PSE as the Modern Euryphaessa in Guiding Humans Past Prometheus' Paradigm and the Climate Change Tautology

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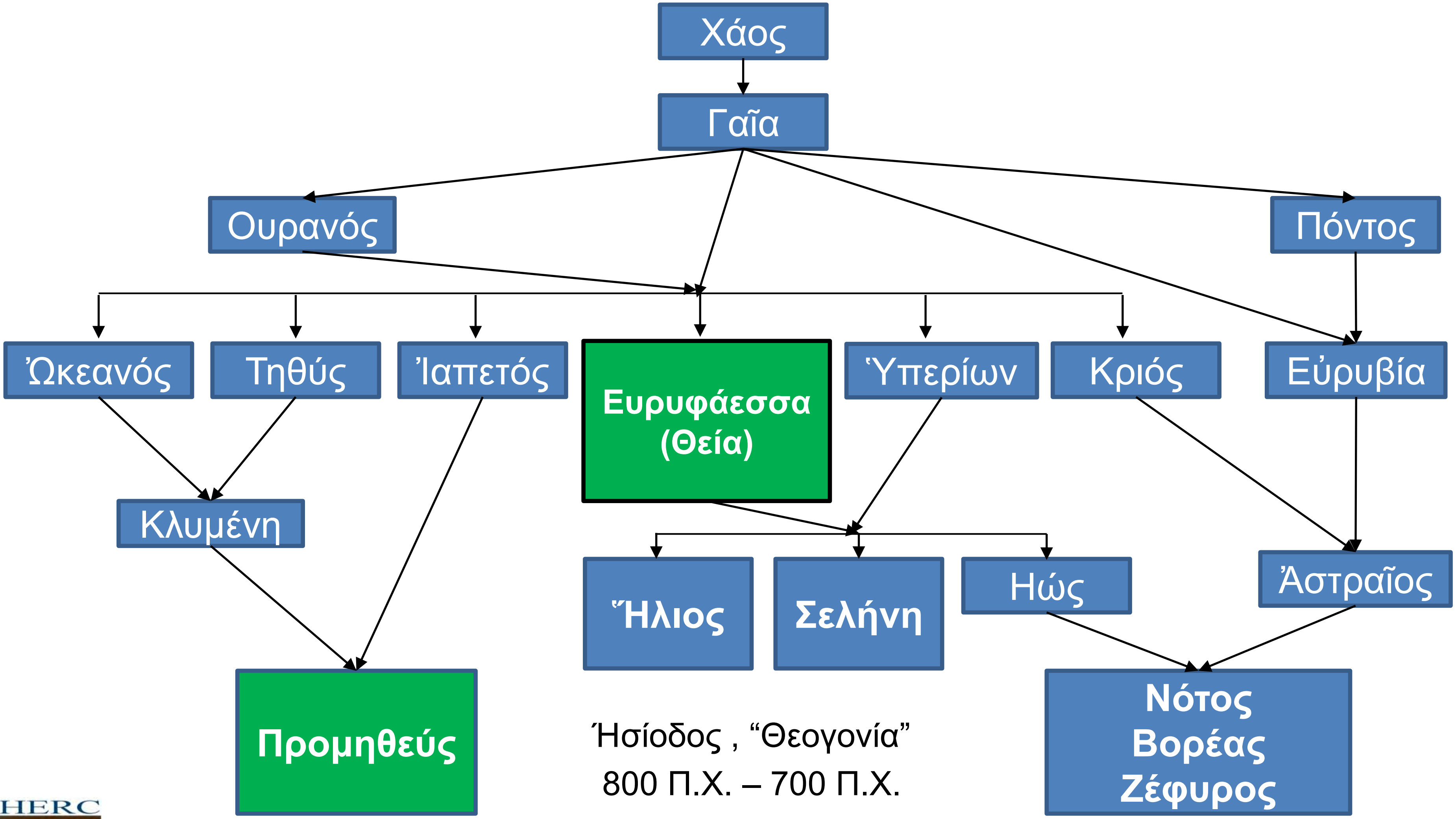
MIT: 2040 Visions of Process Systems Engineering
George Stephanopoulos' Birthday and Retirement Symposium

June 1-2, 2017, Boston, MA
Friday, June 2, 14:30 -15:00
MIT Wong Auditorium, Tang Center, Room E51-115

Outline

- ➢ Euryphaessa, Prometheus, Tautology
- ➢ George’s Impact on My Research/Education
- ➢ Climate Change
- ➢ Process Systems Engineering as Euryphaessa
- ➢ Conclusions
- ➢ Acknowledgments

Θεογονία *



Ησίοδος , “Θεογονία”
800 Π.Χ. – 700 Π.Χ.

Ευρυφάεσσα (Θεία) *

- Euryphaessa means “Wide Shining”
- Theia derived from “Sight” and “Prophesy”
- A Titan
- First Born Daughter of Gaia and Uranus
- Wife of Hyperion (her brother)
- Mother of Sun, Moon, and Dawn (among whose children are the winds (Boreas, Notos, Zefyros)
- Goddess who endowed gold and silver with intrinsic value

. * Ήσίοδος , “Θεογονία”, 800 Π.Χ. – 700 Π.Χ.

Γονιδέλλης Α., “Η Γένεση κατά τούς Αρχαίους ¨Ελληνες, Μέρος Δεύτερο, Τιτάνες, Το Πρώτο Δωδεκάθεο”, 2001

http://www.theoi.com/Titan/TitanisTheia.html

Προμηθεύς *

- ➢ Prometheus’ name derives from “Before” and “Thought”
- ➢ A Titan
- ➢ Third Born Son of Iapetos and Klymene
- ➢ Brother of Atlas, Menoetius, and Epimetheus (1, 2, 4)
- ➢ Considered Benefactor of Mankind
- ➢ God of forethought and crafty counsel, who was given the task of moulding mankind out of clay
- ➢ Designated by Zeus to be in the East (Atlas in the West)

. * Ήσίοδος , “Θεογονία”, 800 Π.Χ. – 700 Π.Χ.
Γονιδέλλης Α., “Η Γένεση κατά τούς Αρχαίους ¨Ελληνες, Μέρος Δεύτερο, Τιτάνες, Το Πρώτο Δωδεκάθεο”, 2001
http://www.theoi.com/Titan/TitanPrometheus.html

Προμηθεύς *

- Prometheus fought on the side of Zeus in the Titan battle
- Following the Titan battle, Prometheus cut a bull into two parts: the meat and intestines inside the skin with the stomach on top; the bones covered in fat
- Zeus chose the latter, and subsequently, in anger, withheld fire from the humans
- Prometheus stole fire, and gave it to humans in a hollow tube
- Prometheus was put in chains, and an eagle was sent to eat his liver during the day, while it was restored every night

. * Ήσίοδος , “Θεογονία”, 800 Π.Χ. – 700 Π.Χ.

Γονιδέλλης Α., “Η Γένεση κατά τούς Αρχαίους ¨Ελληνες, Μέρος Δεύτερο, Τιτάνες, Το Πρώτο Δωδεκάθεο”, 2001

http://www.theoi.com/Titan/TitanPrometheus.html

Prometheus

Prometheus

Prometheus

Prometheus


DUKEART.net
GreekMythology - Prometheus Bound June 2009 Duke Yin

Prometheus

Greek Environmental Catastrophes

12th Century B.C	Mycaenean Civilization is destroyed due to ecological disaster leading to four centuries of “Greek Dark Ages”. Elimination of forests (often through the destruction of the trees’ outer layer, so resulting organic material could be used as swine food), over-cultivation of agricultural land, low brush destruction by sheep and goats, and overpopulation, led to destruction.
4th Century B.C.	Earlier disaster is forgotten, and those that followed Mycaenaean Civilization did not feel responsible. The result is that dense forests of oak, cypress, and olive trees, reaching Attica’s coast, were destroyed. Human impact not as devastating, due to increased sea harnessing and trading.

Μπουρατίνος Α. , “Περιβαλλον και Συνειδηση στην Αρχαια Ελλαδα”, 1997

Προμηθεύς *

- Prometheus traditionally portrayed as benefactor of humankind
- Symbol of human independence from the control of Gods
- Symbol of human ability to determine own path to the future with the help of only external knowledge
- In Nature, the notion of independence does not exist
- No single path is independent of other paths
- Prometheus transformed fire into a simple utilitarian tool
- With no internal awareness, fire can be dangerous
- It may be time to reconsider Prometheus’ burning paradigm

. * Ήσίοδος , “Θεογονία”, 800 Π.Χ. – 700 Π.Χ.
Γονιδέλλης Α., “Η Γένεση κατά τούς Αρχαίους ¨Ελληνες, Μέρος Δεύτερο, Τιτάνες, Το Πρώτο Δωδεκάθεο”, 2001
http://www.theoi.com/Titan/TitanPrometheus.html

Tautology

- From the Greek word “Ταυτολογία”

- “Ταυτολογία” is the composition of

  “Ταυτός” meaning “the same”

  “Λόγος” meaning “”speech”

- In mathematical logic, a tautology is:

  A logical statement in which conclusion and premise are equivalent

  A logical proposition that is always true

- Example: $\{A \Rightarrow B\} \Leftrightarrow \{\neg B \Rightarrow \neg A\}$

Concentrated Solar Power (Ivanpah)

Ivanpah Solar Electric Generating System, California, US
http://inhabitat.com/ivanpah-worlds-largest-solar-thermal-plant-officially-goes-in-service-today/ivanpah-2/

Concentrated Solar Power (Ivanpah)

Ivanpah Solar Electric Generating System, California, US
http://www.marketwatch.com/story/could-californias-massive-ivanpah-solar-power-plant-be-forced-to-go-dark-2016-03-16

Concentrated Solar Power (Ivanpah)

Concentrated Solar Power (Ivanpah)

Tidal Power (Rance River)

Rance River Estuary, Brittany, France
http://tidalenergyassignment.blogspot.com/2014/05/tidal-power-plants-in-world-today.html

Tidal Power (Annapolis)

Annapolis Royal Generating Station, Nova Scotia, Canada
http://brad-bradshaw.blogspot.com/2013/04/tidal-power-investment-surging.html

Tidal Power (Annapolis)

Annapolis Royal Generating Station, Nova Scotia, Canada
http://tidalenergytoday.com/2015/01/20/video-annapolis-tidal-power-station/

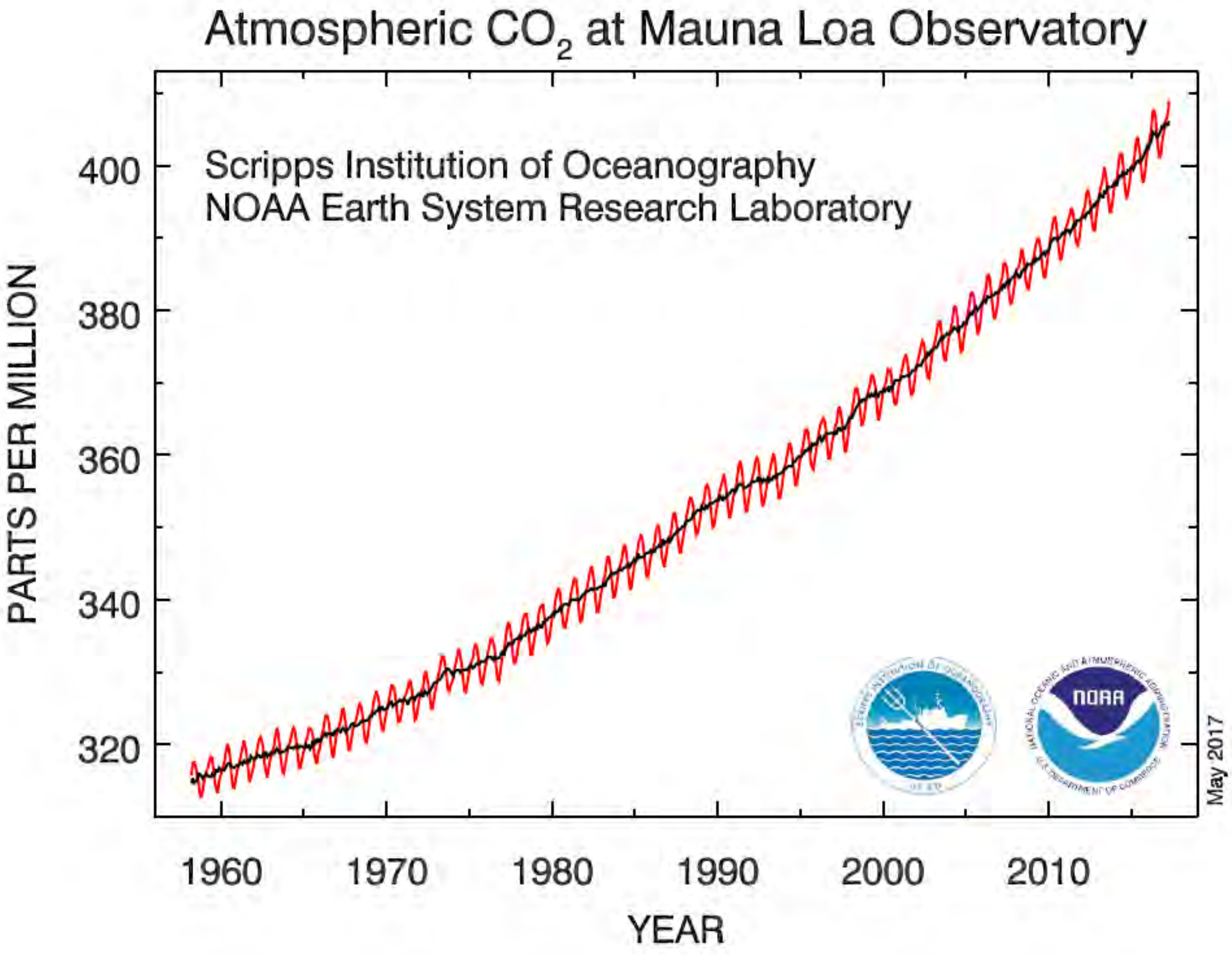
Wind Power (South Fork)

South Fork Wind Farm, Long Island, US
http://gizmodo.com/new-york-state-approves-americas-largest-offshore-wind-1791648822

Climate Change

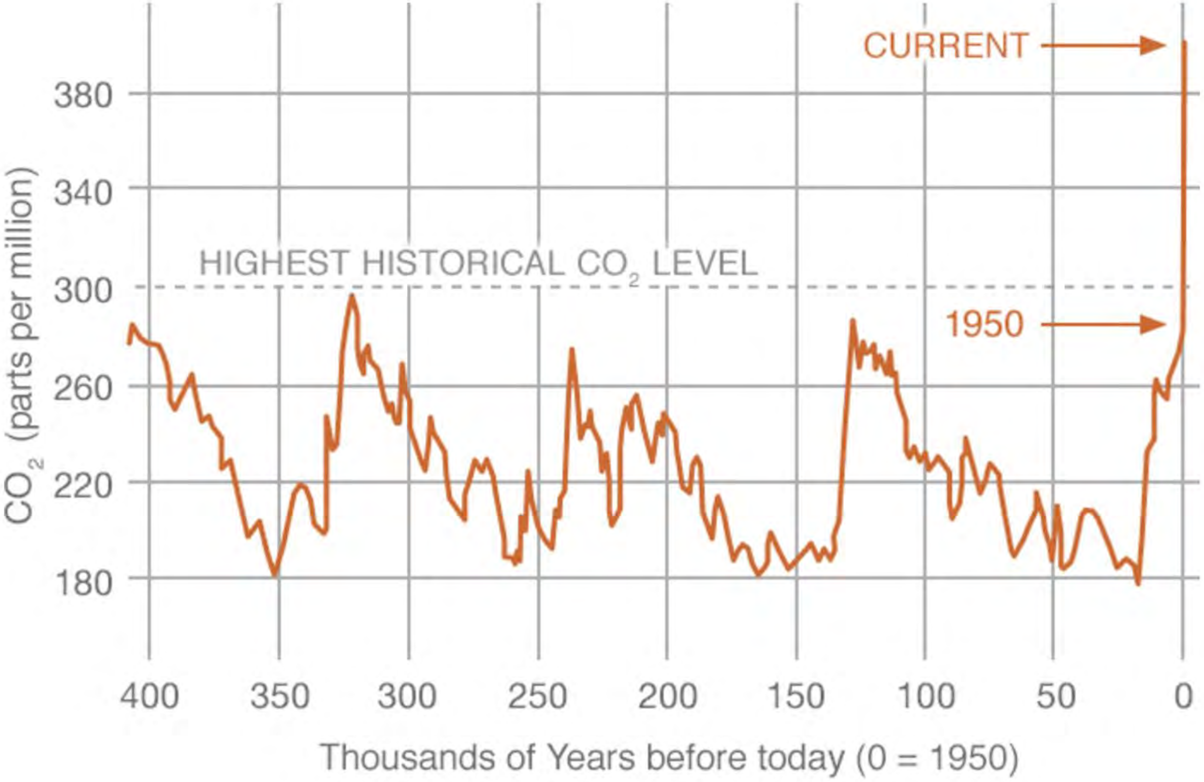
- “Continued Emission of Greenhouse gases will cause further warming and long-lasting changes in all components of the climate system, increasing the likelihood of severe, pervasive, and irreversible impacts for people and eco-systems.” (2014, IPCC)

Atmospheric CO2 Concentrations (Mauna Loa Data)



Atmospheric CO2 Concentrations (Ice Core Data)

Data source: Reconstruction from ice cores.
Credit: NOAA



Global Temperatures

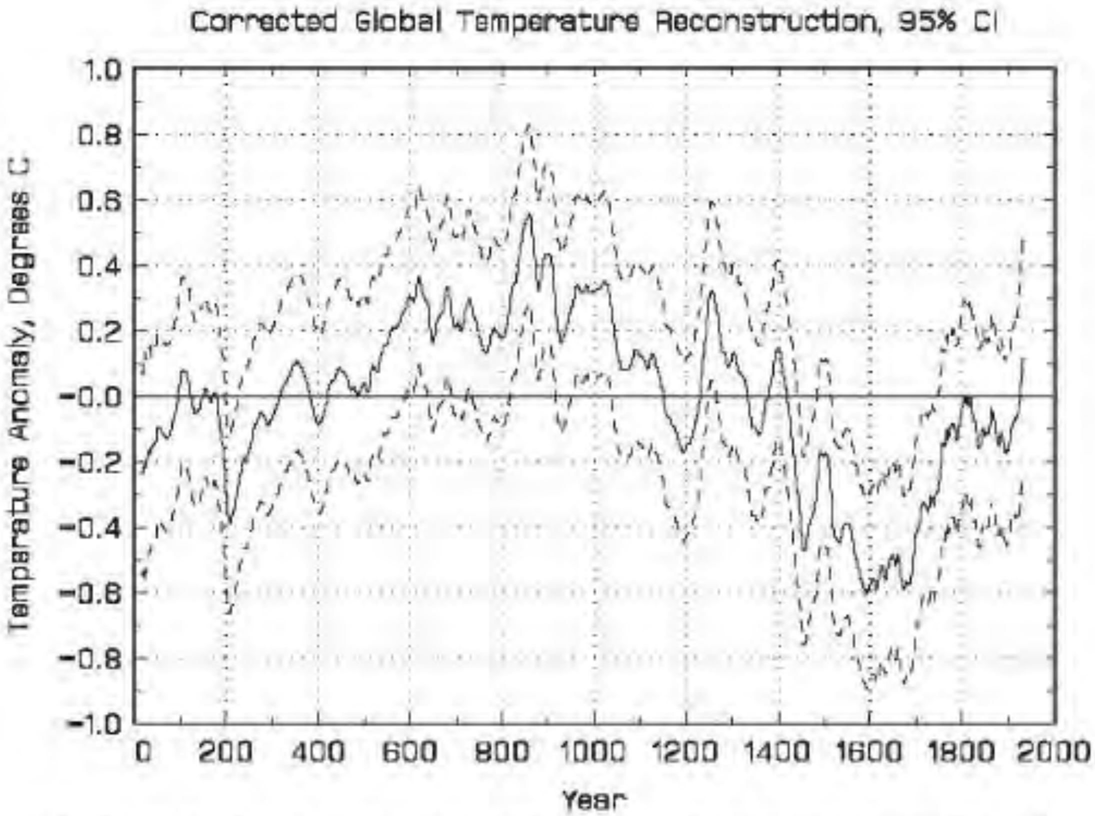
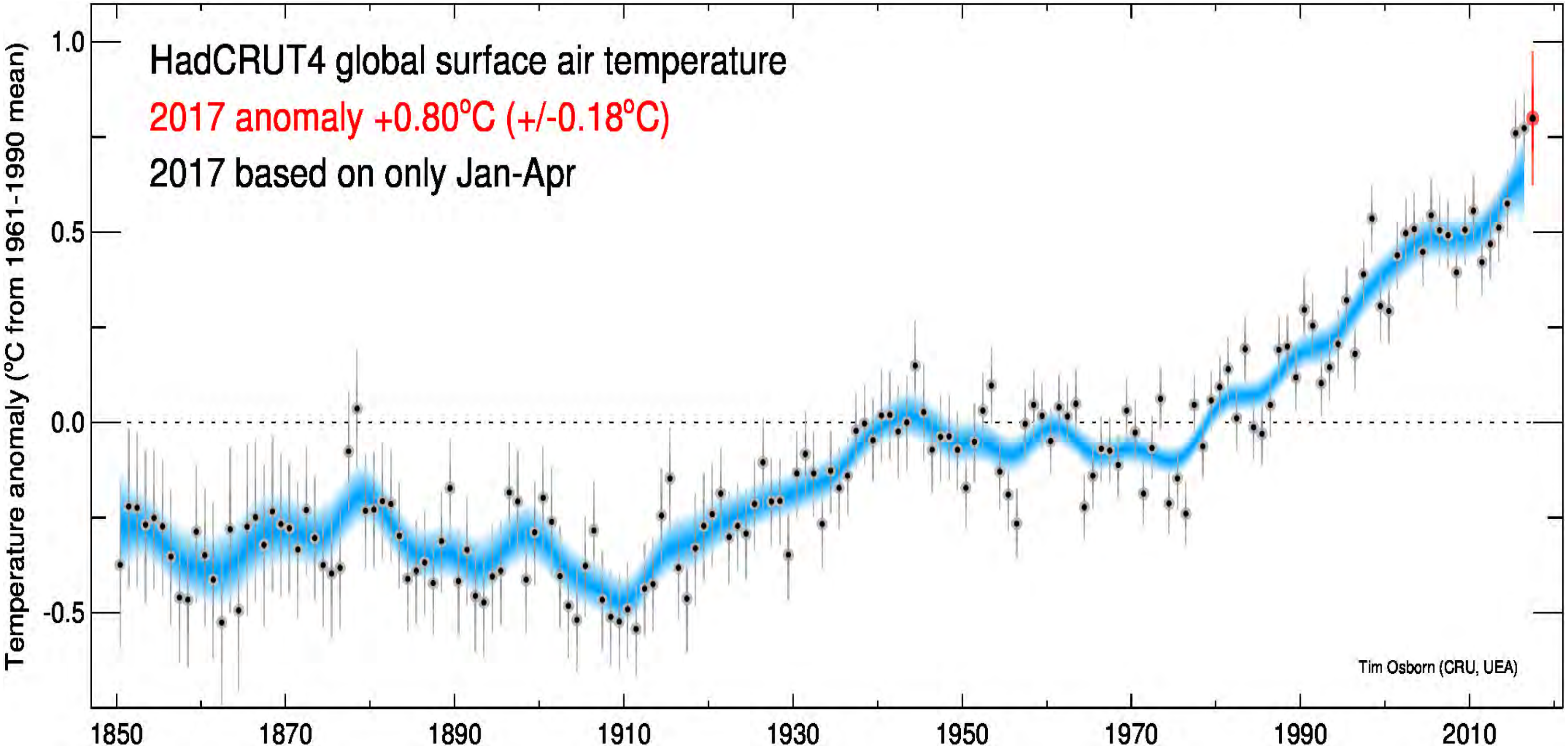


Figure 3. Corrected reconstruction with 95% confidence intervals (from Loehle and McCulloch, 2008)

Global Temperature Deviation Data from 1961-1990 mean



Source: Climatic research unit (CRU)

Global Temperature Deviation Data (cont’d)

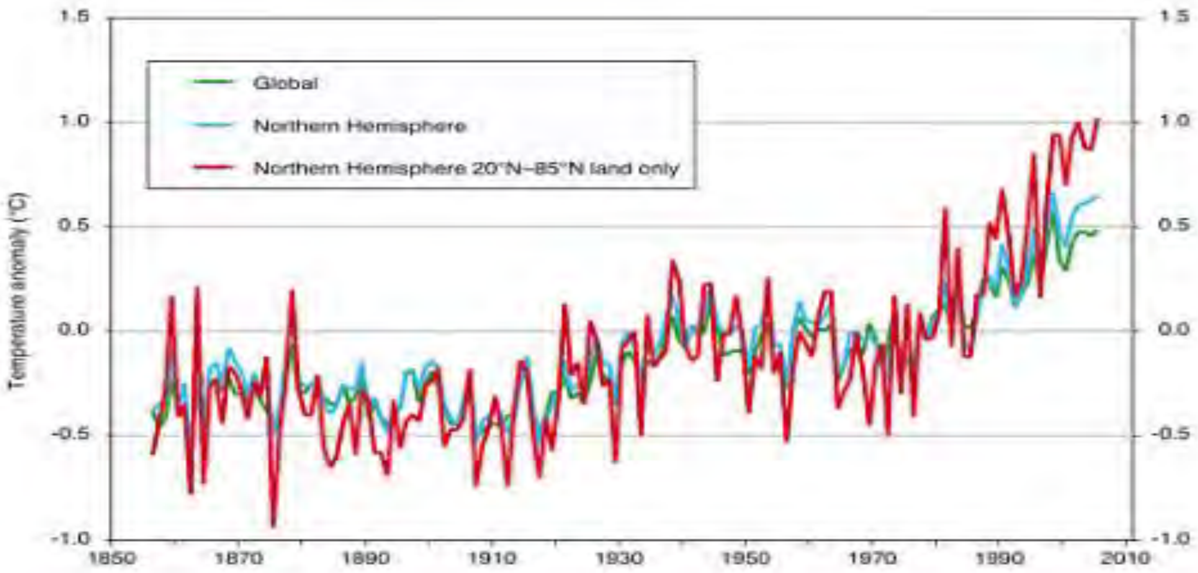
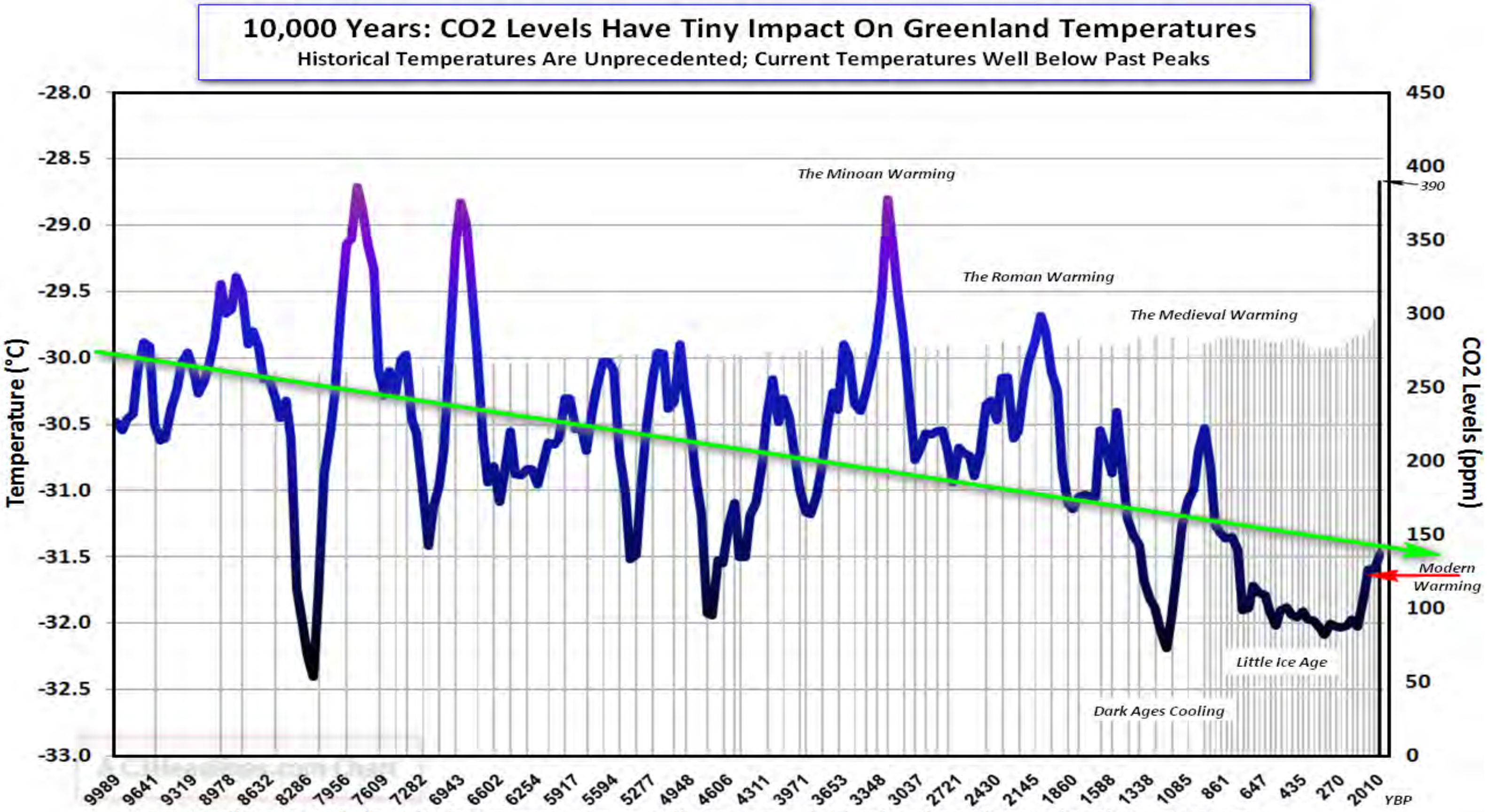


FIGURE 2-1 Global, Northern Hemisphere, and Northern Hemisphere extratropical land area annual temperature anomalies in degrees Celsius from the HadCRUT2v surface temperature dataset. SOURCE: Jones et al. (2001).

