SUPERCRITICAL WATER PARTIAL OXIDATION

Presentation to the

Department of Energy
Hydrogen Program Annual Review
Berkeley, CA

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GENERAL ATOMICS

OBJECTIVES

- Develop a gasification technology that can convert biomass wastes of all types into hydrogen and other high-value products.
- Verify that high-pressure supercritical water is an ideal medium for gasification of biomass.
- Show that high hydrogen yields and gasification efficiencies can be reliably achieved with Supercritical Water Partial Oxidation (SWPO).
- Confirm competitive hydrogen production costs of ~$3/GJ can be achieved with small-size SWPO gasifiers.
- Demonstrate a 5-tpd reduced-scale gasifier at a small municipal POTW.
- Construct a 40-tpd commercial biomass gasifier at a large municipal POTW.

APPROACH

- Build on 20 yrs experience with Supercritical Water Oxidation (SCWO) of hazardous wastes.
- Exploit the inherent characteristics of supercritical water (SCW) to convert wet biomass into hydrogen
  - SCW quickly gasifies all organics with minimum char
  - Water-gas shift contributes significantly to hydrogen yields
  - SCW scrubs particulates and acids from hydrogen-rich gaseous products
  - High pressures aid in separation/storage of hydrogen
- Develop Supercritical Water Gasification System in a four-step program:
  - Phase I: Pilot scale testing / feasibility studies (complete)
  - Phase II: Technology development (expect recompete/award in 2003)
  - Phase III: System integration and design
  - Phase IV: Reduced scale demonstration of 5-tpd system
- Following DOE cost-share program:
  - Design and construct 40-tpd commercial demonstration system

GENERAL ATOMICS

PROJECT TIMELINE

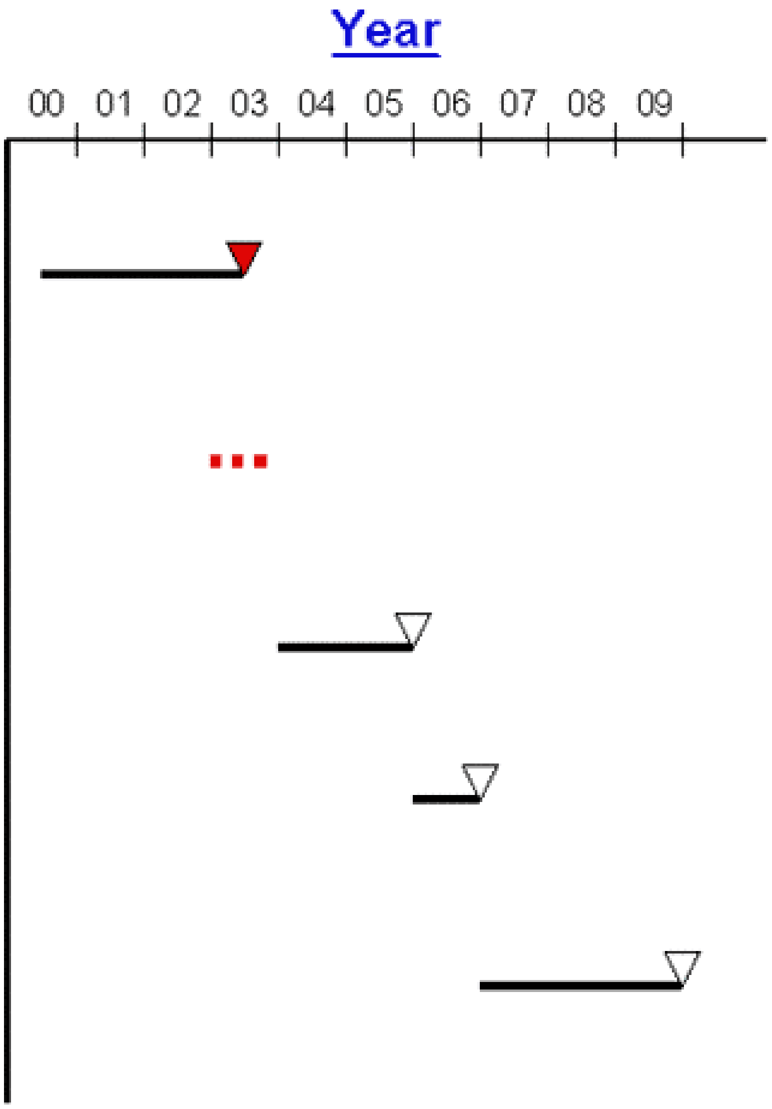
Phase I: Pilot scale testing / feasibility studies (complete) (5/00 – 6/03)

Recompete for H_2 program participation (1/03 – 12/03)

Phase II: Technology development (1/04 – 12/05)

Phase III: System integration and design (1/06 – 12/06)

Phase IV: Reduced scale demonstration of 5-tpd system (1/07 – 12/09)

