Solar thermochemical energy storage; lessons from 40 years of investigation in Australia

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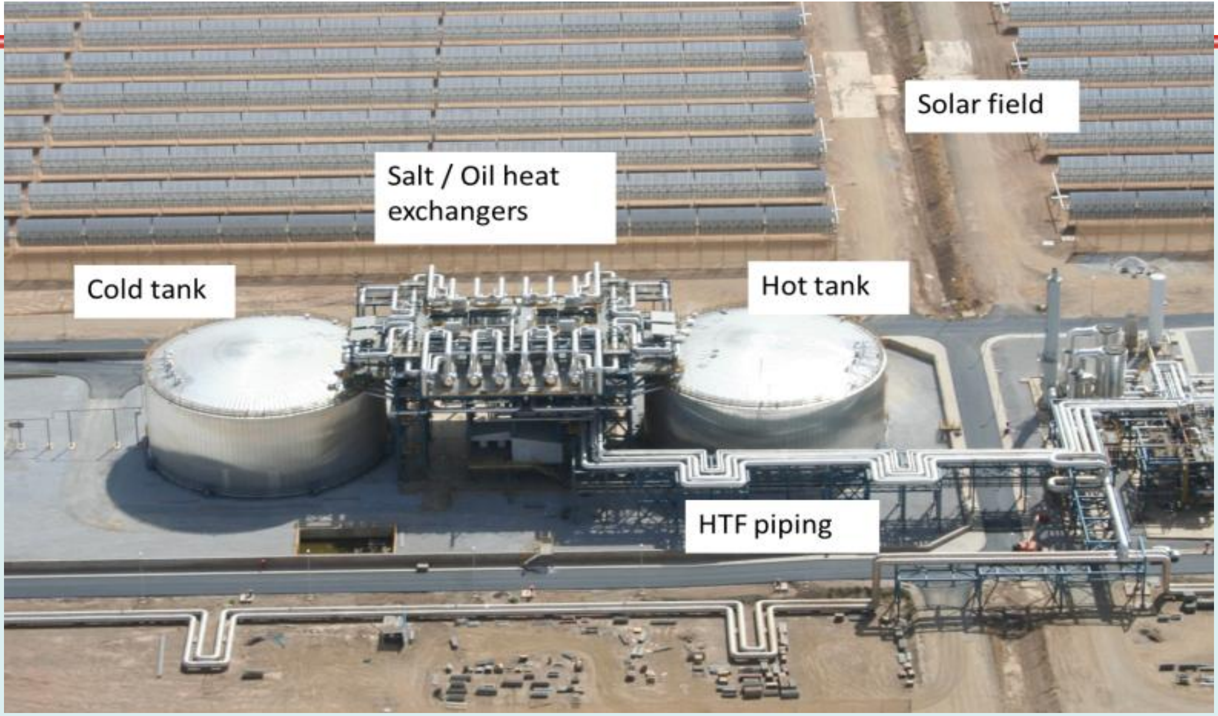
Thermal Energy Storage – the dominant approach with molten salt

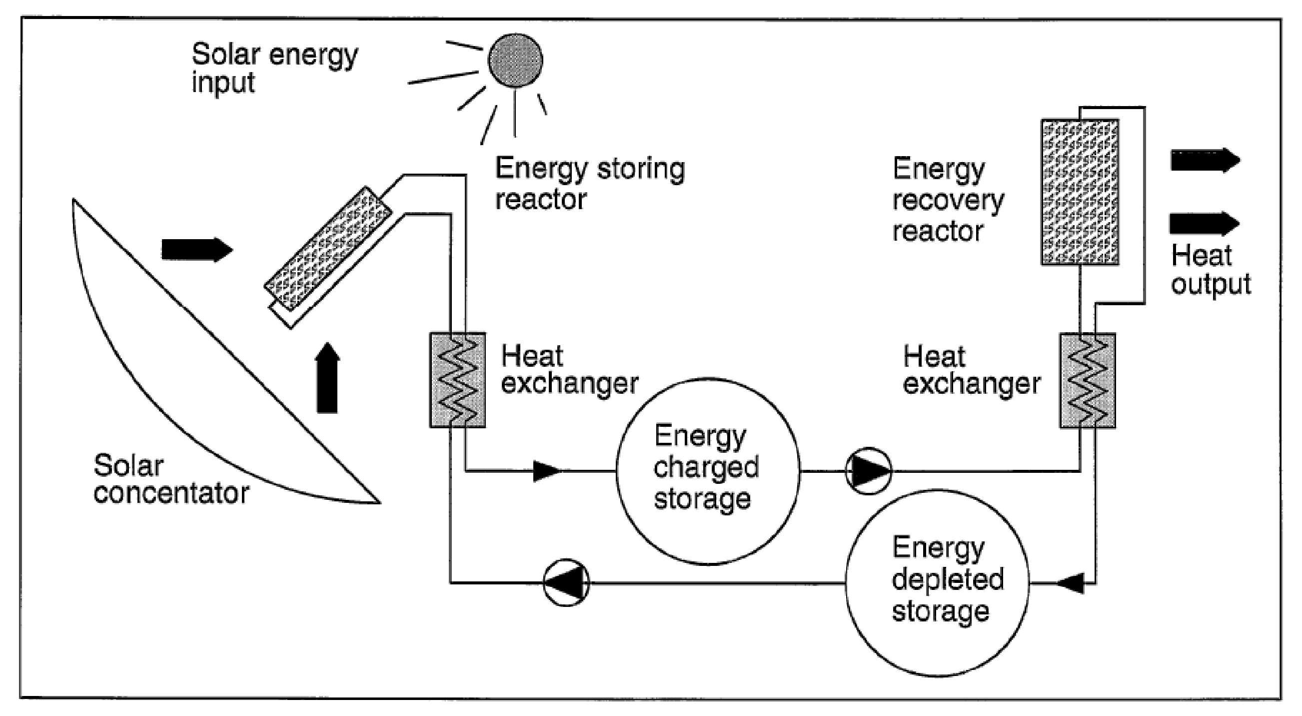


Background pic, Andasol 3 courtesy Ferrostaal

- Thermal storage is “integrated” – improves output, little or no extra cost
- Two tank molten salt is proven / standard (62% plants in Spain)
- A Higher temperature range makes it cheaper
- Steam accumulators are also proven for up to 1 hour storage
- Other options in R&D phase

What is Solar Thermochemical Energy Storage?

- Reversible endothermic chemical reactions driven by solar heat to Store energy over short or long time scales



- “Solar Fuels” are the special case where the endothermic reaction releases oxygen that can be released into the atmosphere and later re-absorbed during combustion / oxidation.

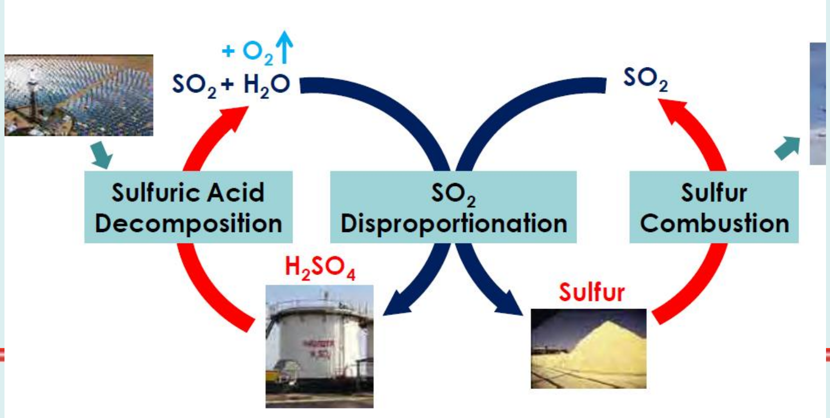
Why Solar Thermochemical Energy Storage?

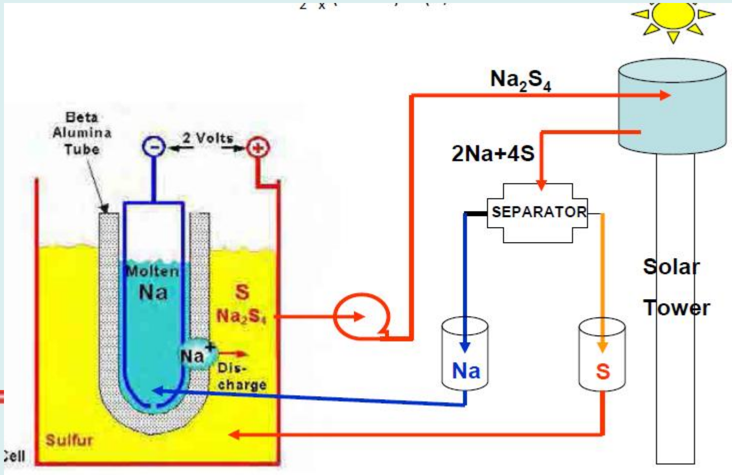
- Use high energy density configurations for centralised energy stores for CSP power systems.
- Use fluid phase reactants to provide energy transport by a “chemical heat pipe”.
  - from collector field to power block or
  - from remote CSP system to load centre..
- Produce “solar fuels” for
  - international energy transport
  - alternative transport fuels
  - Inputs to high efficiency electricity generation

“This workshop is focused exclusively on solar-to-electric conversion and NOT on solar-to-fuels or other applications that do not result in electricity generation” (SunShot whitepaper on TCES).

Point taken, but consider:

- Any “solar fuel” could potentially be used for
  - Combustion in a conventional high efficiency combined cycle power plant
  - Conversion in a fuel cell
- Thermally charged batteries such as zinc/air or Sodium/Sulfur are very interesting new manifestation of a thermally charged fuel cell.

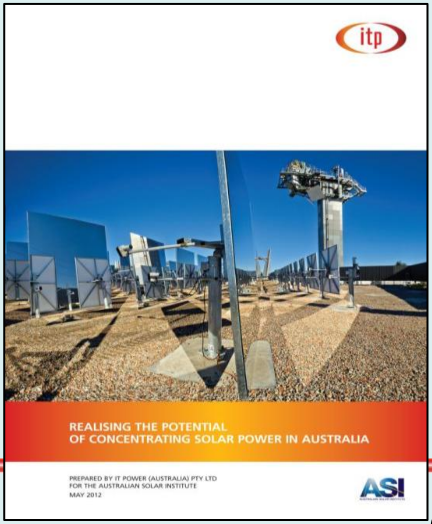




Competitive electricity markets value solar with storage for dispatchability

	Wholesale Market average price	Solar Immediate dispatch average sale price	Ratio immediate / market av	Solar Dispatch from storage average sale price	Ratio Storage / market av
AUSTRALIAN AVERAGE 2005 -2010	**$43.41 / MWh**	**$62.27 / MWh**	**1.43**	**$87.04 / MWh**	**2.01**

- Numbers from “realising the potential of CSP in Australia
- Report by ITPower for the Australian Solar Institute.
- http://www.australiansolarinstitute.com.au/reports/.aspx