Source: Committee on Surface Temperature Reconstructions for the Last 2,000 Years, Board on Atmospheric Sciences and Climate,
Division on Earth and Life Studies, NATIONAL RESEARCH COUNCIL OF THE NATIONAL ACADEMIES

Greenland Temperatures/Atmospheric CO2 Concentrations (Ice Core Data)



10,000 Years: CO2 Levels Have Tiny Impact On Greenland Temperatures
Historical Temperatures Are Unprecedented; Current Temperatures Well Below Past Peaks

Source: http://cdiac.ornl.gov/ftp/trends/co2/lawdome.smoothed.yr75 - ftp://ftp.ncdc.noaa.gov/pub/data/paleo/icecore/antarctica/taylor/taylor_co2-holocene.txt
http://www1.ncdc.noaa.gov/pub/data/paleo/icecore/greenland/summit/gisp2/isotopes/gisp2_temp_accum_alley2000.txt - http://cdiac.esd.ornl.gov/trends/temp/vostok/jouz_tem.htm

Greenland ice core data (GRIP2) reveals an overall cooling trend in the Arctic regions over the last 10,000 years. The gray columns represent atmospheric CO2 levels from Antarctic ice cores. It is clearly obvious that over this brief span of geological time, temperatures and climate change dramatically with CO2 levels remaining almost constant. Since the cold of the Little Ice Age, Greenland temperatures took an upswing well before the massive increase in human CO2 emissions after WWII. 2010 Greenland temps are well below previous peaks.

Global Carbon Cycle

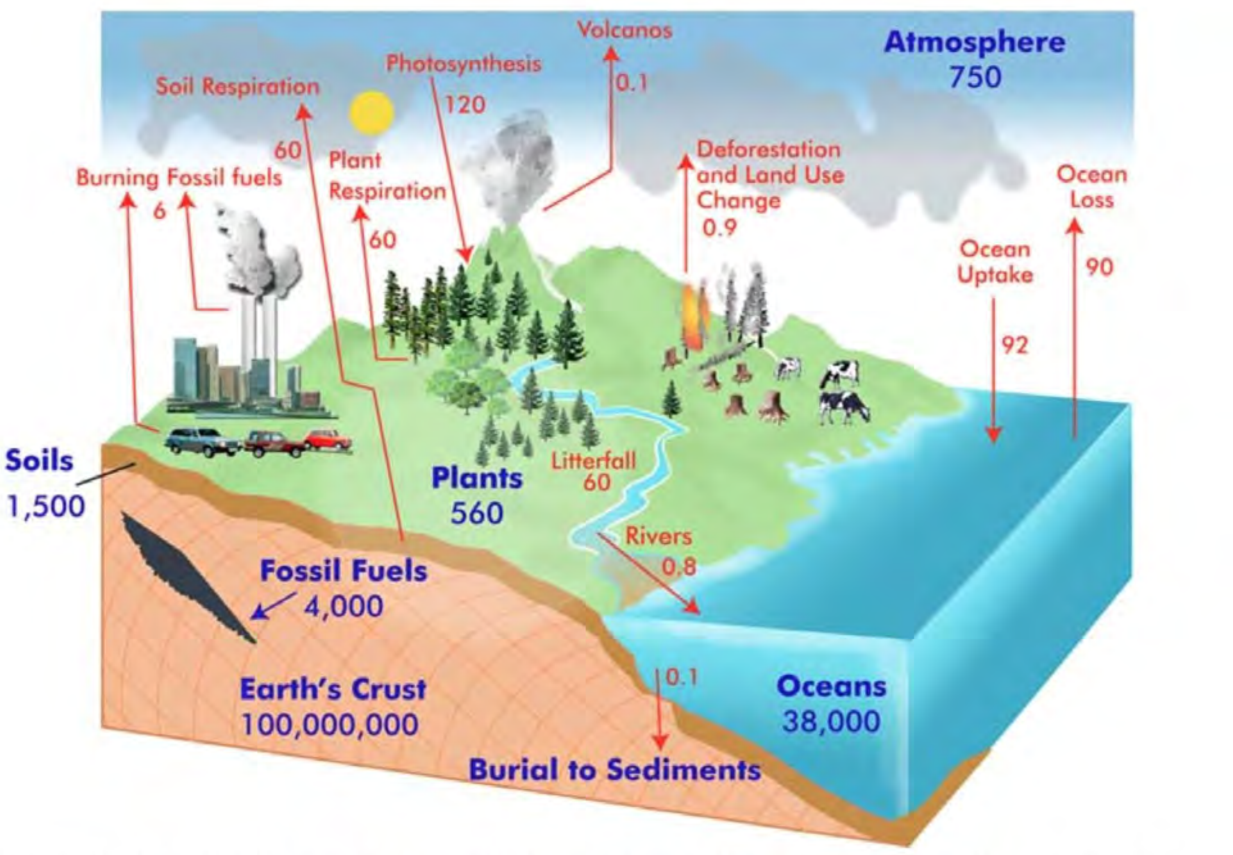
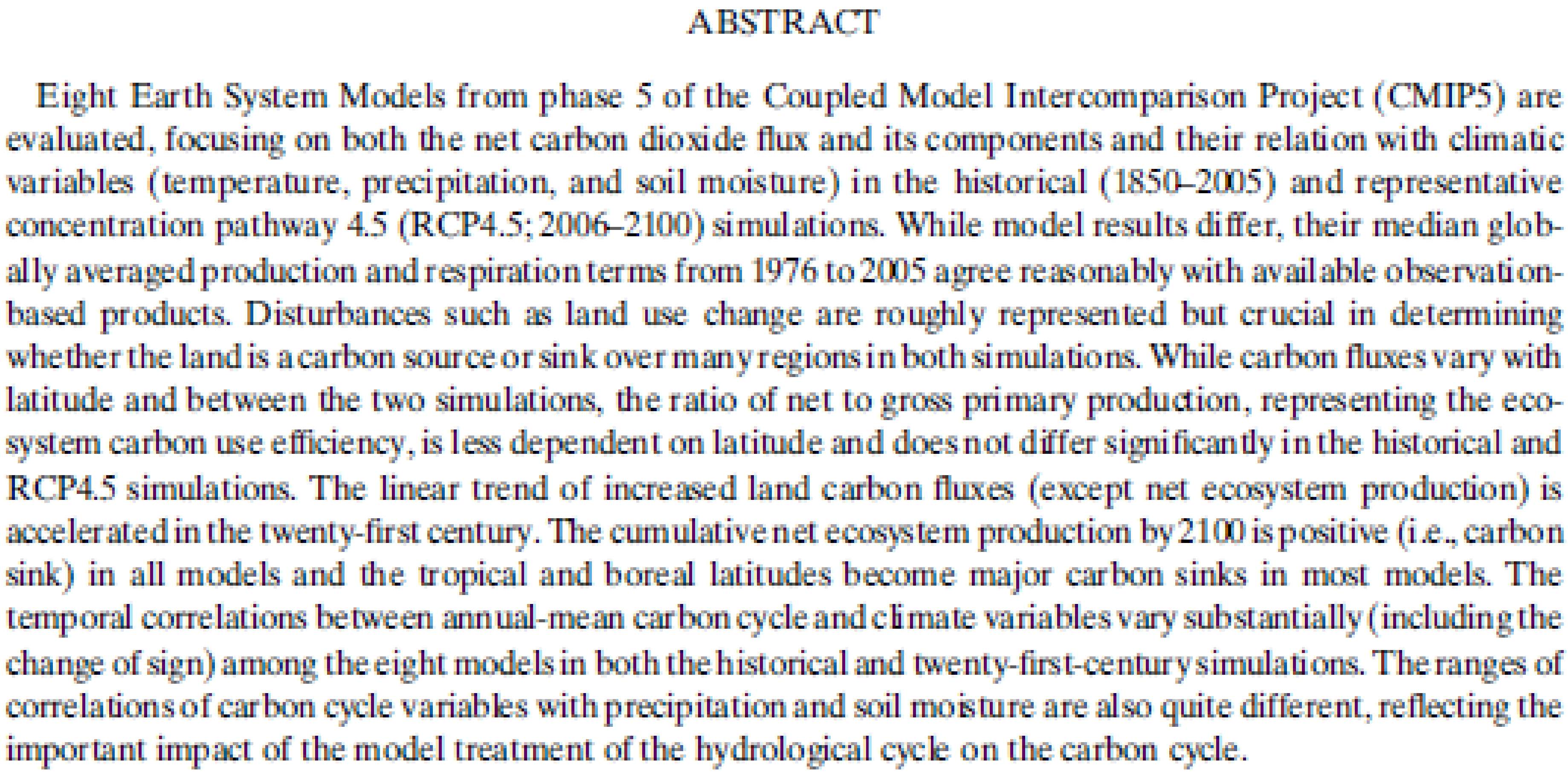


Figure 2. *A simplified diagram of the global carbon cycle. Pool sizes, shown in blue, are given in petagrams (Pg) of carbon. Fluxes, shown in red, are in Pg per year. (www.globe.gov/projects/carbon)*

University of New Hampshire GLOBE Carbon Cycle
http://globecarboncycle.unh.edu/CarbonCycleBackground.pdf

Climate Model Predictions (Carbon Cycle)



ABSTRACT

Eight Earth System Models from phase 5 of the Coupled Model Intercomparison Project (CMIP5) are evaluated, focusing on both the net carbon dioxide flux and its components and their relation with climatic variables (temperature, precipitation, and soil moisture) in the historical (1850–2005) and representative concentration pathway 4.5 (RCP4.5; 2006–2100) simulations. While model results differ, their median globally averaged production and respiration terms from 1976 to 2005 agree reasonably with available observation-based products. Disturbances such as land use change are roughly represented but crucial in determining whether the land is a carbon source or sink over many regions in both simulations. While carbon fluxes vary with latitude and between the two simulations, the ratio of net to gross primary production, representing the ecosystem carbon use efficiency, is less dependent on latitude and does not differ significantly in the historical and RCP4.5 simulations. The linear trend of increased land carbon fluxes (except net ecosystem production) is accelerated in the twenty-first century. The cumulative net ecosystem production by 2100 is positive (i.e., carbon sink) in all models and the tropical and boreal latitudes become major carbon sinks in most models. The temporal correlations between annual-mean carbon cycle and climate variables vary substantially (including the change of sign) among the eight models in both the historical and twenty-first-century simulations. The ranges of correlations of carbon cycle variables with precipitation and soil moisture are also quite different, reflecting the important impact of the model treatment of the hydrological cycle on the carbon cycle.

https://cmip-publications.llnl.gov/, Shao P., Zeng X., Sakaguchi K., Monson R., Zeng X., "Terrestrial Carbon Cycle: Climate Relations in Eight CMIP5 Earth System Models" J. of Climate, Vol. 26, pp 8744-8764, 2013

Climate Model Predictions (Carbon Cycle Cont'd)

"the main advantage of CMIP5 is the representation of land cover change that is considered to be a significant driver for the terrestrial carbon cycle" (Shao et al.)

NEP*: Net Ecosystem Production = Integral of Leaf photosynthesis – Autotrophic Respiration – Heterotrophic Respiration*

D*: Disturbances = Fires + Land Use Change*

NBP*: Net Biome Production*

NBP=NEP - D

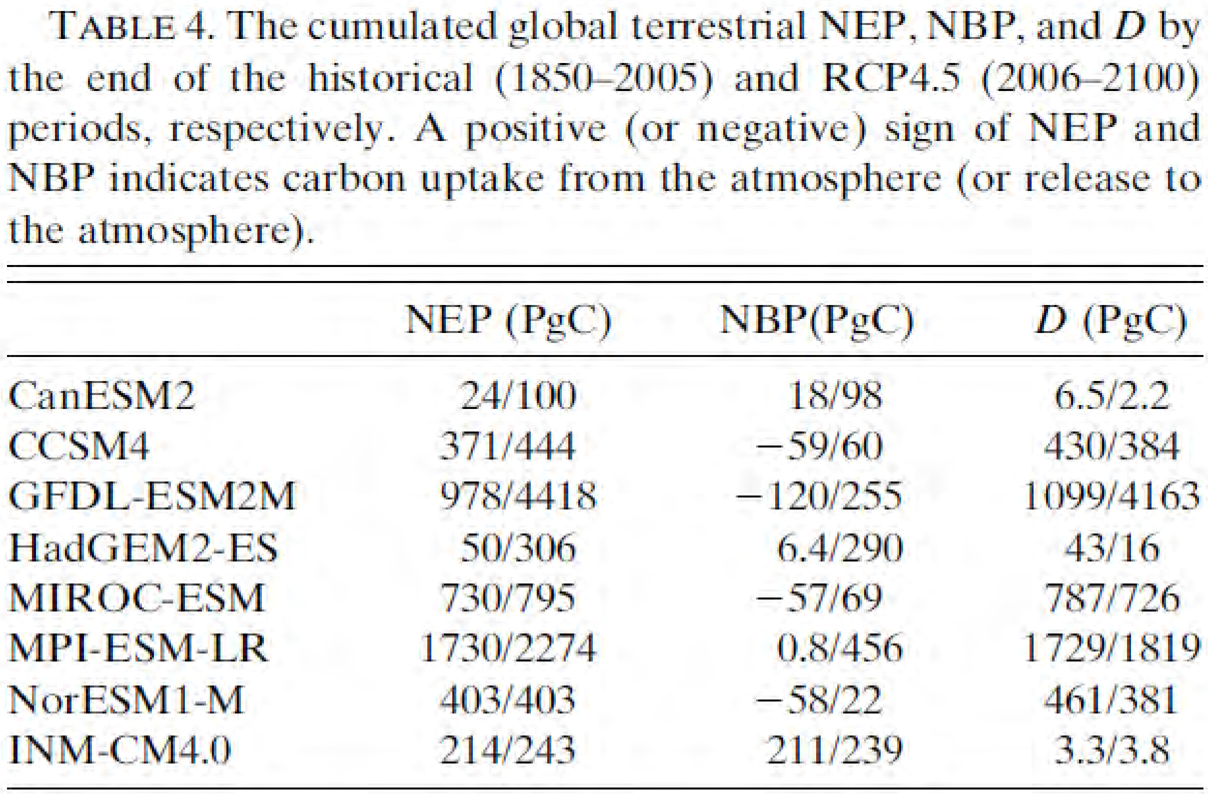
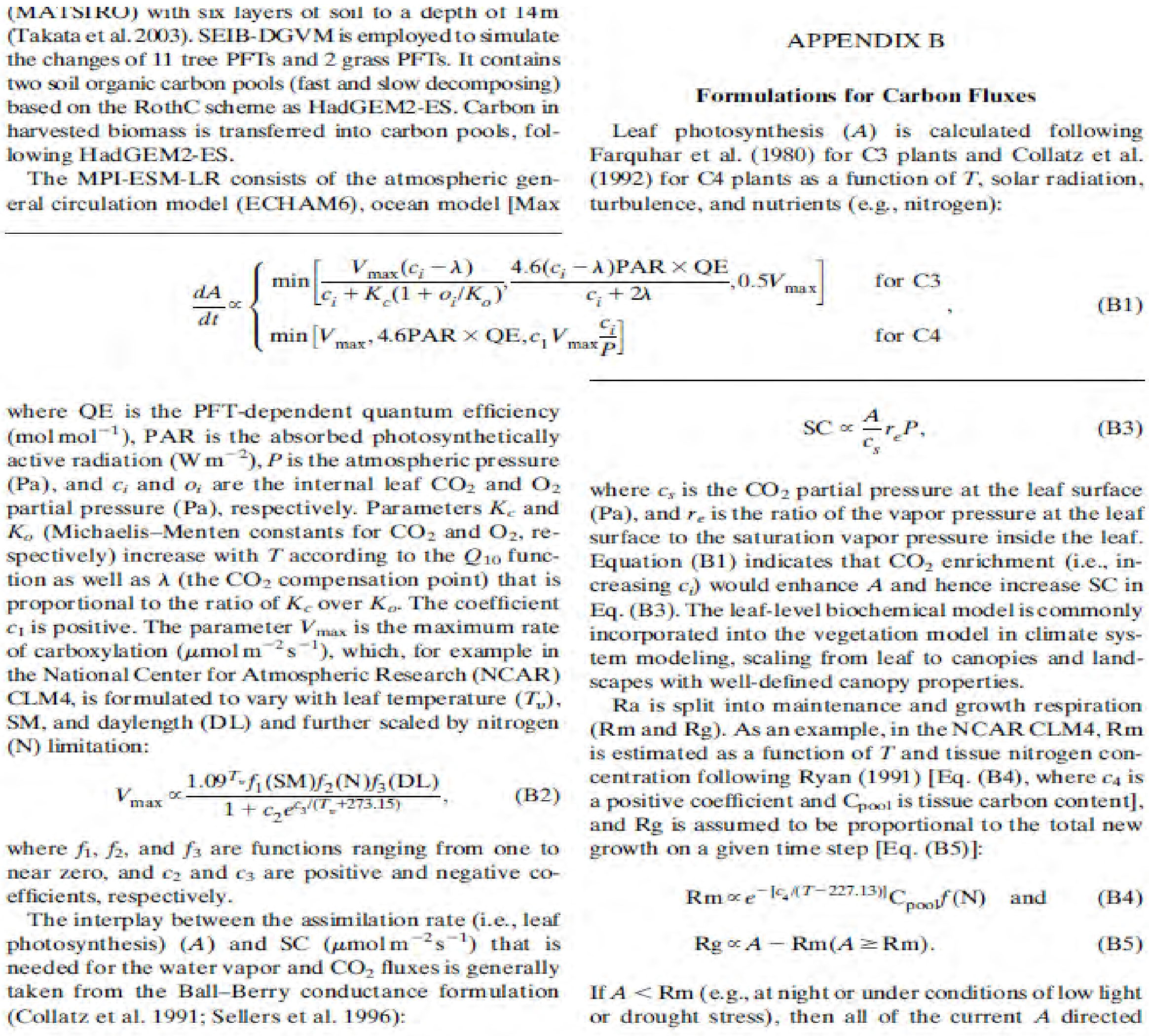


TABLE 4. The cumulated global terrestrial NEP, NBP, and *D* by the end of the historical (1850–2005) and RCP4.5 (2006–2100) periods, respectively. A positive (or negative) sign of NEP and NBP indicates carbon uptake from the atmosphere (or release to the atmosphere).

	NEP (PgC)	NBP(PgC)	*D* (PgC)
CanESM2	24/100	18/98	6.5/2.2
CCSM4	371/444	−59/60	430/384
GFDL-ESM2M	978/4418	−120/255	1099/4163
HadGEM2-ES	50/306	6.4/290	43/16
MIROC-ESM	730/795	−57/69	787/726
MPI-ESM-LR	1730/2274	0.8/456	1729/1819
NorESM1-M	403/403	−58/22	461/381
INM-CM4.0	214/243	211/239	3.3/3.8

Climate Model Predictions (Carbon Cycle Cont'd)



(MATSIRO) with six layers of soil to a depth of 14m (Takata et al. 2003). SEIB-DGVM is employed to simulate the changes of 11 tree PFTs and 2 grass PFTs. It contains two soil organic carbon pools (fast and slow decomposing) based on the RothC scheme as HadGEM2-ES. Carbon in harvested biomass is transferred into carbon pools, following HadGEM2-ES.

The MPI-ESM-LR consists of the atmospheric general circulation model (ECHAM6), ocean model [Max

APPENDIX B

Formulations for Carbon Fluxes

Leaf photosynthesis (A) is calculated following Farquhar et al. (1980) for C3 plants and Collatz et al. (1992) for C4 plants as a function of T, solar radiation, turbulence, and nutrients (e.g., nitrogen):

$$\frac{dA}{dt} \propto \begin{cases} \min\left[\frac{V_{\max}(c_i-\lambda)}{c_i+K_c(1+o_i/K_o)}, \frac{4.6(c_i-\lambda)\mathrm{PAR}\times\mathrm{QE}}{c_i+2\lambda}, 0.5V_{\max}\right] & \text{for C3} \\ \min\left[V_{\max}, 4.6\mathrm{PAR}\times\mathrm{QE}, c_1 V_{\max}\frac{c_i}{P}\right] & \text{for C4} \end{cases}, \qquad \text{(B1)}$$

where QE is the PFT-dependent quantum efficiency (mol mol^{-1}), PAR is the absorbed photosynthetically active radiation (W m^{-2}), P is the atmospheric pressure (Pa), and c_i and o_i are the internal leaf CO_2 and O_2 partial pressure (Pa), respectively. Parameters K_c and K_o (Michaelis–Menten constants for CO_2 and O_2, respectively) increase with T according to the Q_{10} function as well as λ (the CO_2 compensation point) that is proportional to the ratio of K_c over K_o. The coefficient c_1 is positive. The parameter $V_{\max}$ is the maximum rate of carboxylation (μmol m^{-2} s^{-1}), which, for example in the National Center for Atmospheric Research (NCAR) CLM4, is formulated to vary with leaf temperature (T_v), SM, and daylength (DL) and further scaled by nitrogen (N) limitation:

$$V_{\max} \propto \frac{1.09^{T_v} f_1(\mathrm{SM}) f_2(\mathrm{N}) f_3(\mathrm{DL})}{1+c_2 e^{c_3/(T_v+273.15)}}, \qquad \text{(B2)}$$

where f_1, f_2, and f_3 are functions ranging from one to near zero, and c_2 and c_3 are positive and negative coefficients, respectively.

The interplay between the assimilation rate (i.e., leaf photosynthesis) (A) and SC (μmol m^{-2} s^{-1}) that is needed for the water vapor and CO_2 fluxes is generally taken from the Ball–Berry conductance formulation (Collatz et al. 1991; Sellers et al. 1996):

$$\mathrm{SC} \propto \frac{A}{c_s} r_e P, \qquad \text{(B3)}$$

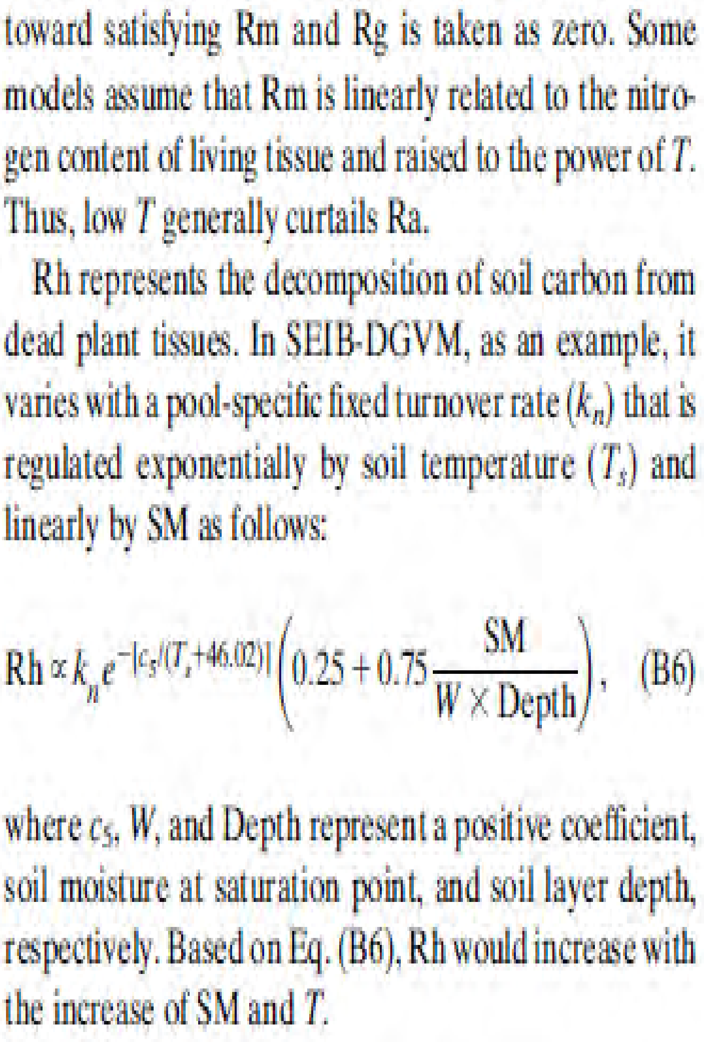
where c_s is the CO_2 partial pressure at the leaf surface (Pa), and r_e is the ratio of the vapor pressure at the leaf surface to the saturation vapor pressure inside the leaf. Equation (B1) indicates that CO_2 enrichment (i.e., increasing c_i) would enhance A and hence increase SC in Eq. (B3). The leaf-level biochemical model is commonly incorporated into the vegetation model in climate system modeling, scaling from leaf to canopies and landscapes with well-defined canopy properties.

Ra is split into maintenance and growth respiration (Rm and Rg). As an example, in the NCAR CLM4, Rm is estimated as a function of T and tissue nitrogen concentration following Ryan (1991) [Eq. (B4), where c_4 is a positive coefficient and C_{pool} is tissue carbon content], and Rg is assumed to be proportional to the total new growth on a given time step [Eq. (B5)]:

$$\mathrm{Rm} \propto e^{-[c_4/(T-227.13)]} C_{\mathrm{pool}} f(\mathrm{N}) \quad \text{and} \qquad \text{(B4)}$$

$$\mathrm{Rg} \propto A - \mathrm{Rm}(A \geq \mathrm{Rm}). \qquad \text{(B5)}$$

If $A < \mathrm{Rm}$ (e.g., at night or under conditions of low light or drought stress), then all of the current A directed



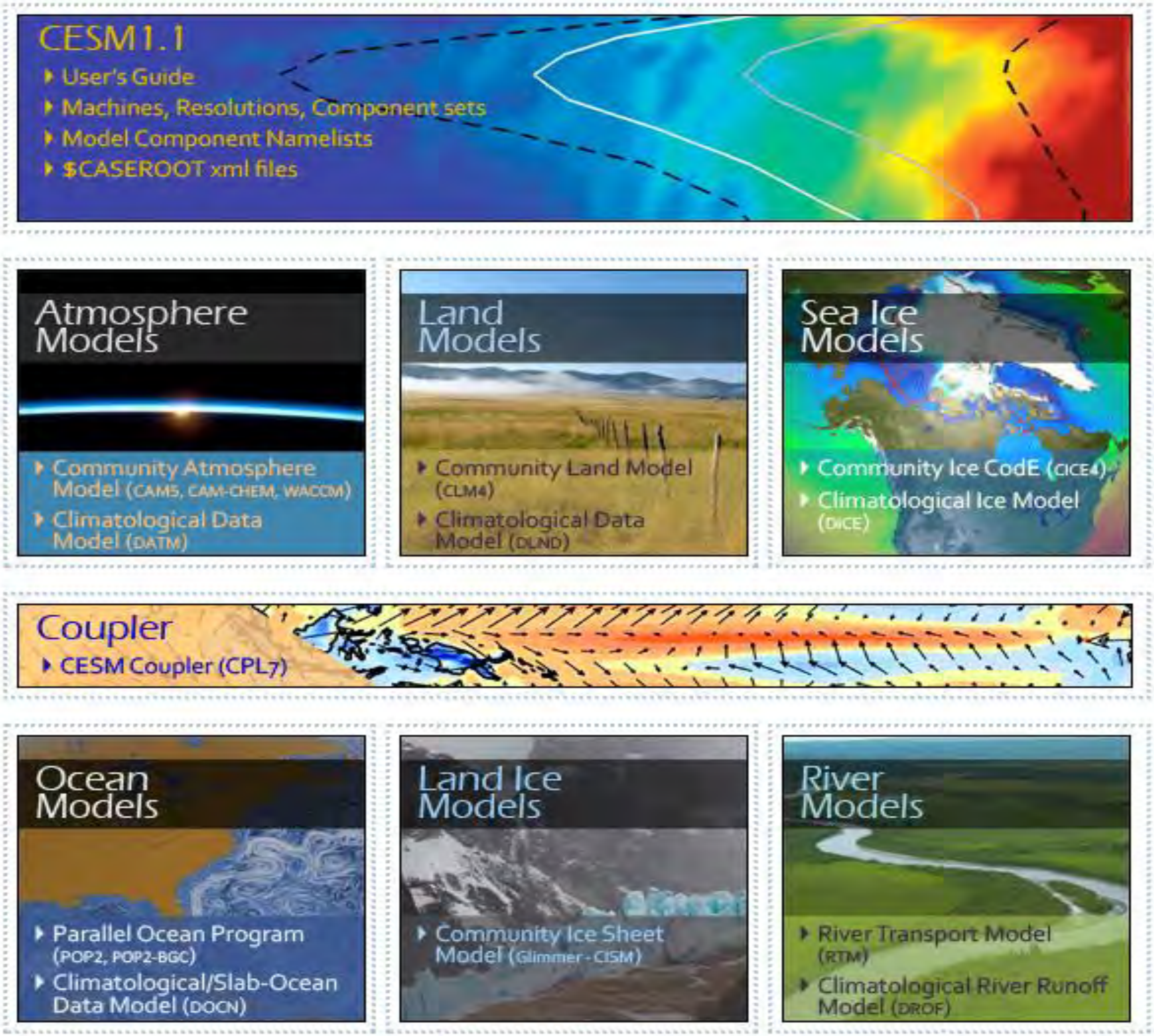
toward satisfying Rm and Rg is taken as zero. Some models assume that Rm is linearly related to the nitrogen content of living tissue and raised to the power of T. Thus, low T generally curtails Ra.

Rh represents the decomposition of soil carbon from dead plant tissues. In SEIB-DGVM, as an example, it varies with a pool-specific fixed turnover rate (k_n) that is regulated exponentially by soil temperature (T_s) and linearly by SM as follows:

$$\mathrm{Rh} \propto k_n e^{-[c_5/(T_s+46.02)]}\left(0.25+0.75\frac{\mathrm{SM}}{W\times\mathrm{Depth}}\right), \qquad \text{(B6)}$$

where c_5, W, and Depth represent a positive coefficient, soil moisture at saturation point, and soil layer depth, respectively. Based on Eq. (B6), Rh would increase with the increase of SM and T.

Climate Change Models



CESM1.1

- User's Guide
- Machines, Resolutions, Component sets
- Model Component Namelists
- $CASEROOT xml files

Atmosphere Models

- Community Atmosphere Model (CAM5, CAM-CHEM, WACCM)
- Climatological Data Model (DATM)

Land Models

- Community Land Model (CLM4)
- Climatological Data Model (DLND)

Sea Ice Models

- Community Ice CodE (CICE4)
- Climatological Ice Model (DICE)

Coupler

- CESM Coupler (CPL7)

Ocean Models

- Parallel Ocean Program (POP2, POP2-BGC)
- Climatological/Slab-Ocean Data Model (DOCN)

Land Ice Models

- Community Ice Sheet Model (Glimmer-CISM)

River Models

- River Transport Model (RTM)
- Climatological River Runoff Model (DROF)

http://www.cesm.ucar.edu/models/

Climate Change Model Metrics: Atmospheric Model (AGCM)

- University of Victoria Model (UViC) Assumptions:
  - Decreasing vertical distribution of energy and relative humidity
  - Parametrization of atmospheric heat and moisture transport by diffusion

$$\rho_a h_t c_{pa} \frac{\partial T_a}{\partial t} = Q_T + Q_{SW} C_A + Q_{LH} + Q_{LW} + Q_{SH} - Q_{PLW}$$

- CLIMate BiosphERe Model (CLIMBER-2) Assumptions:
  - Vertical temperature profile
  - Radiative equilibrium of isothermal stratosphere
  - Exponential vertical profile of specific humidity

$$\begin{aligned}\frac{\partial Q_T}{\partial t} = -\frac{1}{a\cos\phi}\bigg[\frac{\partial}{\partial\lambda}\int_{z_s}^{H_a}\rho(u_n\theta + \widehat{u'\theta'} + M_\lambda^\theta)dz \\ + \frac{\partial}{\partial\phi}\int_{z_s}^{H_a}\cos\phi\,\rho(v_n\theta + \widehat{v'\theta'} + M_\phi^\theta)dz\bigg] - \int_{z_s}^{H_a}\rho w_t(\Gamma_a - \Gamma)dz \\ + c_v^{-1}(S_a + R_s - R_t + L_e P_w + L_s P_s + F_h)\ ,\end{aligned}$$

Climate Change Model Metrics:
Ocean General Circulation Model (OGCM)

- OPA 8.1 (UViC) Assumptions:
  - Thin shell approximations: Negligible ocean depth compared to the radius of the earth
  - Boussinesq hypothesis: Density variations are neglected except where to contribute to buoyancy
  - Hydrostatic hypothesis: Vertical momentum equation is reduced to a balance of the vertical pressure gradient and buoyancy force
  - Boundary conditions are defined by Land-ocean interface, solid earth-ocean interface, atmospheric-ocean interface and sea ice-ocean interface.

$$\frac{\partial \mathbf{U}_h}{\partial t} = -\left[(\nabla \times \mathbf{U}) \times \mathbf{U} + \frac{1}{2}\nabla(\mathbf{U}^2)\right]_h - f\,\mathbf{k} \times \mathbf{U}_h - \frac{1}{\rho_o}\nabla_h p + \mathbf{D}^U$$

$$\frac{\partial p}{\partial z} = -\rho\, g$$

$$\nabla \cdot \mathbf{U} = 0$$

$$\frac{\partial T}{\partial t} = -\nabla.(T\,\mathbf{U}) + D^T$$

$$\frac{\partial S}{\partial t} = -\nabla.(S\,\mathbf{U}) + D^S$$

$$\rho = \rho(T, S, p)$$

Climate Change

- Consistent with other research, the level of agreement on anthropogenic causation correlated with expertise - 90% of those surveyed with more than 10 peer-reviewed papers related to climate (just under half of survey respondents) explicitly agreed that human production of greenhouse gases was the main cause of global warming (Verheggen et al., 2014, Environmental Science & Technology)
- Cook et al. examined 11,944 abstracts from the peer-reviewed scientific literature from 1991–2011 that matched the topics 'global climate change' or 'global warming'.[12] They found that, while 66.4% of them expressed no position on anthropogenic global warming (AGW), of those that did, 97.1% endorsed the consensus position that humans are contributing to global warming. (Cook et al. 2014, Environmental Research Letters)
- In 2007, Harris Interactive surveyed 489 randomly selected members of either the American Meteorological Society or the American Geophysical Union for the Statistical Assessment Service (STATS) at George Mason University. The survey found 97% agreed that global temperatures have increased during the past 100 years; 84% say they personally believe human-induced warming is occurring, and 74% agree that "currently available scientific evidence" substantiates its occurrence. (STATS 2007, US News and World Report)

Climate Change

- “In the APS (American Physical Society) it is ok to discuss whether the mass of the proton changes over time and how a multi-universe behaves, but the evidence of global warming is incontrovertible? The claim (how can you measure the average temperature of the whole earth for a whole year?) is that the temperature has changed from ~288.0 to ~288.8 degree Kelvin in about 150 years, which (if true) means to me is that the temperature has been amazingly stable, and both human health and happiness have definitely improved in this 'warming' period.‘” (Dr. Ivar Giaever, Nobel Laureate)
- “I'm a skeptic. ...Global Warming it's become a new religion. You're not supposed to be against Global Warming. You have basically no choice. And I tell you how many scientists support that. But the number of scientists is not important. The only thing that's important is if the scientists are correct; that's the important part.” (Dr. Ivar Giaever, Nobel Laureate)
- “In questions of science, the authority of a thousand is not worth the humble reasoning of a single individual.” — Galileo Galilei per Biographies of Distinguished Scientific Men (1859) by François Arago, as translated by Baden Powell, Robert Grant, and William Fairbairn, p. 365

Second Edition

Evidence-Based
Climate Science

Data opposing CO_2 emissions as the primary source of global warming

Edited by
Don Easterbrook

Easterbrook, D. (Ed.). (2016). Evidence-based climate science: Data opposing CO2 emissions as the primary source of global warming. Elsevier.

Climate Change

- “If CO2 causes global warming why do we have 30 years of global cooling when it began to escalate. It doesn’t make any sense.”
- “You compare those to actual measurements to see if the models are right. They are totally inaccurate, the models are totally inaccurate… The bottom line is CO2 is not capable of causing significant global warming by itself.”
- “The effect of global warming is to make the oceans more alkaline, not more acidic, because warming drives CO2 out of the ocean”
- “Computer models like any other computing is garbage in garbage out whatever you program the computer will be is what comes out the other end they do not consider real life changes in the atmosphere, in the oceans, they do not consider real physical data.”
- “The models failed miserably they weren’t even close, therefore what trust can you put in models if they cannot even predict 10 years down the line within one degree, they’re useless.” (Dr. Don Easterbrook, Professor Emiritus of Geology, Western WA University)

Climate Change

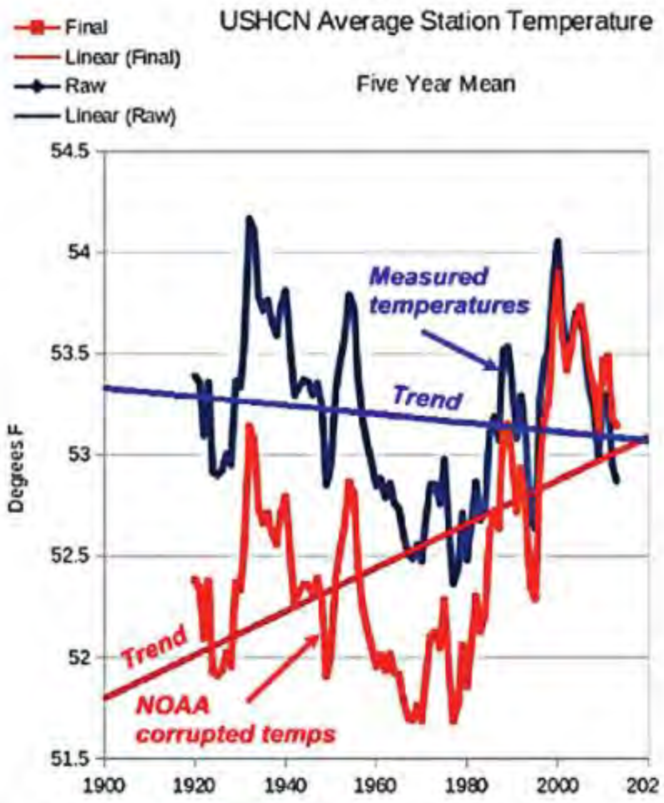
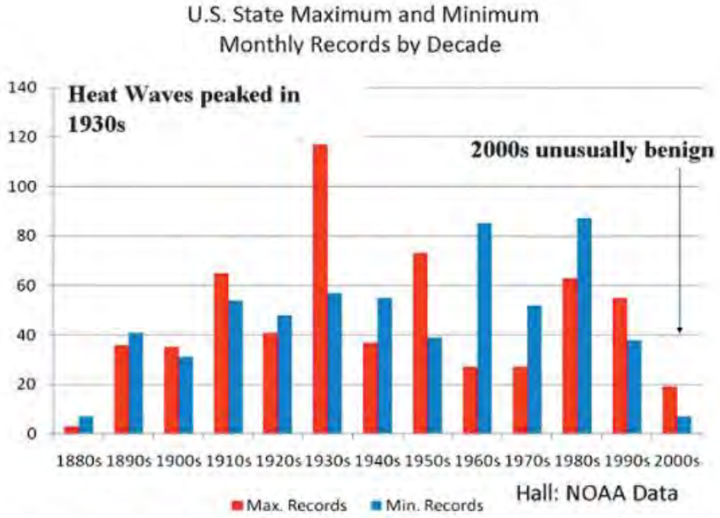


FIGURE 1.4 Temperature data corruption by NOAA. Measured temperatures are shown in blue, corrupted NOAA temperatures are shown in red. Note that NOAA decreased measured temperatures in the 1930s and 1940s by a full degree but made no changes to temperatures from about 1990 onward, thus changing a cooling trend into a warming trend (Heller, 2001, https://stevengoddard.wordpress.com/).

Climate Change

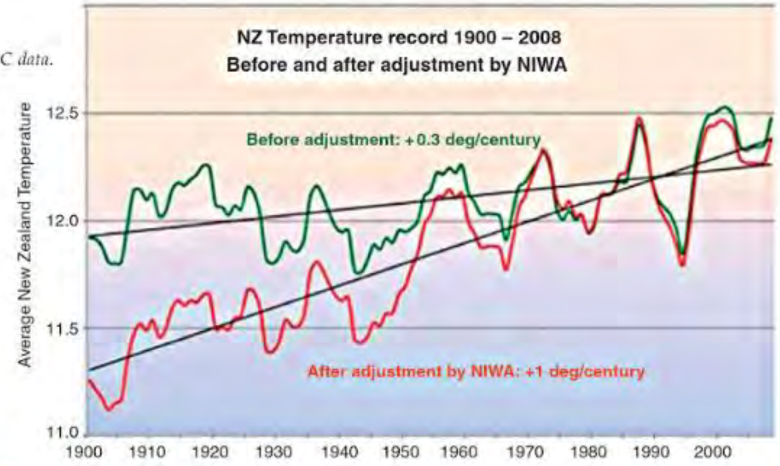

U.S. State Maximum and Minimum Monthly Records by Decade

Heat Waves peaked in 1930s

2000s unusually benign

Hall: NOAA Data

FIGURE 2.19 United States all-time monthly record lows and highs by decade. *Compiled by Hall from NOAA NCDC data.*


NZ Temperature record 1900 – 2008
Before and after adjustment by NIWA

Before adjustment: +0.3 deg/century

After adjustment by NIWA: +1 deg/century

FIGURE 2.37 NIWA raw versus adjusted for Seven Sisters Stations (7SS). Adjusted NIWA becomes GHCN raw.

Climate Change

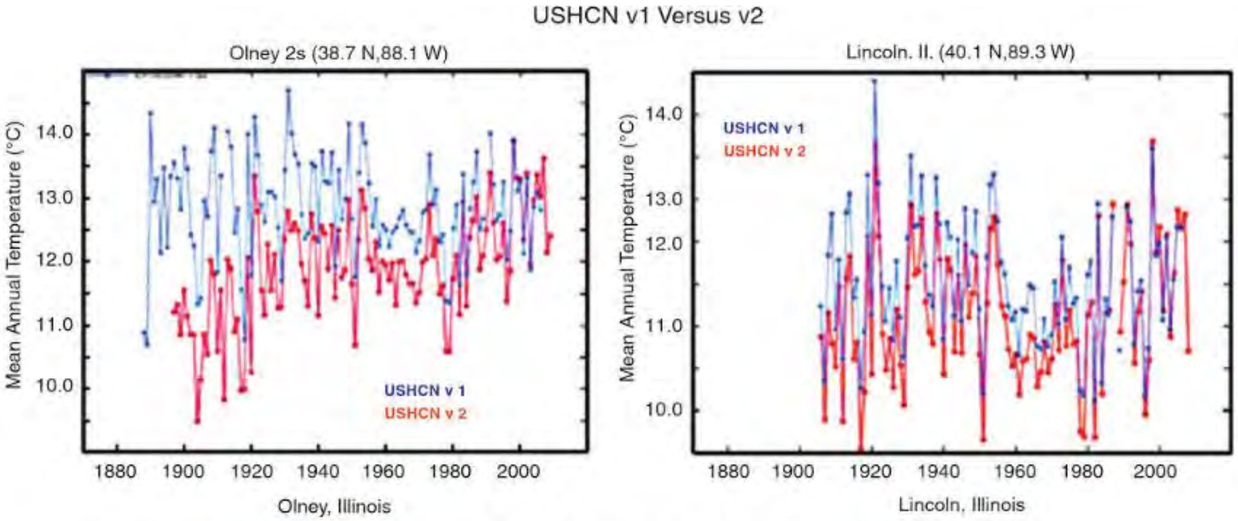


FIGURE 2.22 NOAA USJCN version 1 versus version 2 for Olney and Lincoln, Illinois.

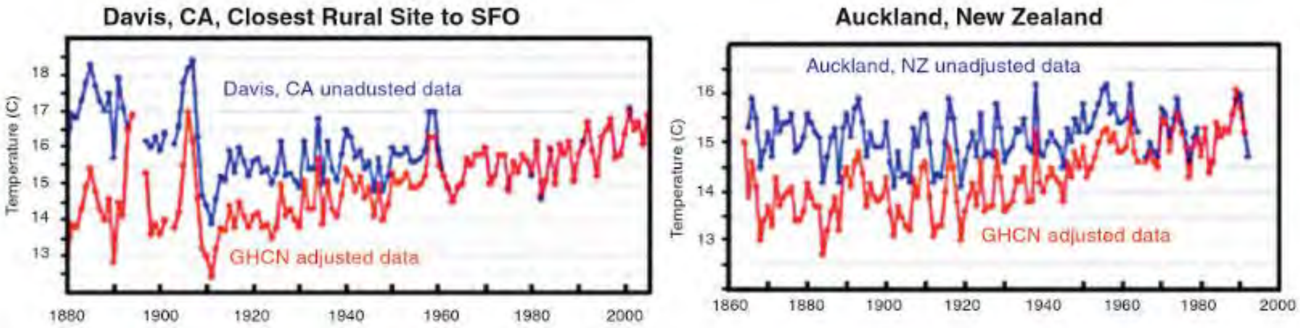
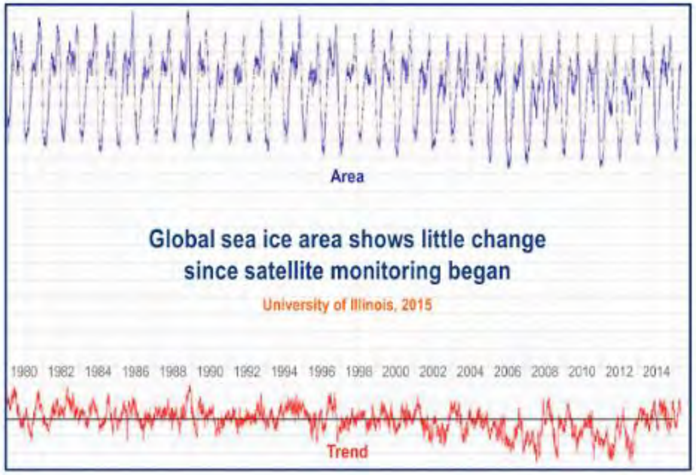
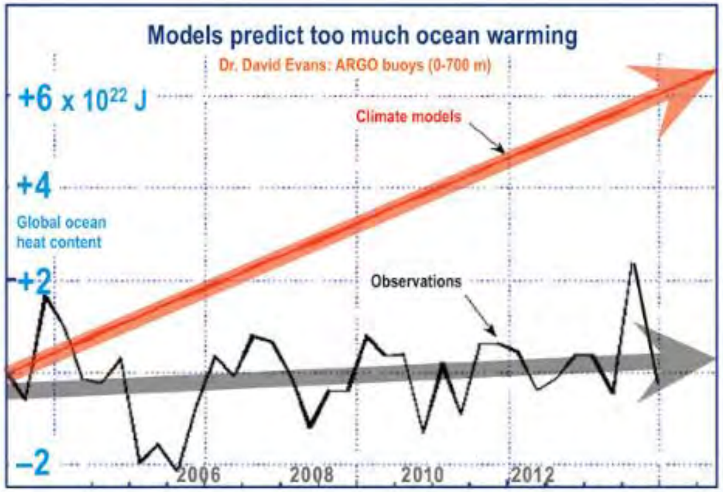


FIGURE 2.36 GHCN raw versus adjusted for Davis, California and Auckland, New Zealand.

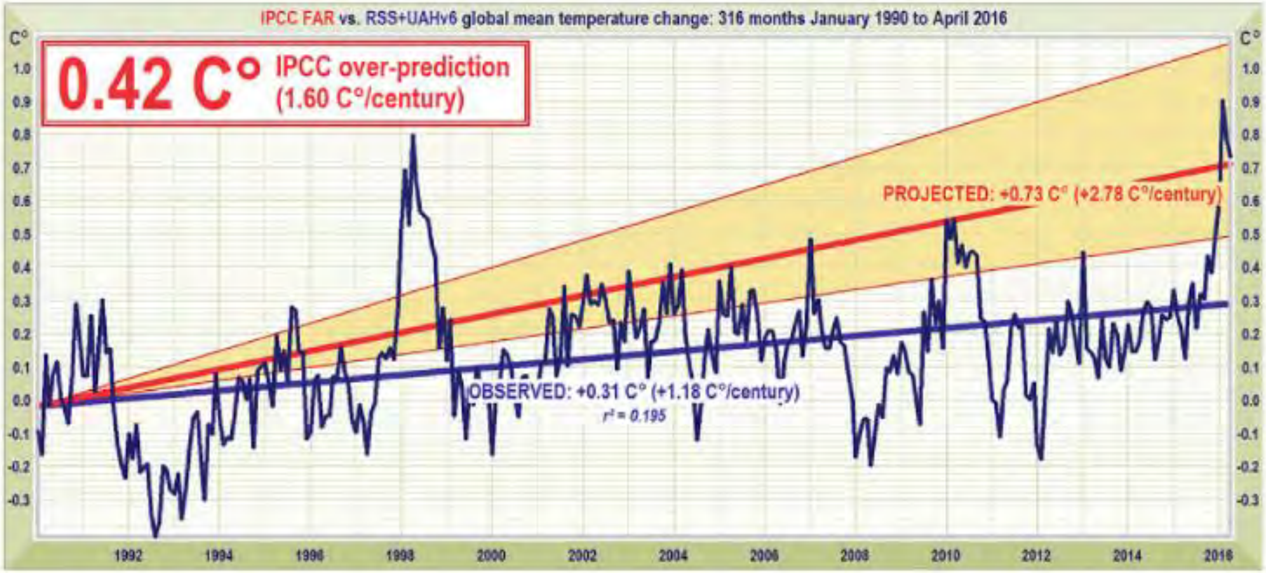
Climate Change Data


Global sea ice area shows little change since satellite monitoring began

University of Illinois, 2015

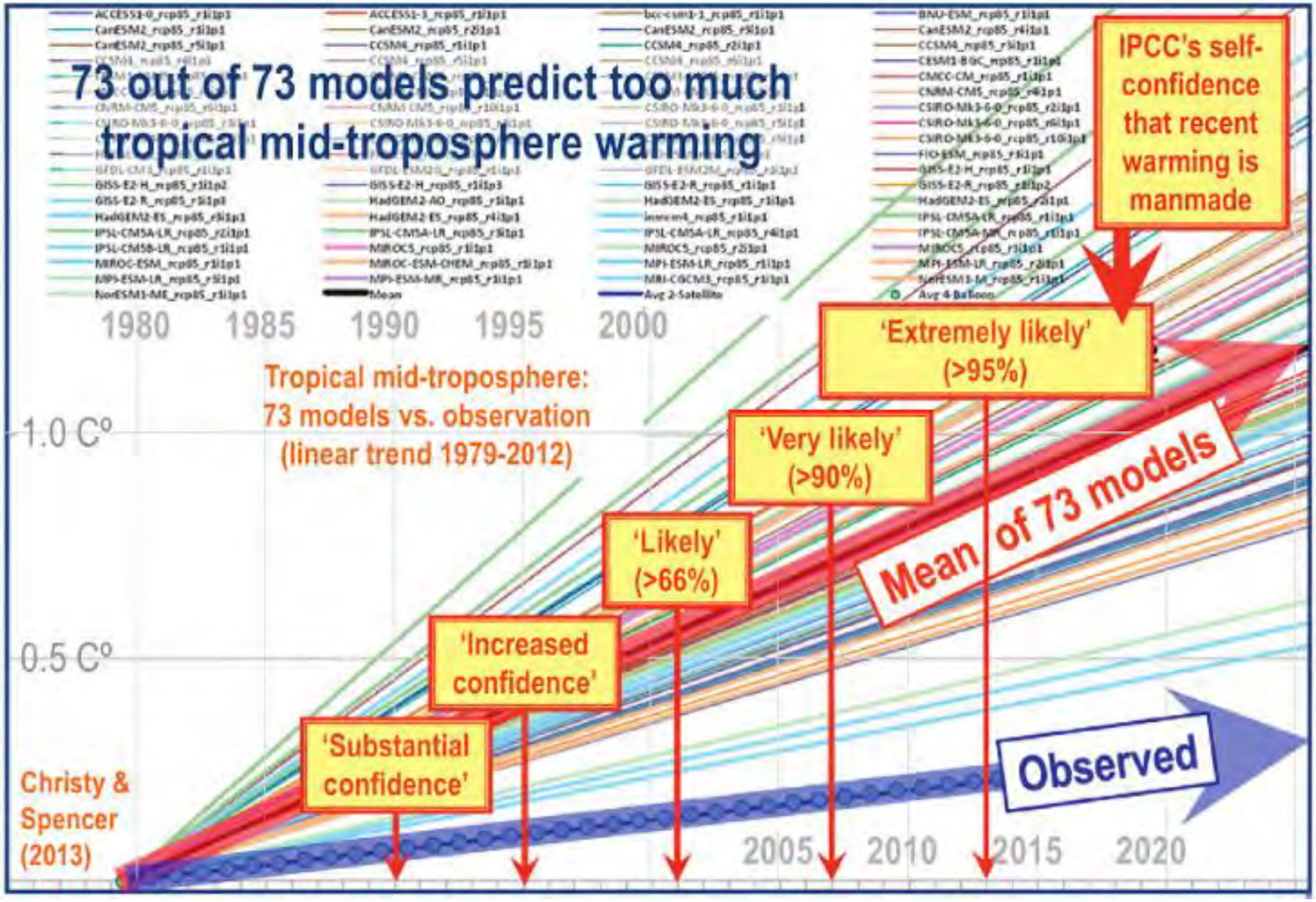

Models predict too much ocean warming

Dr. David Evans: ARGO buoys (0-700 m)


IPCC FAR vs. RSS+UAHv6 global mean temperature change: 316 months January 1990 to April 2016

0.42 C° IPCC over-prediction (1.60 C°/century)

Climate Change



"Climate Change" is a Tautology

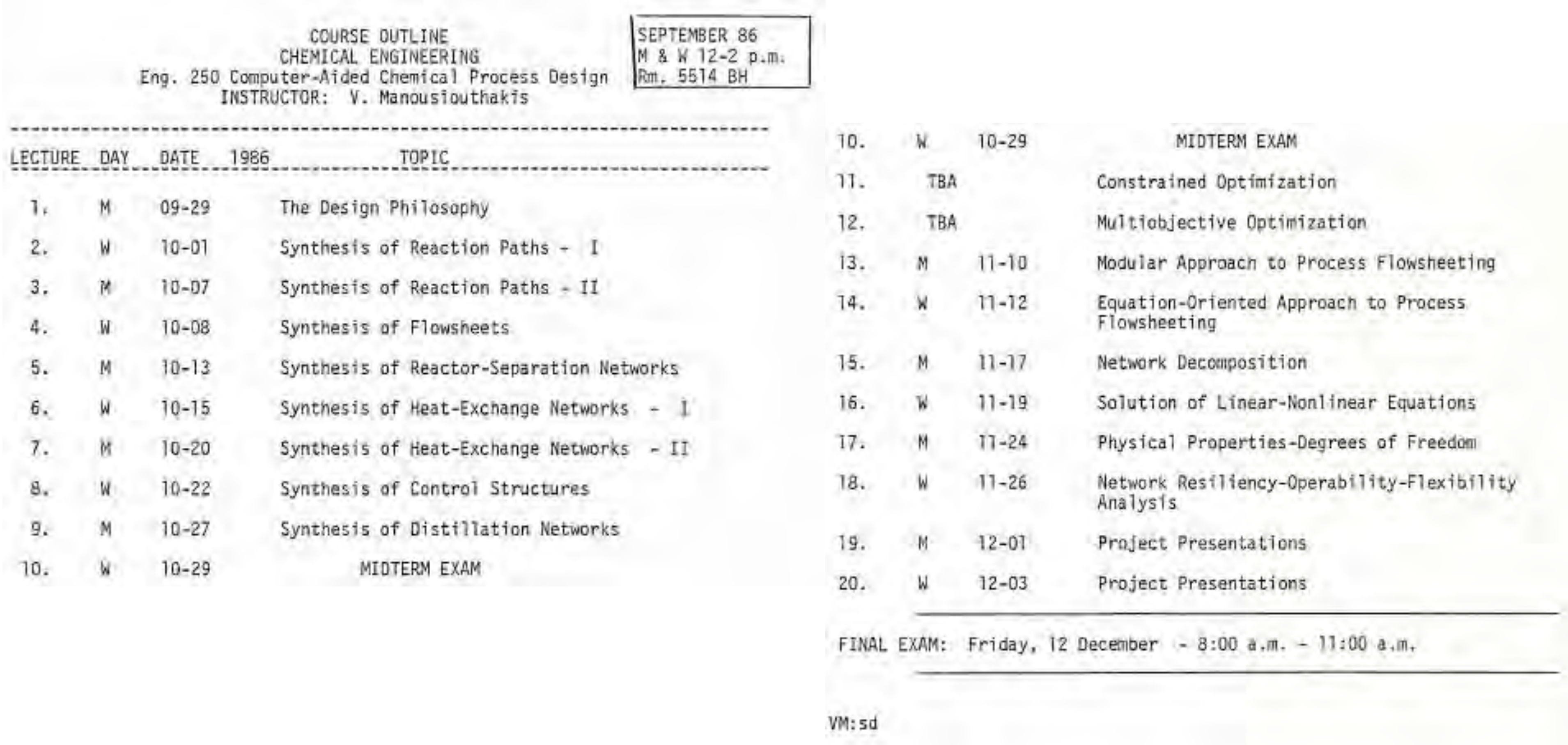
- "Global Warming" is a logical Proposition that could be true or false

- The above historical record suggests that "Climate Change" however is a tautology (i.e. it is always true)

- Below I will describe how PSE ought to assume the role of Euryphaessa to guide humanity past the "Prometheus" Paradigm and the "Climate Change" tautology

- But First!

George’s Impact on My Research/Education: My First Graduate Process Design Syllabus



COURSE OUTLINE
CHEMICAL ENGINEERING
Eng. 250 Computer-Aided Chemical Process Design
INSTRUCTOR: V. Manousiouthakis

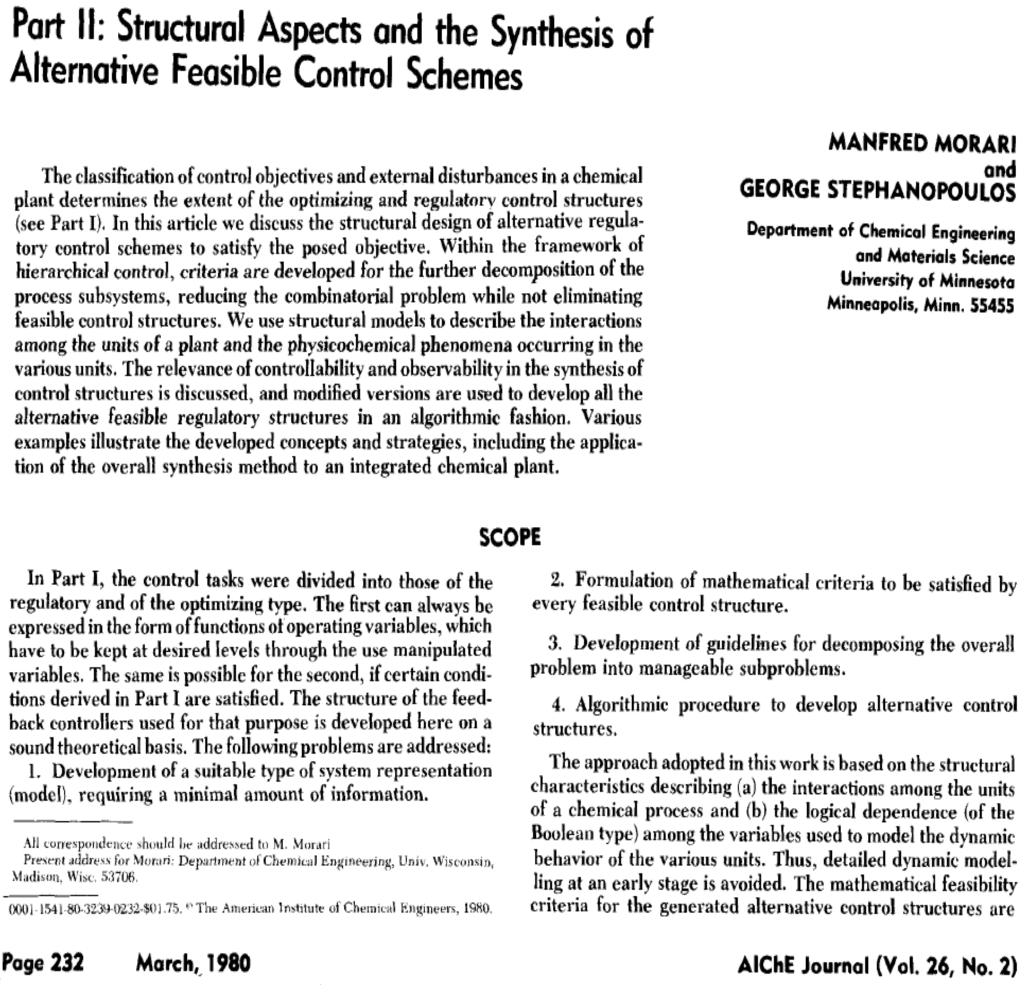
SEPTEMBER 86
M & W 12-2 p.m.
Rm. 5514 BH

LECTURE	DAY	DATE 1986	TOPIC
1.	M	09-29	The Design Philosophy
2.	W	10-01	Synthesis of Reaction Paths - I
3.	M	10-07	Synthesis of Reaction Paths - II
4.	W	10-08	Synthesis of Flowsheets
5.	M	10-13	Synthesis of Reactor-Separation Networks
6.	W	10-15	Synthesis of Heat-Exchange Networks - I
7.	M	10-20	Synthesis of Heat-Exchange Networks - II
8.	W	10-22	Synthesis of Control Structures
9.	M	10-27	Synthesis of Distillation Networks
10.	W	10-29	MIDTERM EXAM
11.	TBA		Constrained Optimization
12.	TBA		Multiobjective Optimization
13.	M	11-10	Modular Approach to Process Flowsheeting
14.	W	11-12	Equation-Oriented Approach to Process Flowsheeting
15.	M	11-17	Network Decomposition
16.	W	11-19	Solution of Linear-Nonlinear Equations
17.	M	11-24	Physical Properties-Degrees of Freedom
18.	W	11-26	Network Resiliency-Operability-Flexibility Analysis
19.	M	12-01	Project Presentations
20.	W	12-03	Project Presentations

FINAL EXAM: Friday, 12 December - 8:00 a.m. - 11:00 a.m.

VM:sd

George's Impact on My Research/Education: Synthesis of Control Structures



Part II: Structural Aspects and the Synthesis of Alternative Feasible Control Schemes

MANFRED MORARI
and
GEORGE STEPHANOPOULOS

Department of Chemical Engineering
and Materials Science
University of Minnesota
Minneapolis, Minn. 55455

The classification of control objectives and external disturbances in a chemical plant determines the extent of the optimizing and regulatory control structures (see Part I). In this article we discuss the structural design of alternative regulatory control schemes to satisfy the posed objective. Within the framework of hierarchical control, criteria are developed for the further decomposition of the process subsystems, reducing the combinatorial problem while not eliminating feasible control structures. We use structural models to describe the interactions among the units of a plant and the physicochemical phenomena occurring in the various units. The relevance of controllability and observability in the synthesis of control structures is discussed, and modified versions are used to develop all the alternative feasible regulatory structures in an algorithmic fashion. Various examples illustrate the developed concepts and strategies, including the application of the overall synthesis method to an integrated chemical plant.

SCOPE

In Part I, the control tasks were divided into those of the regulatory and of the optimizing type. The first can always be expressed in the form of functions of operating variables, which have to be kept at desired levels through the use manipulated variables. The same is possible for the second, if certain conditions derived in Part I are satisfied. The structure of the feedback controllers used for that purpose is developed here on a sound theoretical basis. The following problems are addressed:

1. Development of a suitable type of system representation (model), requiring a minimal amount of information.
2. Formulation of mathematical criteria to be satisfied by every feasible control structure.
3. Development of guidelines for decomposing the overall problem into manageable subproblems.
4. Algorithmic procedure to develop alternative control structures.

The approach adopted in this work is based on the structural characteristics describing (a) the interactions among the units of a chemical process and (b) the logical dependence (of the Boolean type) among the variables used to model the dynamic behavior of the various units. Thus, detailed dynamic modelling at an early stage is avoided. The mathematical feasibility criteria for the generated alternative control structures are

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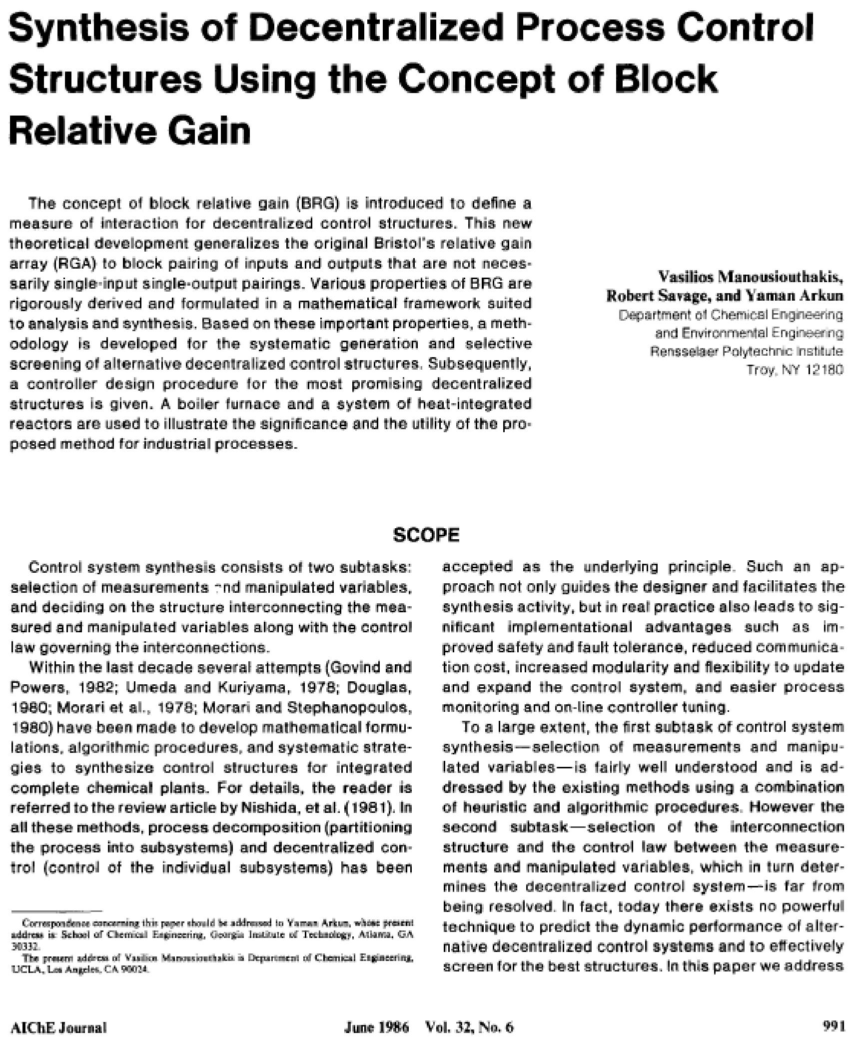
0001-1541-80-3239-0232-$01.75. © The American Institute of Chemical Engineers, 1980.

Page 232 March, 1980 AIChE Journal (Vol. 26, No. 2)



Synthesis of Decentralized Process Control Structures Using the Concept of Block Relative Gain

The concept of block relative gain (BRG) is introduced to define a measure of interaction for decentralized control structures. This new theoretical development generalizes the original Bristol's relative gain array (RGA) to block pairing of inputs and outputs that are not necessarily single-input single-output pairings. Various properties of BRG are rigorously derived and formulated in a mathematical framework suited to analysis and synthesis. Based on these important properties, a methodology is developed for the systematic generation and selective screening of alternative decentralized control structures. Subsequently, a controller design procedure for the most promising decentralized structures is given. A boiler furnace and a system of heat-integrated reactors are used to illustrate the significance and the utility of the proposed method for industrial processes.

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Robert Savage, and Yaman Arkun
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and Environmental Engineering
Rensselaer Polytechnic Institute
Troy, NY 12180

SCOPE

Control system synthesis consists of two subtasks: selection of measurements and manipulated variables, and deciding on the structure interconnecting the measured and manipulated variables along with the control law governing the interconnections.

Within the last decade several attempts (Govind and Powers, 1982; Umeda and Kuriyama, 1978; Douglas, 1980; Morari et al., 1978; Morari and Stephanopoulos, 1980) have been made to develop mathematical formulations, algorithmic procedures, and systematic strategies to synthesize control structures for integrated complete chemical plants. For details, the reader is referred to the review article by Nishida, et al. (1981). In all these methods, process decomposition (partitioning the process into subsystems) and decentralized control (control of the individual subsystems) has been accepted as the underlying principle. Such an approach not only guides the designer and facilitates the synthesis activity, but in real practice also leads to significant implementational advantages such as improved safety and fault tolerance, reduced communication cost, increased modularity and flexibility to update and expand the control system, and easier process monitoring and on-line controller tuning.

To a large extent, the first subtask of control system synthesis—selection of measurements and manipulated variables—is fairly well understood and is addressed by the existing methods using a combination of heuristic and algorithmic procedures. However the second subtask—selection of the interconnection structure and the control law between the measurements and manipulated variables, which in turn determines the decentralized control system—is far from being resolved. In fact, today there exists no powerful technique to predict the dynamic performance of alternative decentralized control systems and to effectively screen for the best structures. In this paper we address

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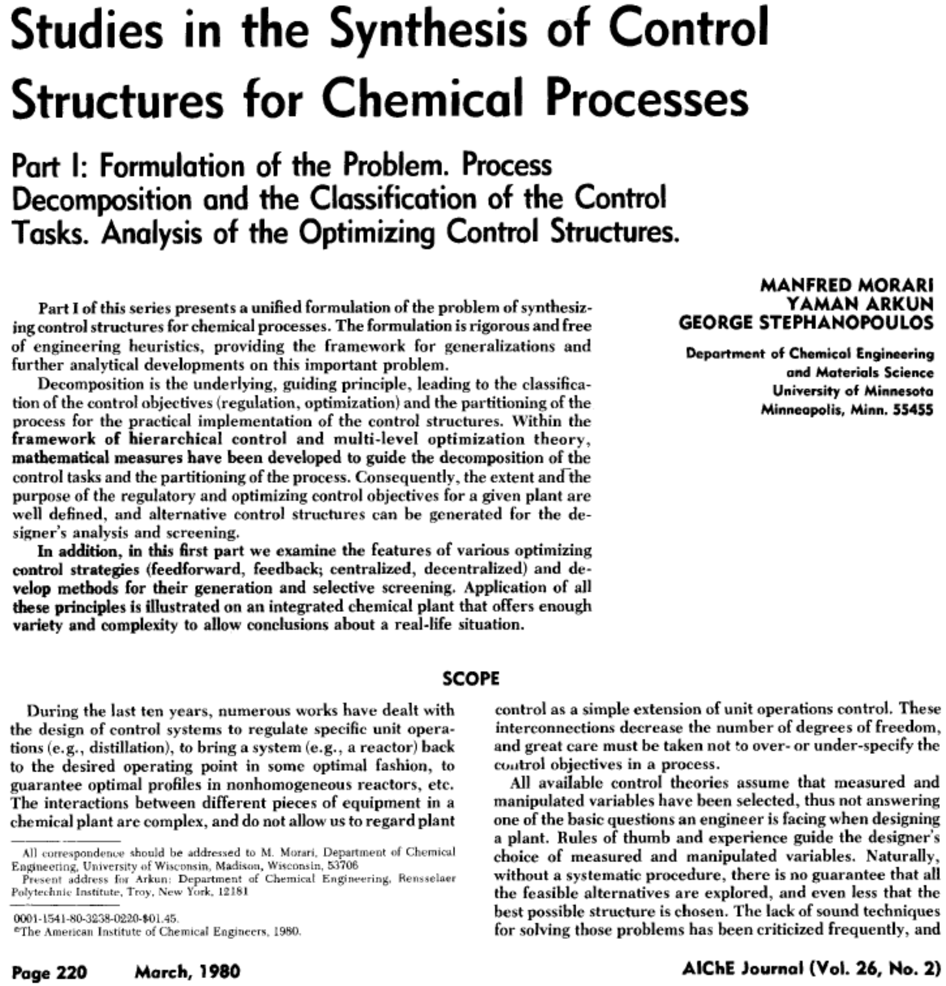
Correspondence concerning this paper should be addressed to Yaman Arkun, whose present address is: School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA 30332.
The present address of Vasilios Manousiouthakis is Department of Chemical Engineering, UCLA, Los Angeles, CA 90024.

AIChE Journal June 1986 Vol. 32, No. 6 991

George’s Impact on My Research/Education: Synthesis of Control Structures for Nonlinear Systems



Studies in the Synthesis of Control Structures for Chemical Processes

Part I: Formulation of the Problem. Process Decomposition and the Classification of the Control Tasks. Analysis of the Optimizing Control Structures.

MANFRED MORARI
YAMAN ARKUN
GEORGE STEPHANOPOULOS

Department of Chemical Engineering
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Minneapolis, Minn. 55455

Part I of this series presents a unified formulation of the problem of synthesizing control structures for chemical processes. The formulation is rigorous and free of engineering heuristics, providing the framework for generalizations and further analytical developments on this important problem.

Decomposition is the underlying, guiding principle, leading to the classification of the control objectives (regulation, optimization) and the partitioning of the process for the practical implementation of the control structures. Within the framework of hierarchical control and multi-level optimization theory, mathematical measures have been developed to guide the decomposition of the control tasks and the partitioning of the process. Consequently, the extent and the purpose of the regulatory and optimizing control objectives for a given plant are well defined, and alternative control structures can be generated for the designer’s analysis and screening.

In addition, in this first part we examine the features of various optimizing control strategies (feedforward, feedback; centralized, decentralized) and develop methods for their generation and selective screening. Application of all these principles is illustrated on an integrated chemical plant that offers enough variety and complexity to allow conclusions about a real-life situation.

SCOPE

During the last ten years, numerous works have dealt with the design of control systems to regulate specific unit operations (e.g., distillation), to bring a system (e.g., a reactor) back to the desired operating point in some optimal fashion, to guarantee optimal profiles in nonhomogeneous reactors, etc. The interactions between different pieces of equipment in a chemical plant are complex, and do not allow us to regard plant control as a simple extension of unit operations control. These interconnections decrease the number of degrees of freedom, and great care must be taken not to over- or under-specify the control objectives in a process.

All available control theories assume that measured and manipulated variables have been selected, thus not answering one of the basic questions an engineer is facing when designing a plant. Rules of thumb and experience guide the designer’s choice of measured and manipulated variables. Naturally, without a systematic procedure, there is no guarantee that all the feasible alternatives are explored, and even less that the best possible structure is chosen. The lack of sound techniques for solving those problems has been criticized frequently, and

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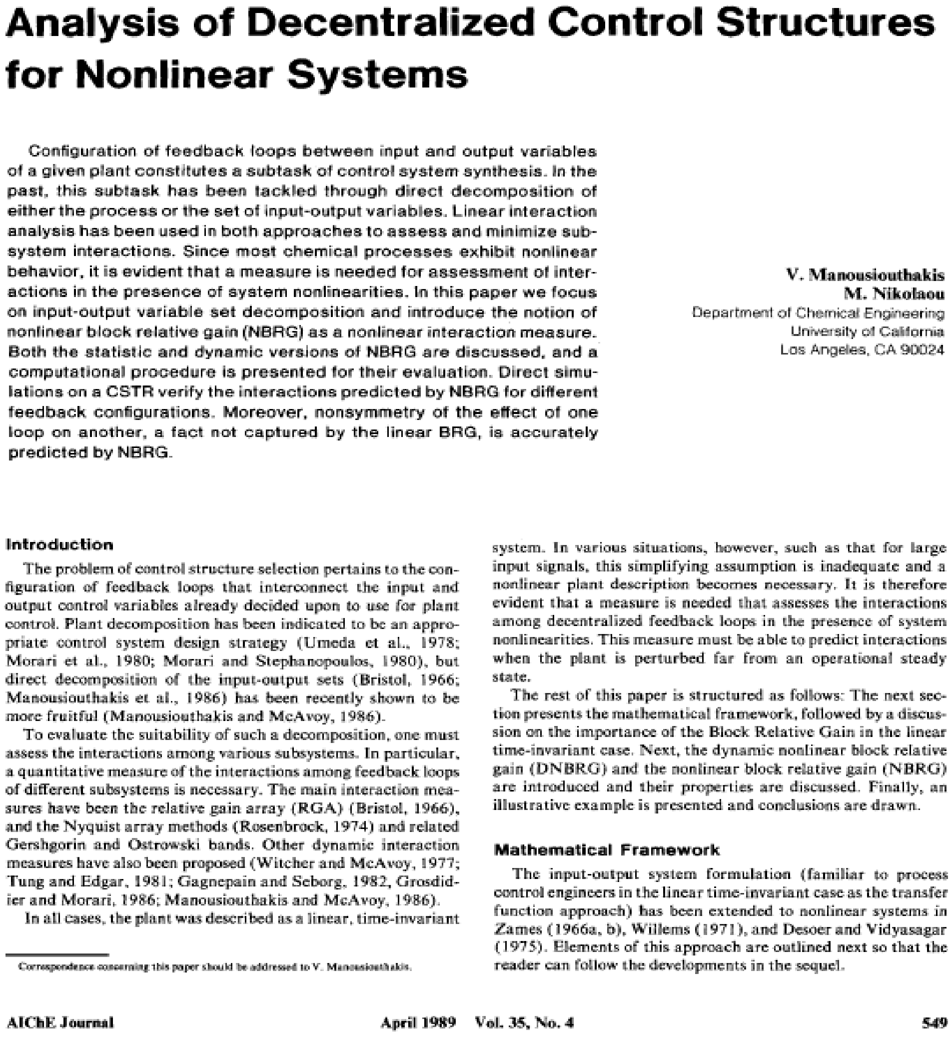

Analysis of Decentralized Control Structures for Nonlinear Systems

Configuration of feedback loops between input and output variables of a given plant constitutes a subtask of control system synthesis. In the past, this subtask has been tackled through direct decomposition of either the process or the set of input-output variables. Linear interaction analysis has been used in both approaches to assess and minimize subsystem interactions. Since most chemical processes exhibit nonlinear behavior, it is evident that a measure is needed for assessment of interactions in the presence of system nonlinearities. In this paper we focus on input-output variable set decomposition and introduce the notion of nonlinear block relative gain (NBRG) as a nonlinear interaction measure. Both the statistic and dynamic versions of NBRG are discussed, and a computational procedure is presented for their evaluation. Direct simulations on a CSTR verify the interactions predicted by NBRG for different feedback configurations. Moreover, nonsymmetry of the effect of one loop on another, a fact not captured by the linear BRG, is accurately predicted by NBRG.

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Introduction

The problem of control structure selection pertains to the configuration of feedback loops that interconnect the input and output control variables already decided upon to use for plant control. Plant decomposition has been indicated to be an appropriate control system design strategy (Umeda et al., 1978; Morari et al., 1980; Morari and Stephanopoulos, 1980), but direct decomposition of the input-output sets (Bristol, 1966; Manousiouthakis et al., 1986) has been recently shown to be more fruitful (Manousiouthakis and McAvoy, 1986).

To evaluate the suitability of such a decomposition, one must assess the interactions among various subsystems. In particular, a quantitative measure of the interactions among feedback loops of different subsystems is necessary. The main interaction measures have been the relative gain array (RGA) (Bristol, 1966), and the Nyquist array methods (Rosenbrock, 1974) and related Gershgorin and Ostrowski bands. Other dynamic interaction measures have also been proposed (Witcher and McAvoy, 1977; Tung and Edgar, 1981; Gagnepain and Seborg, 1982, Grosdidier and Morari, 1986; Manousiouthakis and McAvoy, 1986).

In all cases, the plant was described as a linear, time-invariant system. In various situations, however, such as that for large input signals, this simplifying assumption is inadequate and a nonlinear plant description becomes necessary. It is therefore evident that a measure is needed that assesses the interactions among decentralized feedback loops in the presence of system nonlinearities. This measure must be able to predict interactions when the plant is perturbed far from an operational steady state.

The rest of this paper is structured as follows: The next section presents the mathematical framework, followed by a discussion on the importance of the Block Relative Gain in the linear time-invariant case. Next, the dynamic nonlinear block relative gain (DNBRG) and the nonlinear block relative gain (NBRG) are introduced and their properties are discussed. Finally, an illustrative example is presented and conclusions are drawn.

Mathematical Framework

The input-output system formulation (familiar to process control engineers in the linear time-invariant case as the transfer function approach) has been extended to nonlinear systems in Zames (1966a, b), Willems (1971), and Desoer and Vidyasagar (1975). Elements of this approach are outlined next so that the reader can follow the developments in the sequel.

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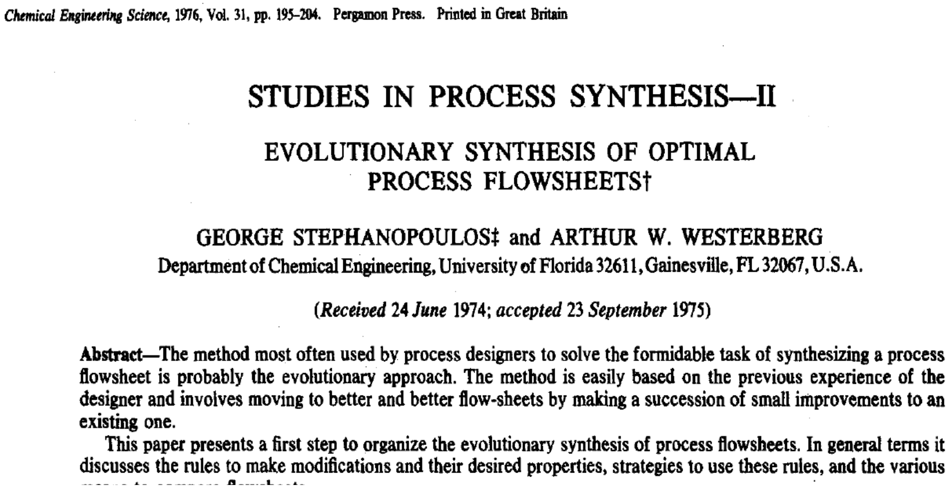
George's Impact on My Research/Education: Synthesis of Mass Exchange Networks



Chemical Engineering Science, 1976, Vol. 31, pp. 195–204. Pergamon Press. Printed in Great Britain

STUDIES IN PROCESS SYNTHESIS—II

EVOLUTIONARY SYNTHESIS OF OPTIMAL PROCESS FLOWSHEETS†

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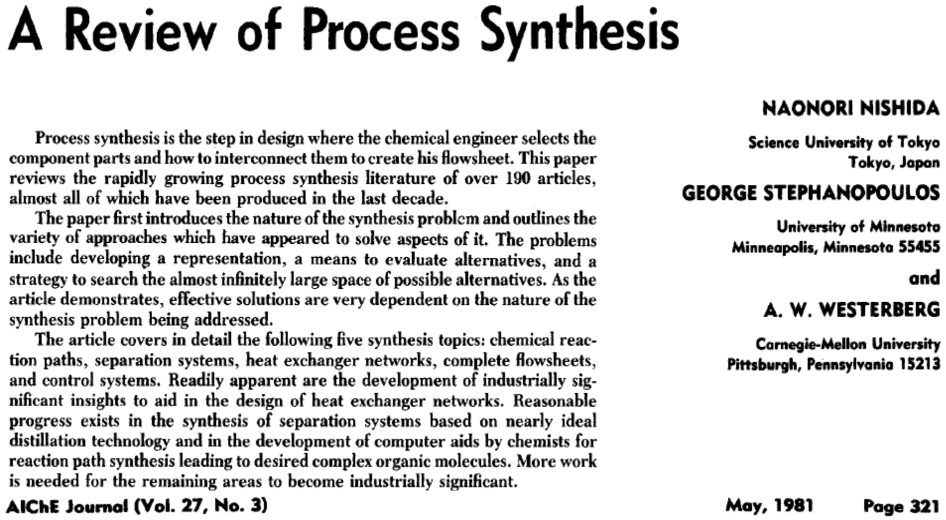
(*Received* 24 *June* 1974; *accepted* 23 *September* 1975)

Abstract—The method most often used by process designers to solve the formidable task of synthesizing a process flowsheet is probably the evolutionary approach. The method is easily based on the previous experience of the designer and involves moving to better and better flow-sheets by making a succession of small improvements to an existing one.

This paper presents a first step to organize the evolutionary synthesis of process flowsheets. In general terms it discusses the rules to make modifications and their desired properties, strategies to use these rules, and the various



A Review of Process Synthesis

NAONORI NISHIDA
Science University of Tokyo
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and

A. W. WESTERBERG
Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

Process synthesis is the step in design where the chemical engineer selects the component parts and how to interconnect them to create his flowsheet. This paper reviews the rapidly growing process synthesis literature of over 190 articles, almost all of which have been produced in the last decade.

The paper first introduces the nature of the synthesis problem and outlines the variety of approaches which have appeared to solve aspects of it. The problems include developing a representation, a means to evaluate alternatives, and a strategy to search the almost infinitely large space of possible alternatives. As the article demonstrates, effective solutions are very dependent on the nature of the synthesis problem being addressed.

The article covers in detail the following five synthesis topics: chemical reaction paths, separation systems, heat exchanger networks, complete flowsheets, and control systems. Readily apparent are the development of industrially significant insights to aid in the design of heat exchanger networks. Reasonable progress exists in the synthesis of separation systems based on nearly ideal distillation technology and in the development of computer aids by chemists for reaction path synthesis leading to desired complex organic molecules. More work is needed for the remaining areas to become industrially significant.

AIChE Journal (Vol. 27, No. 3) May, 1981 Page 321

Synthesis of Mass Exchange Networks

The purpose of this work is to introduce the notion of synthesizing mass-exchange networks (MEN's). A systematic, two-stage, procedure is proposed for the synthesis of cost-effective MEN's. In the first stage, a thermodynamically-oriented procedure is used to identify the thermodynamic bottlenecks (pinch points) that limit the extent of mass exchange between the rich and the lean process streams. Preliminary networks, that feature maximum mass exchange, are generated at this stage. The objective of the second stage is to improve the design of these preliminary networks so as to develop a final configuration of the MEN that satisfies the assigned exchange duty at minimum venture cost. This approach is applied to the synthesis of MEN's with single-component targets as well as multicomponent, compatible targets. An illustrative example on the sweetening of coke-oven gas is presented to demonstrate the applicability of the proposed synthesis procedure.

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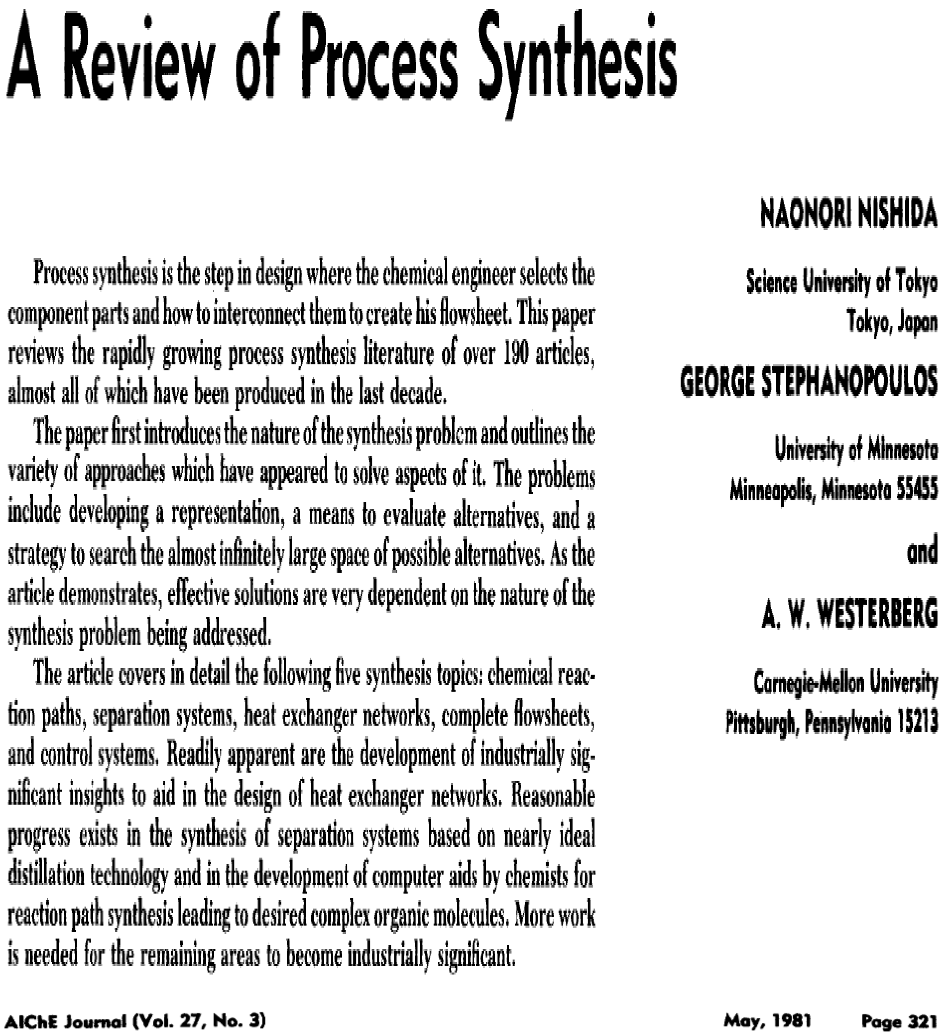
Introduction

The area of chemical process synthesis has received considerable attention over the past two decades. Extensive reviews on the large number of publications in this field can be found in the literature (e.g., Hendry et al., 1973; Hlavacek, 1978; Nishida et al., 1981). In particular, the problem of separation-system synthesis has been the subject of vigorous research effort due to the significant capital and operating costs associated with the separation processes used in chemical plants. The task of separation-system synthesis can be defined as follows (e.g., Floudas, 1987): "Given a set of multicomponent feed streams of known conditions, synthesize a separation sequence that can separate the feed streams into several multicomponent product streams of known conditions with a minimum venture cost." One way of classifying separation processes is according to the nature of the separating agent used which may take the form of energy or mass (King, 1980). Examples of energy-separating-agent processes are distillation, crystallization, and evaporation, while common mass-separating-agent processes are absorption, desorption, ion-exhcnage, etc. Research efforts in the field of separation-system synthesis have primarily been concerned with the synthesis of distillation-based separation systems. A very good reivew of the synthesis approaches for distillation trains is provided by Westerberg (1985). Surprisingly, much less attention has been directed toward the other important category of separators, namely those using mass-separating agents (MSA's) such as solvents, adsorbents, etc.

The earliest attempts to synthesize separation systems which involve the use of MSA's date back to the early 70's. Rudd and coworkers (Siirola et al., 1971; Rudd et al., 1973) developed a heuristic approach for the synthesis of multicomponent separation sequences, as a part of a general process-flowsheeting program called AIDES. Thompson and King (1972) used heuristic and algorithmic programming to select both the sequence and types of separation processes. Stephanopoulos and Westerberg (1976) proposed an evolutionary approach to the synthesis of multicomponent separation sequences. Later, this strategy was refined by Seader and Westerberg (1977), who developed a combined heuristic and evolutionary strategy for the synthesis of simple separation sequences. Motard and coworkers (Mahalec and Motard, 1977; Nath and Motard, 1981; Lu and Motard, 1985) developed a computer methodology for synthesizing preliminary flowsheets, in which separation tasks are synthesized and cost estimated using a set of heuristic and evolutionary rules. Liu and his colleagues (Nadgir and Liu, 1983; Liu 1987; Cheng and Liu, 1988) proposed a simple-ordered heuristic technique for the preliminary synthesis of sloppy multicomponent separation sequences. They developed flexible and effective tools to represent the synthesis problem and to analyze the technical feasibility of separation tasks or product splits. A mixed (real-integer) programming approach for the synthesis of integrated process flowsheets has been proposed by Grossmann (1985). This formulation can serve as a framework for the synthesis of separation systems. Douglas (1985) presented a hierarchical decision procedure for process synthesis which provides useful qualitative criteria for the separation-task selection. Floudas (1987) parametrized the problem using a superstructure, which embeds alternative separation configurations of interest. The solution of a nonlinear programming problem then determines the final network configuration. Muraki and Hayakawa (1988) developed a two-stage evolutionary strat-

AIChE Journal August 1989 Vol. 35, No. 8 1233

George's Impact on My Research/Education: State-Space Approach: Synthesis of Distillation Networks



A Review of Process Synthesis

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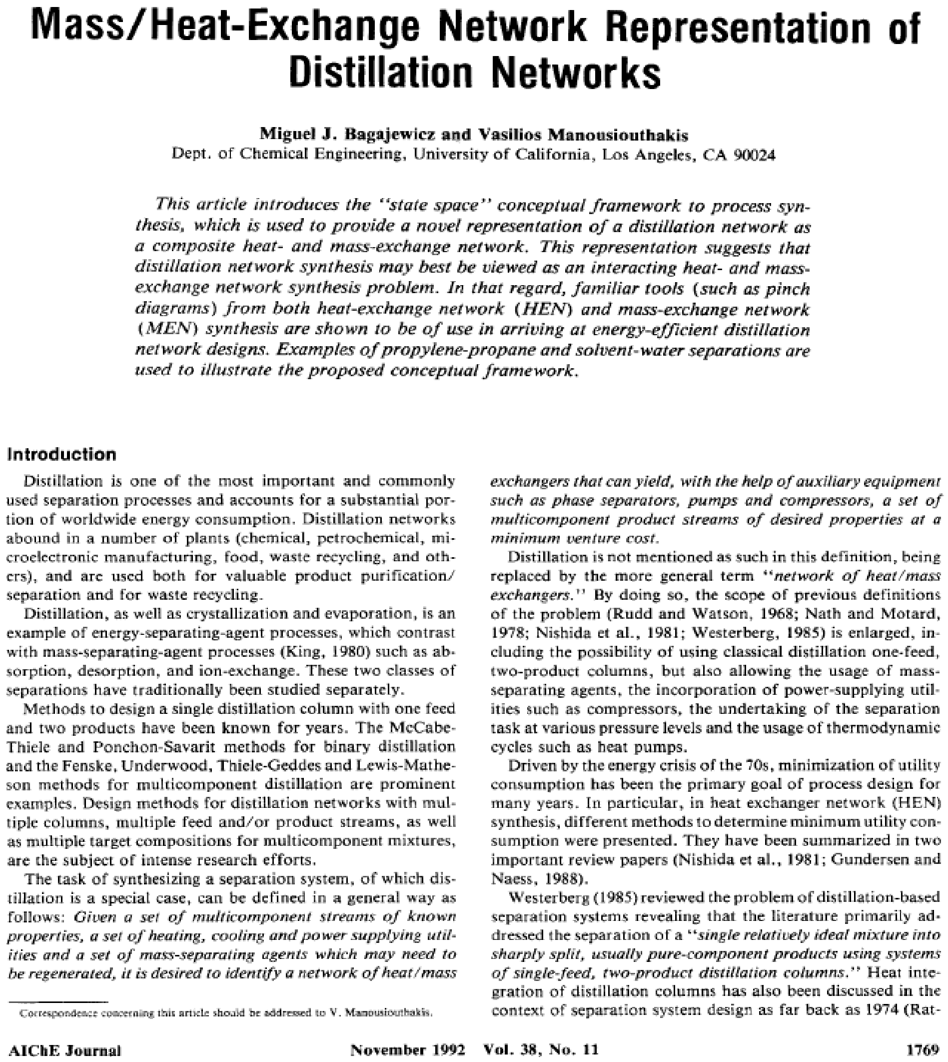
AIChE Journal (Vol. 27, No. 3) **May, 1981** **Page 321**



Mass/Heat-Exchange Network Representation of Distillation Networks

Miguel J. Bagajewicz and Vasilios Manousiouthakis
Dept. of Chemical Engineering, University of California, Los Angeles, CA 90024

This article introduces the "state space" conceptual framework to process synthesis, which is used to provide a novel representation of a distillation network as a composite heat- and mass-exchange network. This representation suggests that distillation network synthesis may best be viewed as an interacting heat- and mass-exchange network synthesis problem. In that regard, familiar tools (such as pinch diagrams) from both heat-exchange network (HEN) and mass-exchange network (MEN) synthesis are shown to be of use in arriving at energy-efficient distillation network designs. Examples of propylene-propane and solvent-water separations are used to illustrate the proposed conceptual framework.

Introduction

Distillation is one of the most important and commonly used separation processes and accounts for a substantial portion of worldwide energy consumption. Distillation networks abound in a number of plants (chemical, petrochemical, microelectronic manufacturing, food, waste recycling, and others), and are used both for valuable product purification/separation and for waste recycling.

Distillation, as well as crystallization and evaporation, is an example of energy-separating-agent processes, which contrast with mass-separating-agent processes (King, 1980) such as absorption, desorption, and ion-exchange. These two classes of separations have traditionally been studied separately.

Methods to design a single distillation column with one feed and two products have been known for years. The McCabe-Thiele and Ponchon-Savarit methods for binary distillation and the Fenske, Underwood, Thiele-Geddes and Lewis-Matheson methods for multicomponent distillation are prominent examples. Design methods for distillation networks with multiple columns, multiple feed and/or product streams, as well as multiple target compositions for multicomponent mixtures, are the subject of intense research efforts.

The task of synthesizing a separation system, of which distillation is a special case, can be defined in a general way as follows: *Given a set of multicomponent streams of known properties, a set of heating, cooling and power supplying utilities and a set of mass-separating agents which may need to be regenerated, it is desired to identify a network of heat/mass exchangers that can yield, with the help of auxiliary equipment such as phase separators, pumps and compressors, a set of multicomponent product streams of desired properties at a minimum venture cost.*

Distillation is not mentioned as such in this definition, being replaced by the more general term "*network of heat/mass exchangers.*" By doing so, the scope of previous definitions of the problem (Rudd and Watson, 1968; Nath and Motard, 1978; Nishida et al., 1981; Westerberg, 1985) is enlarged, including the possibility of using classical distillation one-feed, two-product columns, but also allowing the usage of mass-separating agents, the incorporation of power-supplying utilities such as compressors, the undertaking of the separation task at various pressure levels and the usage of thermodynamic cycles such as heat pumps.

Driven by the energy crisis of the 70s, minimization of utility consumption has been the primary goal of process design for many years. In particular, in heat exchanger network (HEN) synthesis, different methods to determine minimum utility consumption were presented. They have been summarized in two important review papers (Nishida et al., 1981; Gundersen and Naess, 1988).

Westerberg (1985) reviewed the problem of distillation-based separation systems revealing that the literature primarily addressed the separation of a "*single relatively ideal mixture into sharply split, usually pure-component products using systems of single-feed, two-product distillation columns.*" Heat integration of distillation columns has also been discussed in the context of separation system design as far back as 1974 (Rat-

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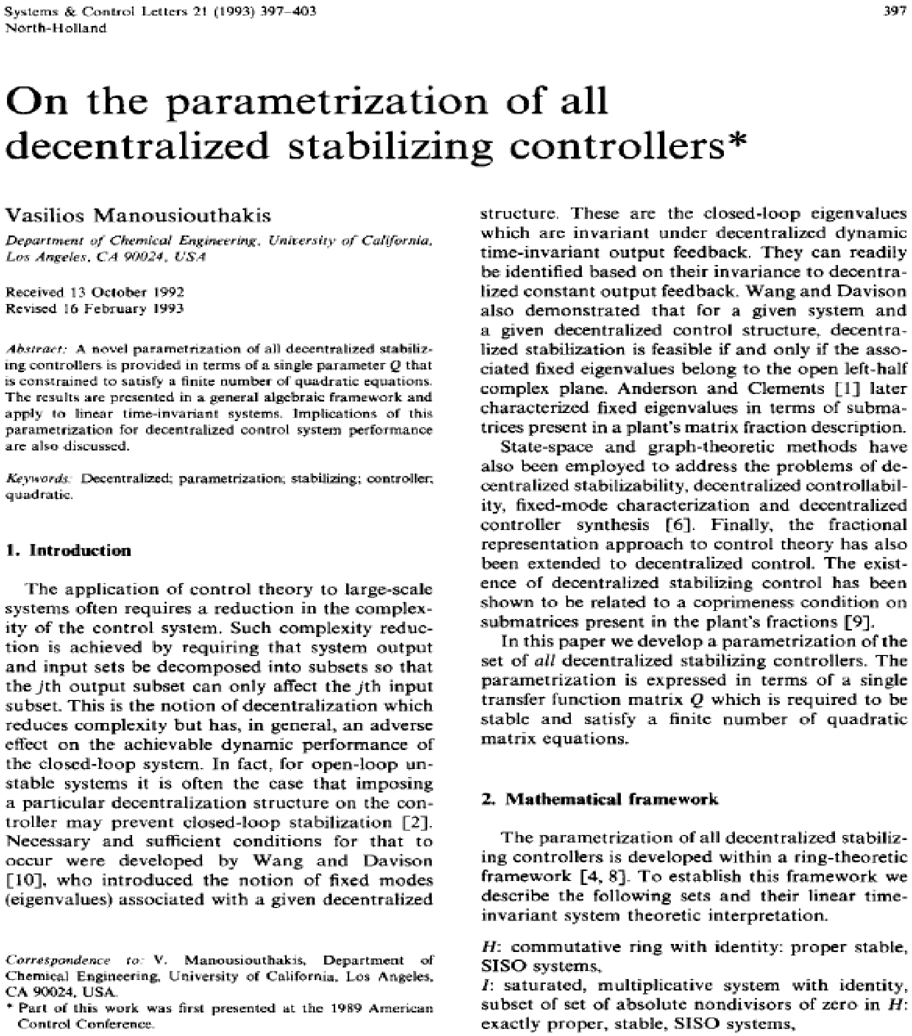
George's Impact on My Research/Education: Stabilizing and Optimal Decentralized Control



Systems & Control Letters 21 (1993) 397–403
North-Holland

On the parametrization of all decentralized stabilizing controllers*

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Abstract: A novel parametrization of all decentralized stabilizing controllers is provided in terms of a single parameter Q that is constrained to satisfy a finite number of quadratic equations. The results are presented in a general algebraic framework and apply to linear time-invariant systems. Implications of this parametrization for decentralized control system performance are also discussed.

Keywords: Decentralized; parametrization; stabilizing; controller; quadratic.

1. Introduction

The application of control theory to large-scale systems often requires a reduction in the complexity of the control system. Such complexity reduction is achieved by requiring that system output and input sets be decomposed into subsets so that the jth output subset can only affect the jth input subset. This is the notion of decentralization which reduces complexity but has, in general, an adverse effect on the achievable dynamic performance of the closed-loop system. In fact, for open-loop unstable systems it is often the case that imposing a particular decentralization structure on the controller may prevent closed-loop stabilization [2]. Necessary and sufficient conditions for that to occur were developed by Wang and Davison [10], who introduced the notion of fixed modes (eigenvalues) associated with a given decentralized structure. These are the closed-loop eigenvalues which are invariant under decentralized dynamic time-invariant output feedback. They can readily be identified based on their invariance to decentralized constant output feedback. Wang and Davison also demonstrated that for a given system and a given decentralized control structure, decentralized stabilization is feasible if and only if the associated fixed eigenvalues belong to the open left-half complex plane. Anderson and Clements [1] later characterized fixed eigenvalues in terms of submatrices present in a plant's matrix fraction description.

State-space and graph-theoretic methods have also been employed to address the problems of decentralized stabilizability, decentralized controllability, fixed-mode characterization and decentralized controller synthesis [6]. Finally, the fractional representation approach to control theory has also been extended to decentralized control. The existence of decentralized stabilizing control has been shown to be related to a coprimeness condition on submatrices present in the plant's fractions [9].

In this paper we develop a parametrization of the set of *all* decentralized stabilizing controllers. The parametrization is expressed in terms of a single transfer function matrix Q which is required to be stable and satisfy a finite number of quadratic matrix equations.

2. Mathematical framework

The parametrization of all decentralized stabilizing controllers is developed within a ring-theoretic framework [4, 8]. To establish this framework we describe the following sets and their linear time-invariant system theoretic interpretation.

H: commutative ring with identity: proper stable, SISO systems,
I: saturated, multiplicative system with identity, subset of set of absolute nondivisors of zero in H: exactly proper, stable, SISO systems,

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* Part of this work was first presented at the 1989 American Control Conference.

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Best Achievable Decentralized Performance

Dennis D. Sourlas and Vasilios Manousiouthakis

***Abstract*— In this paper, a novel parameterization of all decentralized stabilizing controllers is employed in mathematically formulating the best achievable decentralized performance problem as an infinite dimensional optimization problem. Finite dimensional optimization problems are then constructed that have values arbitrarily close to this infinite dimensional problem. An algorithm which identifies the best achievable performance over all linear time-invariant decentralized controllers is then presented. It employs a global optimization approach to the solution of these finite dimensional approximating problems.**

NOTATION

The control problems studied are formulated in a discrete-time framework. The following notation is employed:

G	Set of proper rational transfer functions.
$M(G)$	Set of proper rational transfer function matrices.
S	Set of stable rational transfer functions ($S \subset G$).
$M(S)$	Set of stable rational transfer function matrices ($M(S) \subset M(G)$).
$l^1_{m \times n}$, $\|\cdot\|_{l^1}$	Space of absolutely summable sequences of $m \times n$ real matrices and corresponding norm.
$\phi_0 \subset l^1_{m \times n}$	Set of $l^1_{m \times n}$ sequences with finite number of nonzero elements.
l^∞_m, $\|\cdot\|_\infty$	Space of bounded sequences of m-dimensional real vectors and corresponding norm.
$\|\cdot\|_{i\infty}$	Induced norm of a $l^\infty_m \to l^\infty_n$ map (equal to the $\|\cdot\|_{l^1}$ of the map's impulse response sequence).

I. INTRODUCTION

THE control of most industrial processes involves the measurement and manipulation of a large number of variables. Sometimes, the location of the units that need to be controlled is such that a complex communication network has to be installed if a fully centralized controller is to be designed. The term centralized controller refers to the situation where all measurements are used to determine the values of all manipulations. The complexity of centralized controllers often makes the implementation of such a control strategy impossible. A different approach, which has the benefit of hardware simplicity, is to install local controllers, with each being responsible for the operation of an adjacent unit. In that way, the notion of decentralized control has emerged.

Since the early 1970's, significant research effort has been expended on the subject of decentralized control. Nevertheless, two unanswered questions remain:

a) Given the set of measurements and manipulations, how does one select the appropriate pairings?
b) How can one assess fundamental limitations to decentralized control system performance?

The first question is referred to as the decentralized control structure synthesis problem and has been discussed in [1] and [2]. The second question can be unequivocally addressed only through the optimal decentralized controller synthesis problem. Given the set of measurements and manipulations, the solution of the decentralized control structure synthesis problem determines the flow of information in the control loop, or equivalently the pairings between the measurements and the manipulations. The solution to the second problem determines the best achievable closed-loop dynamic performance for a given decentralized control structure.

It has already been established that, given a plant and a decentralized structure, there may not exist any decentralized stabilizing controllers with that structure. Indeed, Aoki [3] demonstrated that there may exist decentralized control structures that prevent stabilization of the closed loop. Wang and Davison [4] introduced the notion of decentralized fixed eigenvalues, also called fixed modes, associated with a controller structure. A stabilizing decentralized controller exists iff these fixed modes are stable. Algebraic characterizations of the notion of decentralized controllability, which is related to the fixed mode concept, for the two-input vector case are given in [5]–[8]. Anderson and Clements [9] employed algebraic concepts to characterize the decentralized fixed eigenvalues of a system and presented computational tests for the existence of fixed modes. Siljak [10] developed state space and graph theoretic methods to address the problems of decentralized stabilizability, decentralized controllability, fixed mode characterization, and decentralized controller synthesis.

The issue of stability of decentralized control systems has also been addressed within the fractional representation approach to control theory. Gündeş and Desoer [11] characterized the set of all decentralized stabilizing controllers of fixed structure for a given linear time invariant (LTI) process in terms of a number of stable parameters [11, pp. 122, 165]. In this case, stability of the decentralized closed loop is equivalent to the unimodularity of a transfer function matrix which is a function of these stable parameters. For the same class of processes (LTI plants), Manousiouthakis [12], [13] presented a parameterization of all decentralized stabilizing controllers

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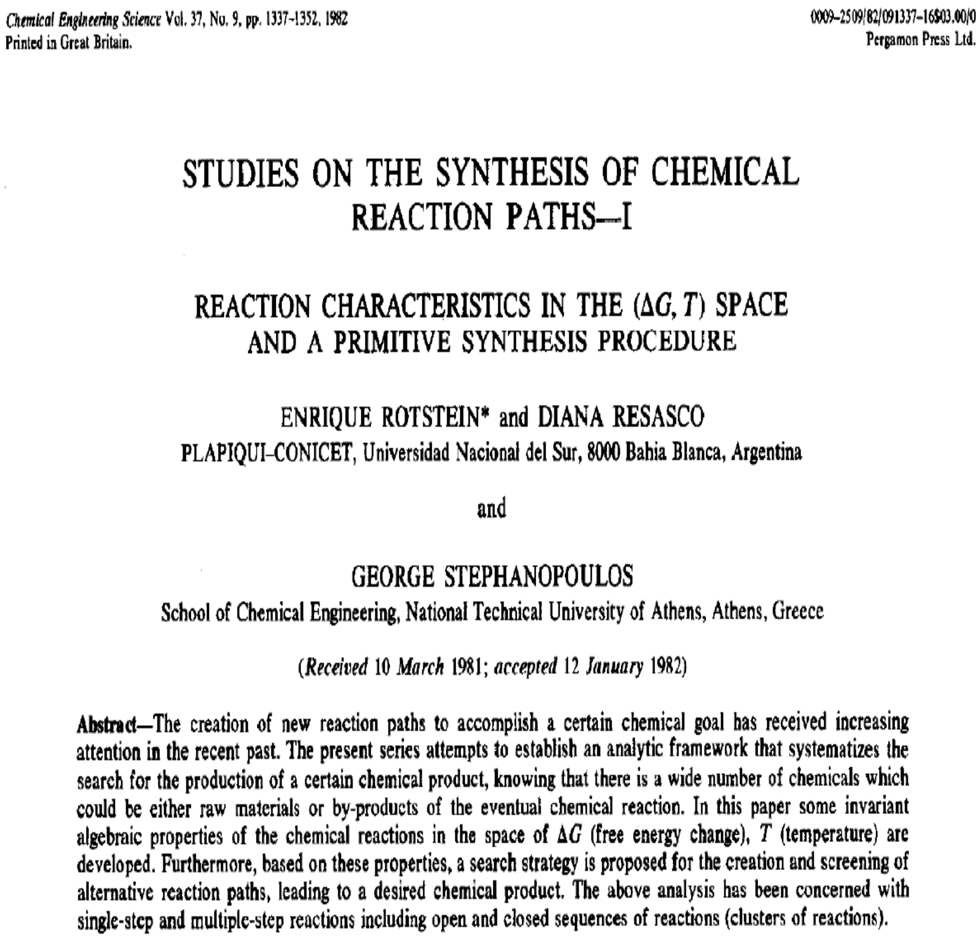
George's Impact on My Research:
Synthesis of Reaction Pathways (Clusters)



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Printed in Great Britain.

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Pergamon Press Ltd.

STUDIES ON THE SYNTHESIS OF CHEMICAL REACTION PATHS—I

REACTION CHARACTERISTICS IN THE $(\Delta G, T)$ SPACE AND A PRIMITIVE SYNTHESIS PROCEDURE

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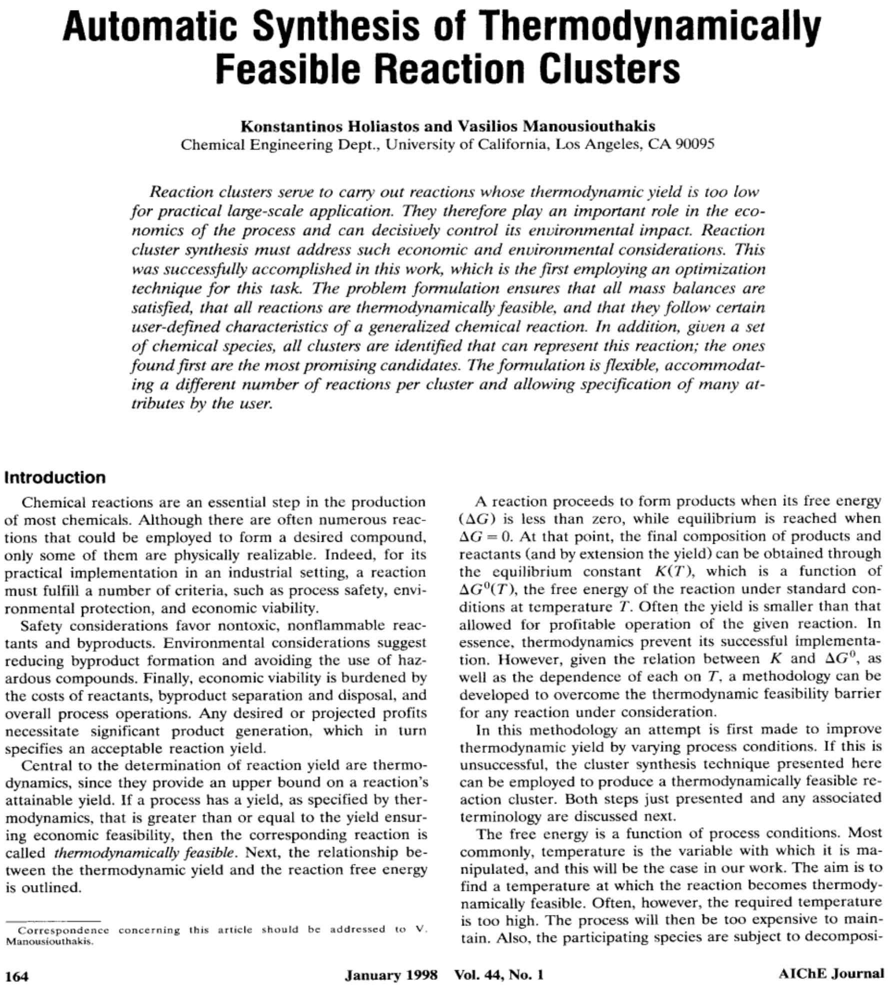
(*Received* 10 *March* 1981; *accepted* 12 *January* 1982)

Abstract—The creation of new reaction paths to accomplish a certain chemical goal has received increasing attention in the recent past. The present series attempts to establish an analytic framework that systematizes the search for the production of a certain chemical product, knowing that there is a wide number of chemicals which could be either raw materials or by-products of the eventual chemical reaction. In this paper some invariant algebraic properties of the chemical reactions in the space of ΔG (free energy change), T (temperature) are developed. Furthermore, based on these properties, a search strategy is proposed for the creation and screening of alternative reaction paths, leading to a desired chemical product. The above analysis has been concerned with single-step and multiple-step reactions including open and closed sequences of reactions (clusters of reactions).



Automatic Synthesis of Thermodynamically Feasible Reaction Clusters

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Reaction clusters serve to carry out reactions whose thermodynamic yield is too low for practical large-scale application. They therefore play an important role in the economics of the process and can decisively control its environmental impact. Reaction cluster synthesis must address such economic and environmental considerations. This was successfully accomplished in this work, which is the first employing an optimization technique for this task. The problem formulation ensures that all mass balances are satisfied, that all reactions are thermodynamically feasible, and that they follow certain user-defined characteristics of a generalized chemical reaction. In addition, given a set of chemical species, all clusters are identified that can represent this reaction; the ones found first are the most promising candidates. The formulation is flexible, accommodating a different number of reactions per cluster and allowing specification of many attributes by the user.

Introduction

Chemical reactions are an essential step in the production of most chemicals. Although there are often numerous reactions that could be employed to form a desired compound, only some of them are physically realizable. Indeed, for its practical implementation in an industrial setting, a reaction must fulfill a number of criteria, such as process safety, environmental protection, and economic viability.

Safety considerations favor nontoxic, nonflammable reactants and byproducts. Environmental considerations suggest reducing byproduct formation and avoiding the use of hazardous compounds. Finally, economic viability is burdened by the costs of reactants, byproduct separation and disposal, and overall process operations. Any desired or projected profits necessitate significant product generation, which in turn specifies an acceptable reaction yield.

Central to the determination of reaction yield are thermodynamics, since they provide an upper bound on a reaction's attainable yield. If a process has a yield, as specified by thermodynamics, that is greater than or equal to the yield ensuring economic feasibility, then the corresponding reaction is called *thermodynamically feasible*. Next, the relationship between the thermodynamic yield and the reaction free energy is outlined.

A reaction proceeds to form products when its free energy (ΔG) is less than zero, while equilibrium is reached when $\Delta G = 0$. At that point, the final composition of products and reactants (and by extension the yield) can be obtained through the equilibrium constant $K(T)$, which is a function of $\Delta G^0(T)$, the free energy of the reaction under standard conditions at temperature T. Often the yield is smaller than that allowed for profitable operation of the given reaction. In essence, thermodynamics prevent its successful implementation. However, given the relation between K and ΔG^0, as well as the dependence of each on T, a methodology can be developed to overcome the thermodynamic feasibility barrier for any reaction under consideration.

In this methodology an attempt is first made to improve thermodynamic yield by varying process conditions. If this is unsuccessful, the cluster synthesis technique presented here can be employed to produce a thermodynamically feasible reaction cluster. Both steps just presented and any associated terminology are discussed next.

The free energy is a function of process conditions. Most commonly, temperature is the variable with which it is manipulated, and this will be the case in our work. The aim is to find a temperature at which the reaction becomes thermodynamically feasible. Often, however, the required temperature is too high. The process will then be too expensive to maintain. Also, the participating species are subject to decomposi-

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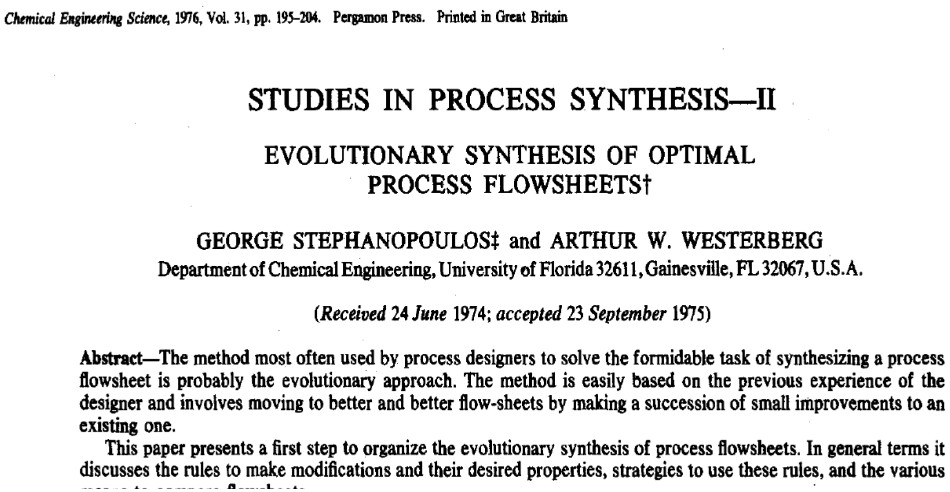
164 January 1998 Vol. 44, No. 1 AIChE Journal

George's Impact on My Research/Education: Synthesis of Mass Exchange Networks



Chemical Engineering Science, 1976, Vol. 31, pp. 195–204. Pergamon Press. Printed in Great Britain

STUDIES IN PROCESS SYNTHESIS—II

EVOLUTIONARY SYNTHESIS OF OPTIMAL PROCESS FLOWSHEETS†

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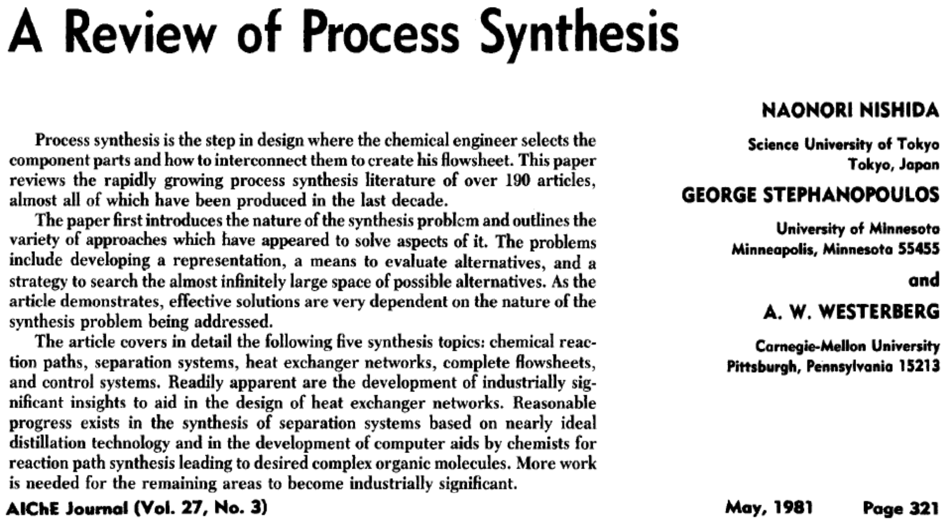
(*Received* 24 *June* 1974; *accepted* 23 *September* 1975)

Abstract—The method most often used by process designers to solve the formidable task of synthesizing a process flowsheet is probably the evolutionary approach. The method is easily based on the previous experience of the designer and involves moving to better and better flow-sheets by making a succession of small improvements to an existing one.

This paper presents a first step to organize the evolutionary synthesis of process flowsheets. In general terms it discusses the rules to make modifications and their desired properties, strategies to use these rules, and the various



A Review of Process Synthesis

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Process synthesis is the step in design where the chemical engineer selects the component parts and how to interconnect them to create his flowsheet. This paper reviews the rapidly growing process synthesis literature of over 190 articles, almost all of which have been produced in the last decade.

The paper first introduces the nature of the synthesis problem and outlines the variety of approaches which have appeared to solve aspects of it. The problems include developing a representation, a means to evaluate alternatives, and a strategy to search the almost infinitely large space of possible alternatives. As the article demonstrates, effective solutions are very dependent on the nature of the synthesis problem being addressed.

The article covers in detail the following five synthesis topics: chemical reaction paths, separation systems, heat exchanger networks, complete flowsheets, and control systems. Readily apparent are the development of industrially significant insights to aid in the design of heat exchanger networks. Reasonable progress exists in the synthesis of separation systems based on nearly ideal distillation technology and in the development of computer aids by chemists for reaction path synthesis leading to desired complex organic molecules. More work is needed for the remaining areas to become industrially significant.

AIChE Journal (Vol. 27, No. 3) **May, 1981** **Page 321**

Synthesis of Mass Exchange Networks

The purpose of this work is to introduce the notion of synthesizing mass-exchange networks (MEN's). A systematic, two-stage, procedure is proposed for the synthesis of cost-effective MEN's. In the first stage, a thermodynamically-oriented procedure is used to identify the thermodynamic bottlenecks (pinch points) that limit the extent of mass exchange between the rich and the lean process streams. Preliminary networks, that feature maximum mass exchange, are generated at this stage. The objective of the second stage is to improve the design of these preliminary networks so as to develop a final configuration of the MEN that satisfies the assigned exchange duty at minimum venture cost. This approach is applied to the synthesis of MEN's with single-component targets as well as multicomponent, compatible targets. An illustrative example on the sweetening of coke-oven gas is presented to demonstrate the applicability of the proposed synthesis procedure.

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Introduction

The area of chemical process synthesis has received considerable attention over the past two decades. Extensive reviews on the large number of publications in this field can be found in the literature (e.g., Hendry et al., 1973; Hlavacek, 1978; Nishida et al., 1981). In particular, the problem of separation-system synthesis has been the subject of vigorous research effort due to the significant capital and operating costs associated with the separation processes used in chemical plants. The task of separation-system synthesis can be defined as follows (e.g., Floudas, 1987): "Given a set of multicomponent feed streams of known conditions, synthesize a separation sequence that can separate the feed streams into several multicomponent product streams of known conditions with a minimum venture cost." One way of classifying separation processes is according to the nature of the separating agent used which may take the form of energy or mass (King, 1980). Examples of energy-separating-agent processes are distillation, crystallization, and evaporation, while common mass-separating-agent processes are absorption, desorption, ion-exhcnage, etc. Research efforts in the field of separation-system synthesis have primarily been concerned with the synthesis of distillation-based separation systems. A very good reivew of the synthesis approaches for distillation trains is provided by Westerberg (1985). Surprisingly, much less attention has been directed toward the other important category of separators, namely those using mass-separating agents (MSA's) such as solvents, adsorbents, etc.

The earliest attempts to synthesize separation systems which involve the use of MSA's date back to the early 70's. Rudd and coworkers (Siirola et al., 1971; Rudd et al., 1973) developed a heuristic approach for the synthesis of multicomponent separation sequences, as a part of a general process-flowsheeting program called AIDES. Thompson and King (1972) used heuristic and algorithmic programming to select both the sequence and types of separation processes. Stephanopoulos and Westerberg (1976) proposed an evolutionary approach to the synthesis of multicomponent separation sequences. Later, this strategy was refined by Seader and Westerberg (1977), who developed a combined heuristic and evolutionary strategy for the synthesis of simple separation sequences. Motard and coworkers (Mahalec and Motard, 1977; Nath and Motard, 1981; Lu and Motard, 1985) developed a computer methodology for synthesizing preliminary flowsheets, in which separation tasks are synthesized and cost estimated using a set of heuristic and evolutionary rules. Liu and his colleagues (Nadgir and Liu, 1983; Liu 1987; Cheng and Liu, 1988) proposed a simple-ordered heuristic technique for the preliminary synthesis of sloppy multicomponent separation sequences. They developed flexible and effective tools to represent the synthesis problem and to analyze the technical feasibility of separation tasks or product splits. A mixed (real-integer) programming approach for the synthesis of integrated process flowsheets has been proposed by Grossmann (1985). This formulation can serve as a framework for the synthesis of separation systems. Douglas (1985) presented a hierarchical decision procedure for process synthesis which provides useful qualitative criteria for the separation-task selection. Floudas (1987) parametrized the problem using a superstructure, which embeds alternative separation configurations of interest. The solution of a nonlinear programming problem then determines the final network configuration. Muraki and Hayakawa (1988) developed a two-stage evolutionary strat-

AIChE Journal **August 1989** **Vol. 35, No. 8** **1233**

Infinite DimEnsionAl State-space (IDEAS) Paradigm

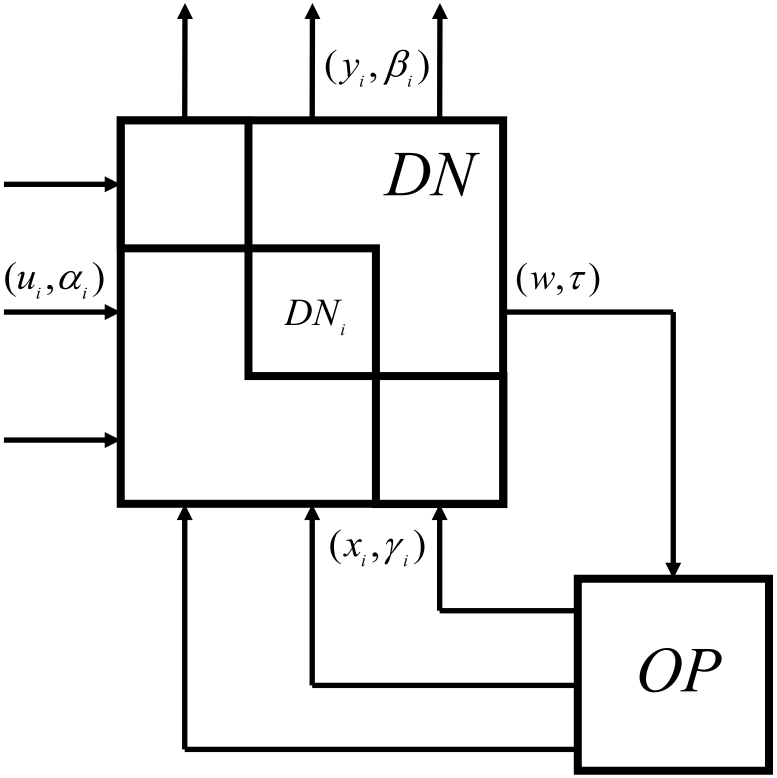
- All feasible network configurations are considered
- No *a priori* network structure is assumed
- Linear feasible region in infinite dimensional space
- Finite approximations are employed which are guaranteed to converge to IDEAS optimum
- Gives rise to Large Scale, Linear Programming (LP) Formulations
- Able to guarantee global optimality
- Over twenty archive journal publications

Infinite DimEnsionAl State-space (IDEAS) Paradigm

The network is decomposed into two blocks of operations:

1. DN (Distribution Network): where all mixing, splitting, bypassing, and recycling operations.

2. OP or the Operator: where the actual unit operation are (mass/heat exchange, reaction, etc.)



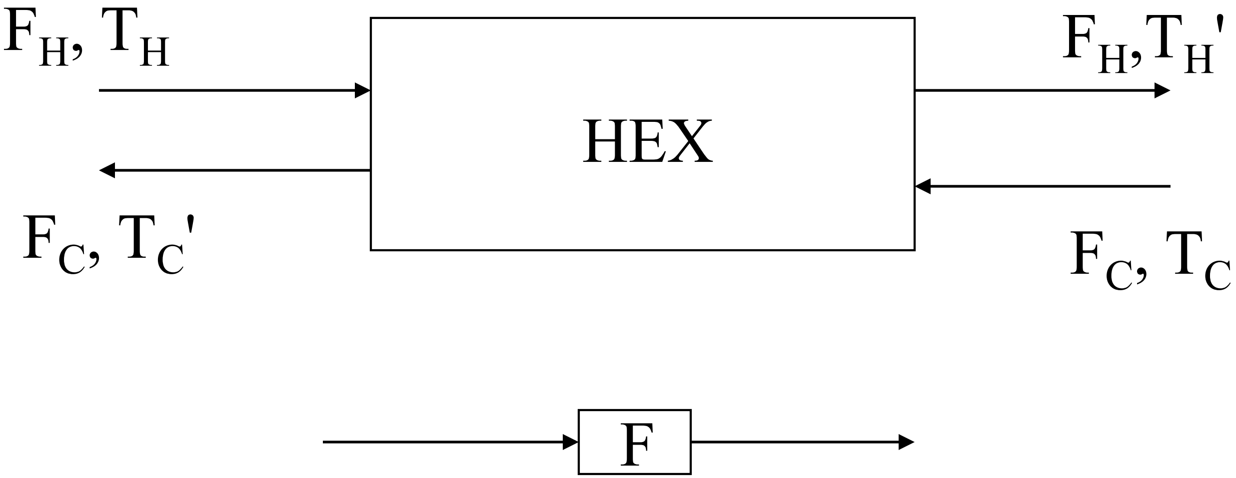
IDEAS Information Map

- Applicability of IDEAS requires satisfaction of the following property by the information map of the process model:

$$N : u = \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} \rightarrow y = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} L_1(u_2) \cdot u_1 \\ N_2(u_2) \end{bmatrix} \quad , \quad L_1(u_2) \ \ is \ \ linear$$

- This property is satisfied by the information map of a wide variety of process models as discussed next

Heat Exchanger Information Map



F_H, T_H

F_H, T_H'

HEX

F_C, T_C'

F_C, T_C

F

$$\left(F_H,\ F_C,\ T_H,\ T_C,\ T_H',\ T_C'\right)^T$$

$$\left(F_H,\ F_C,\ T_H,\ T_C,\ A/F_H,\ T_C'\right)^T \overset{F}{\Longrightarrow} \left(F_H,\ F_C,\ T_H',\ T_C'\right)^T$$

$$\left(F_H,\ F_C,\ T_H,\ T_C,\ A/F_H,\ T_H'\right)^T$$

Heat Exchanger Information Map

F restriction on a single flow variety is a linear map

$$\left(F_H,\ F_C,\ T_H,\ T_C,\ T_H',\ T_C'\right)^T \overset{F}{\Rightarrow} \left(F_H,\ F_C,\ T_H',\ T_C'\right)^T$$

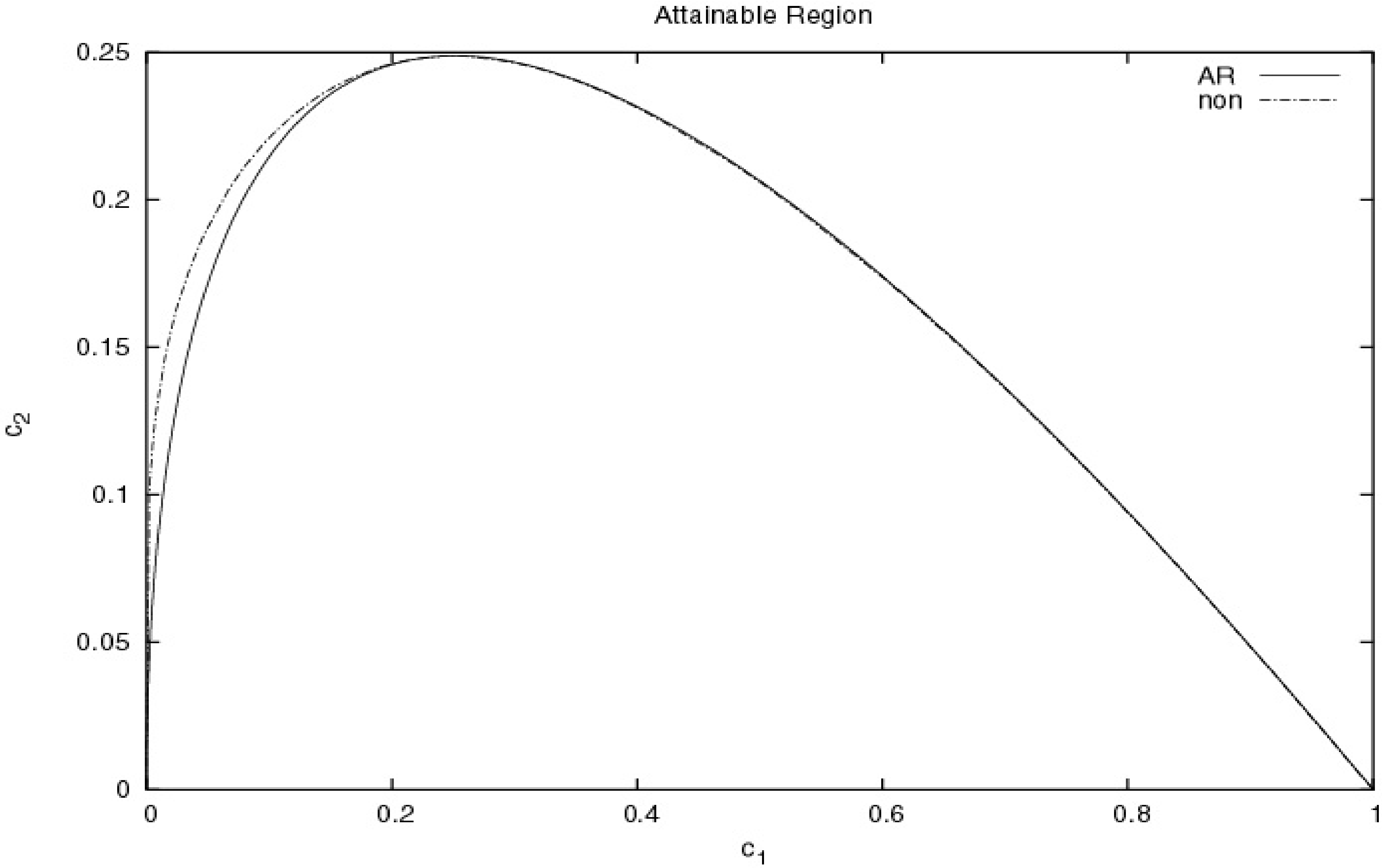
$$\Delta T_{lm} = \frac{(T_H - T_C') - (T_H' - T_C)}{\ln((T_H - T_C')/(T_H' - T_C))}$$

$$U \Delta T_{lm} \alpha = h(T_H) - h(T_H')$$

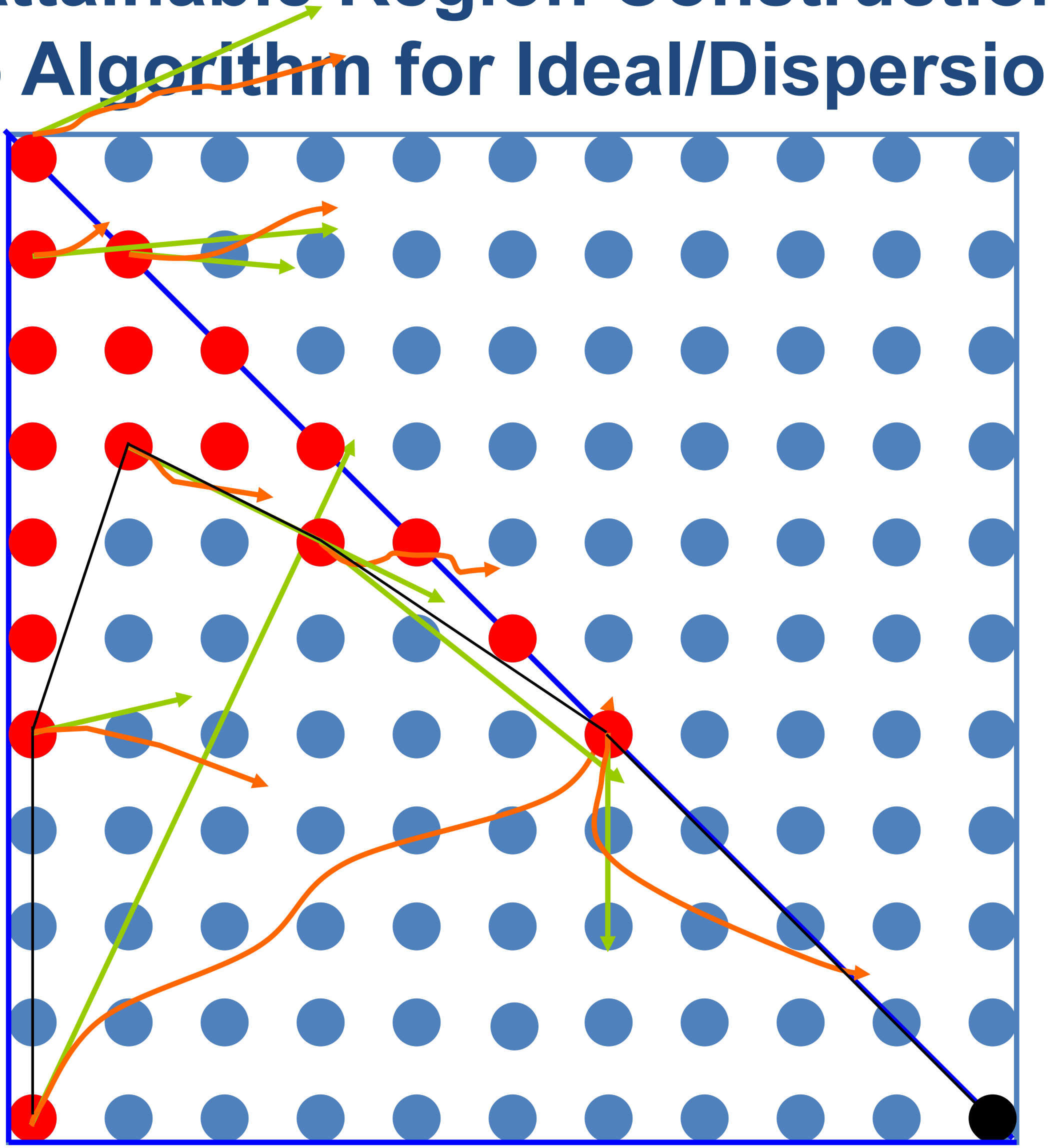
$$U \Delta T_{lm} \alpha = \beta[h(T_C') - h(T_C)]$$

$$A = \alpha F_H \qquad F_C = \beta F_H$$

Attainable Region Construction
Shrinkwrap Algorithm for Ideal/Dispersion Reactors



Attainable Region Construction
Shrinkwrap Algorithm for Ideal/Dispersion Reactors



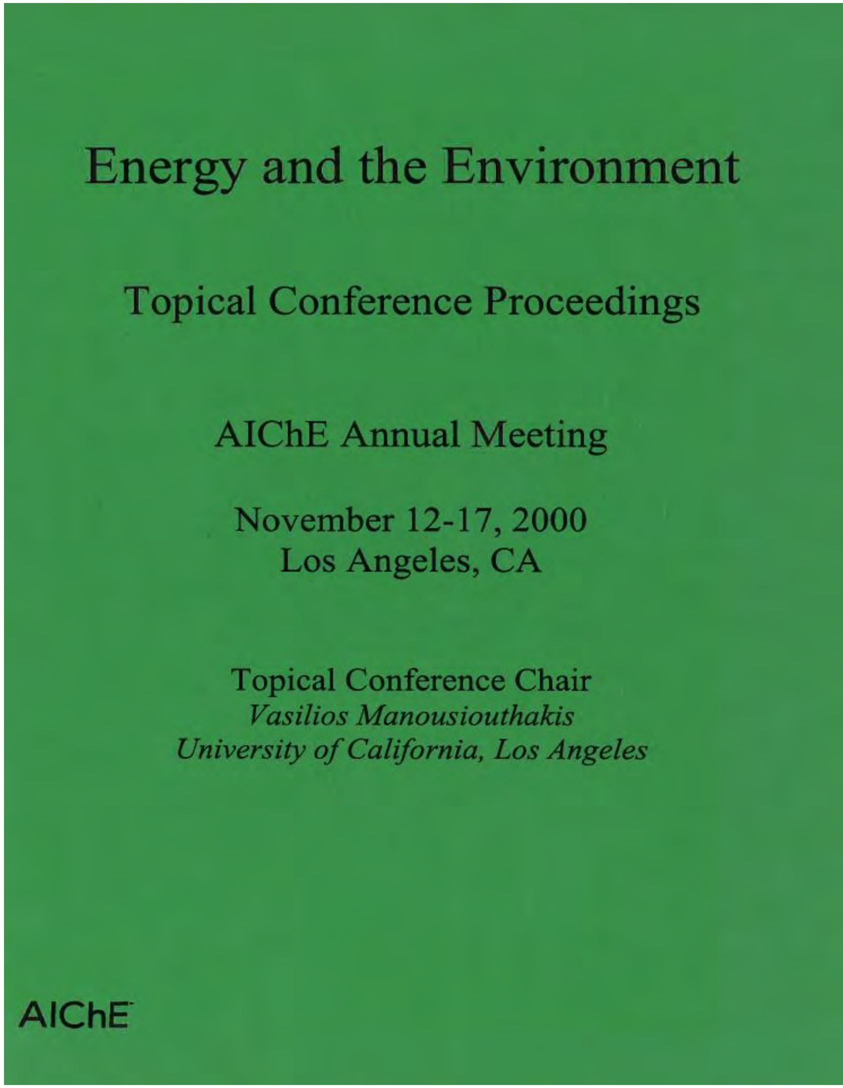
PSE as the Modern Euryphaessa

- Climate Change – CO_2 Profitability
- Air quality – Thermochemical Cycles
- Creation of Hybrid Energy Systems Fossil Fuels – Renewables
- Pursuit of “Green Engineering” (Green Dollars and Green Environment)

PSE as the Modern Euryphaessa

- ➢ Do not have visions for the future
- ➢ Shape the future
- ➢ Become the mother Euryfaessa, that will give birth to the ideas needed to move humanity past:

1. Prometheus’ Burning Paradigm
2. Climate Change Tautology



Energy and the Environment

Topical Conference Proceedings

AIChE Annual Meeting

November 12-17, 2000
Los Angeles, CA

Topical Conference Chair
Vasilios Manousiouthakis
University of California, Los Angeles

AIChE

Climate Change Solution: CO_2 Profitability

- **CO_2**, produced or captured, can **produce useful chemicals** (formic acid, acetic acid, hydrogen or a combination of formic acid/acetic acid and power).

- Process can utilize fossil fuel raw materials (natural gas, coal etc.) to produce above chemicals with **no CO_2 emissions**.

- Process utilizes already **existing commercial technologies** such as SMR, WGS etc.

- Process can be such that it is **energetically self-sufficient** (no energy or work input from surrounding).

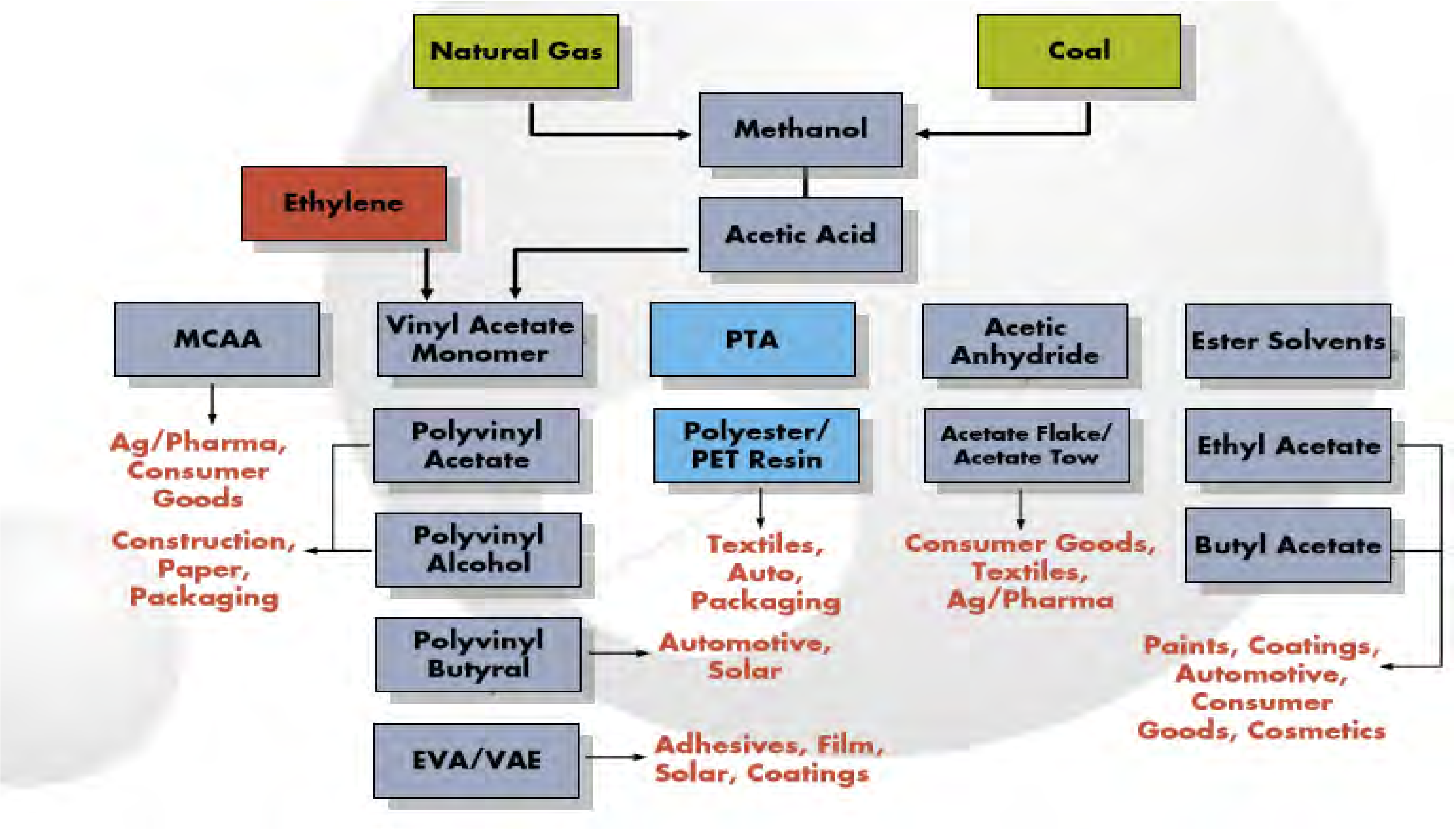
- Sale of products at current market prices **guarantees profit**

CO_2 Profitability: Formic Acid Uses

Neutralization and acidification	- Textiles: dyeing, impregnating, pre-treatment, mercerization - Leather: tanning, bating, dyeing and refining - Rubber: latex coagulation - Waste-gas treatment: desulfurization
Preservation	- Grass silage: preservation of green fodder - Feed: preservation of grain, corn, etc. - Fish silage: prevention of salmonellae - Drinking water: salmonella control
Cleaner and biocide	- Industrial plants: cleaning, descaling, derusting - Household: descaling, cleaning - Wine casks, beer barrels and kegs - Dairy
Reactant	- Plasticizers: epoxidation of soy bean oil to ESO - Paper: sizing agent for surfacing - Artificial sweetener - Semiconductor board soldering
Starting material	- Oilfield chemicals: formate salts (cesium, potassium formates) - Runway deicing (potassium formate) - Refrigerant for cold stores (potassium formate)

Source: BASF

CO_2 Profitability: Acetic Acid Uses



Source: Tecnon OrbiChem

Source: Tecnon OrbiChem, Chemical Market Insight and forecast, Acetic Acid, 2013

Formic acid Reaction cluster – CO_2 to formic

$$(0.5-0.25X)\left[CH_4^{(g)} + 2O_2^{(g)} \rightarrow CO_2^{(g)} + 2H_2O^{(g)}\right]$$

$$(Y)\left[CH_4^{(g)} + 2H_2O^{(g)} \rightleftharpoons CO_2^{(g)} + 4H_2^{(g)}\right]$$

$$(0.5+0.25X-Y)\left[CH_4^{(g)} + H_2O^{(g)} \rightleftharpoons CO^{(g)} + 3H_2^{(g)}\right]$$

$$(0.5+0.25X-Y)\left[CO^{(g)} + H_2O^{(g)} \rightleftharpoons CO_2^{(g)} + H_2^{(g)}\right]$$

$$CO_2^{(g)} + H_2^{(g)} \rightarrow HCOOH^{(aq)}$$

$$CH_4^{(g)} + \left(1-\frac{X}{2}\right)O_2^{(g)} + X\,H_2O^{(g)} \rightleftharpoons HCOOH^{(aq)} + (1+X)H_2^{(g)}$$

Formic acid Reaction cluster – BASF Process

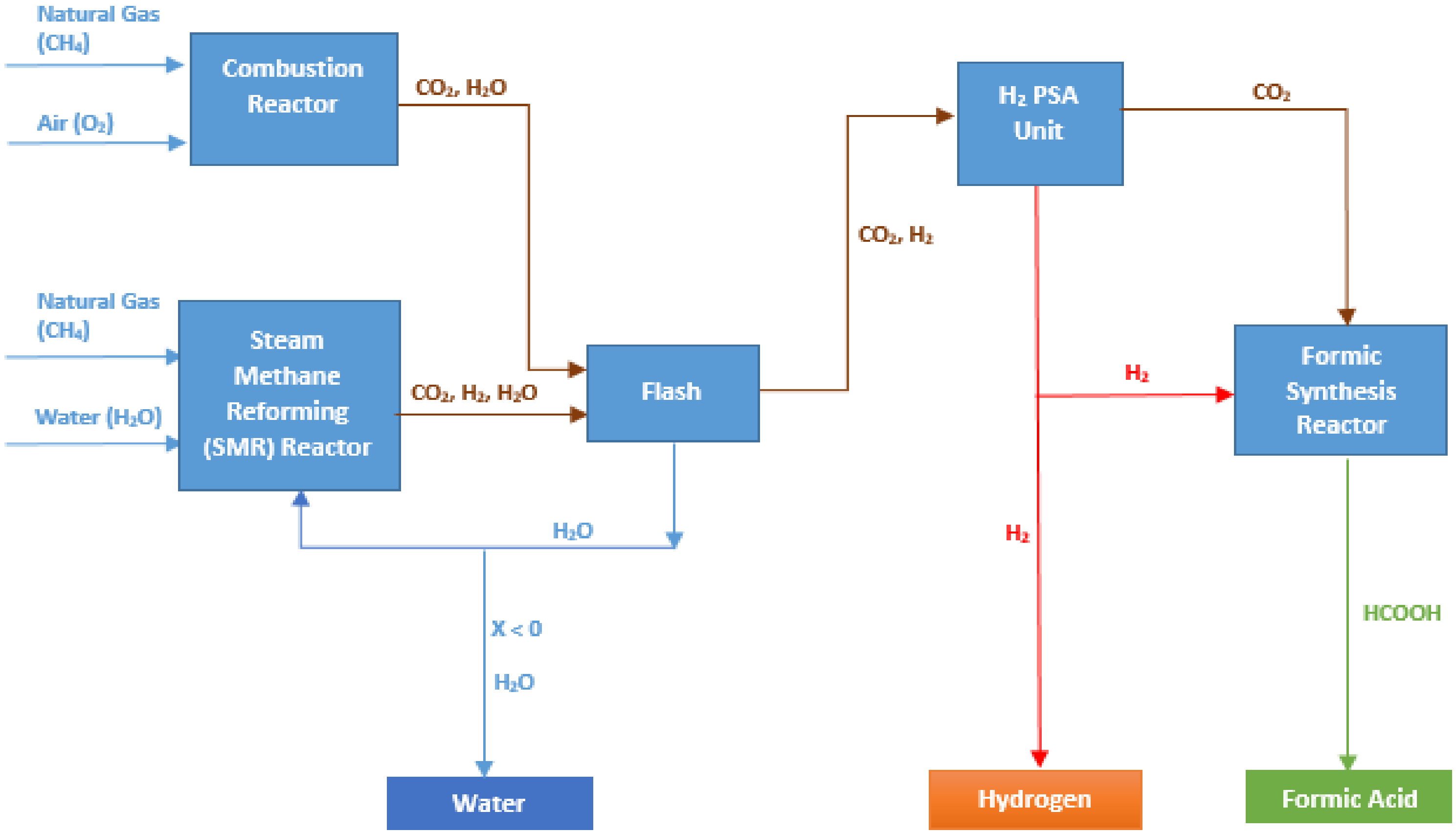
$$
\begin{array}{rcrcrcr}
\left(\frac{3-\Lambda}{4}\right)CH_4^{(g)} & + & \left(\frac{3-\Lambda}{2}\right)O_2^{(g)} & \rightarrow & \left(\frac{3-\Lambda}{4}\right)CO_2^{(g)} & + & \left(\frac{3-\Lambda}{2}\right)H_2O^{(g)} \\
\left(1-\frac{3-\Lambda}{4}\right)CH_4^{(g)} & + & \left(1-\frac{3-\Lambda}{4}\right)CO_2^{(g)} & \rightarrow & \left(2-\frac{3-\Lambda}{2}\right)CO^{(g)} & + & \left(2-\frac{3-\Lambda}{2}\right)H_2^{(g)} \\
\left(1-\frac{3-\Lambda}{2}\right)CO^{(g)} & + & \left(1-\frac{3-\Lambda}{2}\right)H_2O^{(g)} & \rightarrow & \left(1-\frac{3-\Lambda}{2}\right)CO_2^{(g)} & + & \left(1-\frac{3-\Lambda}{2}\right)H_2^{(g)} \\
CO^{(g)} & + & CH_3OH^{(l)} & \rightarrow & HCOOCH_3^{(l)} & & \\
HCOOCH_3^{(l)} & + & H_2O^{(l)} & \rightarrow & HCOOH^{(l)} & + & CH_3OH^{(l)} \\
\hline
\end{array}
$$

$$
CH_4^{(g)} + \left(\frac{3-\Lambda}{2}\right)O_2^{(g)} + (\Lambda-1)H_2O^{(g)} \rightarrow HCOOH^{(l)} + (\Lambda)H_2^{(g)}
$$

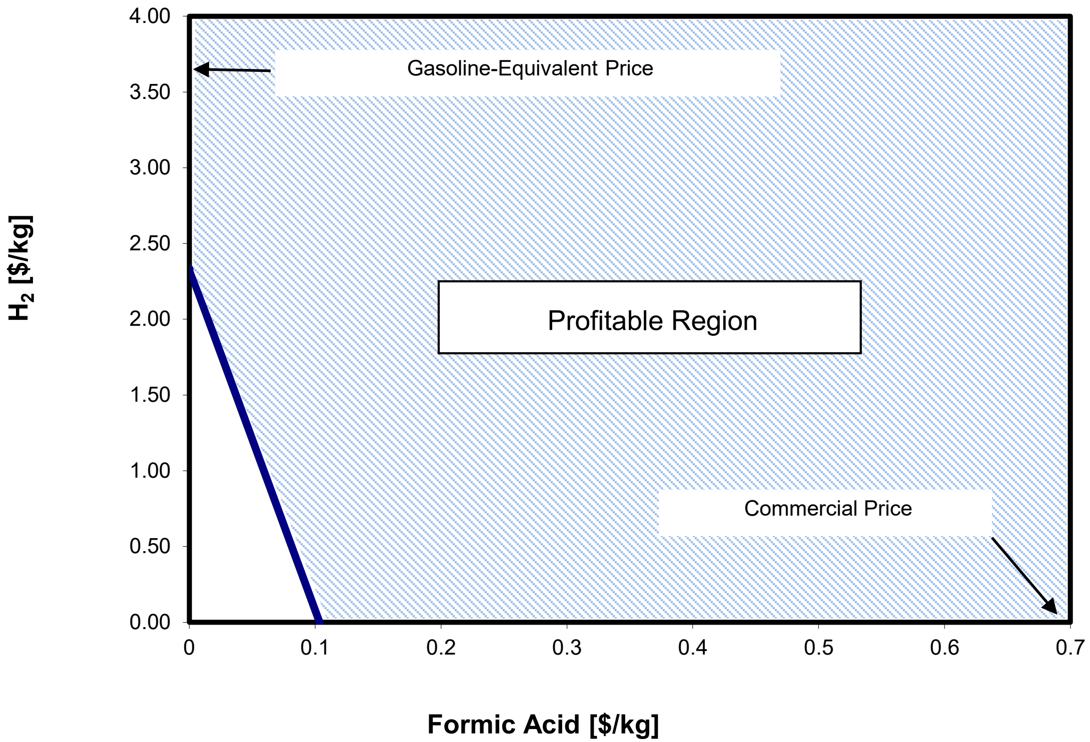
CO_2 Profitability: Formic Acid/Hydrogen

Formic Acid Overall Rxn:

$$CH_4^{(g)} + (1-0.5X)O_2^{(g)} + X\,H_2O^{(g)} \rightarrow HCOOH^{(aq)} + (1+X)H_2^{(g)}$$



Formic acid Profitability region



- Commercial price for formic acid (0.70 $/kg)
- Energy-price equivalent of hydrogen to gasoline (3.64 $/kg) (1 kg of hydrogen is energetically equivalent to 1 gallon of gasoline)

Lopez, Jorge A. Pena, and Vasilios I. Manousiouthakis. "Natural gas based hydrogen production with zero carbon dioxide emissions." international journal of hydrogen energy 36.20 (2011): 12853-12868.

Acetic acid Reaction cluster

$$\left(\frac{2X}{3}\right)\left[CH_4^{(g)} + 1.5O_2^{(g)} \rightarrow CO^{(g)} + 2H_2O^{(g)}\right]$$

$$\left(1-\frac{X}{3}\right)\left[CH_4^{(g)} + H_2O^{(g)} \rightleftharpoons CO^{(g)} + 3H_2^{(g)}\right]$$

$$\left(1-\frac{X}{3}\right)\left[CH_4^{(g)} + 2H_2O^{(g)} \rightleftharpoons CO_2^{(g)} + 4H_2^{(g)}\right]$$

$$\left(1-\frac{X}{3}\right)\left[CO_2^{(g)} + H_2^{(g)} \rightleftharpoons CO^{(g)} + H_2O^{(g)}\right]$$

$$CO^{(g)} + 2H_2^{(g)} \rightarrow CH_3OH^{(g)}$$

$$CO^{(g)} + CH_3OH^{(g)} \rightarrow CH_3COOH^{(l)}$$

$$2CH_4^{(g)} + X\,O_2^{(g)} + 2(1-X)H_2O^{(g)} \rightleftharpoons CH_3COOH^{(l)} + 2(2-X)H_2^{(g)}$$

Formic Acid/Acetic acid Reaction cluster

$$\left\{\begin{array}{l}
(1)\left[C^{(s)}+O_2{}^{(g)}\rightarrow CO_2{}^{(g)}\right]\\
(W+2X+Y-1)\left[CH_4{}^{(g)}+H_2O^{(g)}\rightarrow CO^{(g)}+3H_2{}^{(g)}\right]\\
(1)\left[CO_2{}^{(g)}+H_2{}^{(g)}\rightarrow CO^{(g)}+H_2O^{(g)}\right]\\
(X+Y)\left[CO^{(g)}+2H_2{}^{(g)}\rightarrow CH_3OH^{(l)}\right]\\
(W)\left[CO^{(g)}+CH_3OH^{(g)}\rightarrow HCOOCH_3{}^{(l)}\right]\\
(W)\left[HCOOCH_3{}^{(l)}+H_2O^{(l)}\rightarrow HCOOH^{(l)}+CH_3OH^{(l)}\right]\\
(X)\left[CO^{(g)}+CH_3OH^{(g)}\rightarrow CH_3COOH^{(l)}\right]\\
\dfrac{(3W+4X+Y-4)}{2}\left[2H_2{}^{(g)}+O_2{}^{(g)}\rightarrow 2H_2O^{(l)}\right]
\end{array}\right\}$$

$$\left\{\begin{array}{l}
C+(W+2X+Y-1)CH_4+\left(\dfrac{3W+4X+Y-2}{2}\right)O_2+(2-W-2X)H_2O(l)\rightarrow\\
W\ HCOOH(l)+X\ CH_3COOH(l)+\ Y\ CH_3OH(l)
\end{array}\right\}\ (R5)$$

Acetic acid cluster energy analysis

Baseline: $2\left[CH_4^{(g)} + 2O_2^{(g)} \rightarrow CO_2^{(g)} + 2\,H_2O^{(l)}\right] \quad \Delta h_f^o\left(298\right) = -890.649\,kJ/mol\,CH_4$

Total heat of reaction (Baseline Combustion): $\boxed{\Delta h_f^o\left(298\right) = -1,781.3\ kW}$

Acetic acid cluster

$$\left(\frac{2X}{3}\right)\left[CH_4^{(g)} + 1.5O_2^{(g)} \rightarrow CO^{(g)} + 2H_2O^{(l)}\right] \quad \Delta h_f^o\left(298\right) = -\,607.665\ kJ/mol\,CH_4$$

$$\left(1-\frac{X}{3}\right)\left[CH_4^{(g)} + H_2O^{(l)} \rightleftharpoons CO^{(g)} + 3H_2^{(g)}\right] \quad \Delta h_f^o\left(298\right) = +\,249.825\ kJ/mol\,CH_4$$

$$\left(1-\frac{X}{3}\right)\left[CH_4^{(g)} + 2H_2O^{(l)} \rightleftharpoons CO_2^{(g)} + 4H_2^{(g)}\right] \quad \Delta h_f^o\left(298\right) = +\,252.671\ kJ/mol\,CH_4$$

$$\left(1-\frac{X}{3}\right)\left[CO_2^{(g)} + H_2^{(g)} \rightleftharpoons CO^{(g)} + H_2O^{(g)}\right] \quad \Delta h_f^o\left(298\right) = +\,41.164\ kJ/mol\,CO_2$$

$$CO^{(g)} + 2H_2^{(g)} \rightarrow CH_3OH^{(g)} \quad \Delta h_f^o\left(298\right) = -\,128.135\ kJ/mol\,CO$$

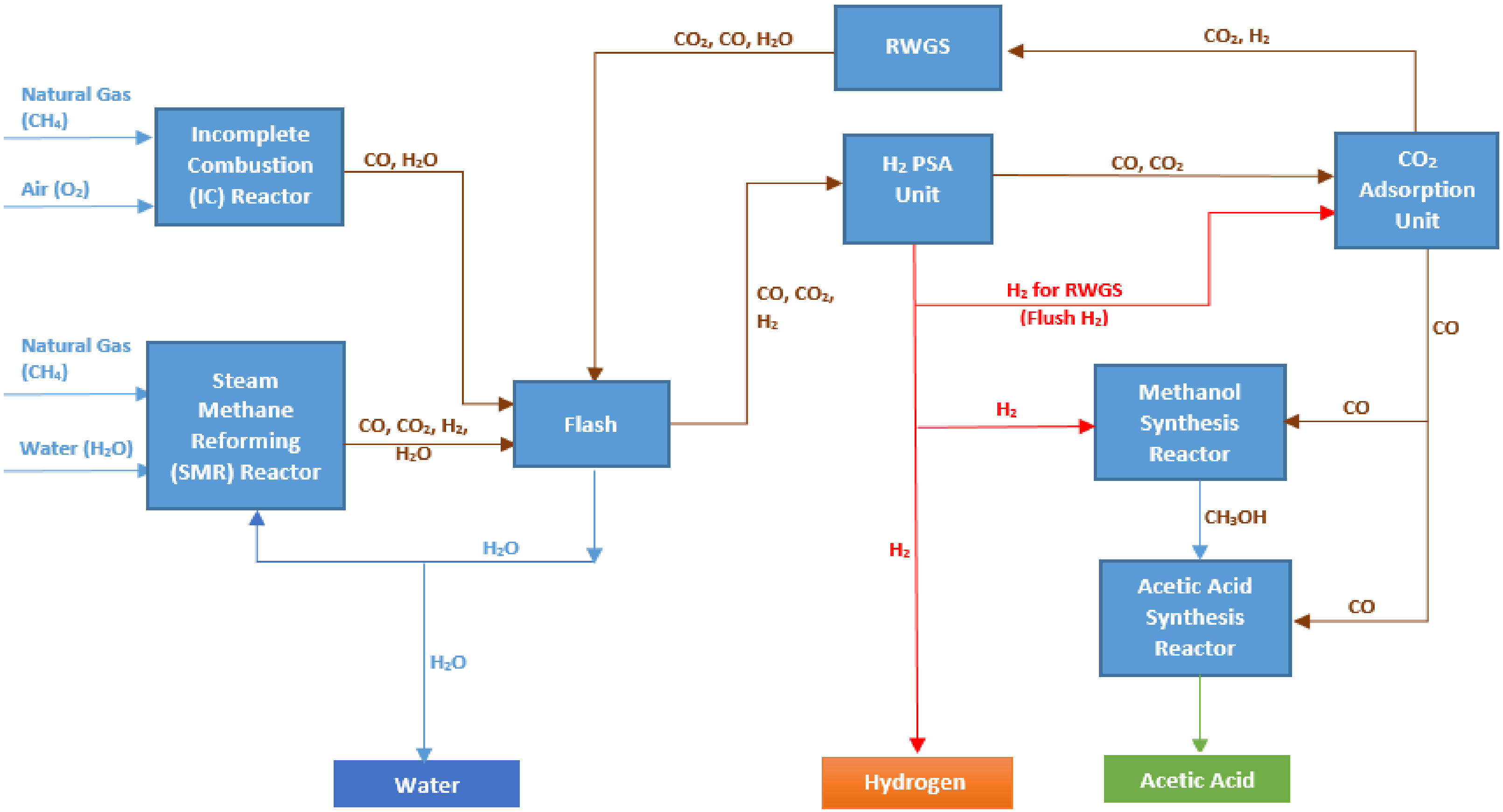
$$CO^{(g)} + CH_3OH^{(g)} \rightarrow CH_3COOH^{(l)} \quad \Delta h_f^o\left(298\right) = -\,135.315\ kJ/mol\,CO$$

Total heat of reaction (Acetic acid cluster): $\boxed{\Delta h_f^o\left(298\right) = 280.21 - 586.325X\ kW}$

CO_2 Profitability: Acetic Acid/Hydrogen

Acetic Acid Overall Rxn:

$$2CH_4^{(g)} + XO_2^{(g)} + 2(1-X)H_2O^{(g)} \rightarrow CH_3COOH^{(aq)} + 2(2-X)H_2^{(g)}$$

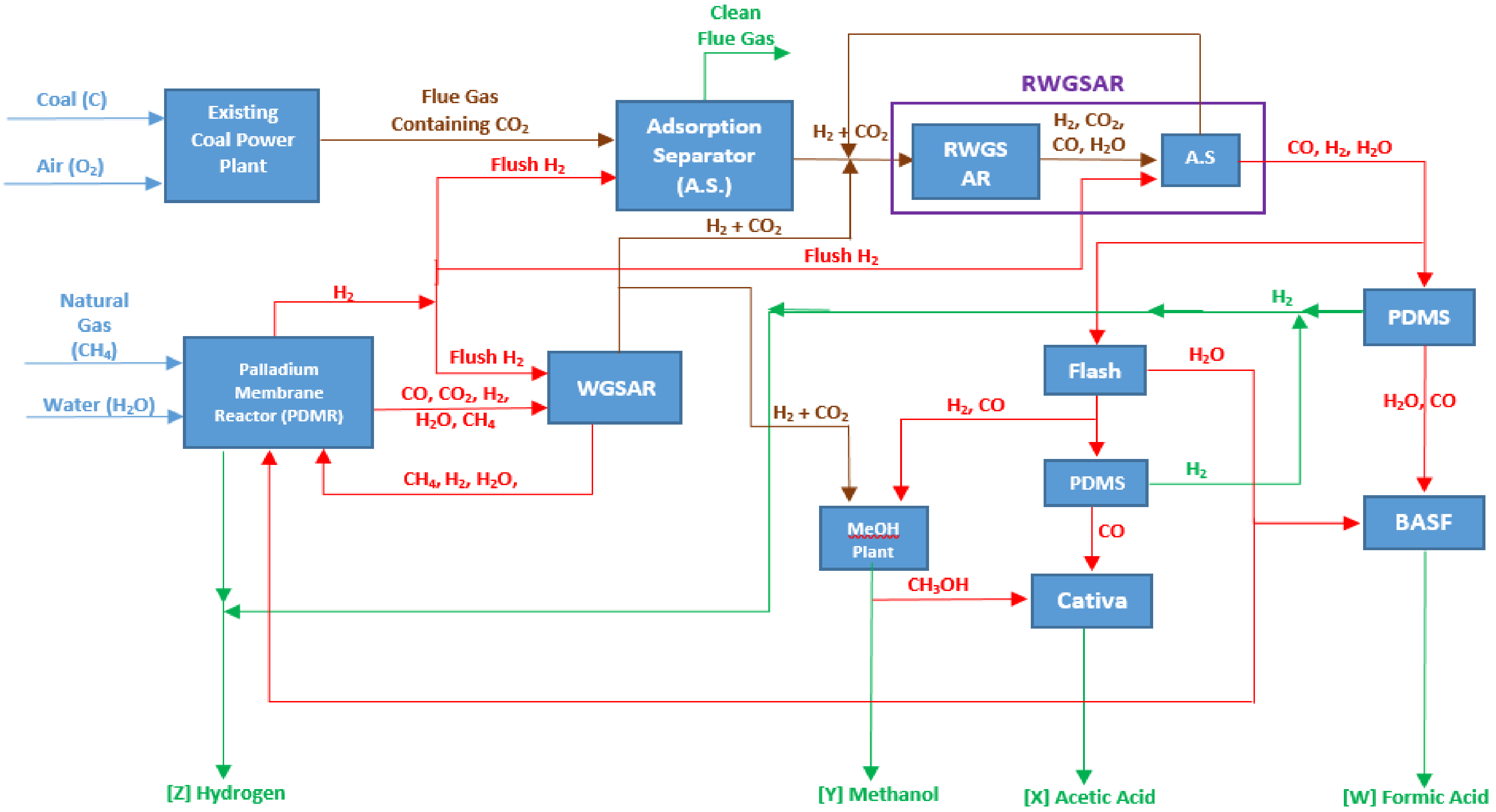


Natural Gas (CH_4)
Air (O_2)
Incomplete Combustion (IC) Reactor
CO, H_2O
Natural Gas (CH_4)
Water (H_2O)
Steam Methane Reforming (SMR) Reactor
CO, CO_2, H_2, H_2O
Flash
H_2O
H_2O
Water
CO_2, CO, H_2O
RWGS
CO_2, H_2
CO, CO_2, H_2
H_2 PSA Unit
CO, CO_2
CO_2 Adsorption Unit
H_2 for RWGS (Flush H_2)
CO
H_2
Methanol Synthesis Reactor
CO
CH_3OH
Acetic Acid Synthesis Reactor
CO
H_2
Hydrogen
Acetic Acid

CO_2 Profitability: Formic Acid/Acetic Acid

Formic/Acetic Acid Overall Rxn:

$$\left\{\begin{aligned}&C^{(s)}+\left(W+2X-1\right)CH_4^{(g)}+\left(1.5W+2X-1\right)O_2^{(g)}+(2-W-2X)H_2O^{(g)}\\&\rightarrow W\,HCOOH^{(aq)}+X\,CH_3COOH^{(aq)};\ \left(Y=Z=0\right)\end{aligned}\right\}$$



Operating Cost Analysis
(per 1 kg/h carbon-containing feed)

	Unit Cost	Unit	Ref.
COST ELEMENTS			
Natural Gas	0.298	(\$/kg)	[2]
Coal	0.03819	(\$/kg)	[2]
Water	0.00044	(\$/kg)	[3, 4]
O_2 Power Consumption	0.105	(\$/kWh)	[2]
REVENUE ELEMENTS			
Formic acid	0.70	(\$/kg)	[5]
Acetic acid	0.50	(\$/kg)	[6]
Hydrogen	3.64	(\$/kg)	[5]

	Selected Operating Point	Profit Margin
CO-PRODUCTION SCENARIOS		
Formic acid/Hydrogen	X = 0.654	**2.40 (\$/h)**
Acetic acid/Hydrogen	X = 1.238	**0.95 (\$/h)**
Formic acid/Acetic acid	W = 1; X = 1	**1.11 (\$/h)**

[2] Rath, L. K. (2010). Assessment of hydrogen production with CO2 capture volume 1: Baseline state-of-the-art plants. DoE/NETL, report, 1434.
[3] Black, J. (2010). Cost and performance baseline for fossil energy plants volume 1: Bituminous coal and natural gas to electricity. National Energy Technology Laboratory: Washington, DC, USA.
[4] Woods, M., Pinkerton, L. R., & Varghese, E. (2012). Updated Costs (June 2011 Basis) for Selected Bituminous Baseline Cases. Washington, DC: DOE/NETL, 49.
[5] Lopez, J. A. P., & Manousiouthakis, V. I. (2011). Natural gas based hydrogen production with zero carbon dioxide emissions. International Journal of Hydrogen Energy, 36(20), 12853-12868.
[6] Tecnon OrbiChem, Chemical Market Insight and forecast, Acetic Acid, 2013

Carbon Containing Chemicals

Chemicals	World Annual Production (million tonnes)
Benzene	42
Buta-1,3-diene	11.9
Ethylene oxide (epoxyethane)	17
Ethylene glycol	18
Ethanol (excluding bioethanol)	0.85
Ethene (ethylene)	156
Methanal (formaldehyde)	30
Methanol	65
Methyl tertiary-butyl ether	15.2
Phenol	10
Propanone (acetone)	6
Propene (propylene)	80

Source: http://www.essentialchemicalindustry.org/chemicals.html

Air Quality - H_2 Production: Thermochemical Cycles

- H_2, can be produced from a low-temperature (< 1000^0C) thermochemical cycle.

- Low-temperature thermochemical cycle can only be achieved via multi-step (> 2) reaction clusters[7].

- Low-temperature thermochemical cycles can be Concentrated Solar Power (CSP) driven.

- A **Sodium carbonate based** reaction cluster is a feasible, low-temperature, 3-step thermochemical cycle for H_2 production[8]. (900^0C**)**

[7] Xu, B., Bhawe, Y., Davis M.E. Low-temperature, manganese oxide-based thermochemical water-splitting cycle. PNAS 2012; 109 (24): 9260-64.

[8] Manousiouthakis VI; Manousiouthakis IV. USPTO No. 7,960,063 B2, 2004.

H_2 Production: Sodium Carbonate based thermochemical cycle

$$2Na_2CO_3^{(l)} \overset{K_{R1}(T)}{\rightleftarrows} 4Na^{(g)} + 2CO_2^{(g)} + O_2^{(g)}$$

$$4Na^{(l)} + 4H_2O^{(g)} \overset{K_{R2}(T)}{\rightleftarrows} 4NaOH^{(l)} + 2H_2^{(g)}$$

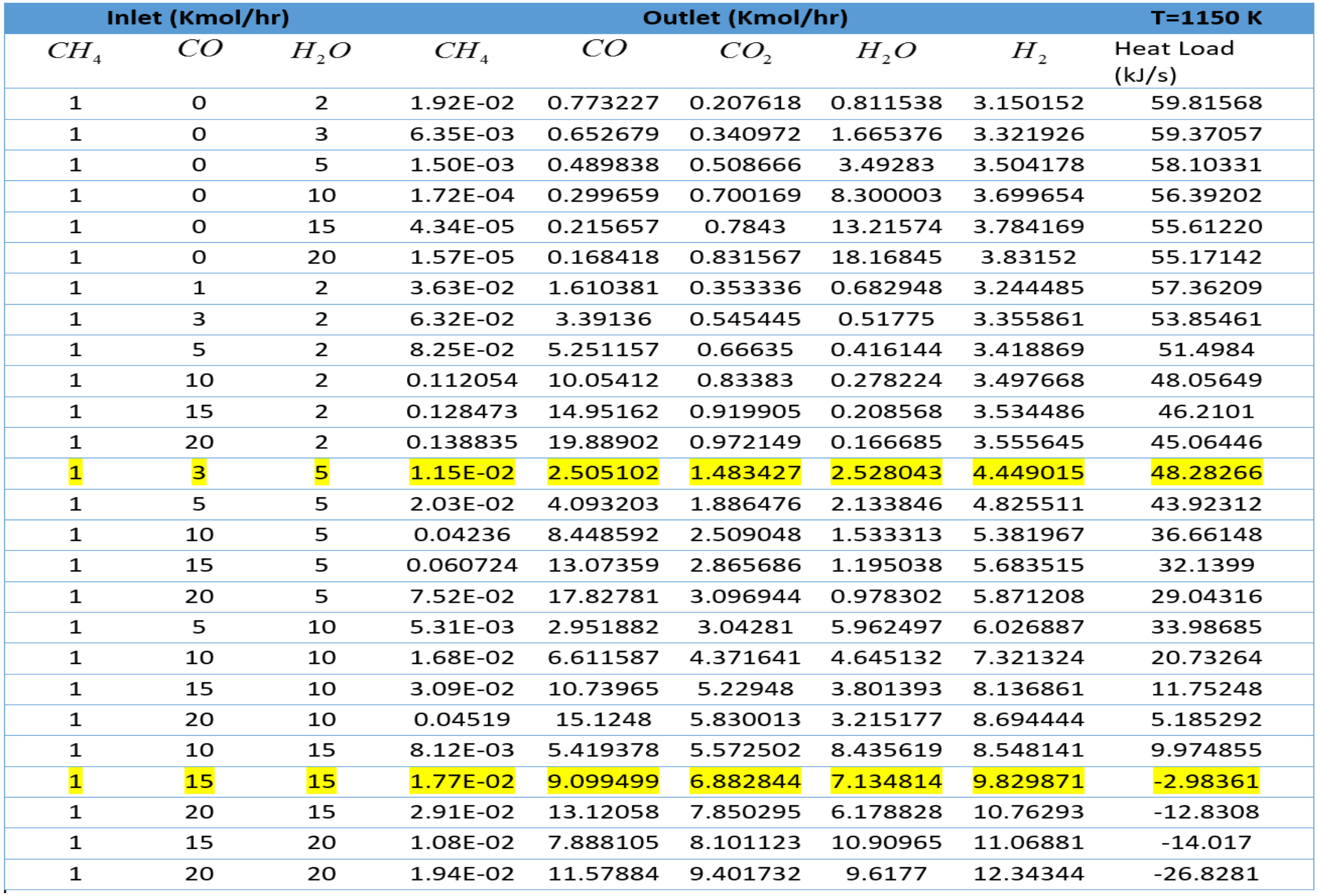
$$\underline{4NaOH^{(l)} + 2CO_2^{(g)} \overset{K_{R3}(T)}{\rightleftarrows} 2Na_2CO_3^{(l)} + 2H_2O^{(g)}}$$

$$2H_2O^{(g)} \rightarrow 2H_2^{(g)} + O_2^{(g)}$$

- ➢Maximum temperature of the Sodium carbonate based thermochemical cycle is 900^{0}C.
- ➢Feasible operating points are determined using either the Gibbs minimization method or Equilibrium constant method.
- ➢Operating point is such that the formation of sodium oxide is limited

Reducing CO_2 emissions – Exothermic reforming

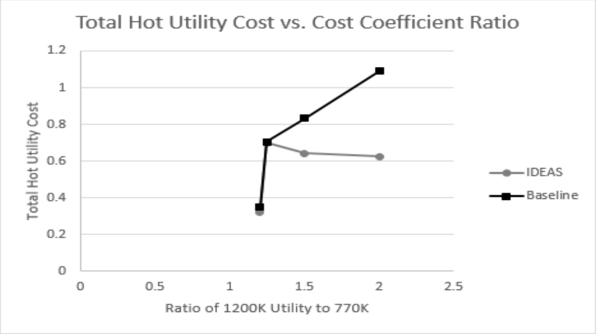
- Reduces CO_2 emissions by eliminating the need to burn methane to power reformer



Inlet (Kmol/hr)			Outlet (Kmol/hr)					T=1150 K
CH_4	CO	H_2O	CH_4	CO	CO_2	H_2O	H_2	Heat Load (kJ/s)
1	0	2	1.92E-02	0.773227	0.207618	0.811538	3.150152	59.81568
1	0	3	6.35E-03	0.652679	0.340972	1.665376	3.321926	59.37057
1	0	5	1.50E-03	0.489838	0.508666	3.49283	3.504178	58.10331
1	0	10	1.72E-04	0.299659	0.700169	8.300003	3.699654	56.39202
1	0	15	4.34E-05	0.215657	0.7843	13.21574	3.784169	55.61220
1	0	20	1.57E-05	0.168418	0.831567	18.16845	3.83152	55.17142
1	1	2	3.63E-02	1.610381	0.353336	0.682948	3.244485	57.36209
1	3	2	6.32E-02	3.39136	0.545445	0.51775	3.355861	53.85461
1	5	2	8.25E-02	5.251157	0.66635	0.416144	3.418869	51.4984
1	10	2	0.112054	10.05412	0.83383	0.278224	3.497668	48.05649
1	15	2	0.128473	14.95162	0.919905	0.208568	3.534486	46.2101
1	20	2	0.138835	19.88902	0.972149	0.166685	3.555645	45.06446
1	3	5	1.15E-02	2.505102	1.483427	2.528043	4.449015	48.28266
1	5	5	2.03E-02	4.093203	1.886476	2.133846	4.825511	43.92312
1	10	5	0.04236	8.448592	2.509048	1.533313	5.381967	36.66148
1	15	5	0.060724	13.07359	2.865686	1.195038	5.683515	32.1399
1	20	5	7.52E-02	17.82781	3.096944	0.978302	5.871208	29.04316
1	5	10	5.31E-03	2.951882	3.04281	5.962497	6.026887	33.98685
1	10	10	1.68E-02	6.611587	4.371641	4.645132	7.321324	20.73264
1	15	10	3.09E-02	10.73965	5.22948	3.801393	8.136861	11.75248
1	20	10	0.04519	15.1248	5.830013	3.215177	8.694444	5.185292
1	10	15	8.12E-03	5.419378	5.572502	8.435619	8.548141	9.974855
1	15	15	1.77E-02	9.099499	6.882844	7.134814	9.829871	-2.98361
1	20	15	2.91E-02	13.12058	7.850295	6.178828	10.76293	-12.8308
1	15	20	1.08E-02	7.888105	8.101123	10.90965	11.06881	-14.017
1	20	20	1.94E-02	11.57884	9.401732	9.6177	12.34344	-26.8281

[1] Manousiouthakis, V. I., Albassam, A. M., & Conner, J. A. (2016). U.S. Patent Application No. 15/202,411.

IDEAS Based Process Intensification CH4 and CSP Based Hydrogen Production

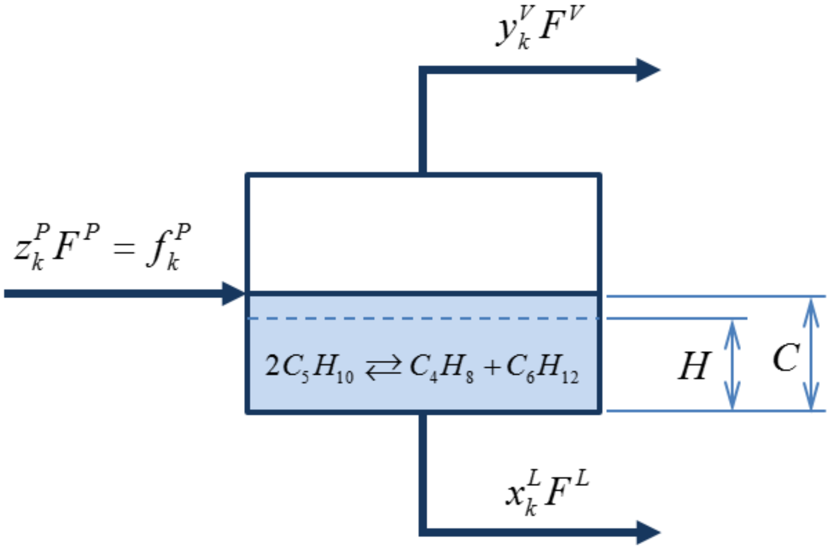


Metric	Baseline	IDEAS 24:2:1	IDEAS 4:2:1	IDEAS 3:2:1	IDEAS 2.5:2:1	IDEAS 1.2:1:1
Total Hot Utility Cost (24:2:1) ($/s)	6.22	0.62				
Total Hot Utility Cost (4:2:1) ($/s)	1.10		0.62			
Total Hot Utility Cost (3:2:1) ($/s)	0.83			0.64		
Total Hot Utility Cost (2.5:2:1) ($/s)	0.71				0.69	
Total Hot Utility Cost (1.2:1:1) ($/s)	0.35					0.32
HU at 1200K, (kJ/s)	60.3	0	0	3.37	26.26	48.72
HU at 770K, (kJ/s)	6.06	68.97	68.97	66.6	46.73	14.56
HU at 420K, (kJ/s)	3.29	8.9	8.9	7.64	5.14	3.00

Pichardo, Patricia, and Vasilios I. Manousiouthakis. "Infinite DimEnsionAl State-space as a systematic process intensification tool: Energetic intensification of hydrogen production." Chemical Engineering Research and Design 120 (2017): 372-395.

IDEAS Based Process Intensification
Olefin Metathesis

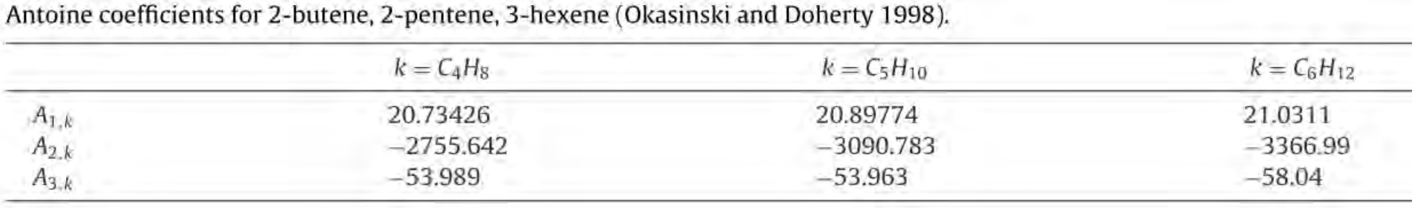
IDEAS framework applied in the design of an intensified RD network for the metathesis of 2-pentene to form 2-butene and 3-hexene



$$R = k_f\left(a_{C_5H_{10}}^2 - \frac{a_{C_4H_8}\,a_{C_6H_{12}}}{K_{eq}}\right)$$

$$K_{eq} = 0.25$$

$$k_f = 1.0661\times 10^5\ e^{(-3321.2/T(K))}\ \left(h^{-1}\right)$$

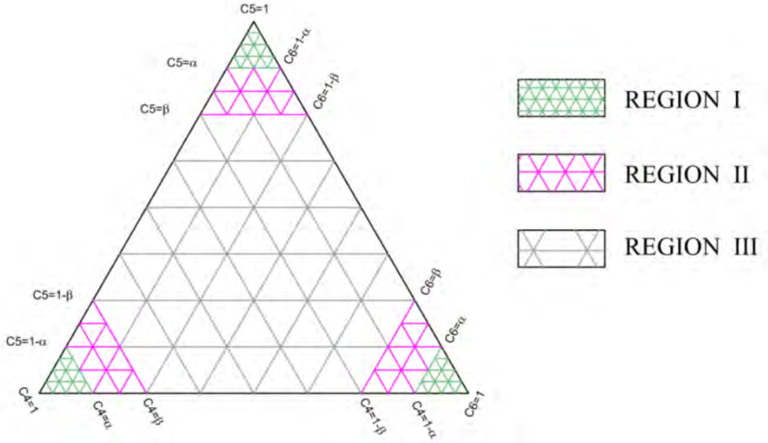


Antoine coefficients for 2-butene, 2-pentene, 3-hexene (Okasinski and Doherty 1998).

	$k = C_4H_8$	$k = C_5H_{10}$	$k = C_6H_{12}$
$A_{1,k}$	20.73426	20.89774	21.0311
$A_{2,k}$	−2755.642	−3090.783	−3366.99
$A_{3,k}$	−53.989	−53.963	−58.04

IDEAS Based Process Intensification
Olefin Metathesis

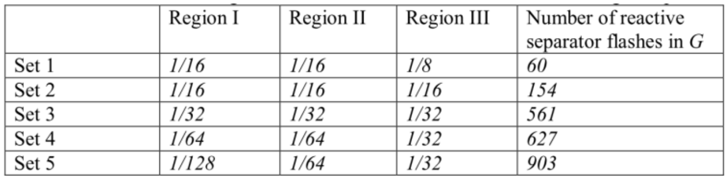
Feed Flow (kmol/h)	100
Outlet Flow 1 (Distillate) (kmol/h)	50
Outlet Flow 2 (Bottom) (kmol/h)	50
Residence Time (s)	60
Operating pressure (bar)	1
Inlet molar fractions	
C4H8	0.0000
C5H10	1.0000
C6H12	0.0000
Outlet molar fraction target bounds	
Outlet Flow 1	
C4H8	0.9800 - 1.0000
C5H10	0.0000 - 0.2000
C6H12	0.0000 - 0.2000
Outlet Flow 2	
C4H8	0.0000 - 0.2000
C5H10	0.0000 - 0.2000
C6H12	0.9800 - 1.0000



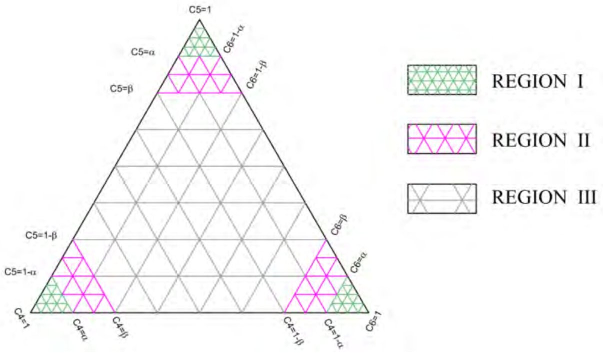
Optimal total reactive holdup (87.5% purity) per discretized set in regions I, II and III

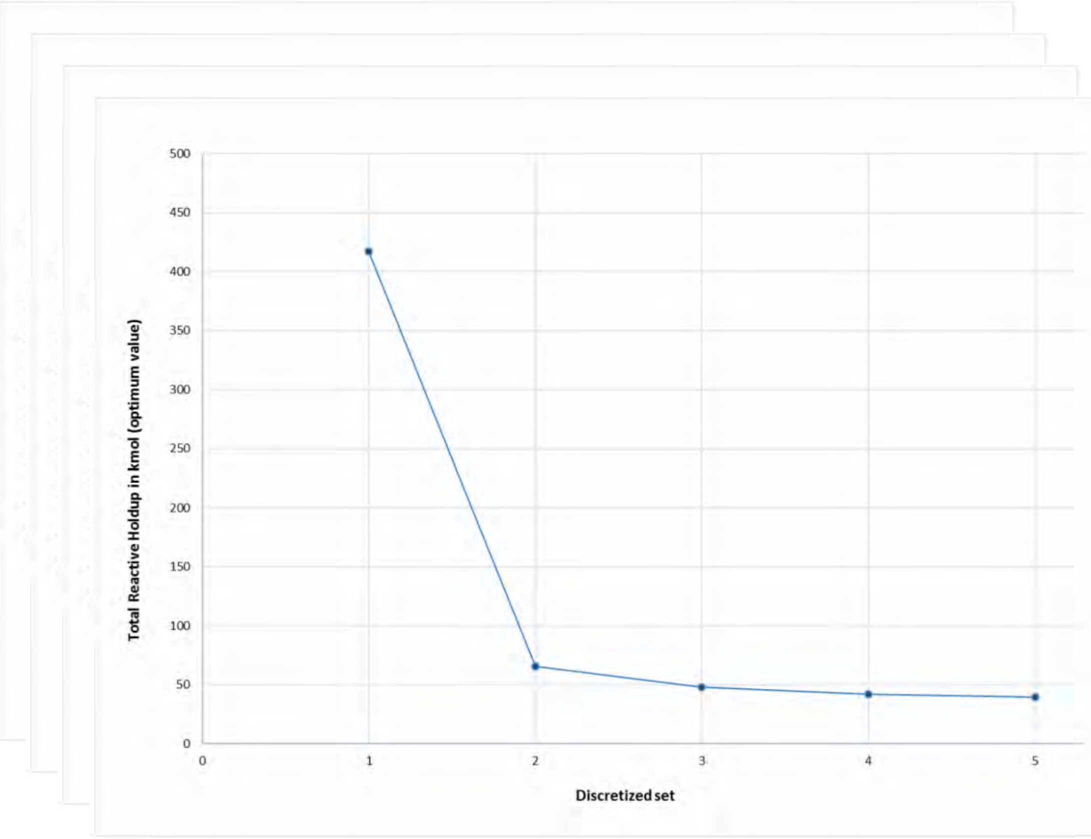
Discretized step size			Optimum total reactive holdup
Region I	Region II	Region III	
1/8	1/8	1/8	Infeasible
1/16	1/8	1/8	Infeasible
1/32	1/8	1/8	Infeasible
1/64	1/8	1/8	596.74
1/128	1/8	1/8	378.66
1/16	1/16	1/8	416.99
1/32	1/16	1/8	394.15
1/64	1/16	1/8	381.46
1/128	1/16	1/8	376.79
1/16	1/16	1/16	65.44
1/32	1/16	1/16	61.6
1/64	1/16	1/16	42.24
1/128	1/16	1/16	39.64
1/32	1/32	1/16	48.31
1/64	1/32	1/16	42.24
1/128	1/32	1/16	39.64
1/32	1/32	1/32	48.31
1/64	1/32	1/32	42.24
1/128	1/32	1/32	39.64
1/64	1/64	1/16	42.24
1/128	1/64	1/16	39.64
1/64	1/64	1/32	42.24
1/128	1/64	1/32	39.64

IDEAS Based Process Intensification
Olefin Metathesis, IDEAS Convergence

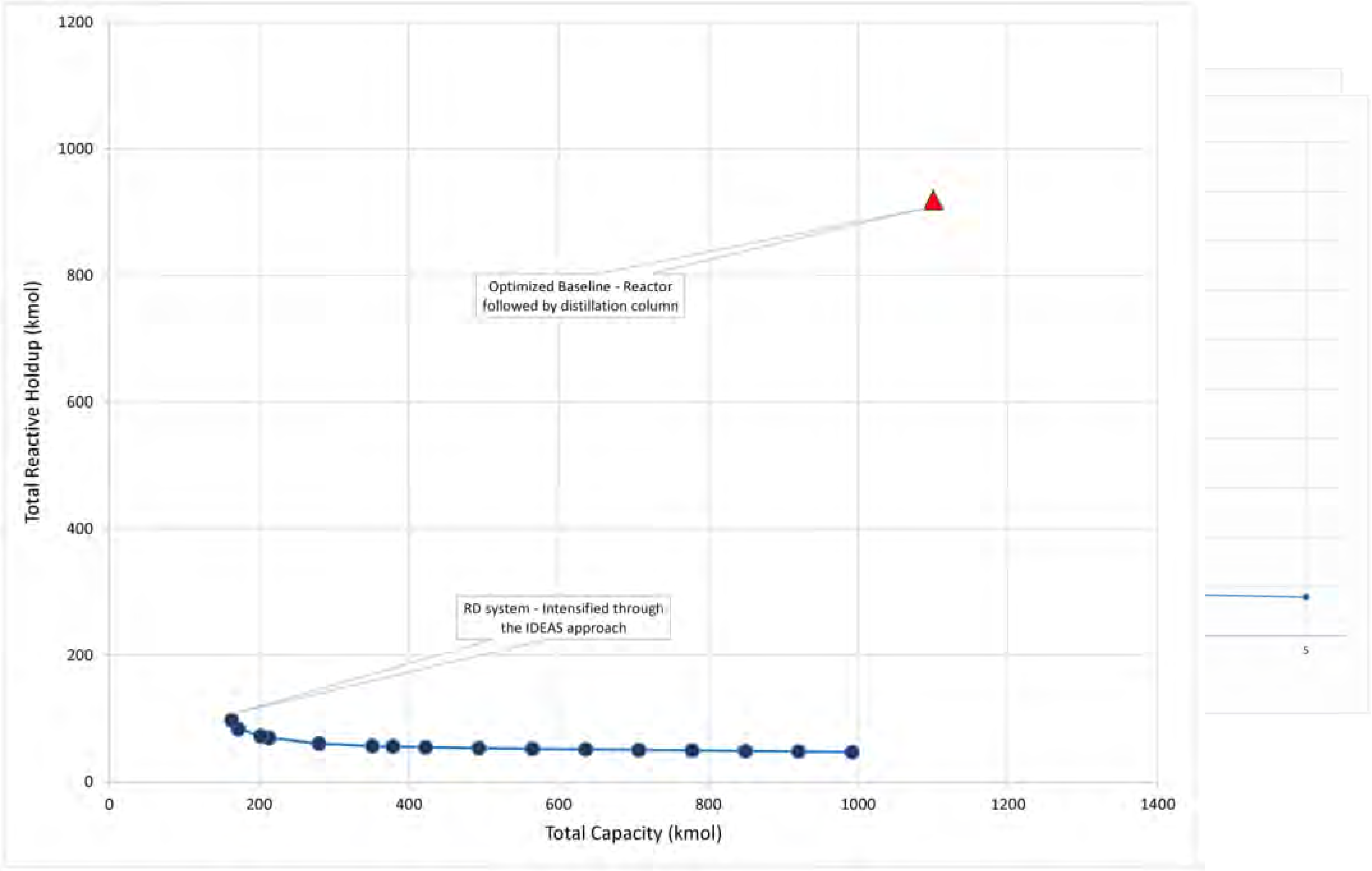


	Region I	Region II	Region III	Number of reactive separator flashes in *G*
Set 1	*1/16*	*1/16*	*1/8*	*60*
Set 2	*1/16*	*1/16*	*1/16*	*154*
Set 3	*1/32*	*1/32*	*1/32*	*561*
Set 4	*1/64*	*1/64*	*1/32*	*627*
Set 5	*1/128*	*1/64*	*1/32*	*903*

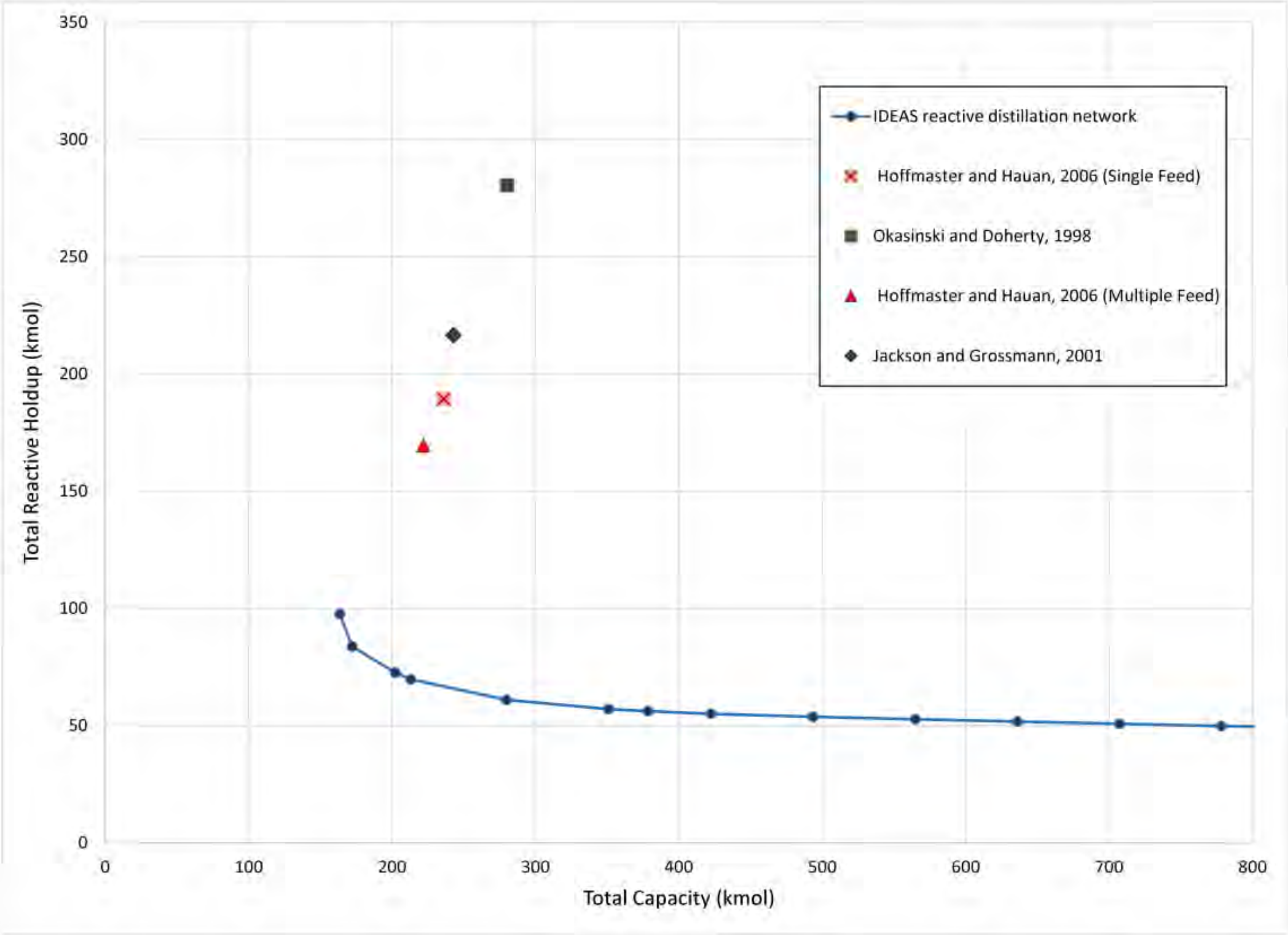




IDEAS Based Process Intensification Olefin Metathesis, Results



IDEAS Based Process Intensification Olefin Metathesis, Results



IDEAS Based Process Intensification
Olefin Metathesis, Conclusions

- Through IDEAS, we found reactive distillation networks that can reduce the total reactive holdup and total capacity by 94.5% and 84.3% respectively (compared to baseline).

- Comparing the IDEAS networks with the best equivalent RD study through non-linear optimization, reduction in reactive holdup and capacity are 42.1% and 22.7%.

- The rigorous quantification of the performance limit for a given technology, such as in this RD case, can greatly benefit Process Intensification (PI) initiatives.

Sustainability Over Sets (S.O.S.)

- **Critical questions to be answered?**
  - Is a system sustainable?
  - Can human input be incorporated into the sustainability assessment process?
  - