Design of Hybrid Power Generation Cycles Employing Ammonia-Water-Carbon Dioxide Mixtures

Final Technical Report

Reporting Period: September 1, 2000 to August 31, 2001

Principal Author: Ashish Gupta

June 2002

DOE Award No. DE-FG26-00NT40826

Submitted by the Research Foundation of State University of New York
On behalf of
University at Buffalo

Title	Design of Hybrid Power Generation Cycles Employing Ammonia-Water-Carbon Dioxide Mixtures.
PI:	Ashish Gupta
Institution:	University at Buffalo Department of Chemical Engineering Buffalo, NY 14260 Phone: (716) 645-2911 x2221 Fax: (716) 645-3822 ashishgbuffalo.edu
Grant No.:	DE-FG26-00NT40826
Period of Performance:	September 1, 2000-August 30, 2001

Abstract

A *power cycle* generates electricity from the heat of combustion of *fossil fuels*. Its *efficiency* is governed by the cycle configuration, the operating parameters, and the working fluid. Typical designs use pure water as the fluid. In the last two decades, hybrid cycles based on *ammonia-water*, and *carbon-dioxide* mixtures as the working fluid have been proposed. These cycles may improve the power generation efficiency of Rankine cycles by 15%. Improved efficiency is important for two reasons: it lowers the cost of electricity being produced, and by reducing the consumption of fossil fuels per unit power, it reduces the generation of environmental pollutants.

The goal of this project is to develop a computational optimization-based method for the design and analysis of hybrid bottoming power cycles to minimize the usage of fossil fuels. The development of this methodology has been achieved by formulating this task as that of selecting the least cost power cycle design from all possible configurations. We employ a detailed thermodynamic property prediction package we have developed under a DOE-FETC grant to model working fluid mixtures. Preliminary results from this work suggest that a pure NH_3 cycle outperforms steam or the expensive Kalina cycle.

The lack of a unified framework to systematically develop cycle design alternatives results in missed opportunities. Hence, for process representation, we propose *a new graph theoretic approach to power cycle design.* The **key feature** of this representation is that it reformulates the nonconvex problems (with multiple minima) that result from an *optimization based formulation of the power cycle synthesis task* as a linear program which can be solved globally. We have applied this method to save energy costs in other chemical process design problems, such as in liquid-liquid extraction, and in air separation.

This work in progress provides the basis for a general method to evaluate and design *Vision 21 plant configurations*. Though bottoming cycles are only a component of the energyplex, our design methodology can be modified to design the entire complex with water-gas shift reactions, fuel cells, and gas turbine cycles. The proposed innovative concept work will develop this capability for this component of the Vision 21 plant: the bottoming cycle to recover heat from the stack gases. a 10% improvement in fossil fuel power plant efficiency may lead to a 5% increase in U.S. power generation capacity, without any increase in fuel consumption.

Presentations and Student Support

Journal Articles (Peer Reviewed)

1. Patra, A. and Gupta, A. "A Systematic Strategy For Simultaneous Adaptive *hp* Finite Element Mesh Modification Using Nonlinear Programming," *J. Applied Comp. Mech.*, 190 (2001), 3797-3818.

2. Sourlas, D.D. and A. Gupta *A Pollution Prevention Course for the Chemical Engineering Curriculum.* Chemical Engineering Education in the New Millenium, Topical Conference Proceedings, AIChE Annual Meeting, Editors: R.P. Hesketh, C.S. Howat and D.S. Dixon, pp. 662-675, November 12-17, 2000, Los Angeles, CA.

Conference Presentations

1. Gupta, A. (Invited) *A Graph Theoretic Approach to Process Synthesis.* Praxair Seminar Series, Industrial Engineering Department, University at Buffalo, NY, December 2000.

2. Gupta, A., *A Graph Theoretic Approach to Process Synthesis.* FMC Technical Center, Tonawanda, NY, November 2000.

3. Gupta, A. and Sourlas, D.D., *Minimum Utility Bounds For Liquid-Liquid Extraction Systems.* Paper #49g. AIChE Annual Meeting, Los Angeles, CA, November 2000.

4. Gupta, A. and D.D. Sourlas (Speaker), *A Pollution Prevention Course for the Chemical Engineering Curriculum.* Paper #67f. AIChE Annual Meeting, Los Angeles, CA, November 2000.

5. Gupta, A., *A Graph Theoretic Approach to Mixed Fluid Power Cycle Synthesis.* Paper #242i. AIChE Annual Meeting, Los Angeles, CA, November 2000.

6. Gupta, A. (Speaker) and A. Patra, *Solution of Reaction Diffusion Equations Through Systematically Modified Adaptive hp Meshes.* Paper #272j. AIChE Annual Meeting, Los Angeles, CA, November 2000.

7. Gupta, A. (Speaker) and A. Patra, *Solution of Reaction-Diffusion Equations With A Systematic Adaptive hp Finite Element Mesh Modification Strategy.* First SIAM Computational Science and Engineering Meeting, September 2000. Two presentations.

8. Gupta, A., *A Graph Theoretic Approach to Synthesis of Reactive Distillation Systems.* Gordon Research Conference on Separations & Purifications, August 2000.

Students Supported Under This Grant

- Ananda Viraha Venkata, graduate student, 1/2001-3/2001, in Chemical Engineering, University at Buffalo

A Graph Theoretic Approach For Mixed Fluid Power Cycle Synthesis

Ashish Gupta
Process Synthesis Group
Department of Chemical Engineering
University at Buffalo, Buffalo, NY 14260

Funded by the Department of Energy
November 2000
AIChE Annual Meeting, Los Angeles, CA

Outline

1. Problem Statement
2. Existing Power Cycle Designs
3. Nonlinear Programming Based Approach
4. Graph Theoretic Approach
5. Conclusions

Problem Statement: Power Cycle Synthesis

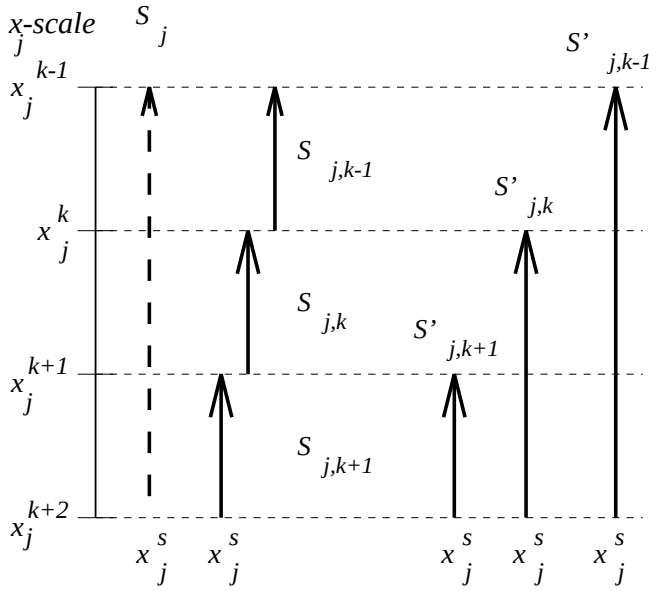
We develop here a general approach for power cycle synthesis:

Given a set of waste hot streams and cold utilities with their thermodynamic properties, a working fluid mixture with a thermodynamic model, and a set of unit operations with operating costs, design a power cycle composed of these unit operations and the working fluid that transfers heat from the hot streams to the cold streams thereby generating power at maximum operating profit.

Existing Separation System Synthesis Approaches

- Process representation: Process design hierarchy (Douglas, 1985): design decisions are: (1) batch vs. continuous, (2) input-output structure, (3) recycle structure, (4) separation system synthesis, (5) heat recovery network.
- For decisions 3-5, a process representation methodology that captures several alternatives is necessary for design generation and evaluation.
- Abstract diagrams: Process represented as a diagram or graph with states (streams) and operations. Simplified unit operation description. Useful in conceptual design. Quantitative data is restricted by assumptions: sharp splits, ideal mixtures, pure component streams. Rudd et al, Nath and Motard, Seader et al, Friedler, Fan et al, 1970's-80's.
- Detailed descriptions: Superstructures that include detailed unit operation descriptions and (all) flows between them. Quantitative analysis possible. Large nonconvex problems. Proposed for specific systems: heat exchangers, binary mass/heat exchange (distillation), reactor networks. Grossmann et al, Floudas et al, Manousiouthakis et al, 1980's-90's
- Process theory: Governing equations restrict design choices. Assess feasibility rapidly. 'One process' systems: attainable regions, residue/distillation curves in composition space, mass/heat pinch curves. Least cost alternative may not be found, or interactions between processes not captured. Horn, Perkins/Doherty/Malone, Westerberg et al, Manousiouthakis et al, Last several decades.

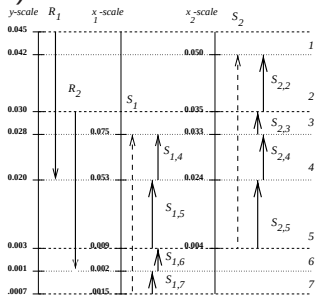
Stream Decomposition



- Variable target MEN synthesis is a nonlinear problem
- Variable target stream has uncountably infinite possible exit compositions. The key is that this stream can be decomposed into:
  - Parallel or serial streams (as many as intervals spanned by the original)
  - Each substream has a fixed target composition: its upper interval edge.

Graph Theoretic Approach

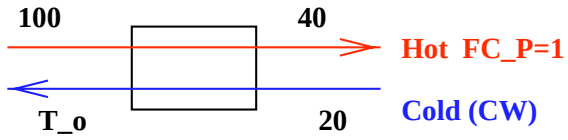
1. We generalize the stream decomposition approach used in variable target mass exchange network synthesis (Gupta and Manousiouthakis, 1996).



2. Stream states define nodes and flowrates define connecting edges.
3. Accurate thermodynamics can be incorporated easily for node definition.
4. Detailed process description is used for edge definition.
5. All possible process configurations are embedded.
6. Process theory and insight is incorporated *a priori* in determining feasible node values.
7. Contraint logic programming and object oriented modeling can be used to develop a computational tool.
8. Resulting large linear program provides a solution that is near the optimal solution.

Graph Theoretic Approach: Example

Consider the task of designing a single heat exchanger:



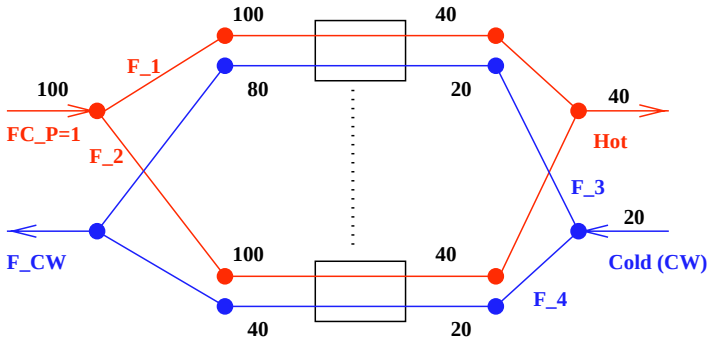
$$\min .05 \cdot F_{CW}$$

s.t.

$$1 \cdot (100 - 40) - F_{CW}(To - 20) = 0$$

$$100 - T_o - (\Delta T_{\min} = 20) \geq 0$$

Nonconvex problem



$$\min .05 \cdot F_{CW}$$

s.t.

$$F_1 + \ldots + F_2 = 1$$

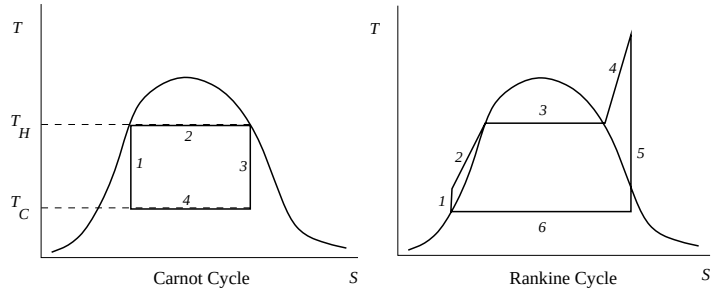
$$F_1(100-40) - F_3(80-20) = 0 \quad \ldots$$

$$\ldots \quad F_2(100-40) - F_4(40-20) = 0$$

$$F_3 + \ldots + F_4 = F_{CW}$$

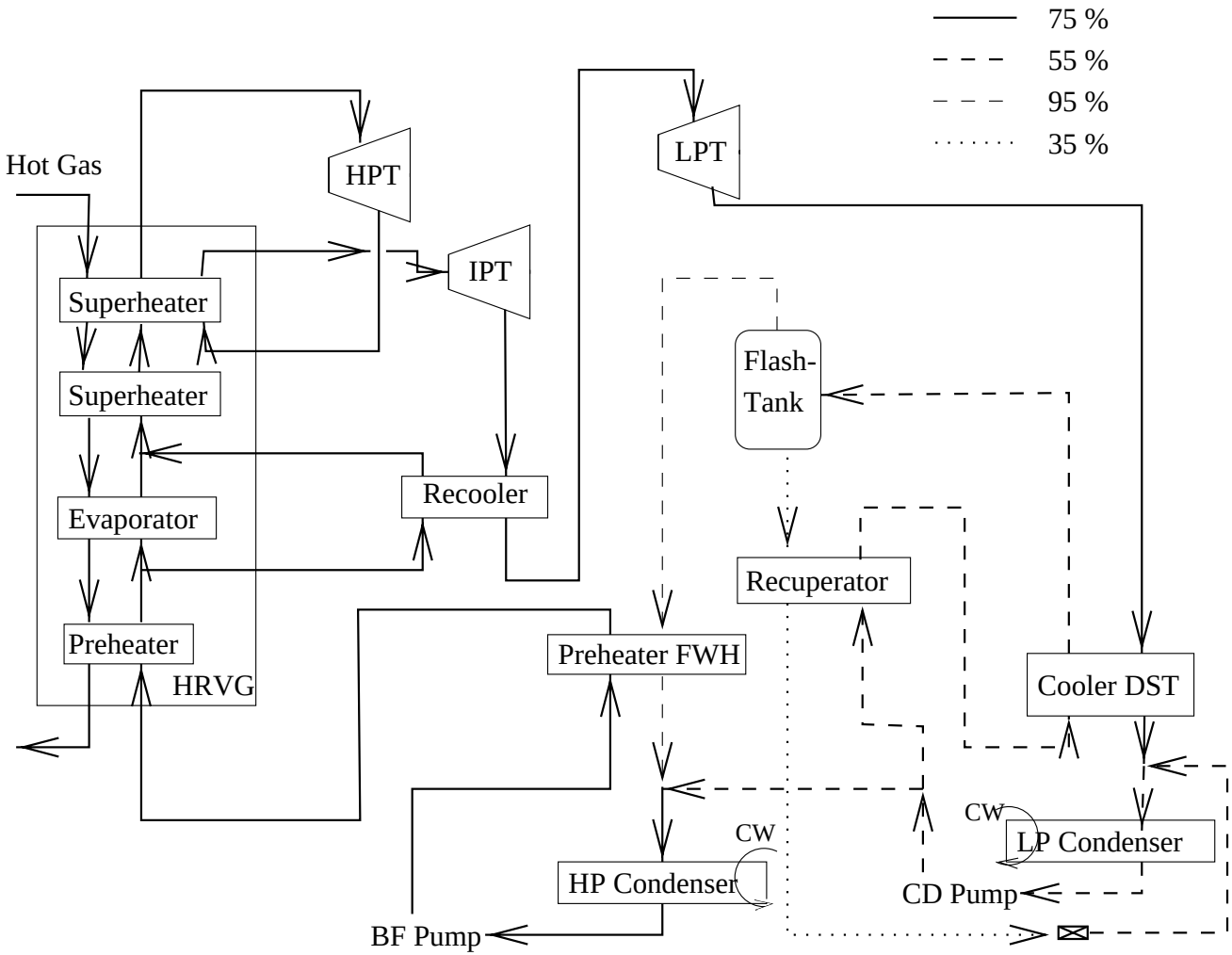
Linear problem

Existing Power Cycle Designs



1. **Rankine Cycle**
   - The working fluid is pure water.
2. **Kalina Cycle**
   - Uses NH_3-H_2O (binary) mixture as the working fluid.
   - Nonisothermal vaporization (dew point-bubble point gap) decreases the gap between the hot and cold curves.
3. **NH_3-CO_2-H_2O Cycle**
   - Addition of CO_2 to the NH_3/H_2O mixture leads to ionic species that raise the mixture bubble point and lower its dew point.

Kalina Bottoming Cycle



Objective Function

$$\max \mathcal{F} = \left\{ \begin{array}{l} \text{Turbine} \\ \text{Work} \end{array} \right\} - \left\{ \begin{array}{l} \text{Pumping} \\ \text{Costs} \end{array} \right\} - \left\{ \begin{array}{l} \text{Hot} \\ \text{Utility} \\ \text{Costs} \end{array} \right\} - \left\{ \begin{array}{l} \text{Cold} \\ \text{Utility} \\ \text{Costs} \end{array} \right\}$$

- Turbine efficiency: 90%.
- Pump efficiency: 70%.
- Electricity cost factor: 3,000.
- Cooling water cost factor: 200.