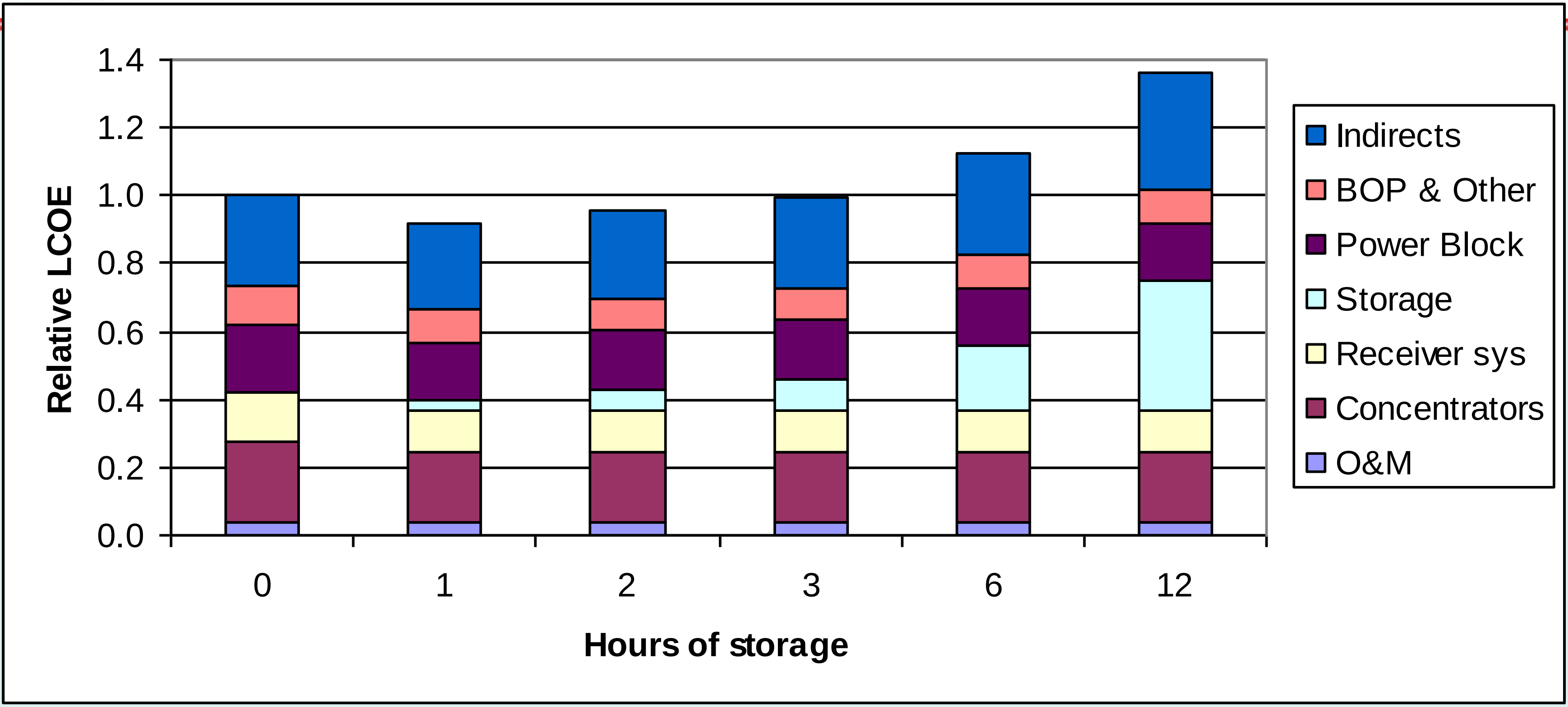
REALISING THE POTENTIAL
OF CONCENTRATING SOLAR POWER IN AUSTRALIA

PREPARED BY IT POWER (AUSTRALIA) PTY LTD
FOR THE AUSTRALIAN SOLAR INSTITUTE
MAY 2012

But systems with storage are higher capital cost

	No storage (lowest capital cost)	2 hours storage (approx min LCOE)	5 hours storage (earns higher value)
Configuration	100 MW_e block, 350 MW_{th} field, 21% cap factor at 2,400 $kWh/m^2/year$	100 MW_e block, 395 MW_{th} field, 30% cap factor at 2,400 $kWh/m^2/year$	100 MW_e block, 526 MW_{th} field, 40% cap factor at 2,400 $kWh/m^2/year$
Specific installed cost (AUD 2012)	\$4653 / kW_e	\$5534 / kW_e	\$7350 / kW_e

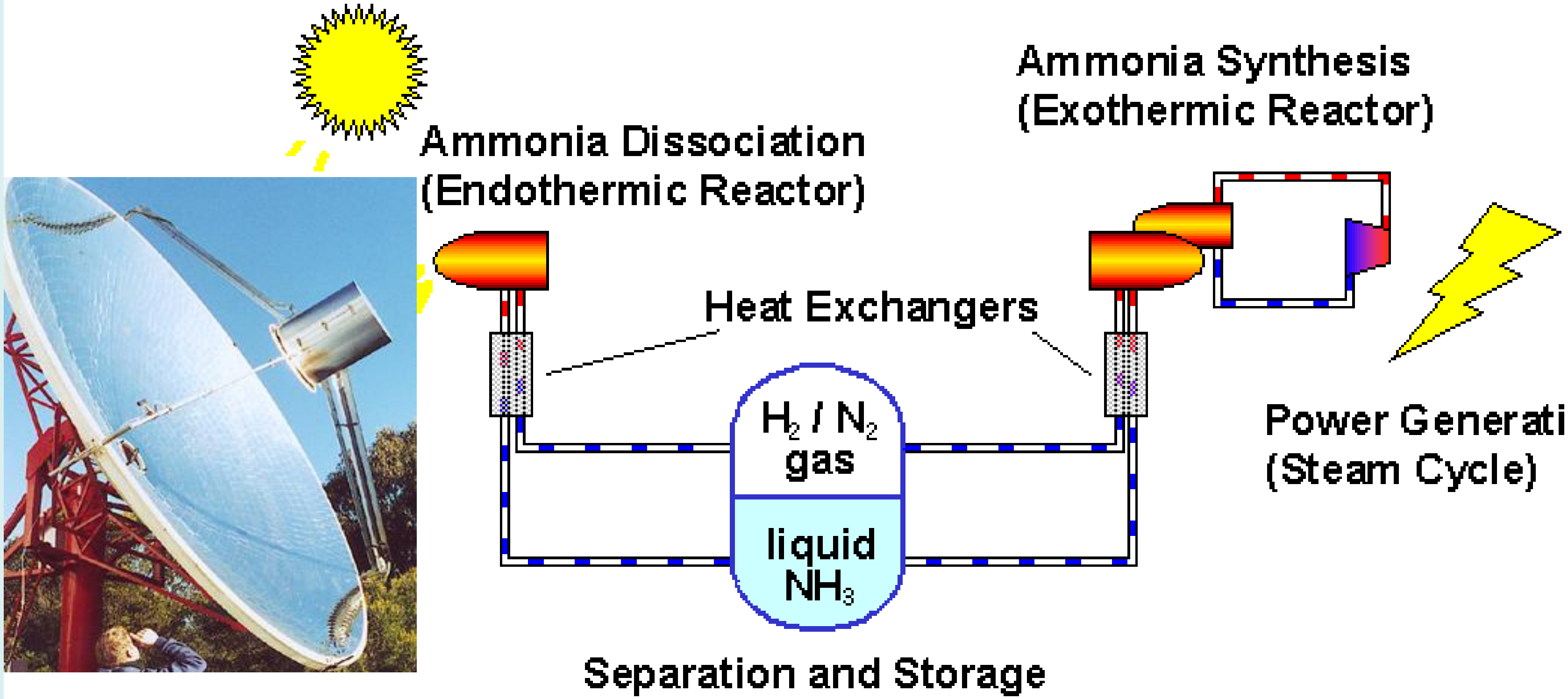
Some storage reduces LCOE



- More storage is higher LCOE but offers higher “value” energy
- “The goal of the Concentrating Solar Power (CSP) Program within the SunShot Initiative is to reduce the cost of electricity generated from a CSP power plant to $0.06/kWhe, without subsidy, by the year 2020.”

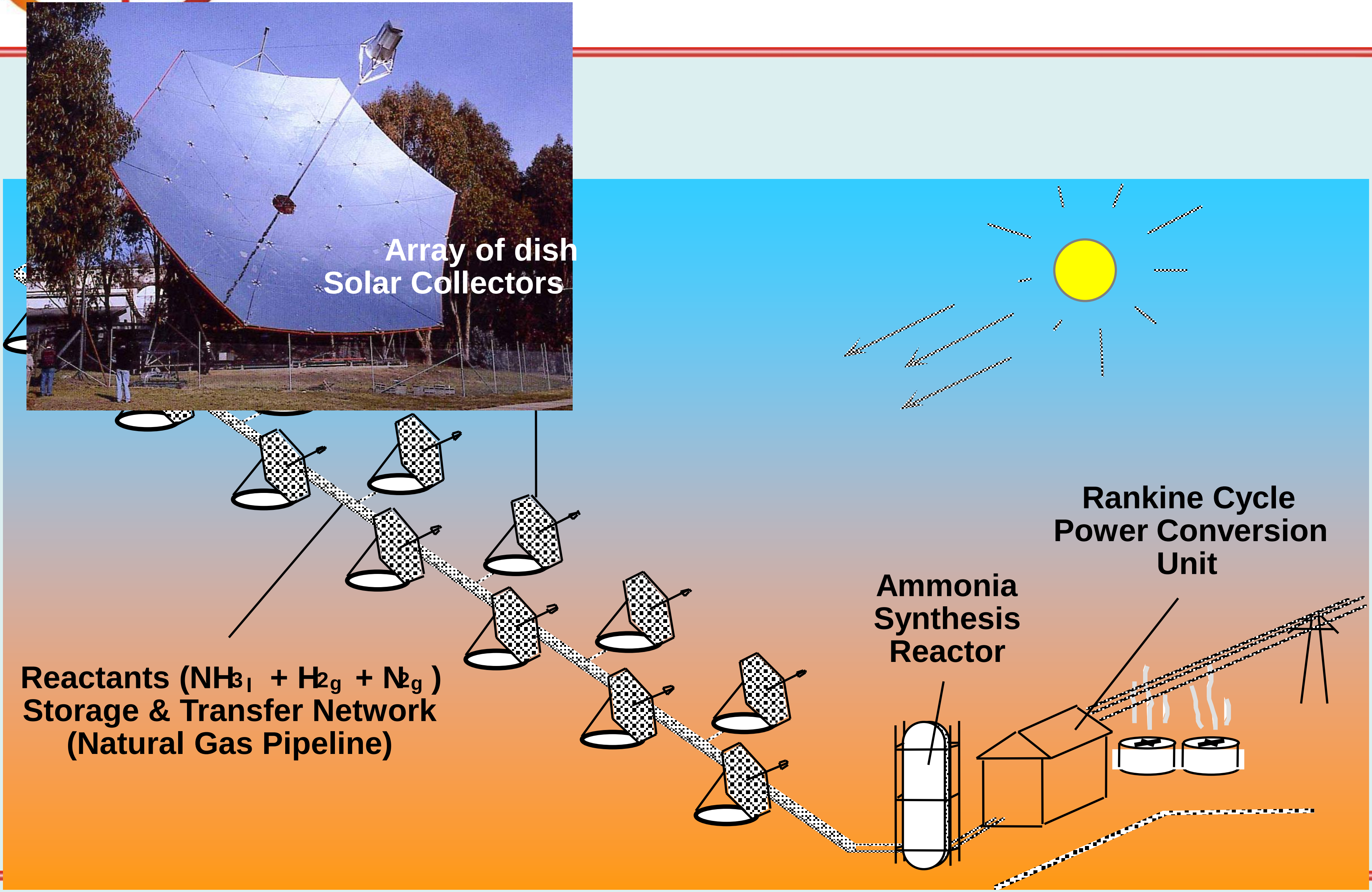
Beware of perverse outcomes from LCOE based targets!!!

Ammonia based thermochemical Energy Storage



$$NH_3 + 66.8\text{kJ/mol} \rightleftharpoons 1/2N_2 + 3/2H_2$$

Dish Power Plant concept



Array of dish Solar Collectors

Rankine Cycle Power Conversion Unit

Ammonia Synthesis Reactor

Reactants ($NH_{3\,l} + H_{2\,g} + N_{2\,g}$)
Storage & Transfer Network
(Natural Gas Pipeline)

Dishes, ammonia thermochemical energy storage at ANU over 40 years

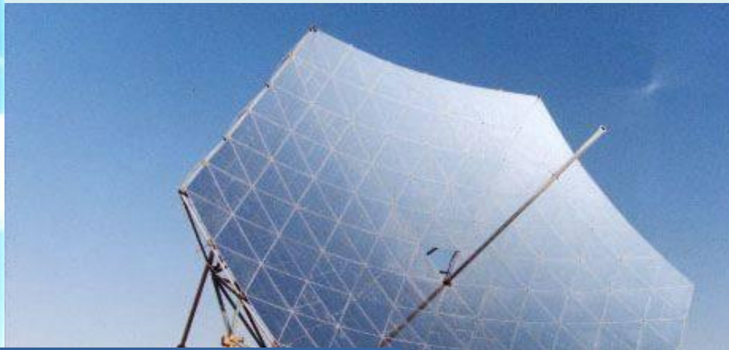
- Invented 1971 – Peter Carden, various studies during 70’s and 80’s
- First solar reactor 1994
- 10MWe System study Dec 1997
- First lab closed loop 10th April 98
- First solar (1kWsol) loop 26th Sept 98
- Full size (15kWsol) closed loop Dec 99 (IEAust award)
- 24 hr continuous operation May 2002
- 2002 – 2012 Alternative catalysts, trough operation and receiver optimisation

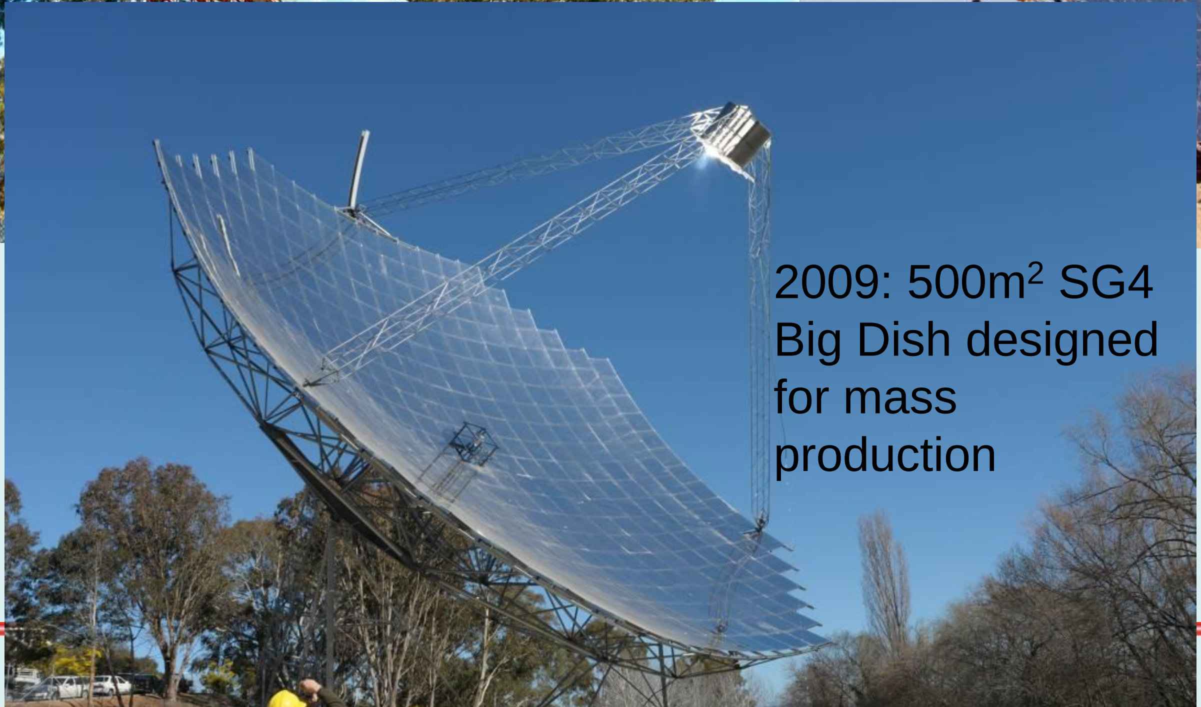
In parallel with dish development – a combined systems approach

