reactant and product concentrations.

Solution (2/2):

- Because reaction is not equimolar: the Methane coking reaction will be driven forward while the Boudouard coking reaction will reverse.
- reverse reaction of CO-reduction stimulated by excess steam will increase the presence of CO, driving the Boudouard coking reaction forward.
- Overall, **the addition of steam is useful** at preventing soot from ruining the expensive catalysts used in reformers and fuel cell systems. Too much steam, however, simply adds an unnecessary operating cost.
- When temperature drops to about 750 ºC, kinetic limitations preclude sooting.
- Typically, steam reformers have operated with steam to carbon ratios of **2 to 3**, depending on the operating conditions in order to provide an adequate safety margin.