Constraints

- Mass balance, component balance and energy balance at the mixing and split points.
- Liquid, vapor and mixed phase stream constraints
- 2^{nd} law of thermodynamics constraints
- Heat exchanger constraints
- Power-pressure isentropic turbine relations
- Pump energy (Bernoulli) equations

NH_3-H_2O Thermodynamics

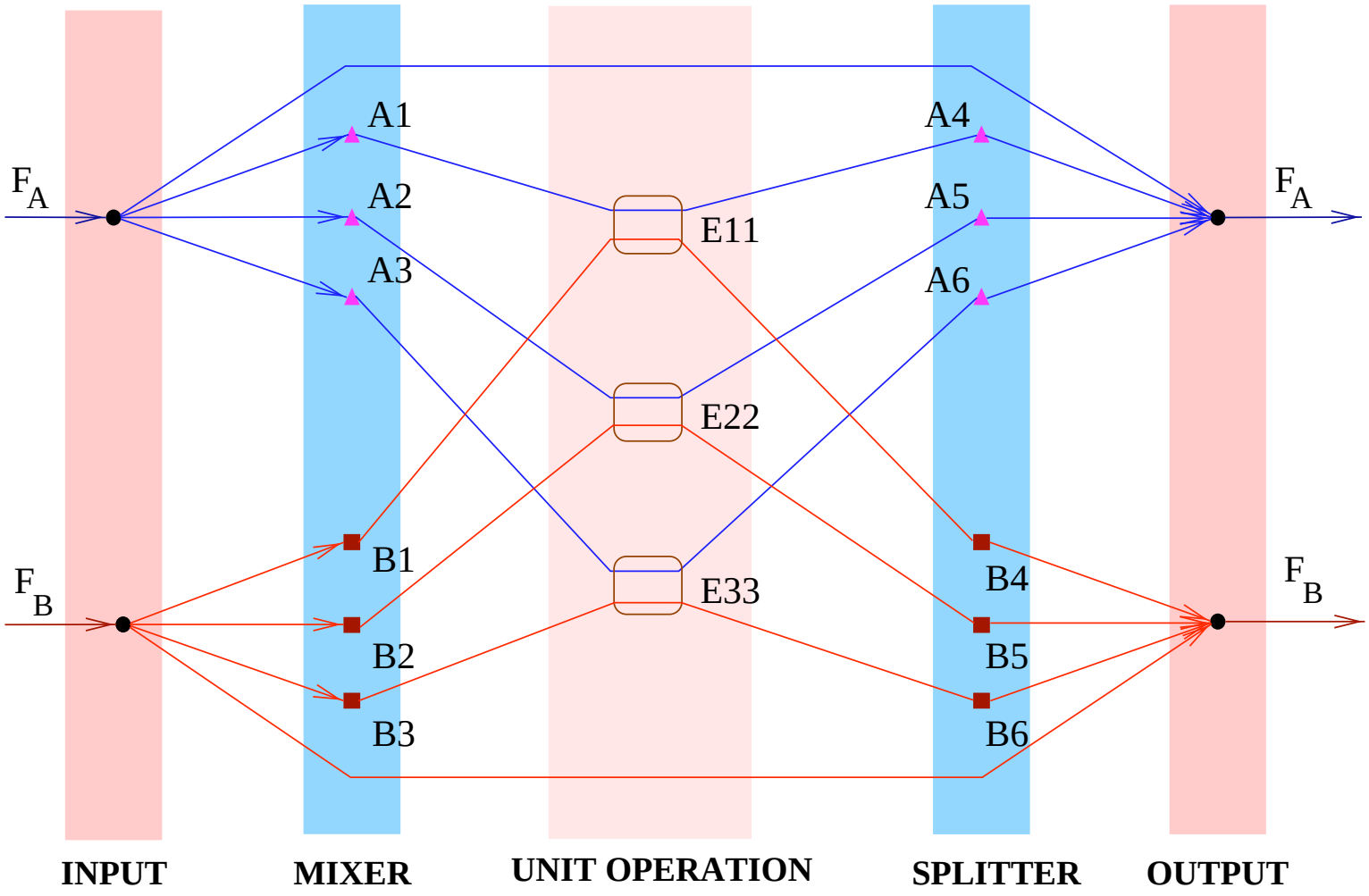
$$\phi_i(T,P)\cdot P\cdot y_i \;=\; f_i^{sat}(T)\cdot\gamma_i(T,P,x_i)\cdot x_i\cdot\delta_i, \quad i=\;\mathrm{NH_3},\,\mathrm{H_2O}$$

- Ideal vapor phase mixture
- Redlich-Kwong-Soave equation for fugacity coefficient of NH_3
- Empirical equation of states for pure components suggested by Ibrahim & Klein (1993)

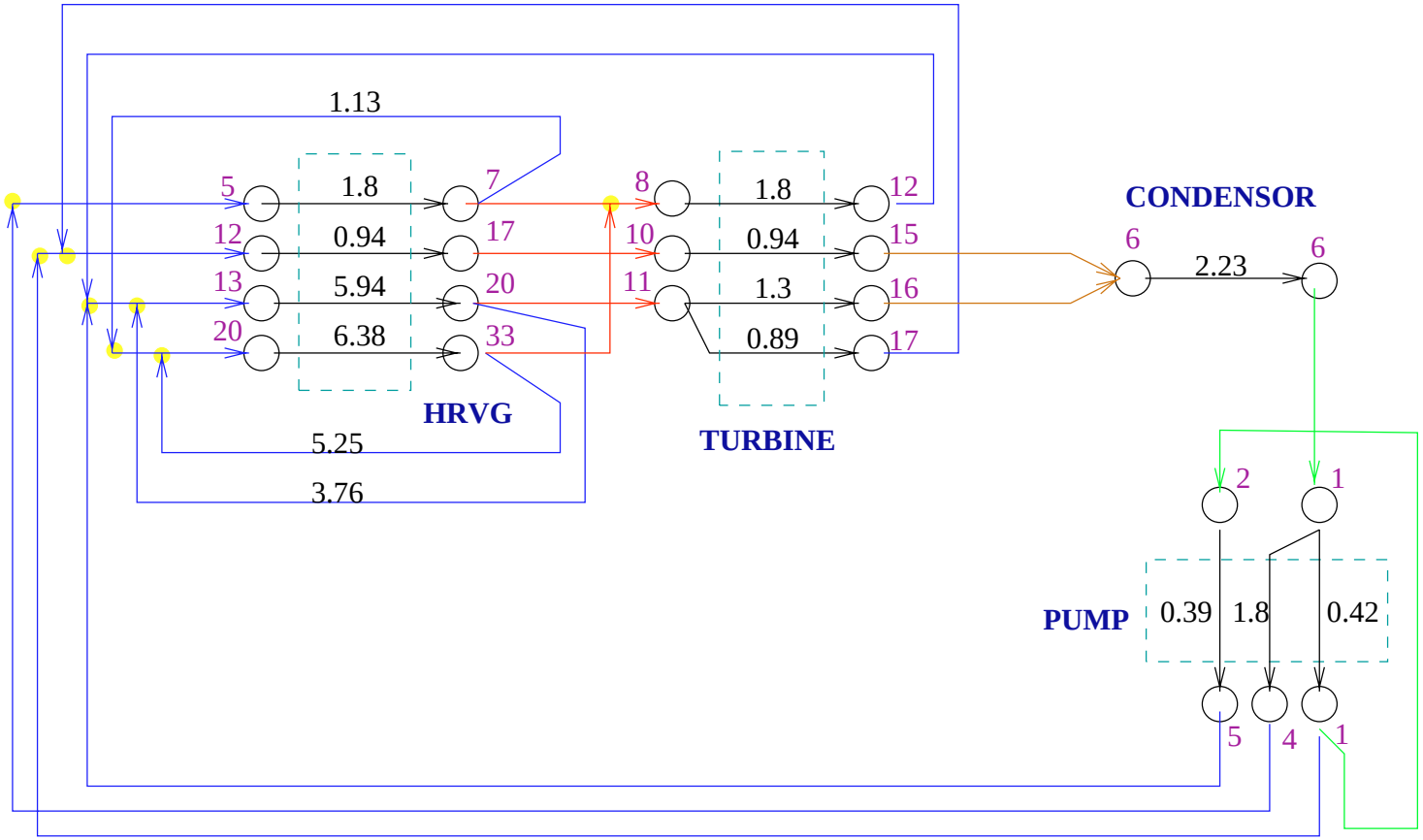
$$\begin{aligned} v^l &= a_1 + a_2P + a_3T + a_4T^2 \\ v^g &= \frac{RT}{P} + c_1 + \frac{c_2}{T^3} + \frac{c_3}{T^{11}} + \frac{c_4P^2}{T^{11}} \end{aligned}$$

- Four suffix Margule's equation for the excess free energy
- Robustness of the VLE calculation requires analytical gradients for the nonlinear phase equilibrium equations.

Graph Theoretic Approach



Graph Theoretic Approach: Results



Efficiency: Work done/Heat absorbed = 25.785%

Graph Theoretic Approach: Results

	Inlet Node	T(K)	P(bar)	Outlet Node	T(K)	P(bar)
HRVG	5	290	100	7	380	100
	12	470	31	17	550	31
	13	470	54	20	550	54
	20	560	100	33	650	100
Turbine:	8	470	100	12	406.1	8
	10	550	31	15	411.8	8
	11	550	54	16	357.1	8
				17	496.5	31
Condenser:	6	370	8	6	290	8
Pump:	1	290	8	1	290	31
	2	290	31	4	290	100
				5	290	54

Graph Theoretic Approach: Assumptions

1. Only vapor phase streams can enter or leave a turbine.
2. Only liquid phase streams can enter or leave a pump.
3. Only streams with equal pressures can mix.
4. Hot gas properties: $T_{in} = 655$ K, $FC_{pg} = 20.0$.
5. Minimum temperature difference: 5 K
6. Cooling water inlet temperature = 285 K
7. Objective value(Ibrahim *Energy* **21**(10).1996.): 1.198×10^5

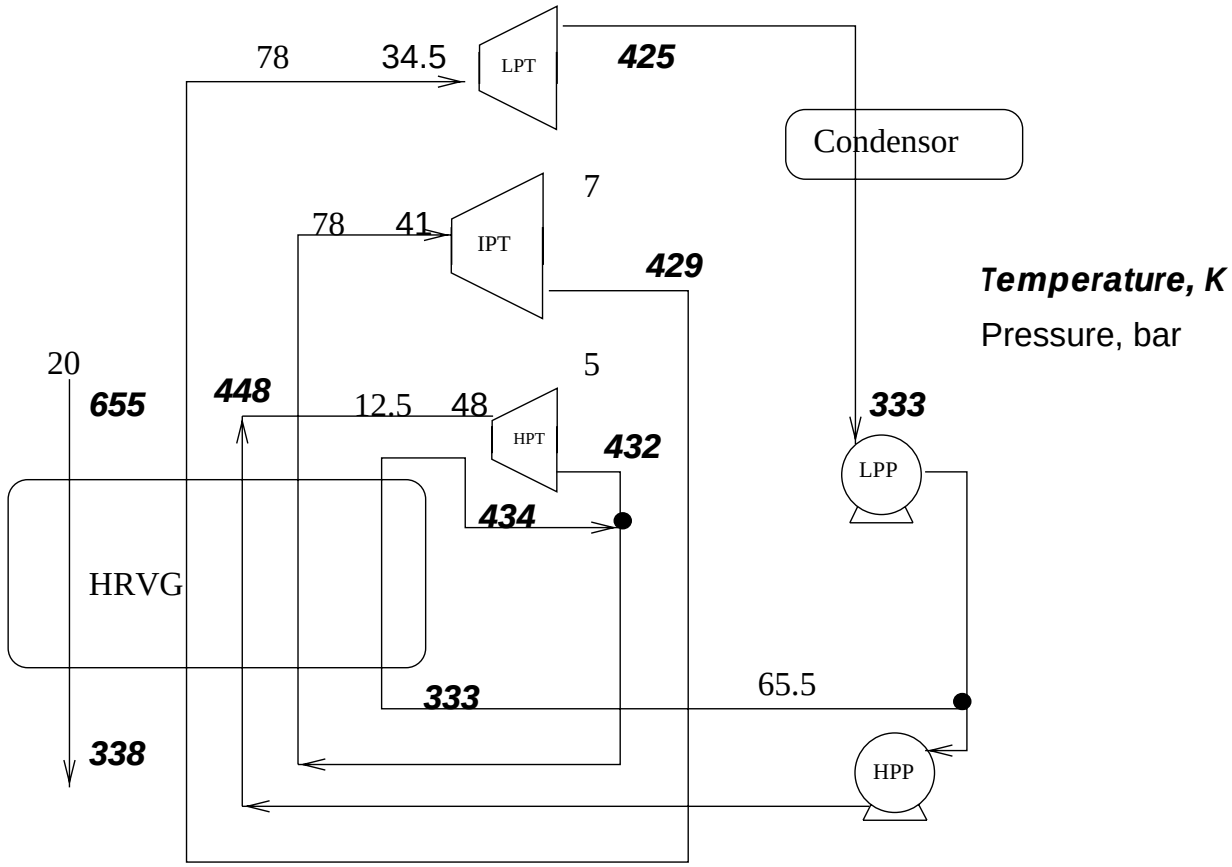
Graph Theoretic Approach: Results

1. Used both simplex method (MINOS) and interior point method (PCx).
2. PCx converges faster than MINOS.

Constraints	**Variables**	**PCx** CPU Time(s)	**MINOS** CPU Time(s)	**PCx** Iterations	**MINOS** Iterations
429	2704	0.72	1.0	19	1262
1390	20352	29.82	44.83	26	12375
2463	39029	161.56	223.5	31	28947
2222	51630	164.95	346.96	31	40354
3570	116737	870.66	2321.92	35	115459
5231	220882	5625.91	8674.66	65	215862

CPLEX 6.6 is nearly 10 times faster.

Graph Theoretic Approach: Results

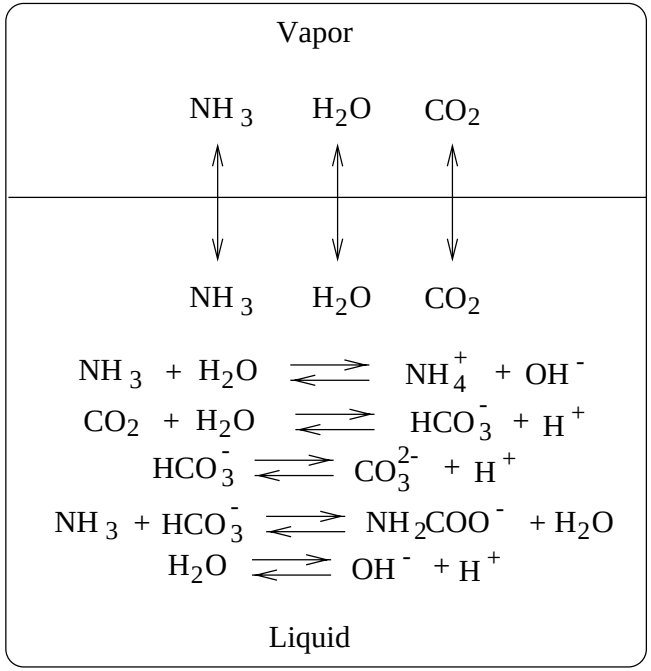


Optimal cycle using 90% ammonia working fluid. Profit= \$19M/yr

Conclusions

1. The task of designing an optimal power cycle leads to a nonlinear programming problem.
2. We formulated this task to consider ammonia-water mixture as the working fluid.
3. Created a graph theoretic approach for power cycle synthesis.
4. A mixed ammonia-water cycle seems to be the best cycle.

NH_3-CO_2-H_2O Thermodynamics



- Reaction equilibrium and phase equilibrium have to solved simultaneously.

$$
\begin{aligned}
K_R(T) &= \Pi_i a_i^{\nu_{i,R}}, \quad R = 1, \cdots, 5 \\
\phi_w \cdot P \cdot y_w &= f_w^{sat} \cdot \gamma_w \cdot \delta_w \cdot x_w \\
\phi_i \cdot P \cdot y_i &= H_{iw} \cdot \gamma_i \cdot \delta_i \cdot x_i, \quad i = \mathrm{NH_3}, \mathrm{CO_2}
\end{aligned}
$$

NH_3-CO_2-H_2O Thermodynamics

- Truncated virial equation of state for CO_2 fugacity coefficient in vapor phase.

$$\log \phi_{i,gas}(T, P, y_j) = \left(2 \sum_j y_j B_{ij} - \sum_i \sum_j y_i y_j B_{ij} \right) \frac{P}{RT}$$

- Second virial coefficients, Henry's constants, and reaction equilibrium constants from Kurz et al.
- Pitzer's model for the excess free energy.

$$\frac{G^E}{RTn_w M_w} = f_1(I) + \sum_{(i,j)\neq w} m_i m_j \left(\beta_{i,j}^{(0)} + \beta_{i,j}^{(1)} f_2(I) \right) + \sum_{(i,j,k)\neq w} m_i m_j m_k \tau_{i,j,k}$$

- Binary and ternary interaction terms and dielectric constant from Kurz et al.
- Solid formation (carbamate) needs to be incorporated.
- Available experimental data is limited.