1980: White Cliffs 14 x 20m^2 dishes

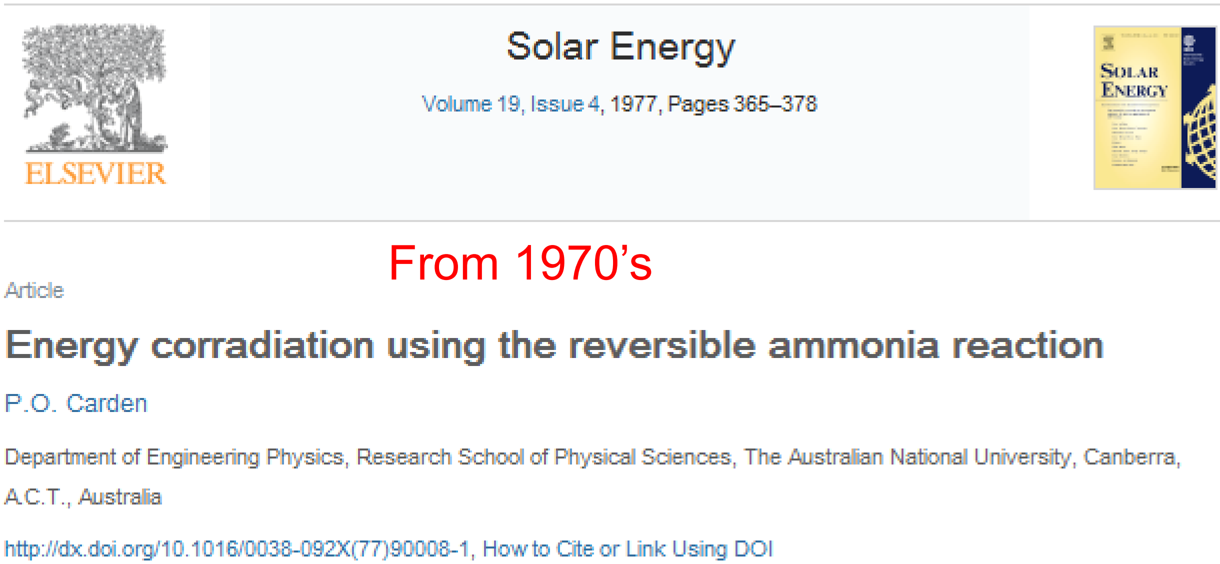
1994: 400m^2 SG3 Big Dish

1998: 400m^2 System for BGU Israel





2009: 500m^2 SG4 Big Dish designed for mass production


ELSEVIER

Solar Energy

Volume 19, Issue 4, 1977, Pages 365–378

Article

Energy corradiation using the reversible ammonia reaction

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http://dx.doi.org/10.1016/0038-092X(77)90008-1, How to Cite or Link Using DOI

From 1970's

Lesson #1: It only takes 40 years if your don't have enough money!

Lesson #2: Having no money makes you inventive – avoid the pitfalls of too much money!!!


INVITED PAPER

A Review of Ammonia-Based Thermochemical Energy Storage for Concentrating Solar Power

To 2012 and beyond….

By Rebecca Dunn, Keith Lovegrove, and Greg Burgess

ABSTRACT | The development of a thermochemical energy storage system based on ammonia, for use with concentrating solar power is discussed in this paper. This is one of a group of storage options for concentrating solar power, some of which are already operating commercially using molten salts. The ammonia storage development has involved prototype solar receiver/reactors operated in conjunction with a 20-m² dish concentrator, as well as closed-loop storage demonstrations. An ongoing computational study deals with the performance of an ammonia receiver for a 489-m² dish concentrator. The ammonia storage system could employ industry-standard ammonia synthesis converters for superheated steam production. A standard 1500 t/day ammonia synthesis reactor would suffice for a 10-MW$_e$ baseload plant with 330 large 489-m² dishes. At this stage, an updated economic assessment of the system would be valuable.

KEYWORDS | Ammonia; concentrating solar power; dish concentrators; energy storage; thermochemical storage

I. INTRODUCTION

This paper discusses the ammonia-based thermochemical storage system which has been developed for use with concentrating solar power (CSP) systems. As described in several papers within this special issue, CSP systems can AQ provide energy storage fully integrated within the electricity-generating plant—a commercial reality at several CSP plants using molten salt in Spain [1], [2]. Parabolic mirrors in the form of troughs, linear Fresnel, power towers, or dishes are used to concentrate solar radiation to a hot focus. The concentration ratio can be up to 100 for parabolic troughs and linear Fresnel systems, or in excess of 1000 for power towers (central receivers) and dishes—the geometric concentration ratio being the ratio of the area of the receiver aperture to the area of mirror aperture. The heat collected at the focus can be used to produce steam for immediate electricity generation, or alternatively it can be stored prior to electricity generation using molten salt [3], sensible heat storage in solids [4]–[6], phase change salts [7], or thermochemical storage cycles [8].

The thermal approach to energy storage using CSP systems has several potential advantages.

- Because the storage occurs before the conversion of heat to electricity at the turbine/generator set, the difference in overall solar-to-electric conversion efficiency between a system with storage and one without can be close to zero. For example, in commercial molten-salt storage systems, the storage system can have an effective efficiency of 99% [3].
- The actual energy storing components are relatively simple and potentially cost effective.
- Full integration into the system means that some components may actually be reduced in size

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Choosing a reaction – selection criteria include:

- Environmental and health impacts of leaks
- Cost of reactants (LCA basis)
- Presence of undesirable side reactions
- Ease of handling (Fluid / solid)
- Turning temperature in accessible range
- Δh of reaction (high give better storage density)
- Δg/Δh (indicates limit to conversion efficiency)
- Level of industrial experience

"An ideal TCES system would be one that uses liquid reactants, has 100% reversibility, is 100% exergetically efficient, requires the use of no catalyst, uses earth-abundant materials, and takes place at ambient temperature and pressure" (Sunshot TCES white paper).

Criteria should be weighted and different weights apply for different:

- **Locations**
- **Developers**
- **Concentrator technologies**

Fluid Phase favourites

Reaction	**Turning temp (K)**	**DelH at 298k (kj/mol)**	**R&D institutions**
$SO_3 \leftrightarrow SO_2 + 1/2O_2$	1000	98.2	Sandia Labs
$NH_4HSO_4 \leftrightarrow NH3 + H_2SO_4$	1013	132	University of Houston
$CH_4 + H_2O \leftrightarrow 3H_2 + CO$	1285	206.2	University of Houston, CSIRO, DLR
$CH_4 + CO_2 \leftrightarrow 3H_2 + 2CO$	1285	246.8	Sandia, Uni of Houston, DLR, Weizmann Inst, CSIRO, Boreskov Inst
$NH_3 \leftrightarrow 3/2H_2 + 1/2N_2$	751	66.5	ANU, Colorado State Uni

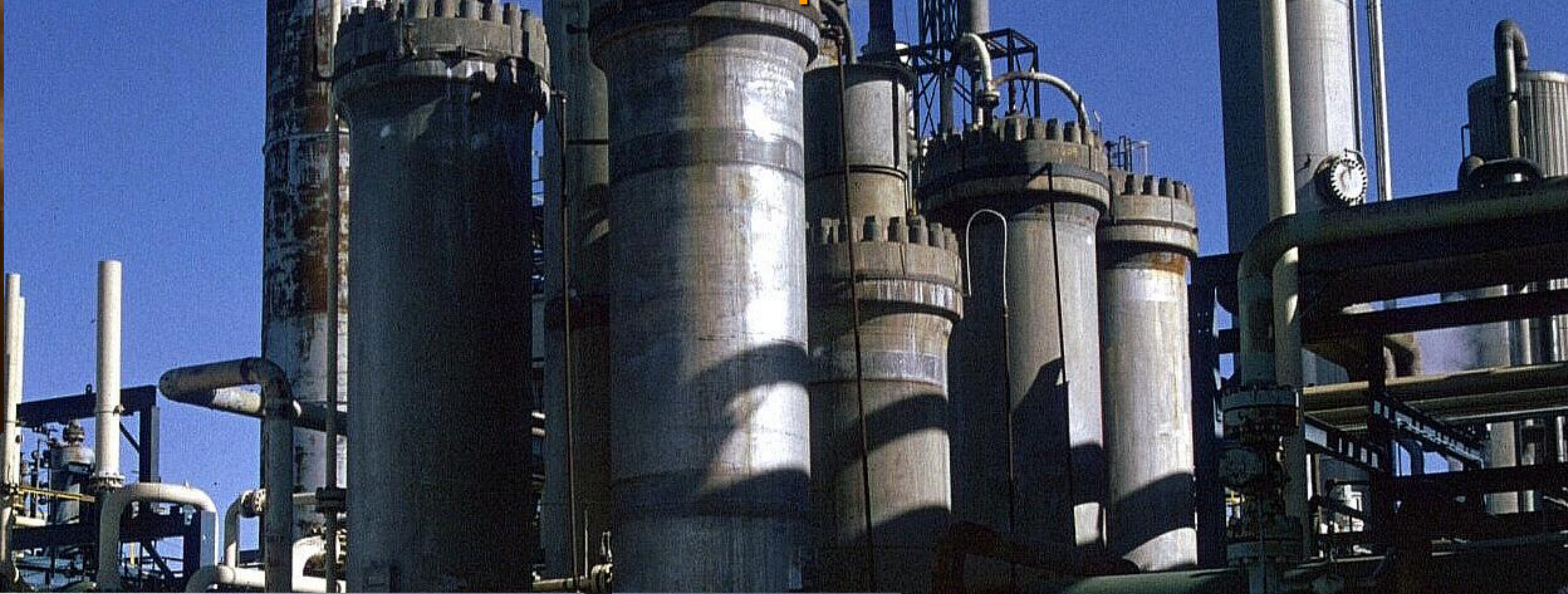
The ammonia based system has

- No undesirable side reactions
- A range of standard catalysts available
- A large background of industrial experience with Haber Bosch process
- Use of mild steel components for handling and storage
- Phase separation of reactants and products at ambient temperature
- No problems with solar transients
- Lower operating temp for higher receiver efficiency and less materials constraints

But

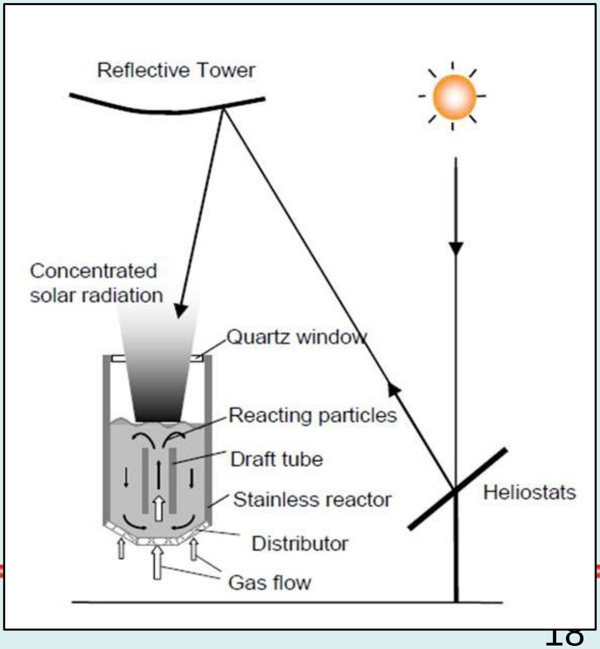
- High operating pressures
- Smallish enthalpy of reaction
- Conversion efficiency limited by low characteristic temperature

Builds on 100 Years of industrial ammonia production based on the Haber Bosch process



A Systems approach to design is essential

- Don’t let the tail wag the dog !
- The ammonia TCES system was developed specifically for a distributed collector field CSP application
- A provocative question: are beam down tower systems for ground mounted reactors really an optimum mix of cost and performance across the system???



A Systems approach to design is essential

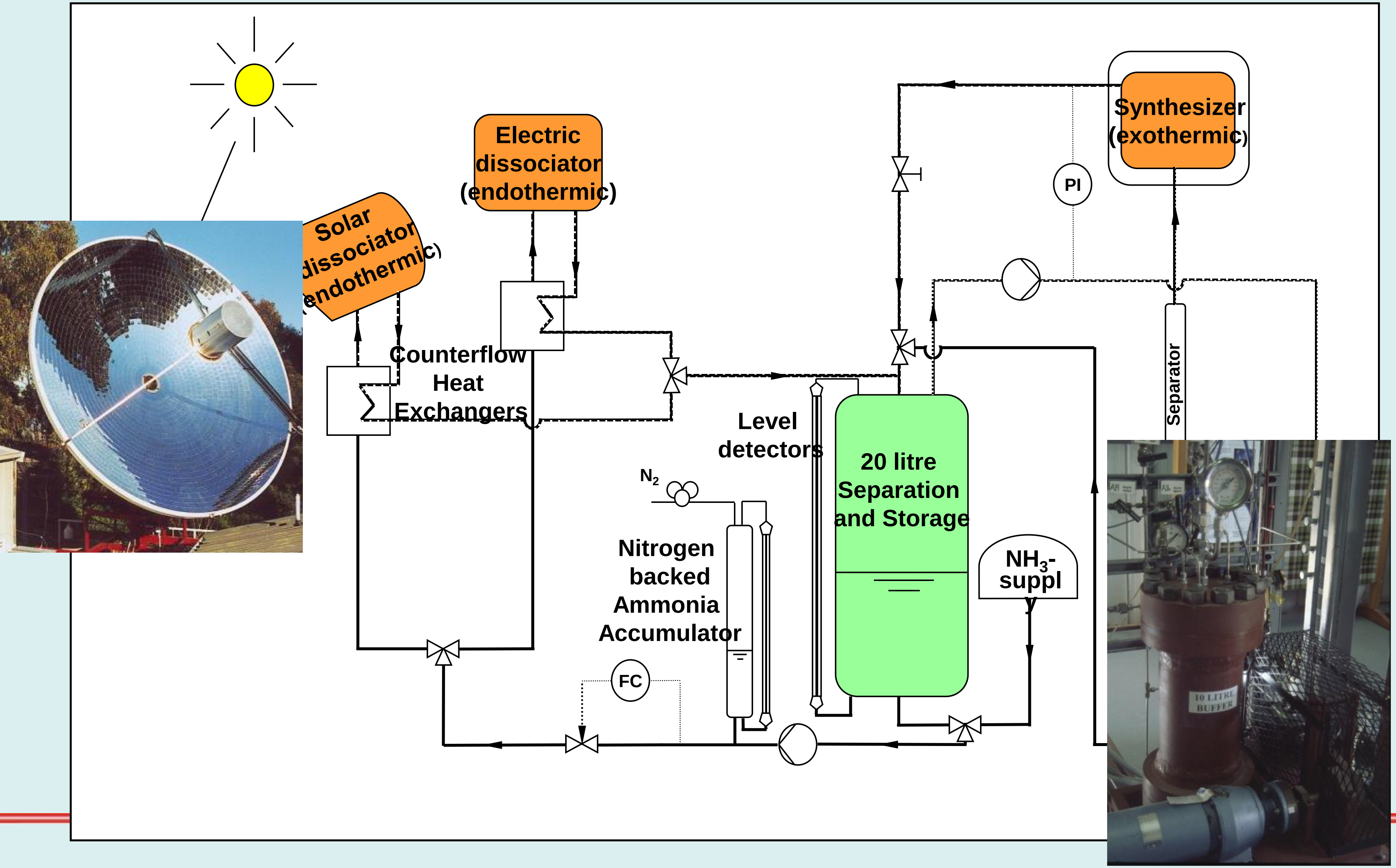
Things to consider:

- A chemical heat pipe avoids thermal losses from HTF lines
- High pressures and low Δh are challenging, but actually help to improve heat transfer rates
- Could an exothermic reactor be a thermal as well as thermochemical store?
- Direct work output from exothermic reactor has potential to improve performance and reduce cost
- Could storage volumes double as
  - structural elements
  - heat sinks
  - long distance chemical heat pipes?

Modular vs Integrated design

- Modular = Careful interface specification and separate subsystem design
- Integrated = making one thing do multiple jobs
- High O&M elements like receivers are best modular eg
  - Reveiver tube modules designed for mass production
  - Receiver units designed for rapid replacement
- High capital cost, complex items are likely to be more economic if integrated eg
  - Direct work recovery from reactants instead of heat transfer to steam
- Integrated design is harder to develop and riskier through the development phase, but can pay off in the long run

Solar Closed Loop Project



Solar dissociator (endothermic)

Electric dissociator (endothermic)

Synthesizer (exothermic)

PI

Counterflow Heat Exchangers

Level detectors

20 litre Separation and Storage

Separator

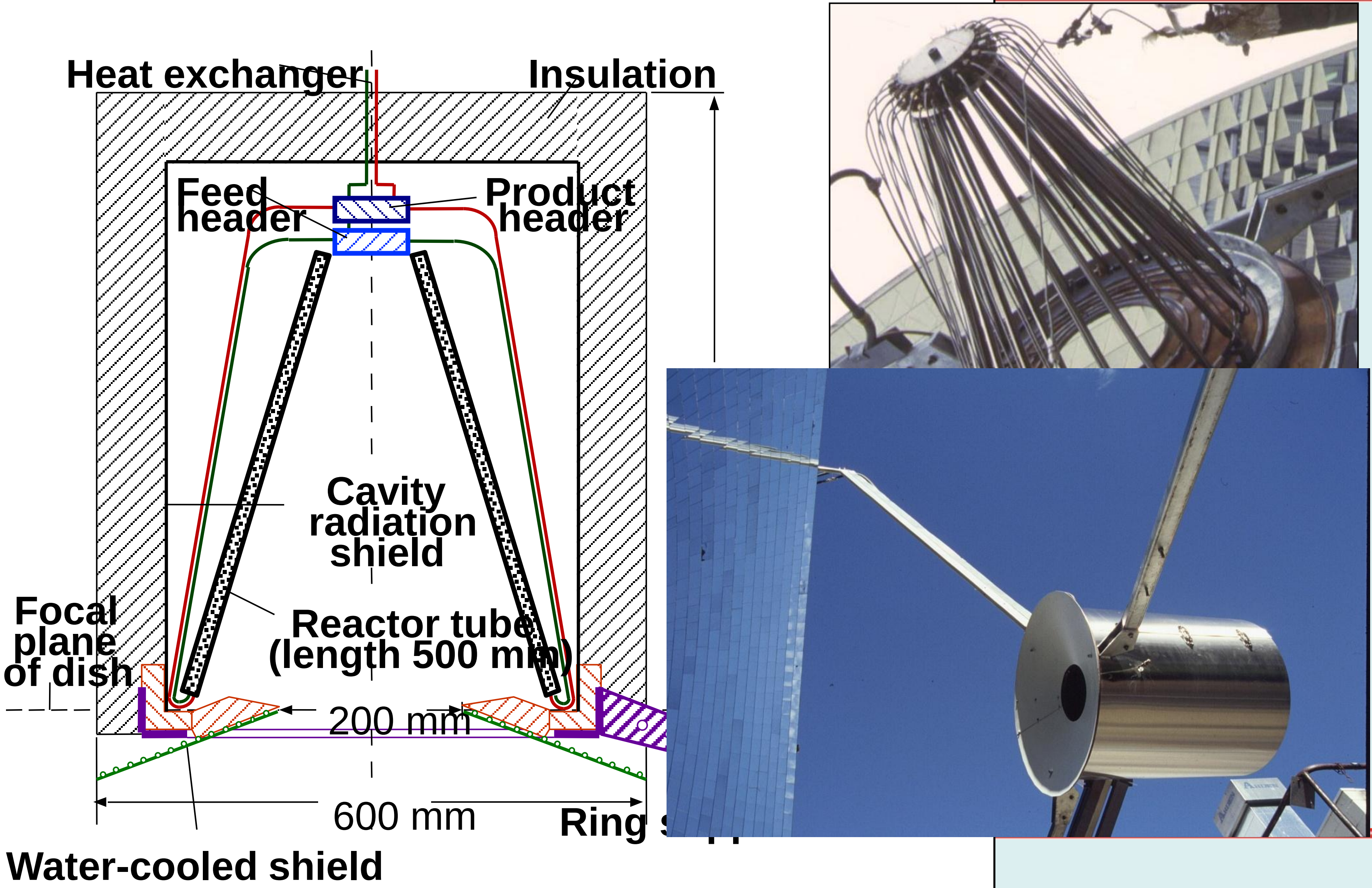
N_2

Nitrogen backed Ammonia Accumulator

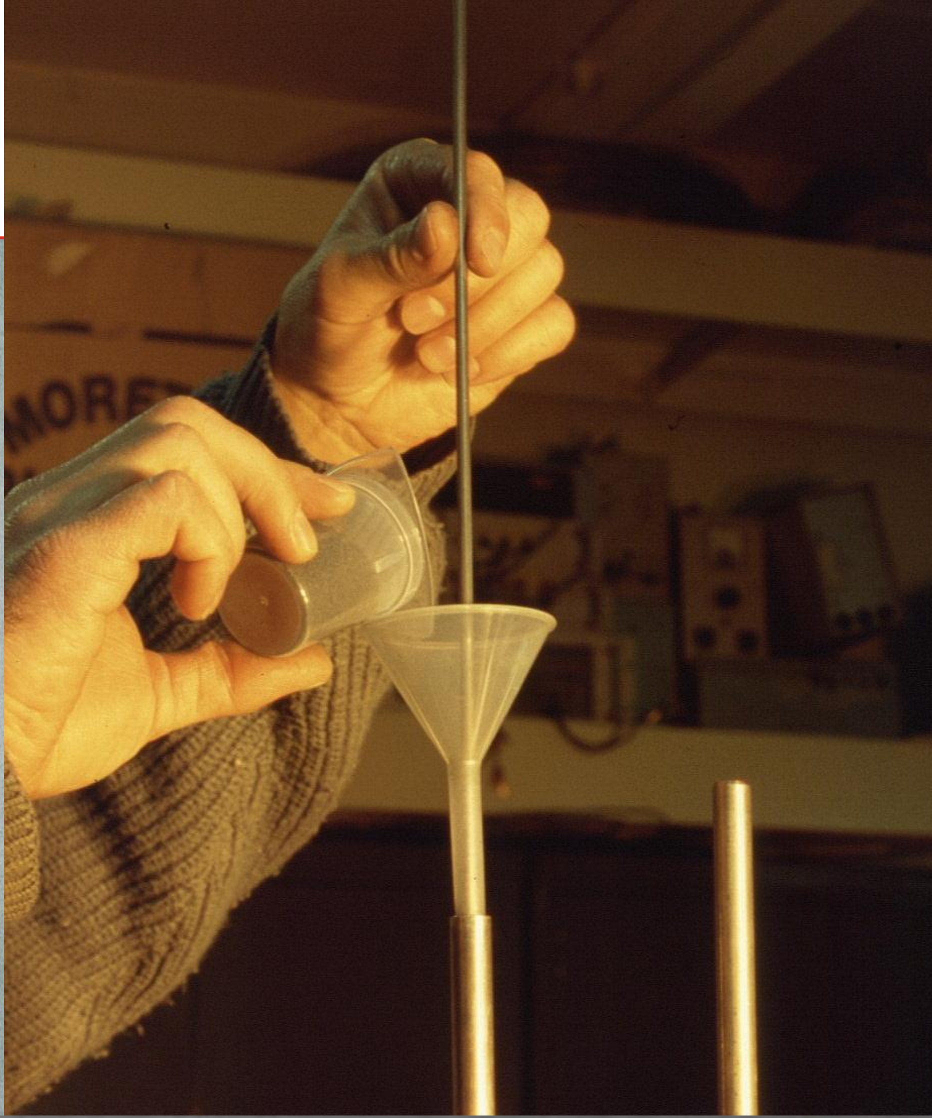
FC

NH_3-supply

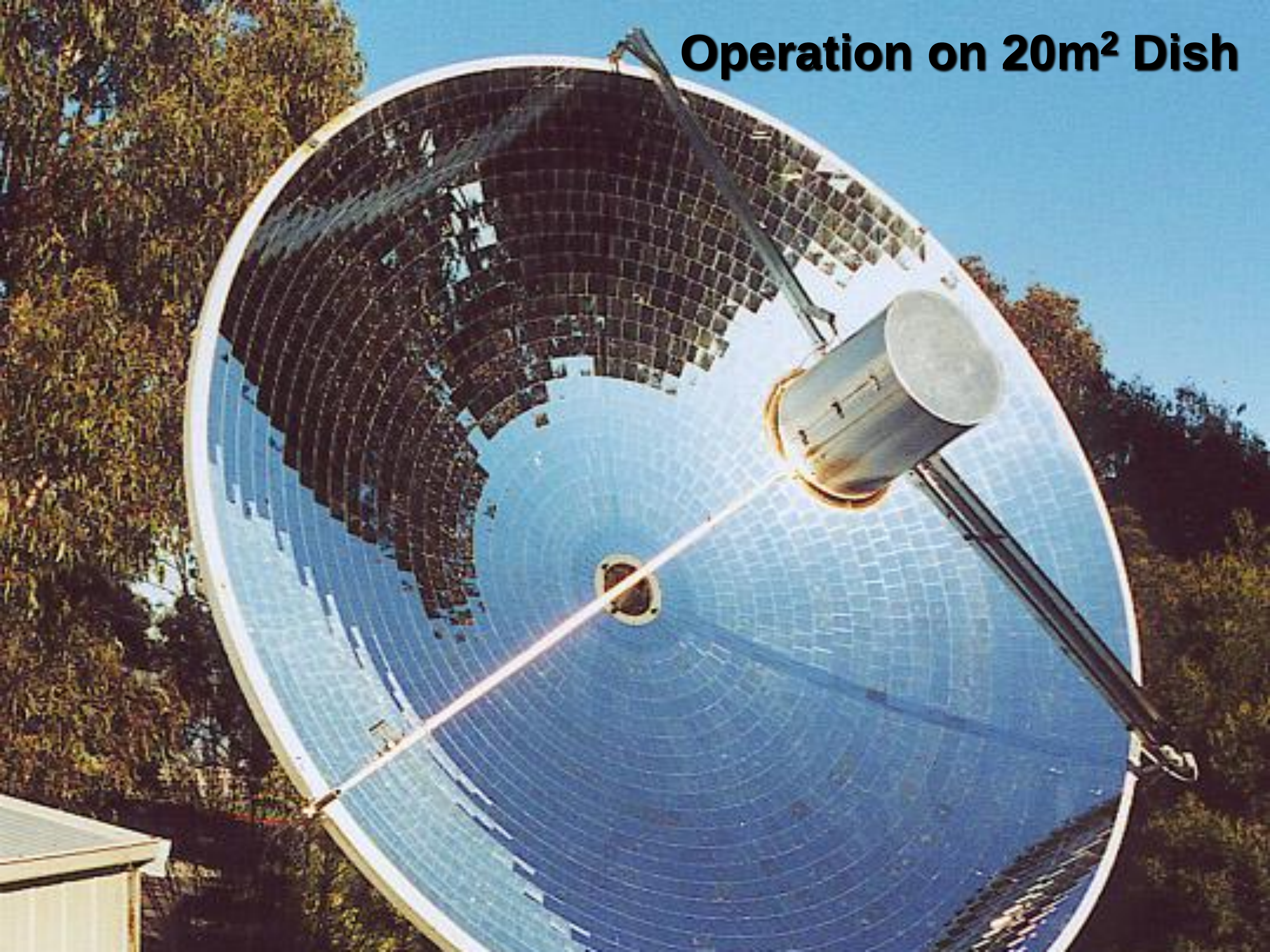
12 kW Receiver / Reactor



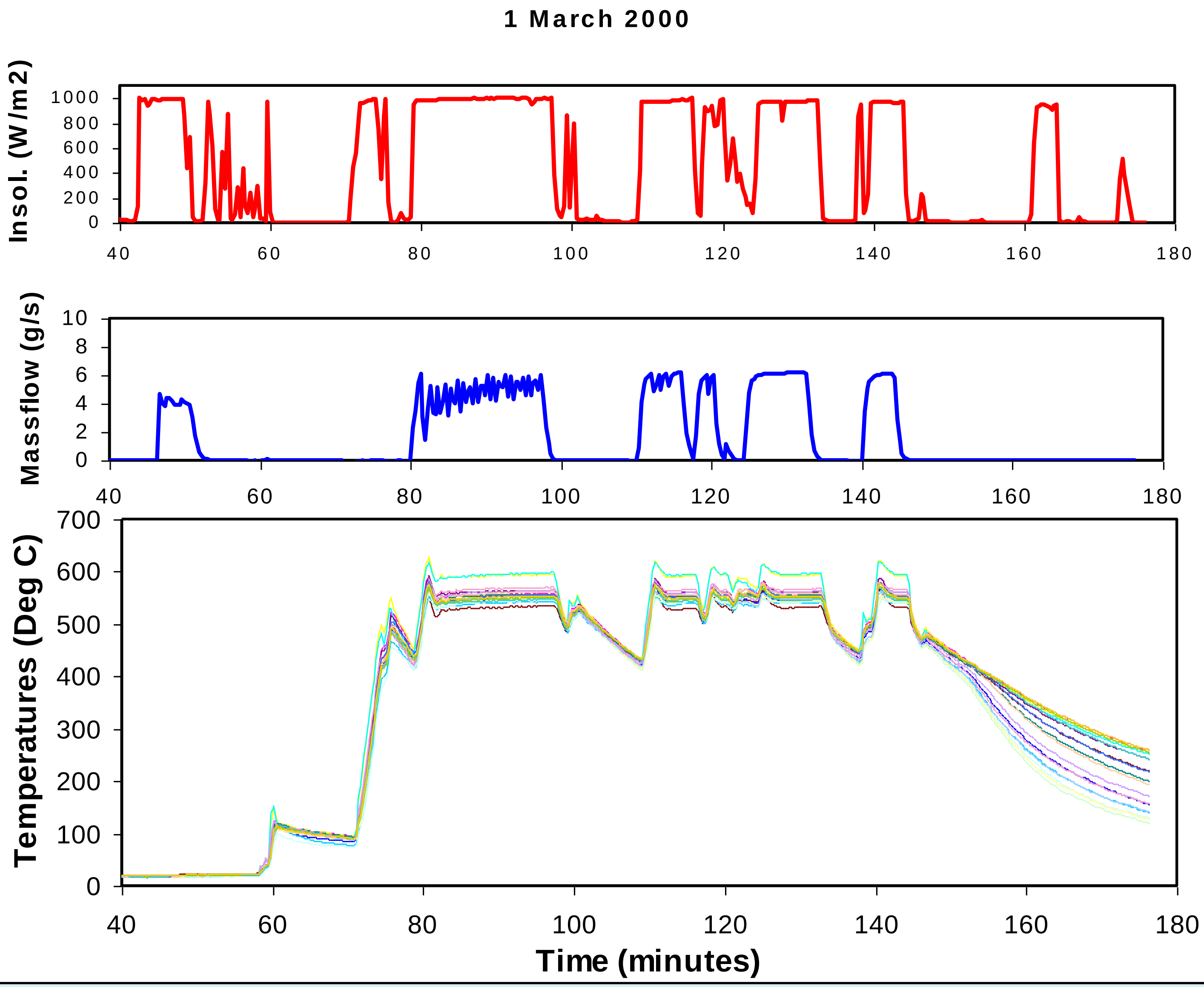
Modular, mass-produceable easily replaceable reactor tubes



Operation on 20m^2 Dish

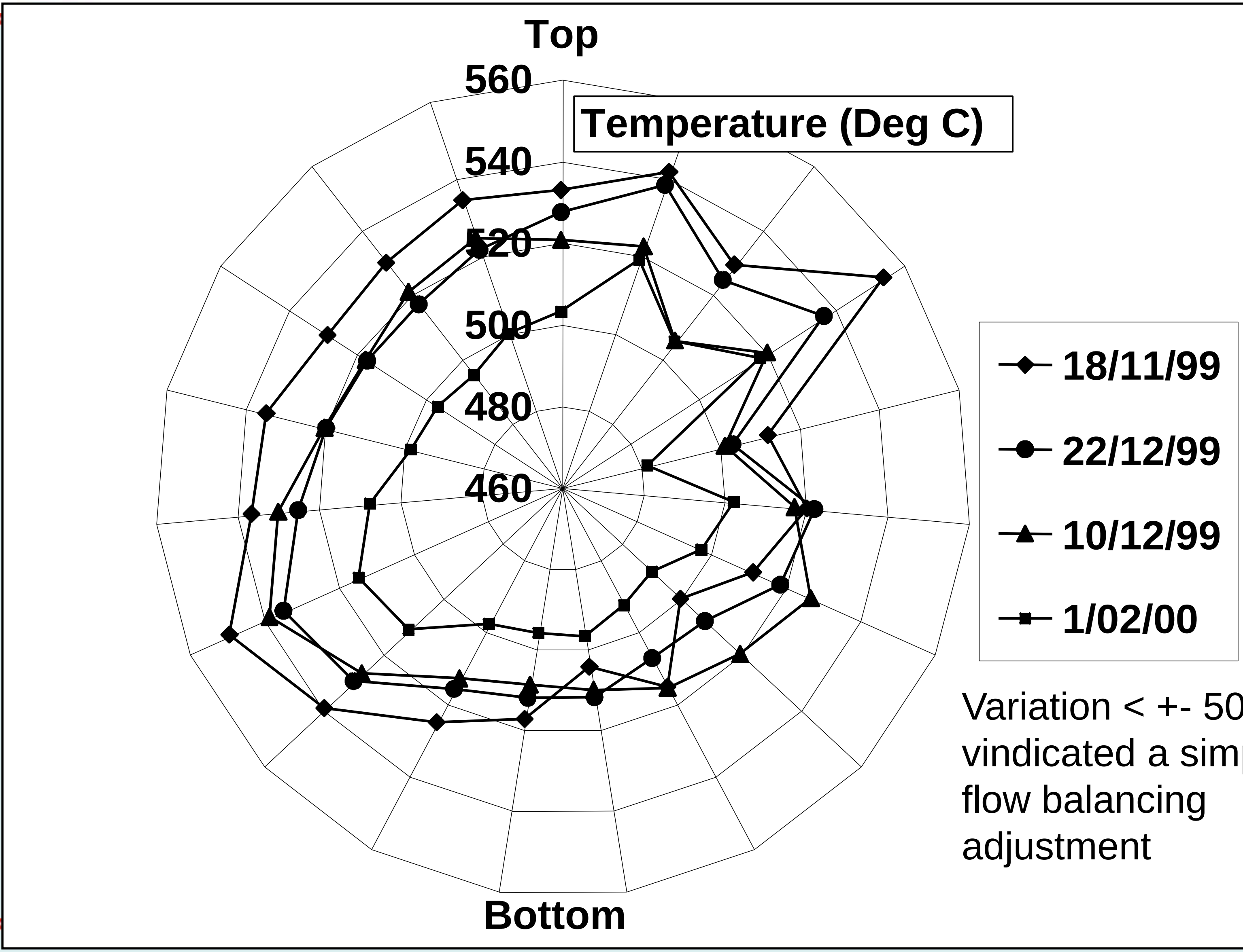


T control via massflow



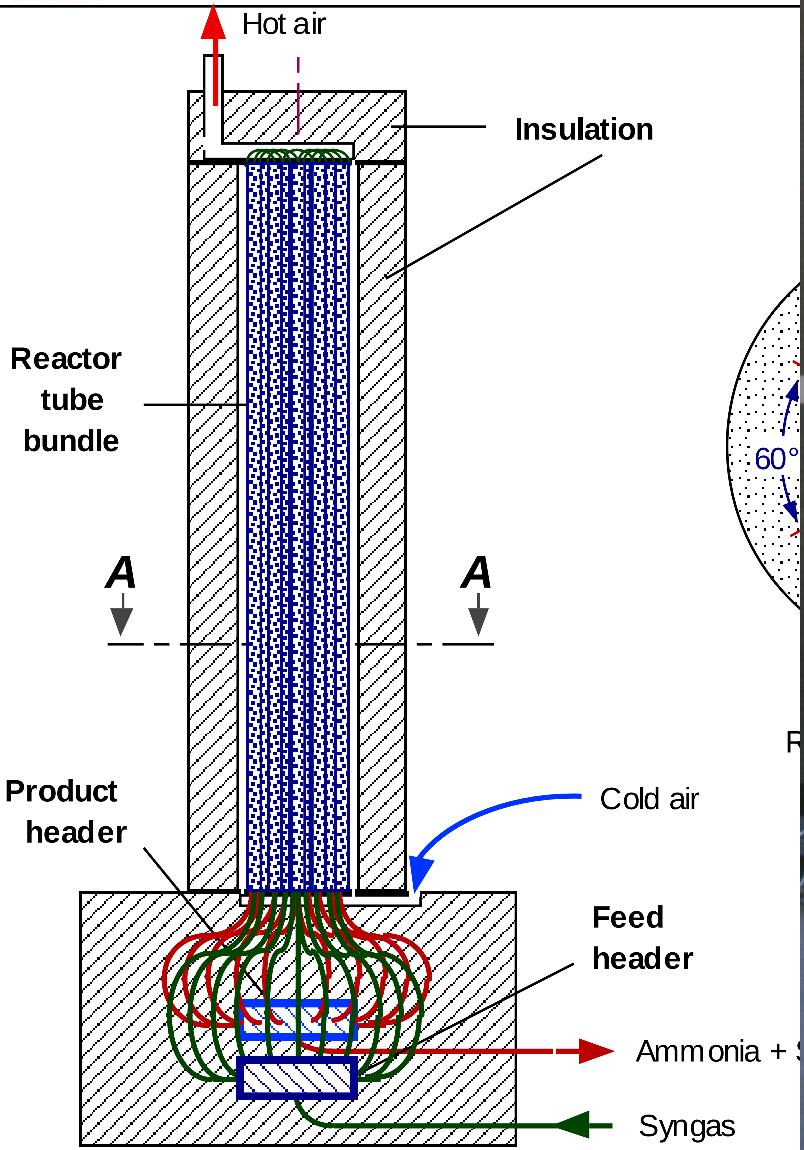
Simple, robust and handles transients with ease

Variation between tubes



Variation < +- 50°C, vindicated a simple fixed flow balancing adjustment

10kW Heat Recovery Reactor


Hot air

Insulation

Reactor tube bundle

A

A

Product header

Cold air

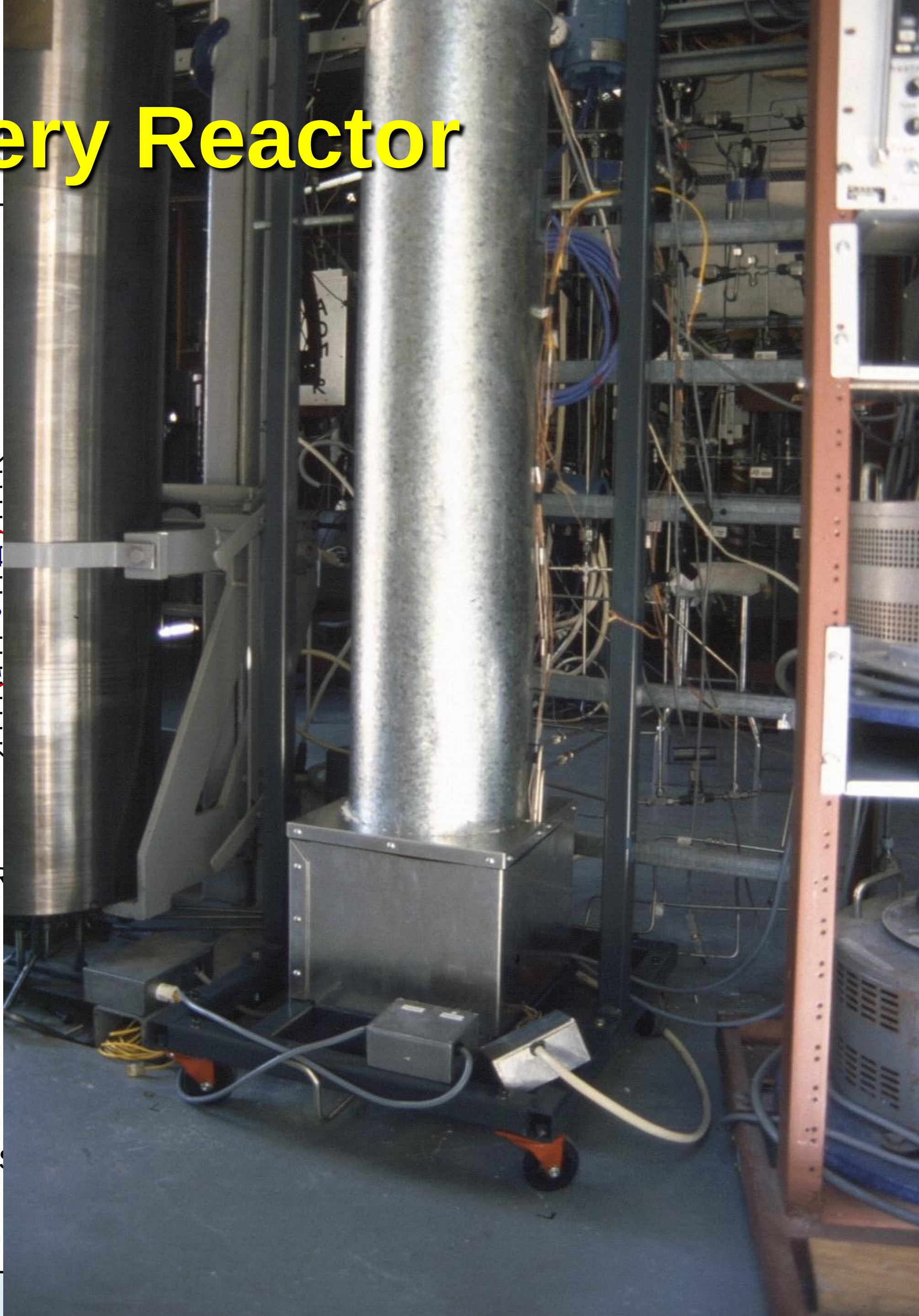
Feed header

Ammonia +

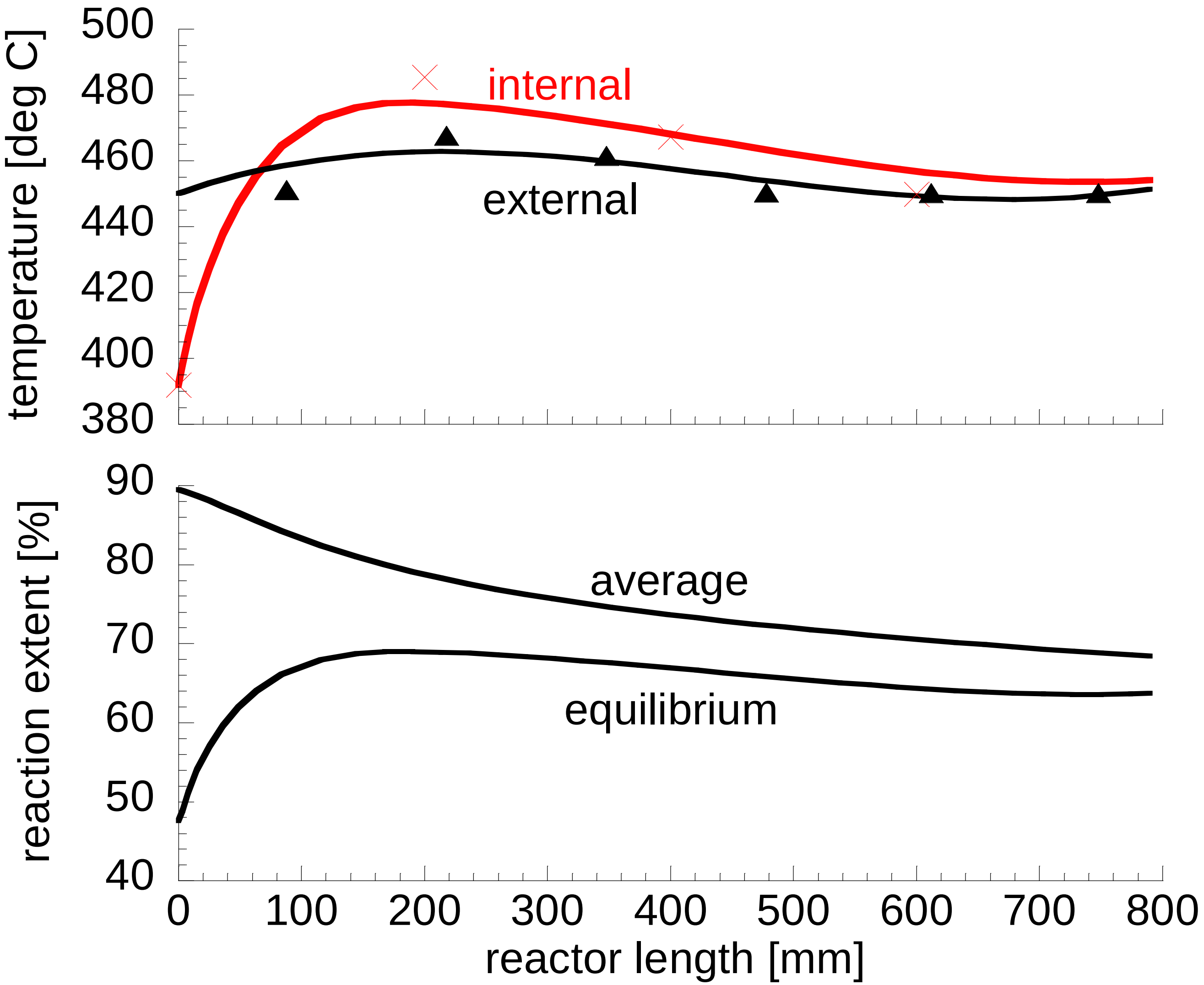
Syngas

60°

R



Heat recovery temperatures



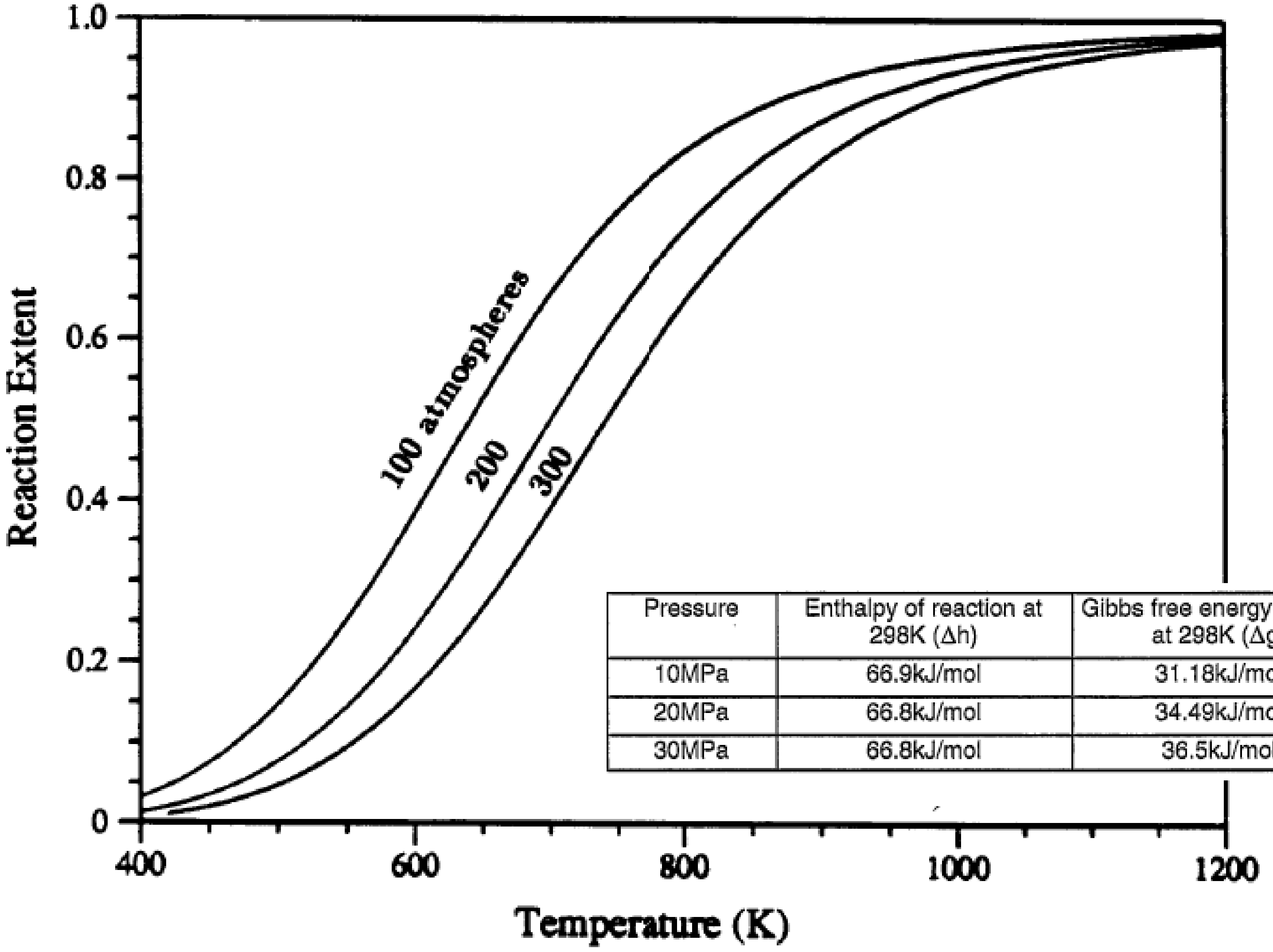
1997 System Study

- Alice Springs baseload 10 MW_e
- 400 dishes (400 m^2 each), 1500t/day ammonia converter
- Net solar-to-electric efficiency of 18 %
- 40hrs storage using 11,500m^3 from 162km of 300mm od pressure pipe.
- Capacity factor 70%, SM 2.2
- Using industry standard components

→ Generation costs the same as a steam plant could be expected

Item	**Fraction**
Dishes	41%
Receivers	7.5%
Heat exchangers	6.4%
Flexible couplings	1.5%
Ammonia synthesiser	2.5%
Compressors	1.4%
Other syn-loop components	2.6%
Reactant storage (pipes)	22.8%
Rankine Cycle	3.6%
Ammonia inventory	<1%
Balance of plant	6.7%
Infrastructure	3.3%

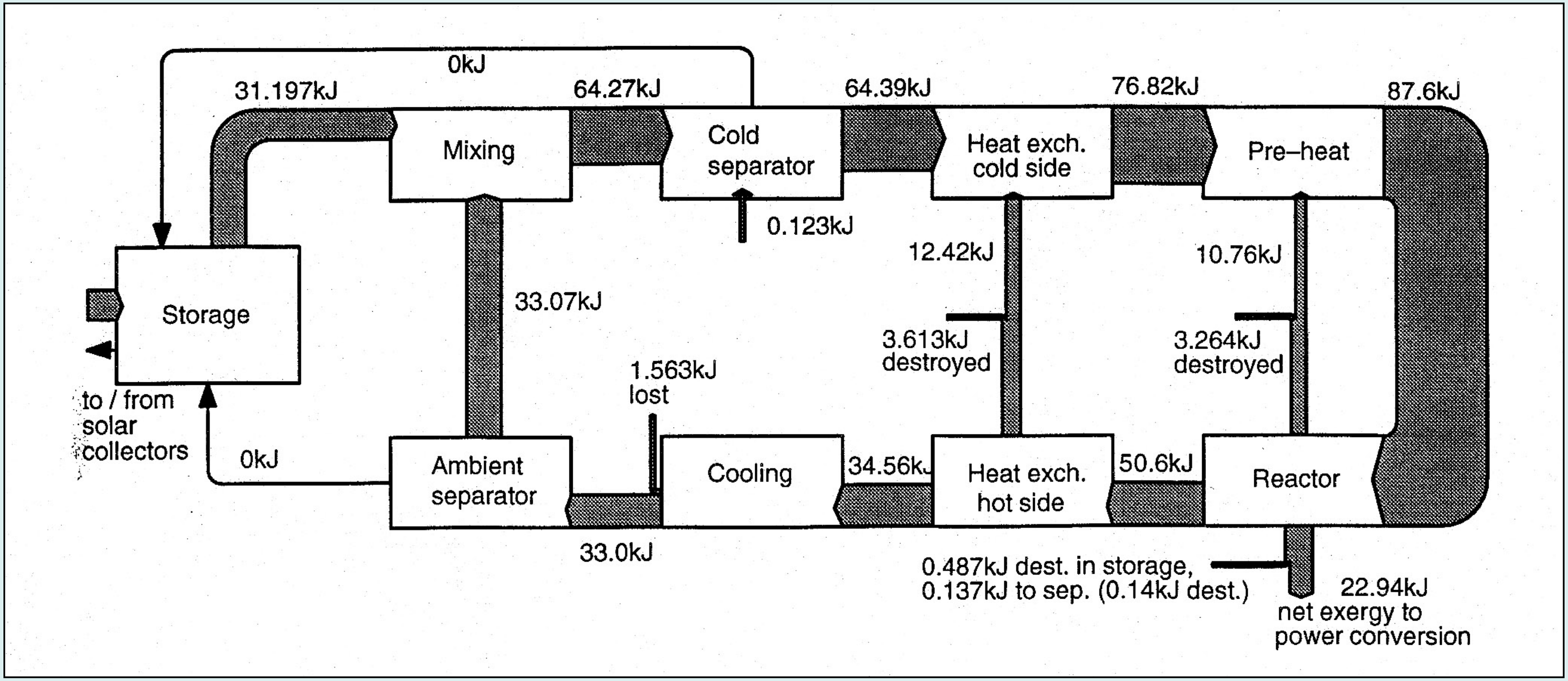
Chemical equilibrium determines maximum work recovery



Pressure	Enthalpy of reaction at 298K (Δh)	Gibbs free energy change at 298K (Δg)	Max. work recovery efficiency (Δg/Δh)
10MPa	66.9kJ/mol	31.18kJ/mol	46.6%
20MPa	66.8kJ/mol	34.49kJ/mol	51.6%
30MPa	66.8kJ/mol	36.5kJ/mol	54.6%

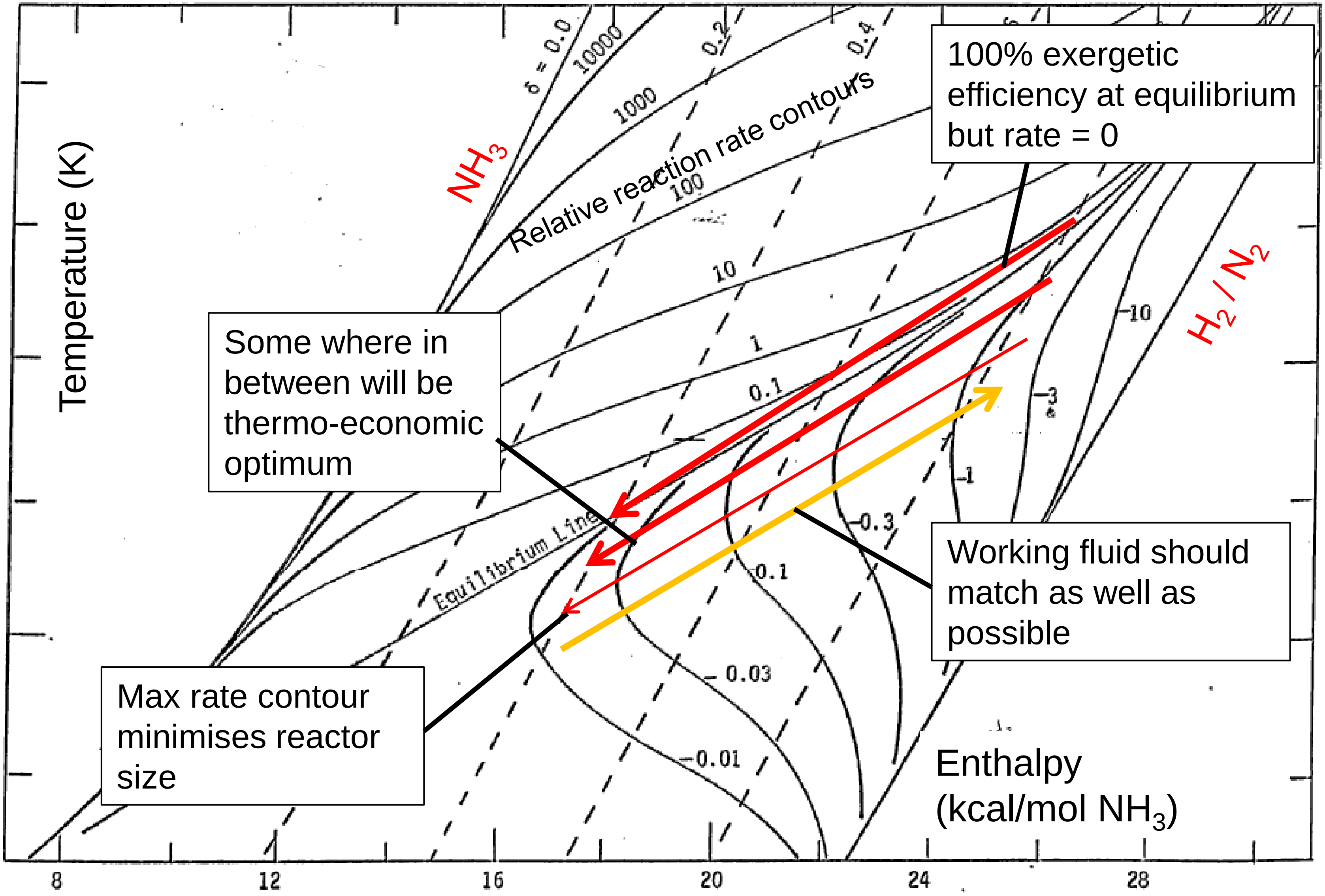
Chemical equilibrium mixture compositions for the ammonia reaction.

Exergy analysis – an essential tool



- Realistic 71% exergetic efficiency for heat recovery → 20% Solar to electric conversion

Thermo-economic optimisation of heat recovery is needed



100% exergetic efficiency at equilibrium but rate = 0

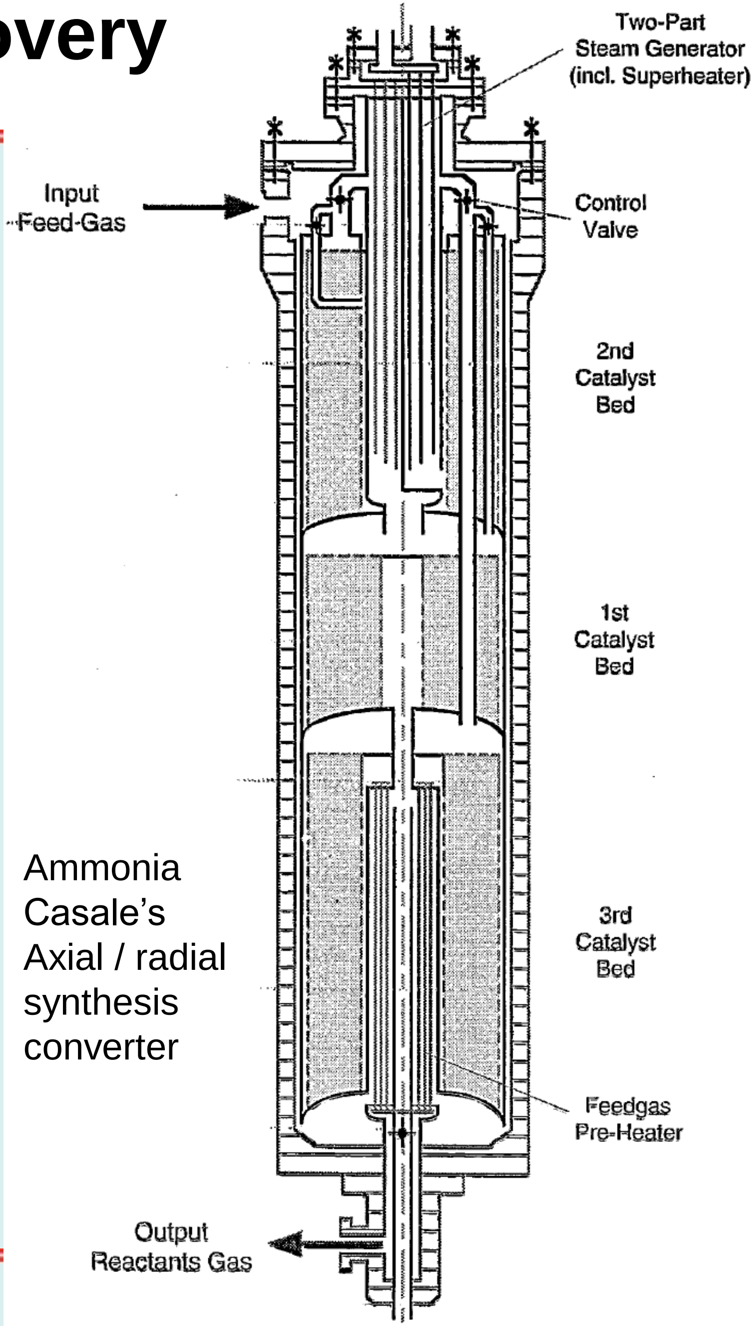
Some where in between will be thermo-economic optimum

Working fluid should match as well as possible

Max rate contour minimises reactor size

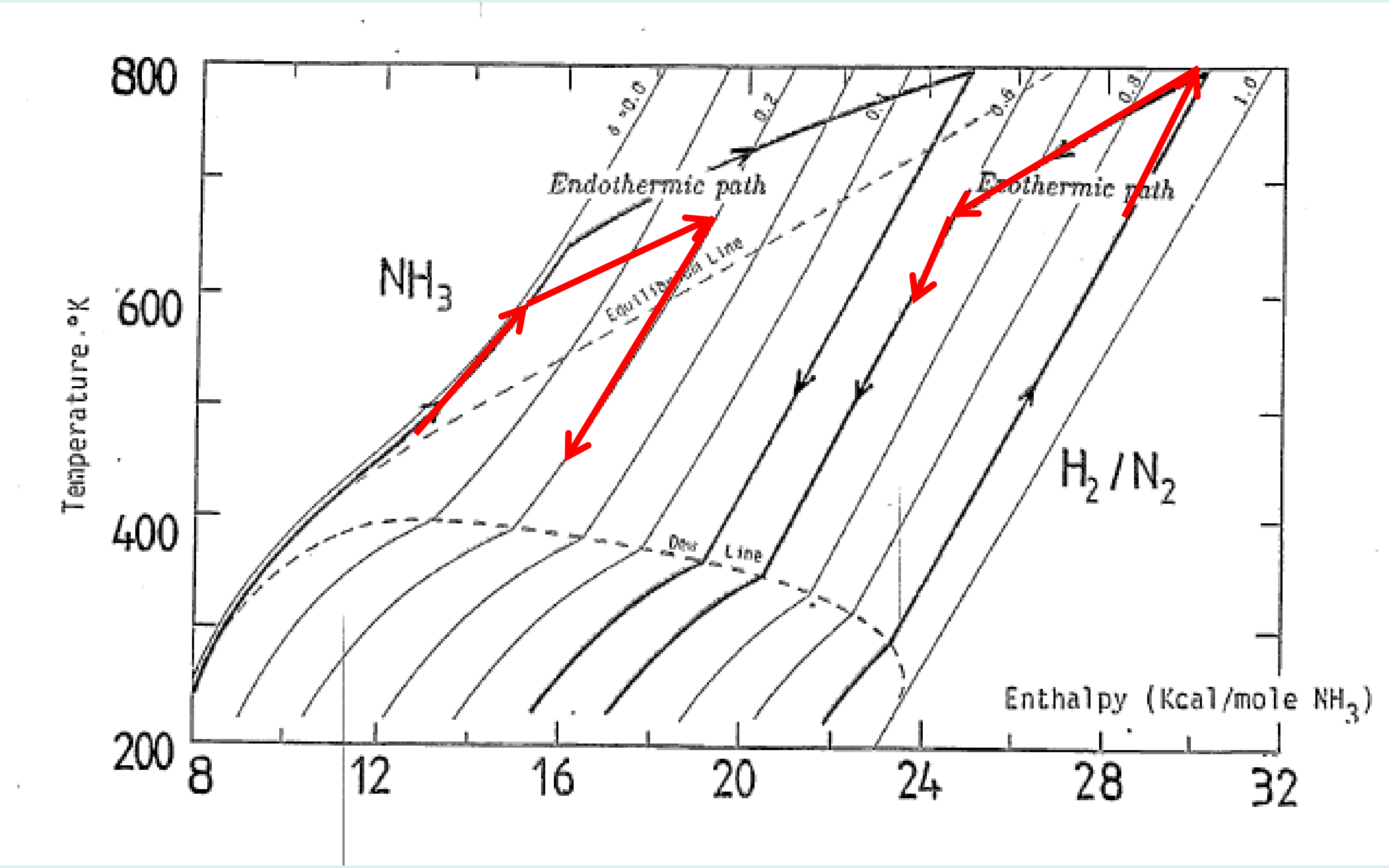
Maximising work recovery

- The equilibrium temperature enthalpy profile matches a constant specific heat working fluid better than a phase change (steam)
- Industrial exothermic reactor designs are maximised for production of product rather than exergy
- For the ammonia system, the concept of Direct Work recovery, where the reactants double as the working fluid was proposed
  - Improves exergetic efficiency
  - Avoid need for separate working fluid and reduces inventory of components
  - Uses high system pressure to advantage
  - BUT needs development of appropriate turbines



Ammonia Casale's Axial / radial synthesis converter

Thermochemical heat pump?

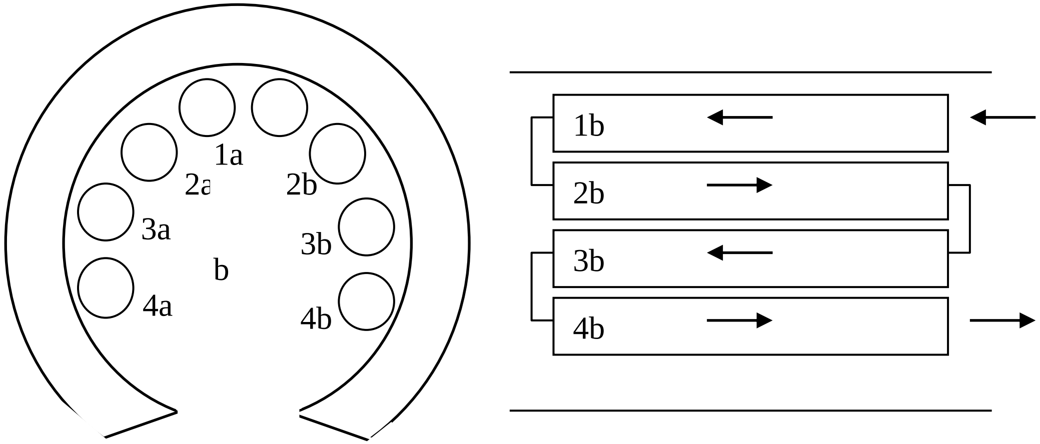


Ammonia thermochem for troughs?

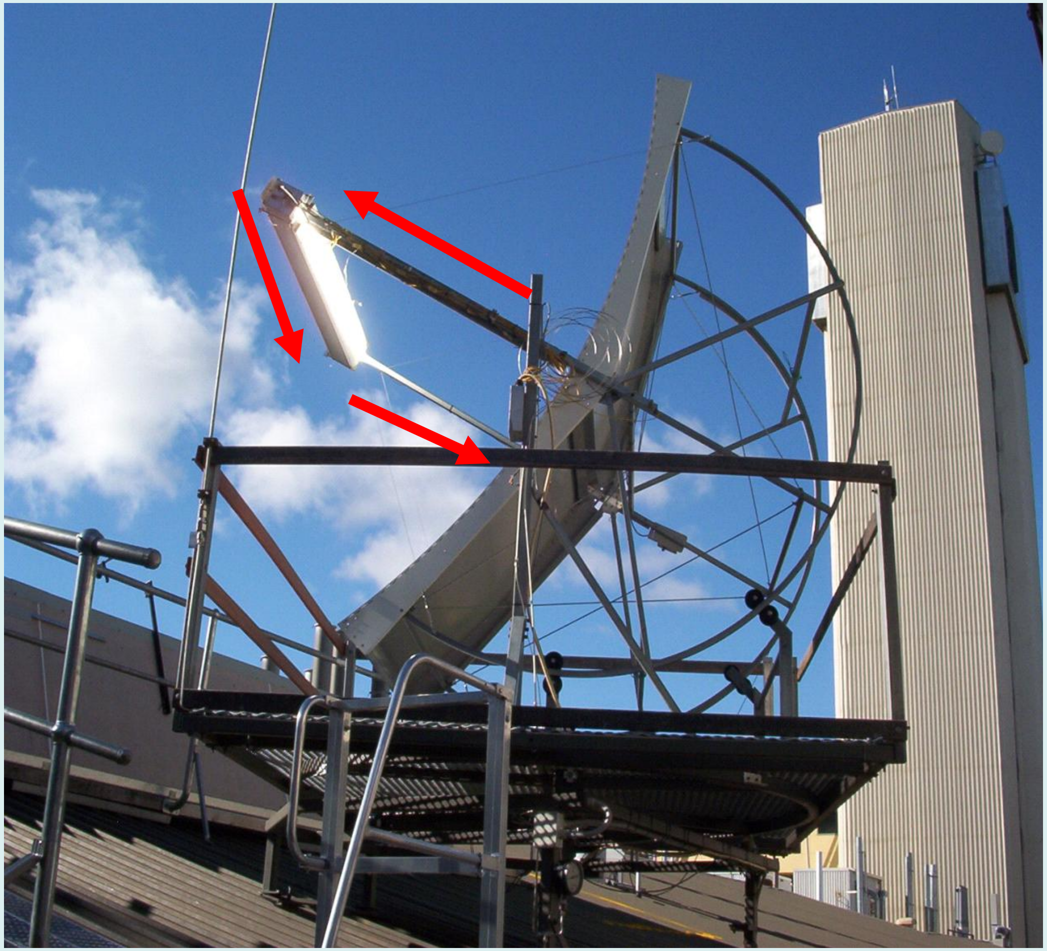
- Storage (of course)
- Relatively low T chemical cycle
- No phase change in receiver
- No network thermal losses
- Large body of industry experience
- Provide a “heat pump” effect which could benefit system efficiency via higher T at turbine

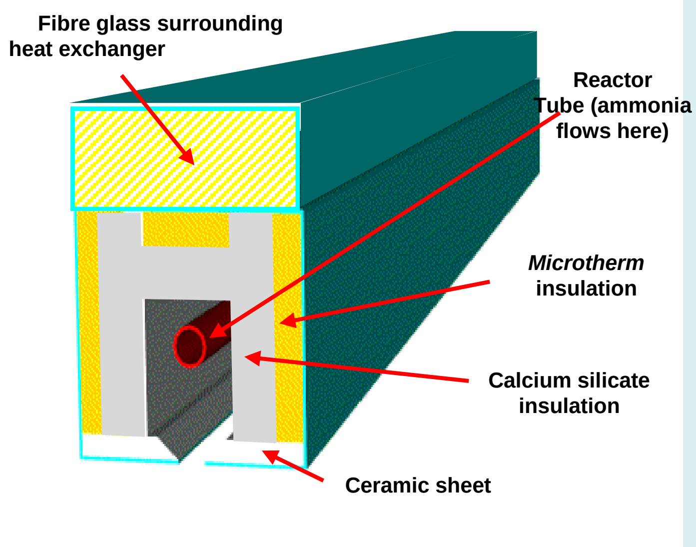
Modeling study

- Assume LS3 trough, Haldoe Topse DNK2R catalysts with ANU performance data.
- Standard evacuated tube receiver won't work, a cavity receiver could.
- Aim for 400^{o}C operation.
- 6 2" schedule 40 pipes operated as 2 x 3 in series.
- Exit reaction extent 36.8%
  - $\eta_{thermal}$ =70%
  - $\eta_{Heat\ ex}$ =74%
  - $\eta_{overall}$=52%



Test of single tube reactor





My critique of the TCES white paper

- “recovery of waste heat are important for optimizing efficiency”

  Very

- “Expertise …. from the chemical industry should be leveraged”

  Yes but don’t treat everything they say as gospel

- “Reactors will be required to have a 30 year lifetime”

  Errr…. Why?

- “versatile enough to respond to both cloud transients”

  Definitely

- “effective transport of mass is required”

  Or bring the energy to the mass…??

- “exergetic efficiency …. is bound by the choice of chemical compounds”

  This is rule #1!!!

My critique of the TCES white paper ctd.

- “catalyst-free systems are ideal”

  Umm.. There are no free lunches

- “equilibrium temperature of the discharge reaction ….is between 650°C and 1400°C”.

  mmm... remember, If it comes out that hot it goes in even hotter

- “Challenges in the modeling arena, if any, need to be considered”

  That is straightforward

- “Elements that are hazardous or toxic should be avoided”

  …. A bit limiting

- “should be readily integrated with current and future CSP systems”

  Definitely…. Don’t let the tail wag the dog

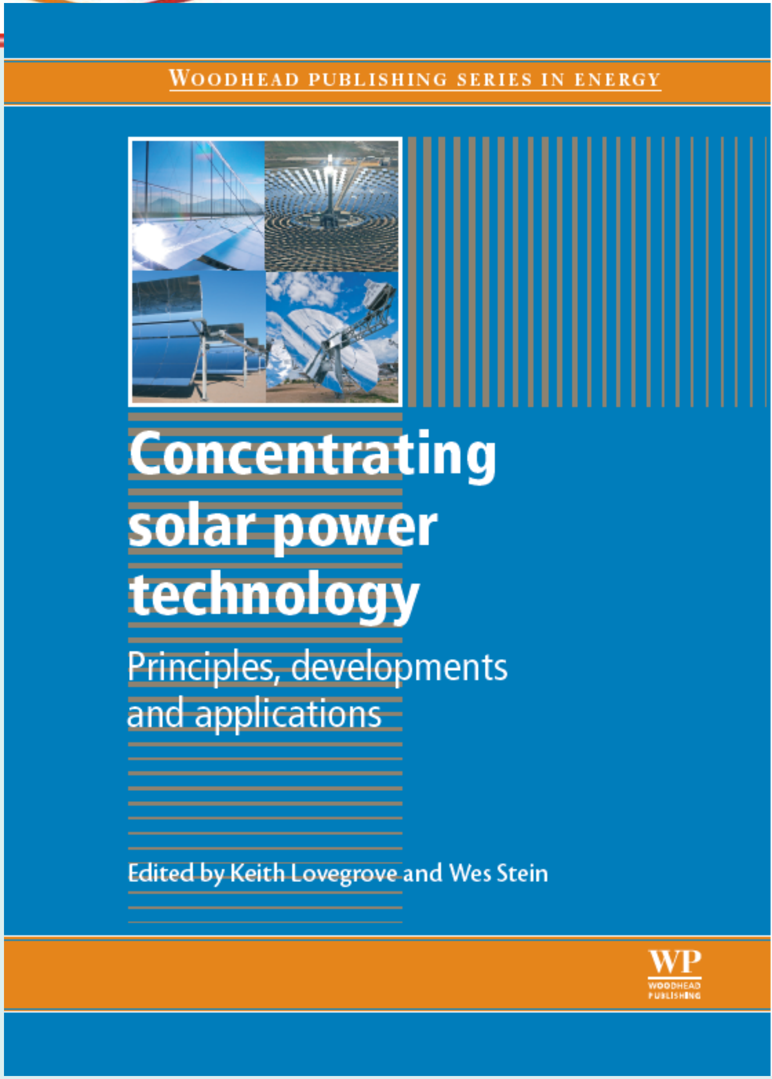
- “systems considerations must drive the science and engineering”

  Is the right answer!!!!!!

Other final thoughts

- Think of thermochemical processes as a tool for CSP system design rather than a TES black box
- Consider the benefits of phase or membrane separation
- Fluidised catalysts, matrix catalysts and membrane reactors are worth attention
- Direct work output ideas have promise
- Consider the possibilities of chemical heat pumping
- TCES is as much about a loss free heat transfer mechanism as it is about storage
- Long distance chemical heat pipes could offset transmission lines to high DNI areas whilst providing storage at the same time.

New CSP Book on the shelves



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