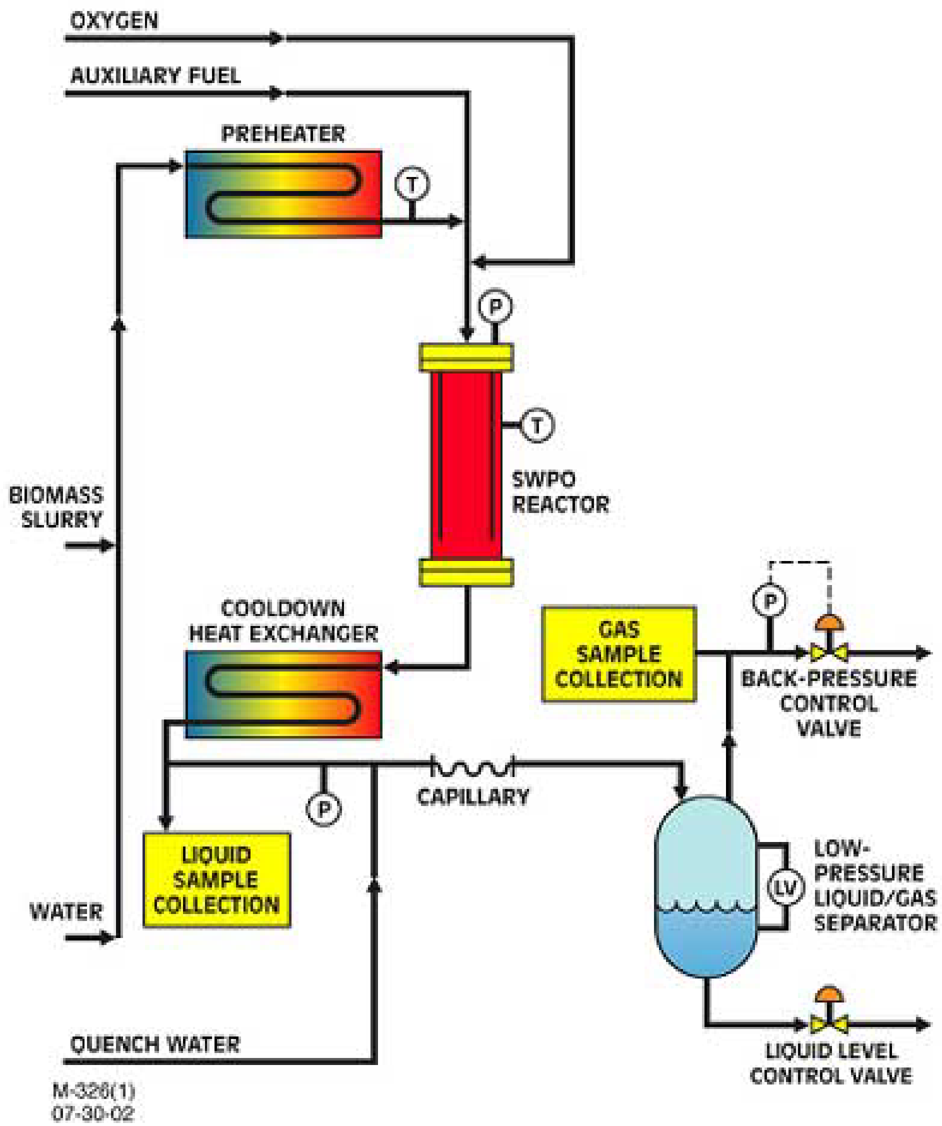


GENERAL ATOMICS

PHASE-I MILESTONES
PILOT-SCALE TESTING/FEASIBILITY STUDIES

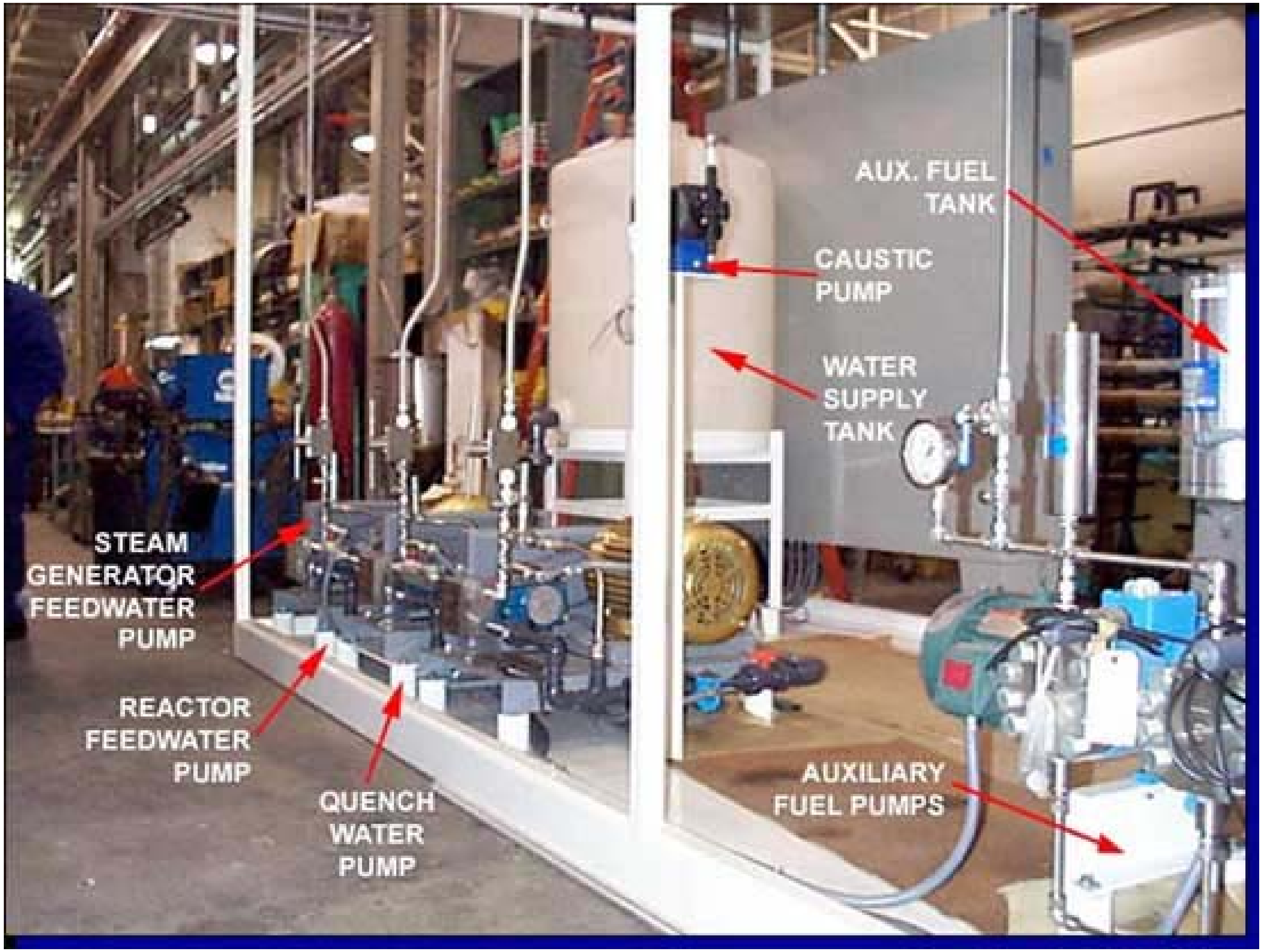
- **5/02 – Complete Pilot-Scale SWPO Tests (Complete)**
- **6/02 - Perform pilot-scale design concept for Phase II (Complete)**
- **6/02 - Perform analysis to predict when/how H_2 production goals can be met (Complete)**
- **8/02 - Prepare a SWPO Development Plan with cost and schedule estimates (Complete)**
- **8/02 - Prepare a Business Plan to identify SWPO market potential (Complete)**
- **12/02 - Define follow-on Phase II Technology Development activities and a follow-on Phase II Proposal (Complete)**
- **12/02 – Issue Phase I Final Report (Complete)**

SIMPLIFIED SWPO PROCESS FLOW DIAGRAM



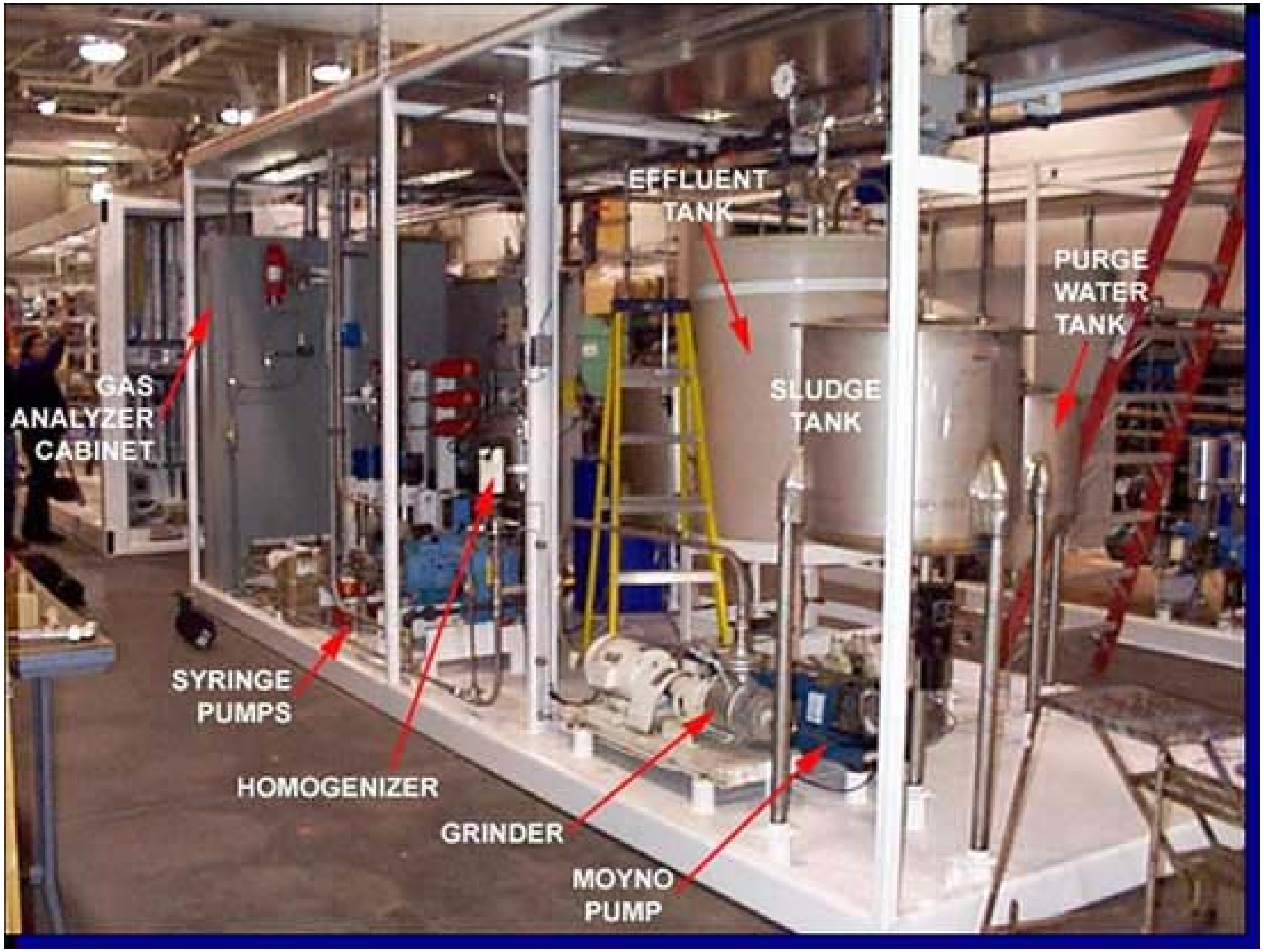
GENERAL ATOMICS

SWPO PILOT-PLANT PUMP SKID



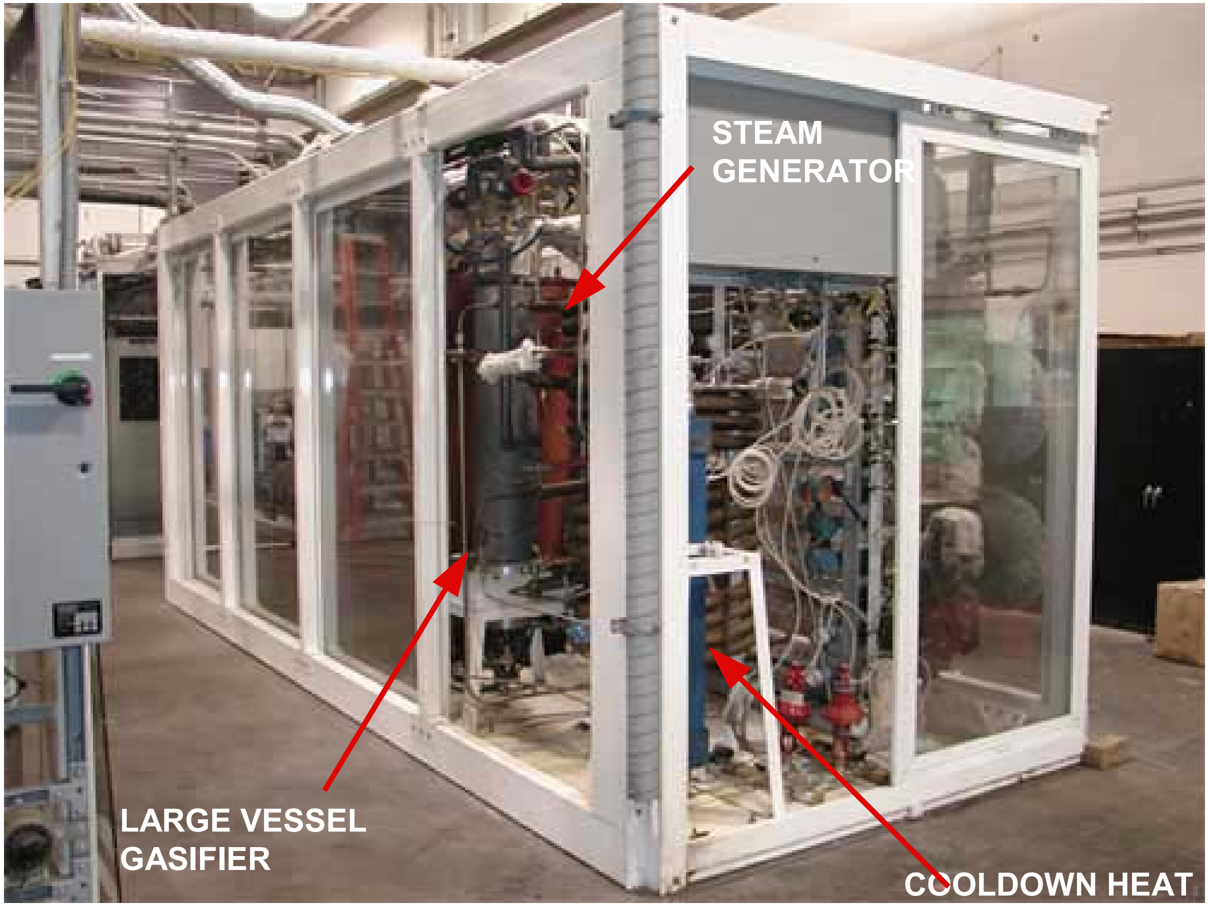
GENERAL ATOMICS

SWPO PILOT-PLANT SLURRY AND EFFLUENT SKID



GENERAL ATOMICS

SWPO PILOT- PLANT REACTOR SKID WITH LARGE VESSEL GASIFIER



SWPO LARGE VESSEL GASIFIER

GENERAL ATOMICS

ACCOMPLISHMENTS

Key findings during Phase I testing:

1. Pumping tests indicate that a biomass slurry feed concentration of about 12 wt% solids is a practical maximum.
2. Feed preheat should be limited to 260°C to avoid char formation and plugging.
3. A high-heating value waste must be coprocessed with biomass in order to attain the desired gasifier temperature and still have sufficient feedstock for gasification. Suitable high-heating value wastes are trap grease, plastics, rubber, or coal.
4. A vessel-type gasifier is required to achieve higher gasifier operating temperatures and minimize heat losses.
5. A catalyst-free gasifier is required to enable long-term operation with dirty feed materials without plugging.
6. A high-energy nozzle is required for high dispersion of the incoming feed to improve mixing and attain high gasification yields.
7. A methane-steam reformer is required on the clean SWPO product gas to reform the methane-rich gas to hydrogen.

GENERAL ATOMICS

SUMMARY OF WOODY BIOMASS GASIFICATION TESTS

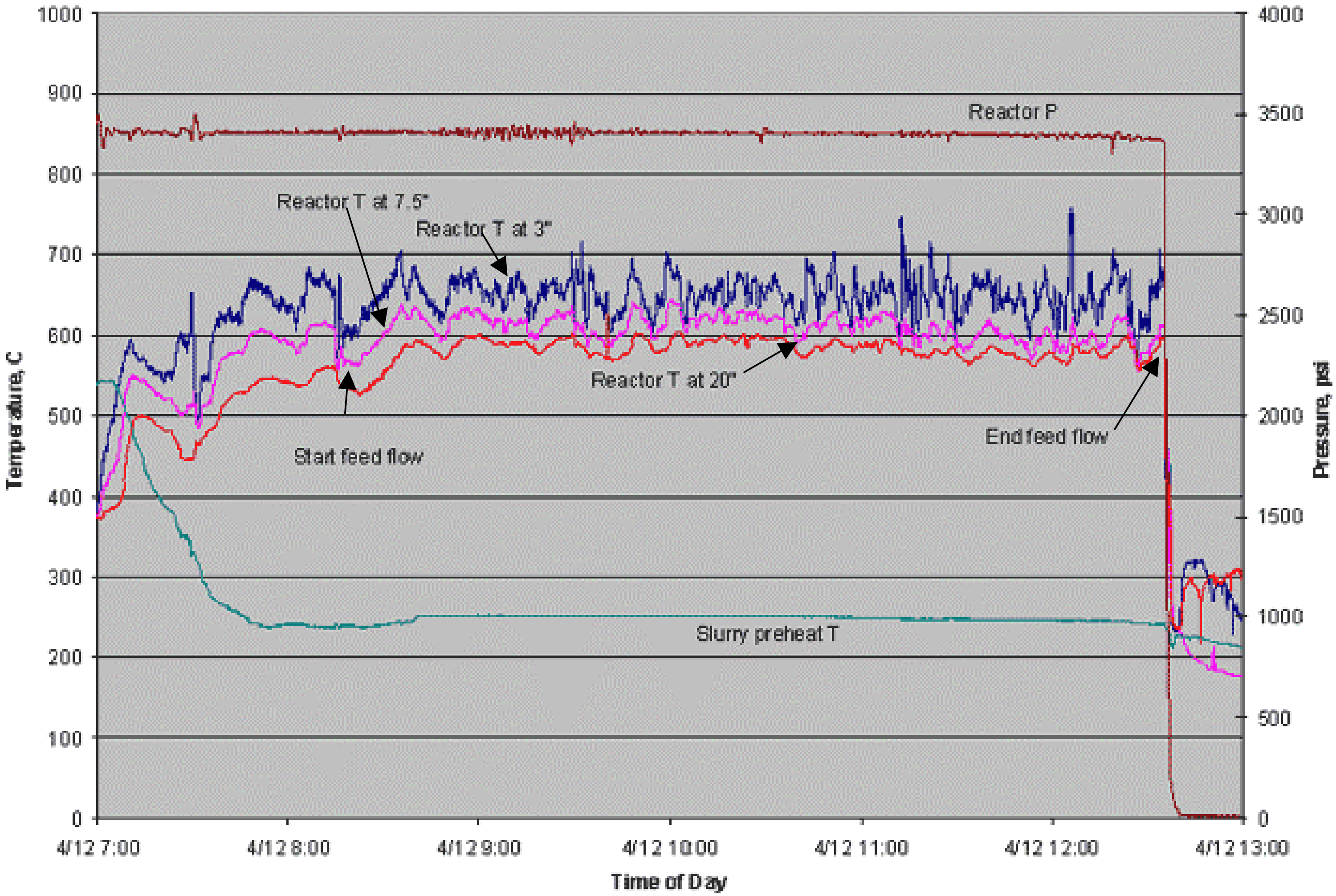
Run Date:	4/10/2002	4/12/2002	4/17/2002	4/18/2002	4/23/2002	4/24/2002
Feed (dry basis)	9% wood	9% wood	9% wood	9% wood	9% wood	9% wood
Gasifier T, C	650	650	800	800	650	800
Input						
Run time min	105	250	242	195	128	132
Oxygen g/min	109	104	110	112	86	113
Stoich. EtOH g/min	52.2	49.8	52.7	53.7	41.2	54.1
Excess EtOH g/min	16.8	22.2	10.3	3.3	17.8	7.4
Feed g/min	367	345	350	336	330	347
CMC %(1)	2.5	2.5	2.5	2.5	2.5	2.5
Output						
Gas SCFM	4.5	5.1	4.6	4.7	4.3	4.9
H_2 %	18.6	21.1	17.0	18.8	25.3	16.9
CH_4 %	16.3	16.7	13.6	14.9	15.7	13.3
C_2H_6 %	0.1	0.1	0.1	0.1	0.2	0.1
CO %	2.7	2.9	1.9	2.2	4.1	1.7
CO_2 %	48.6	48.6	54.5	48.7	43.7	54.9
N_2 %	10.4	8.0	9.5	11.2	8.1	9.7
O_2 %	3.5	2.7	3.5	4.1	3.0	3.5
% Feed C in solid (char)	6.9	2.7	3.5	2.7	0.5	0.2
% Feed C in liquid (tar)	2.3	2.9	6.0	0.0	8.7	5.0
Carbon balance %	79	88	90	90	83	94

Notes:

(1) – CMC is a suspension agent to prevent settling in the feed slurry.

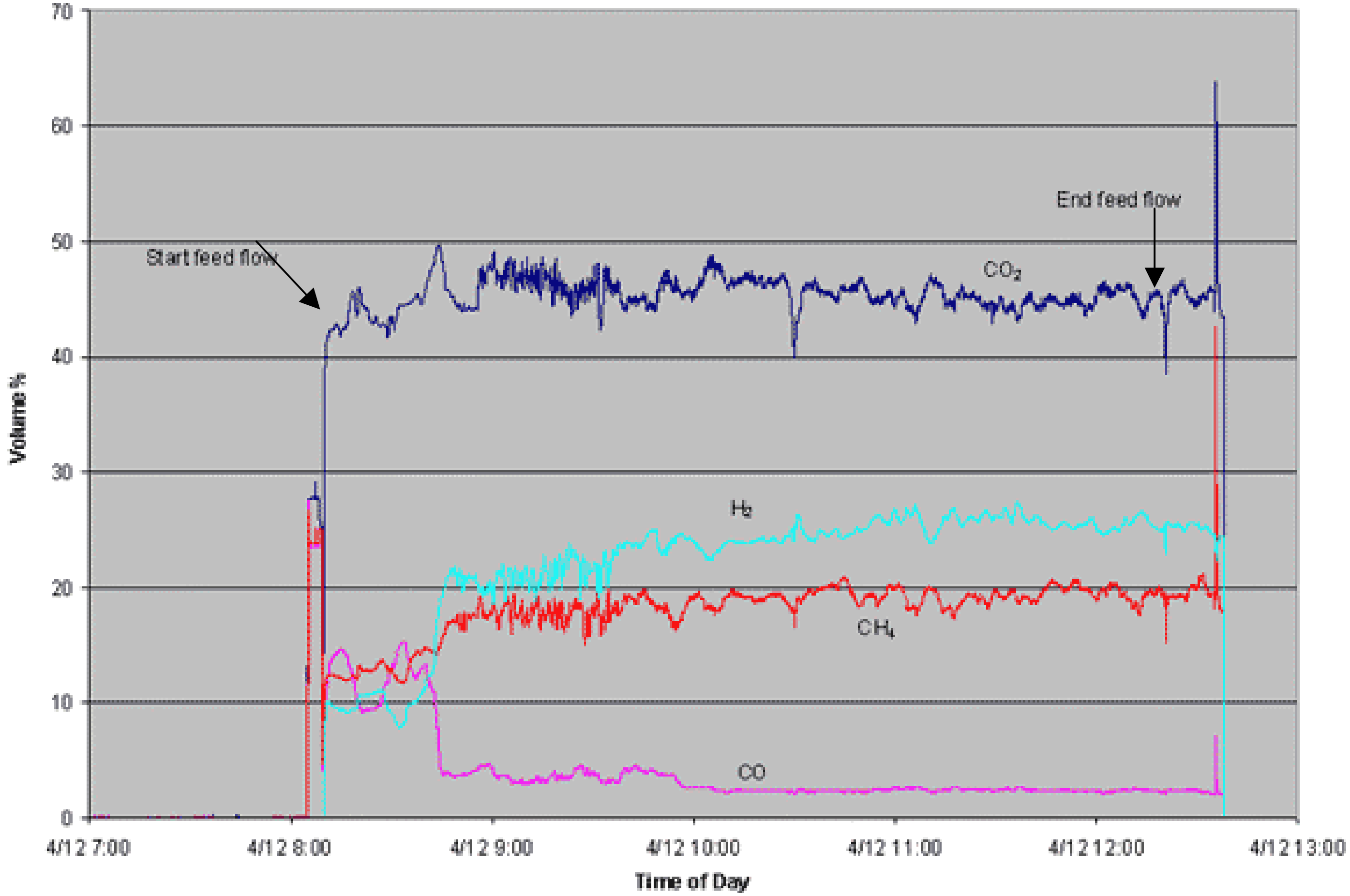
GENERAL ATOMICS

SWPO T-P DATA AT 650°C



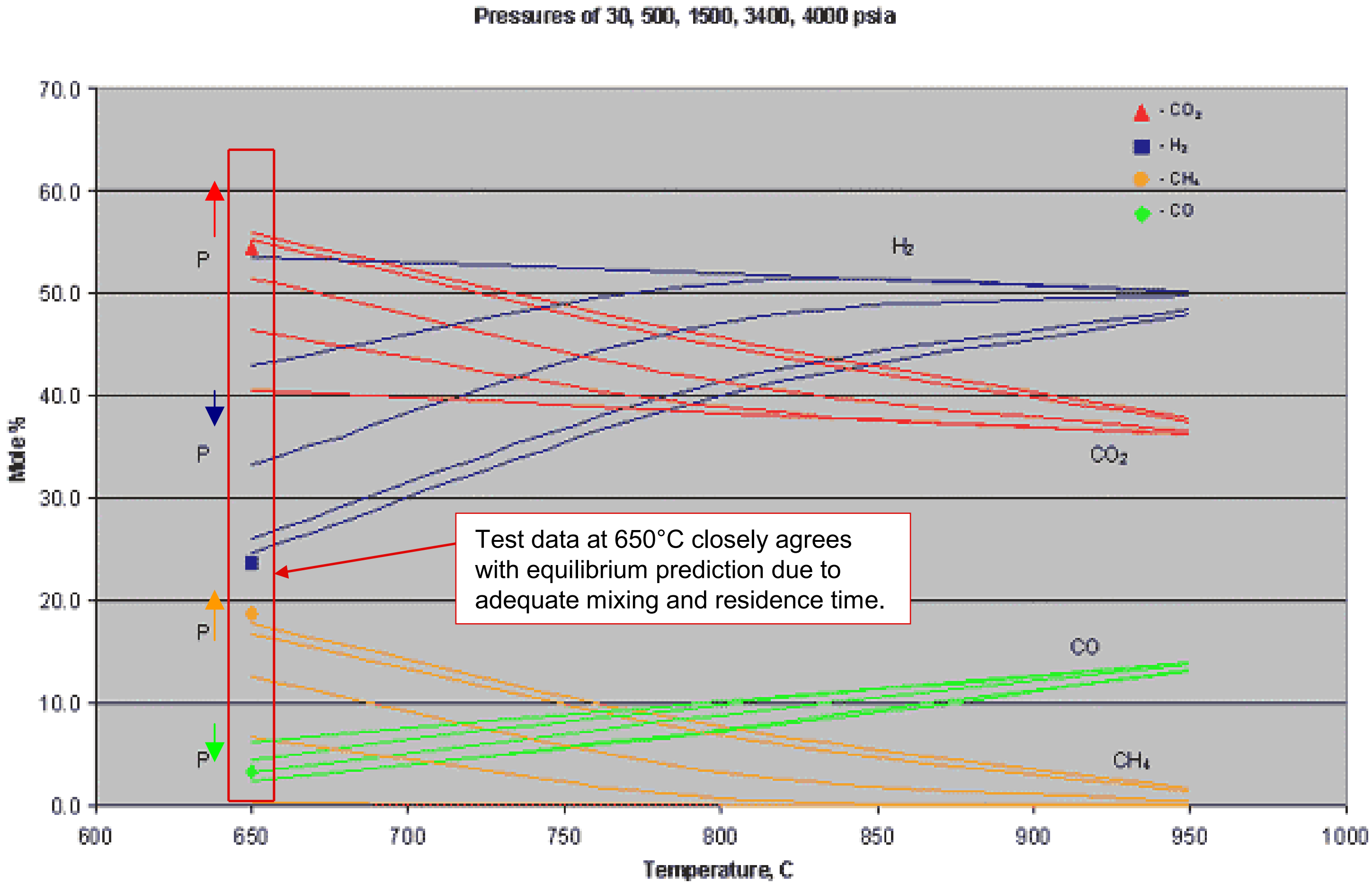
GENERAL ATOMICS

SWPO GAS ANALYZER DATA AT 650°C

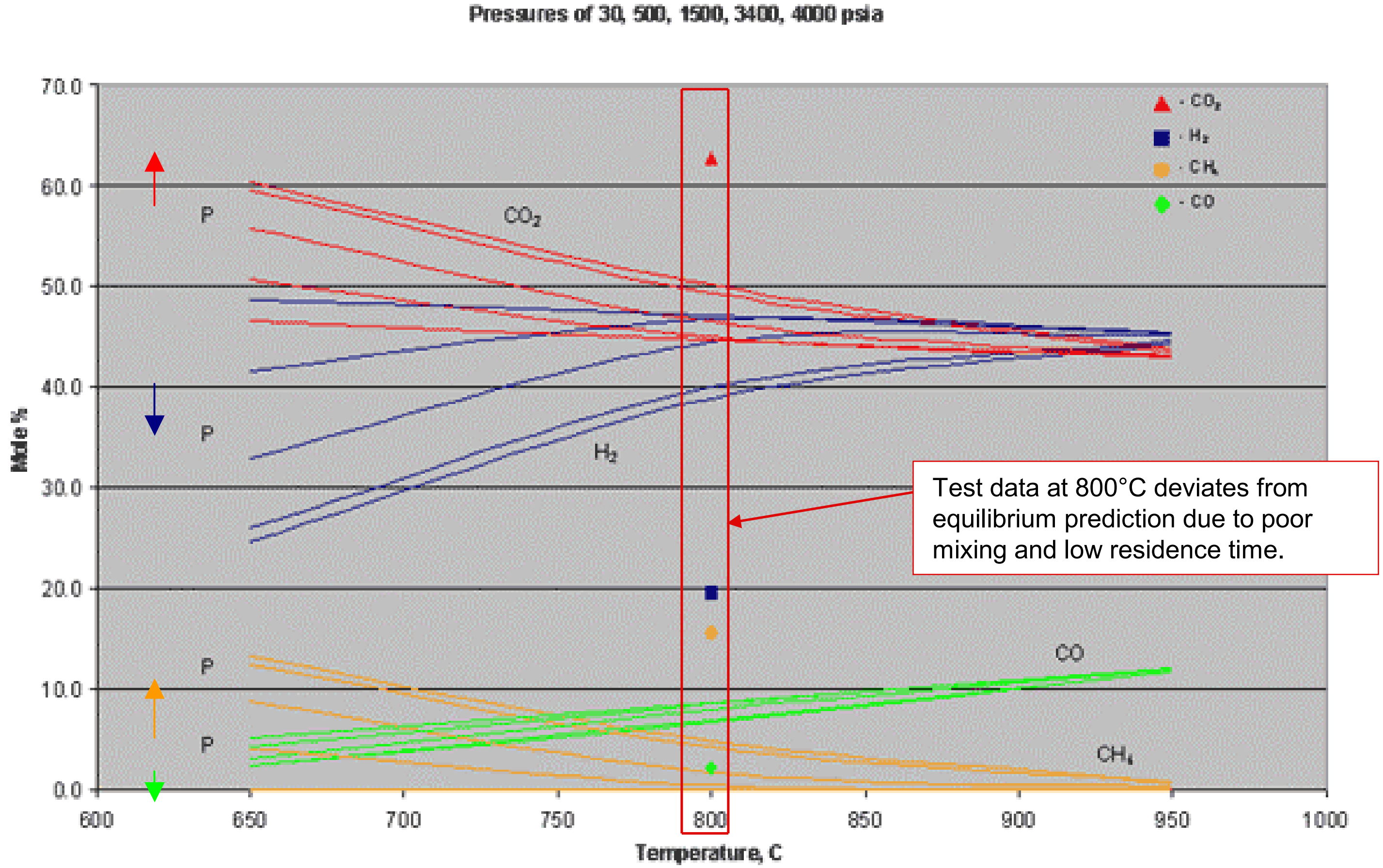


GENERAL ATOMICS

SWPO DATA AT 650°C COMPARED TO EQUILIBRIA PREDICTIONS



SWPO DATA AT 800°C COMPARED TO EQUILIBRIA PREDICTIONS



GENERAL ATOMICS

COMPARISON OF SWPO GAS PRODUCTION WITH INDIRECTLY-HEATED GASIFIERS

Organization	Feed	T °C	P psi	H_2O:C ratio	Product gas mol%					Max possible H_2 yield, g/100g feed		Max possible gasification efficiency, %	Notes
					H_2	CH_4	C_2+	CO	CO_2	Feed	Product gas		
GA	9% wood + 2.5% CMC[1]	650	3400	7.5	43.6	38.3	0.2	6.3	11.5	19.4	15.3	79	Yields based on unoxidized organic
GA	9% wood + 2.5% CMC[1]	650	3400	6.7	40.0	31.6	0.3	5.6	22.5	20.1	17.5	87	Yields based on unoxidized organic
GA	9% wood + 2.5% CMC[1]	800	3400	8.4	38.5	30.8	0.2	4.3	26.2	18.6	15.6	84	Yields based on unoxidized organic
GA	9% wood + 2.5% CMC[1]	800	3400	9.9	44.7	35.4	0.2	5.2	14.5	17.5	21.1	121	Yields based on unoxidized organic
GA	9% wood + 2.5% CMC[1]	650	3400	7.1	47.4	29.5	0.4	7.7	15.0	19.7	16.8	85	Yields based on unoxidized organic
GA	9% wood + 2.5% CMC[1]	800	3400	9.0	37.6	29.6	0.2	3.8	28.8	18.2	17.2	94	Yields based on unoxidized organic
UHM	10.4% CS[2]	650	4061	14.0	45	14	0.0	2	35	13.7	14.5	105	UHM, 1997a
UHM	5% wood + 5.5% CS[2]	650	4061	12.6	34	23	0.2	3	45	15.2	13.3	87	UHM, 1997a
UHM	5% wood + 5.6% CS[2]	650	4061	12.6	50	10	0.0	4	39	15.2	15.5	102	UHM, 1997a
UHM	5% wood + 6.1% CS[2]	650	4061	11.9	43	14	0.2	3	37	15.1	13.5	89	UHM, 1997a
UHM	11.5% wood + 4.2% CS[2]	650	4061	7.6	57	6	0.0	4	33	15.9	15.2	95	UHM, 1997b
TNO	Waste biomass	600	4351	NA	54	9	NA	3	34	NA	NA	NA	TNO, 1998
Battelle	Wood	826	25	0.8	21	16	5.8	43	13	18.0	12.5	70	Craig and Mann, 1996
Battelle	Wood	927	15	0.6	21	15	6.0	47	11	18.5	13.2	72	Katofsky, 1993
Wright-Malta	Wood	600	218	1.1	21	35	0.0	7	38	17.2	17.3	101	Katofsky, 1993
MTCI	Wood	697	15	2.6	50	8	0.4	22	19	17.8	14.9	84	Katofsky, 1993

Notes:
1. CMC is carboxymethylcellulose suspension agent.
2. Activated carbon catalyst. CS is corn starch.

GENERAL ATOMICS

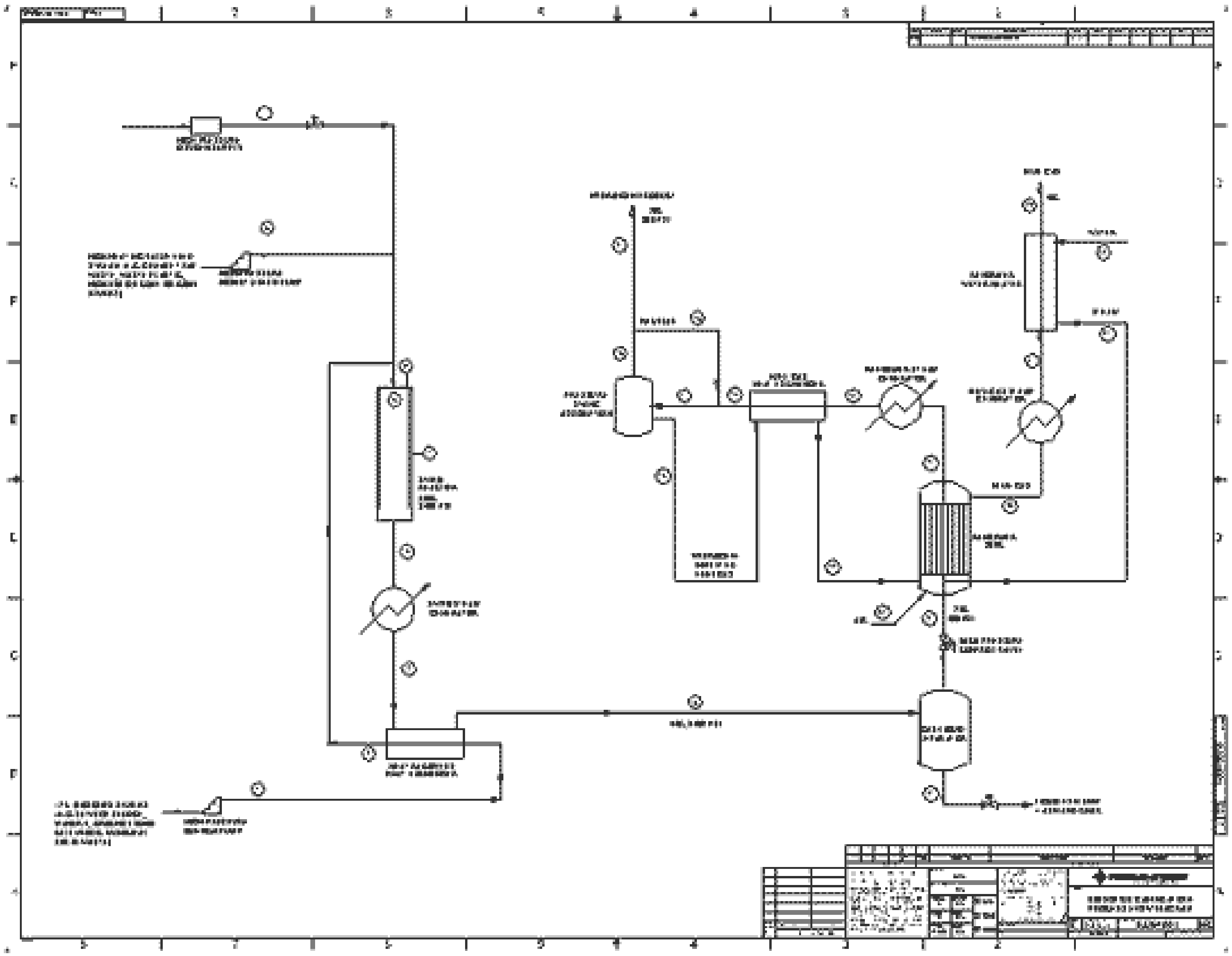
COMPARISON OF SWPO GAS PRODUCTION WITH DIRECTLY-HEATED GASIFIERS

Organization	Feed	T °C	P psi	H_2O:C ratio	O_2:Feed mass ratio	Product gas mol%					Max possible H_2 yield, g/100g feed		Max possible gasification efficiency, %	Notes
						H_2	CH_4	C_2+	CO	CO_2	Feed	Product gas		
GA	9% wood + 2.5% CMC[1,2]	650	3400	3.9	1.0	21.5	18.9	0.1	3.1	56.3	21.9	8.1	37	Yields based on all organic
GA	9% wood + 2.5% CMC[1,2]	650	3400	3.6	0.9	23.6	18.6	0.2	3.3	54.3	21.9	9.7	44	Yields based on all organic
GA	9% wood + 2.5% CMC[1,2]	800	3400	4.0	1.1	19.5	15.6	0.1	2.2	62.5	22.0	7.7	35	Yields based on all organic
GA	9% wood + 2.5% CMC[1,2]	800	3400	4.1	1.2	22.2	17.6	0.1	2.6	57.5	22.2	9.3	42	Yields based on all organic
GA	9% wood + 2.5% CMC[1,2]	650	3400	4.0	0.9	28.4	17.7	0.2	4.6	49.1	21.6	9.7	45	Yields based on all organic
GA	9% wood + 2.5% CMC[1,2]	800	3400	4.0	1.1	19.4	15.3	0.1	2.0	63.2	22.1	8.0	36	Yields based on all organic
IGT	Wood, air-blown[3]	830	460	0.7	0.3	25	18	0.2	19	38	17.3	10.6	62	Craig and Mann, 1996
IGT	Wood, O_2-blown	982	500	0.7	0.3	31	12	0.5	22	35	17.0	11.6	68	Katofsky, 1993
TPS	Wood, air-blown[3]	870	20	0.3	0.5	37	0	0	46	16	17.3	11.1	64	Craig and Mann, 1996
Shell-bio	Wood O_2-blown	1085	352	0.2	0.5	38	0	0	48	14	17.0	11.1	65	Katofsky, 1993

Notes:
1.CMC is carboxymethylcellulose suspension agent.
2.Nitrogen- and oxygen-free basis used for product gas.
3.Nitrogen-free basis used for product gas.

GENERAL ATOMICS

SWPO COMMERCIAL GASIFIER PROCESS FLOW DIAGRAM



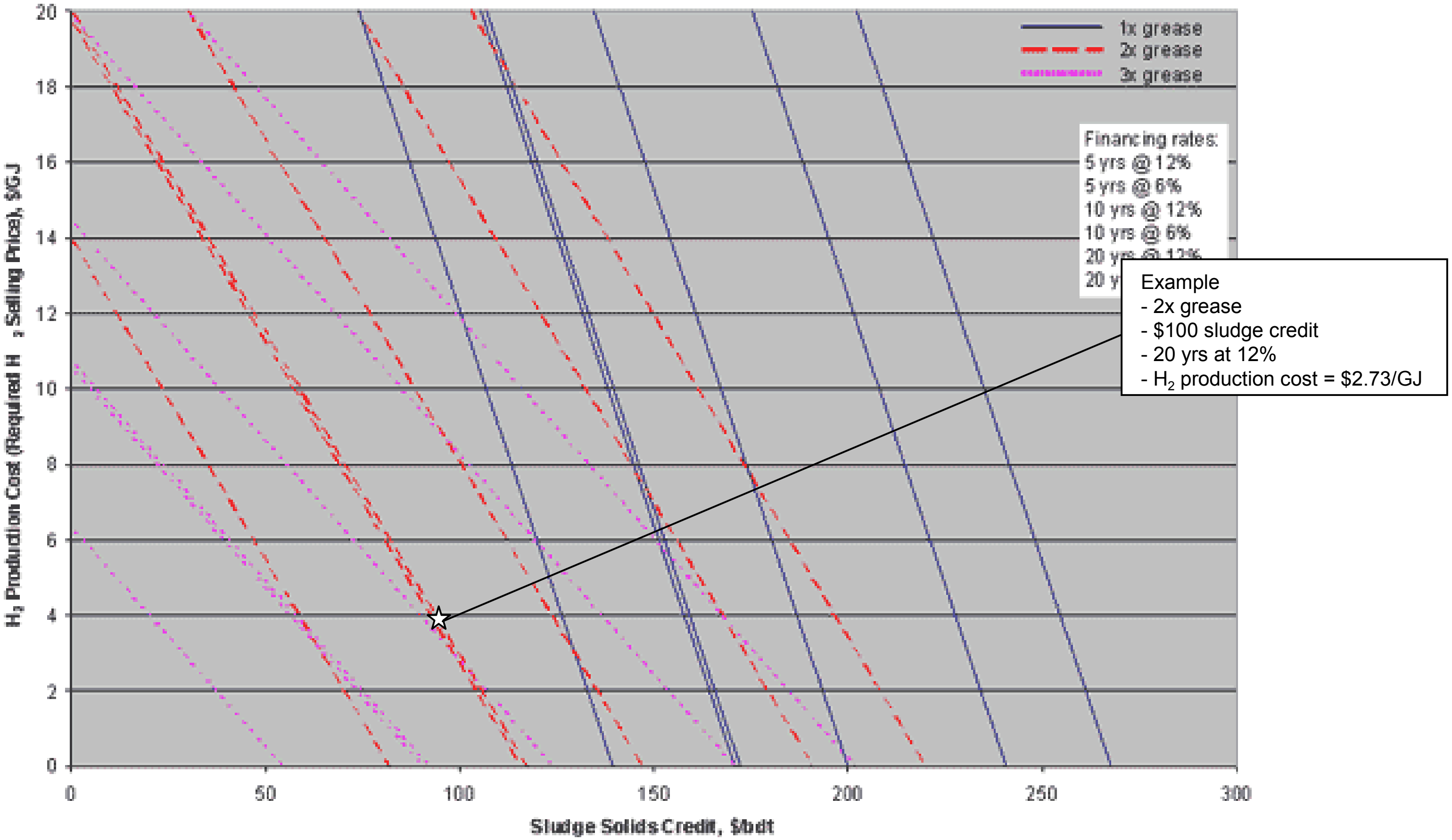
GENERAL ATOMICS

SWPO ECONOMIC ANALYSIS BASES

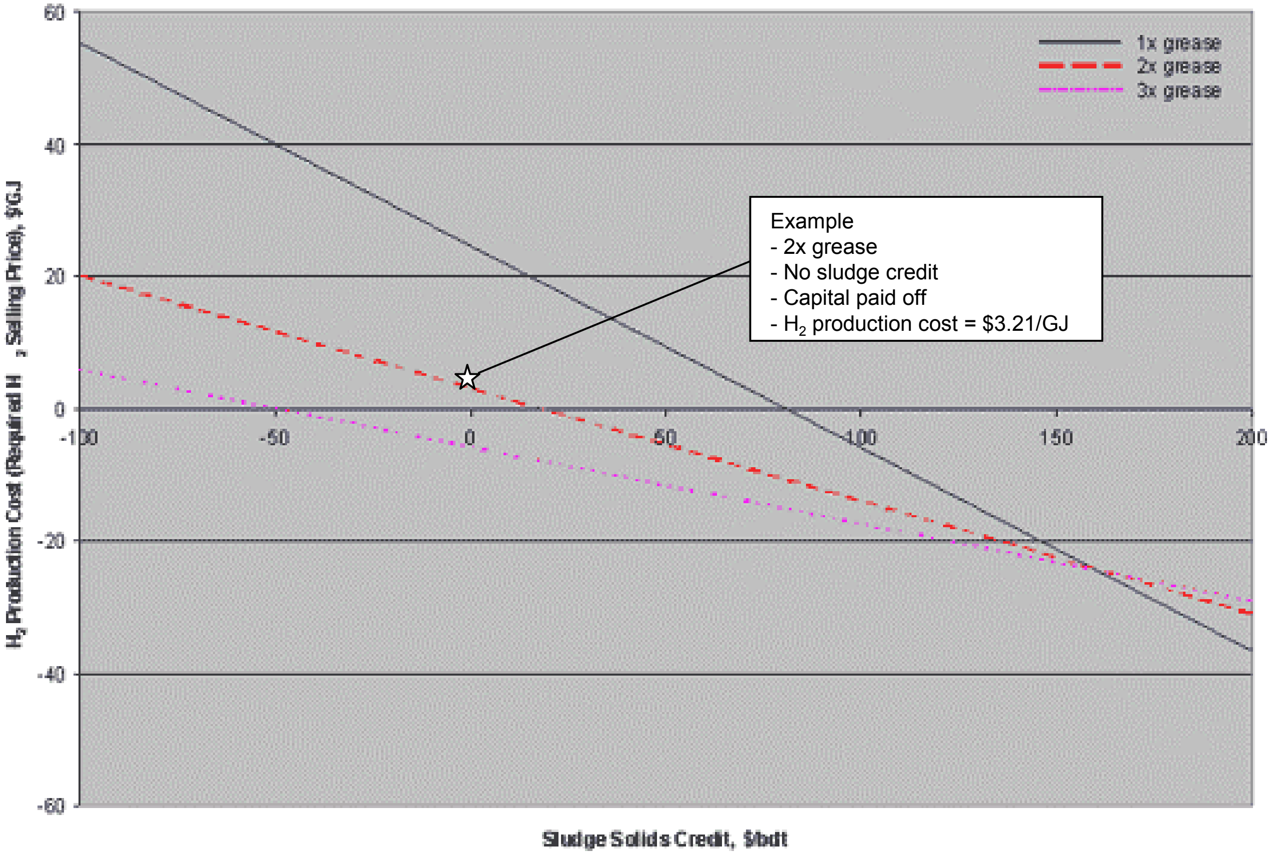
Description	Assumption	Reference
Plant size	40 tpd total solids, 30 tons/day organic sludge solids (not grease)	Numerous plants of this size in the US and worldwide
Sludge solids credit	\$0-300 per dry ton	SDSU survey (Appendix D)
Gasifier residence time	20 seconds	15 seconds for UHM, 1998a
Trap grease credit	\$0.08 per gallon	Darling/Al Max telecons
Steam credit	\$3.50 per MMBtu (≈ 1000 lb)	Yeboah et al., 2002
Cost of liquid oxygen (LOX)	\$0.04 per pound	Vendor discussions
Financing rate	6 to 12%	Current prime interest rate is below 5%
Financing period	Up to 20 years	City of San Diego methane contract is a 20-yr term

GENERAL ATOMICS

HYDROGEN PRODUCTION COST FOR SEWAGE SLUDGE WITH TRAP GREASE



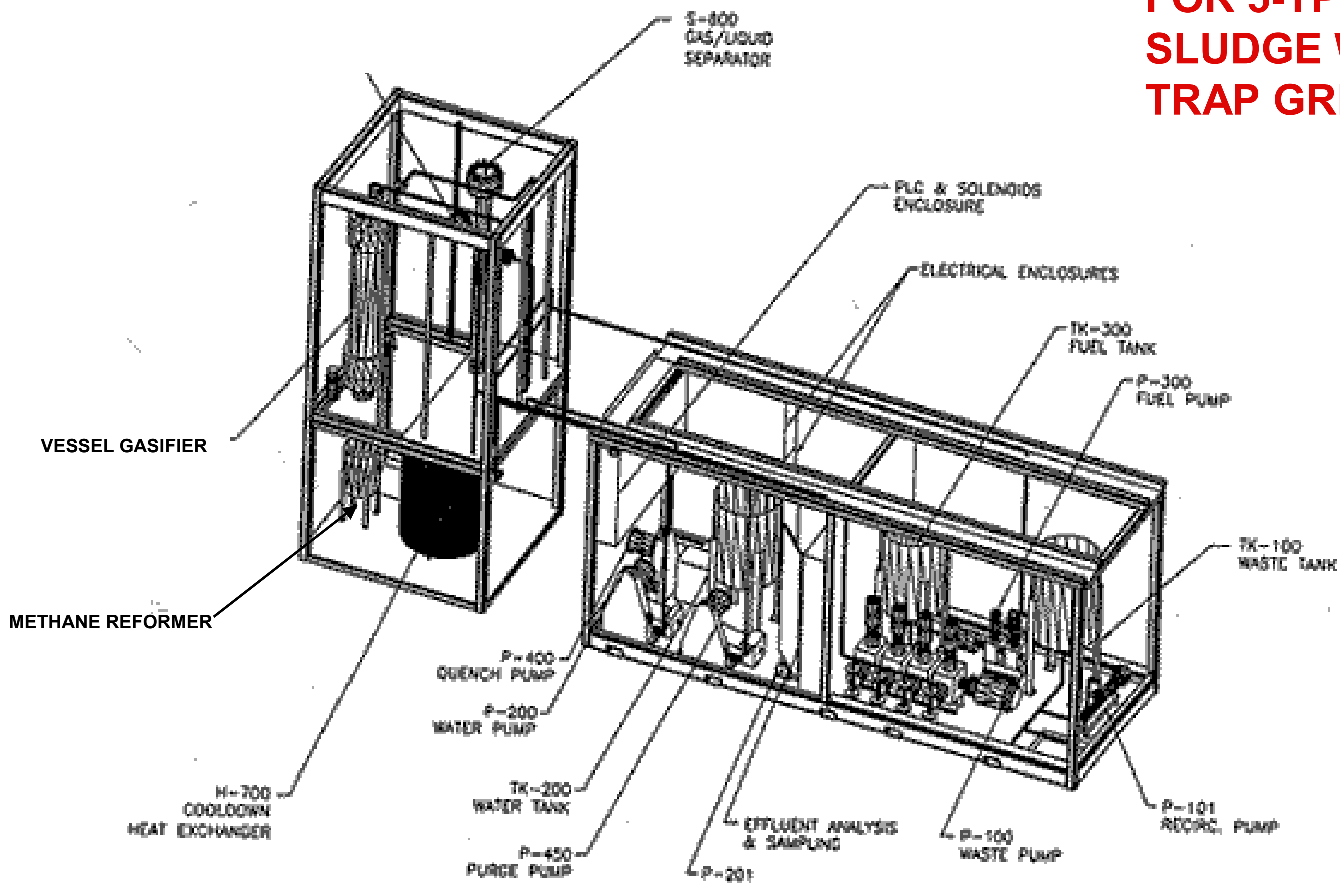
HYDROGEN PRODUCTION COST FOLLOWING CAPITAL RECOVERY



GENERAL ATOMICS

SWPO REDUCED-SCALE DEMONSTRATION SYSTEM

FOR 5-TPD SEWAGE SLUDGE WITH TRAP GREASE



GENERAL ATOMICS

COLLABORATIONS

- GA SWPO pilot plant is supporting multiple project sponsors with synergistic goals – DOE H_2 Program, U.S. Air Force waste gasification, DOE Mixed Waste Focus Area, other projects.
- In contact with the International Energy Agreement (IEA) Hydrogen Programme.
- Sponsored MBA study of U.S. and Canada waste water treatment plants for potential opportunities for SWPO gasification.
- Identified two new collaborations – Regional Economic Research (RER) and University of California, Riverside (UCR) who are doing related research for the California Energy Commission.
- Pursuing related programs with City of Los Angeles.

PLANS, FUTURE MILESTONES

- **Phase II: Technology Development: (1/04 to 12/05)**
  - Design, fabricate and test advanced pilot-scale SWPO reactor
  - Optimize SWPO operating parameters and H_2 yields during extended-duration tests
  - Revise market, economic and life cycle cost assessments and define scale-up requirements.
- **Phase III: System Integration & Design: (1/06 to 12/06)**
  - Perform safety, RAM, and permitting studies
  - Perform process design and long-lead procurement for Phase IV
  - Update development plan for Phase IV
- **Phase IV: Reduced-scale Demonstration of 5-tpd System: (1/07 to 12/09)**
  - Implement requirements defined during Phase III studies
  - Match reduced-scale SWPO system to industrial H_2 separation and storage systems

GENERAL ATOMICS

PEER REVIEW QUESTION #1 – WHY SWPO AS OPPOSED TO TRADITIONAL STEAM GASIFICATION?

- SWPO utilizes negative value feedstocks with high water content (sewage sludge, yard wastes, etc.).
- SWPO gasifier operates efficiently at much higher steam/carbon ratios than traditional gasifiers (no need for feedstock drying).
- Less energy required to vaporize water at supercritical pressures.
- High water content in SWPO reduces CO in product gas and reduces or eliminates the need for shift reactors.
- SWPO gasifiers are more compact than traditional gasifiers, with less surface area for heat loss.
- While supercritical pressures tend to reduce hydrogen yields and increase methane yields, the effects are virtually eliminated at gasification temperatures of about 950°C (see equilibria plots).
- GA's proprietary SWPO gasifier can operate at temperatures of 800°C, or higher.
- SWPO is expected to perform as well as traditional steam gasifiers, but with dirty, wet biomass feedstocks – a fundamental improvement.

PEER REVIEW QUESTION #2 – WHY USE INTERNAL FUEL HEATING FOR PRODUCTION OF DELICATE GASES?

- Most traditional coal gasifiers (Texaco, Shell) and some biomass gasifiers (IGT) are directly fired by partial oxidation of the feed.
- Partial oxidation is beneficial in SWPO by:
  - minimizing heat transfer across surfaces that are easily fouled with low-value, dirty biomass feeds (tar, char, mineral salts, etc.)
  - rapidly heating the biomass feed through the char-formation temperature range thus minimizing char formation
  - allowing gasification temperatures above 800°C to be internally generated without overheating the high-pressure alloy vessel
- While partial oxidation reduces the amount of hydrogen generated, it greatly simplifies the heating process – a worthwhile tradeoff, especially with low-grade, dirty biomass feedstreams.

GENERAL ATOMICS

PEER REVIEW QUESTION #3 – CAN ENOUGH HYDROGEN BE PRODUCED AT ANY ONE TREATMENT FACILITY TO BE WORTH COLLECTING?

- Commercial-scale 40-tpd sewage sludge gasifier is ideal size for distributed hydrogen generation at hundreds of municipal waste-water treatment plants throughout the U.S.
- A 40-tpd Publicly Owned Treatment Works serves a population of about 200,000.
- Economic analysis of a 40-tpd SWPO gasifier predicts hydrogen generation of ~80,000 GJ/year at a cost of ~$3/GJ.
- This is sufficient hydrogen to power about 1200 households or 600 automobiles for a year, about 0.5 - 5% of the population requirement.
- Additional 40-tpd (or larger) SWPO plants for MSW can add further to the municipal energy requirements for urban centers.
- Based on the above, we believe SWPO of municipal biomass wastes is an economically viable distributed hydrogen production technology.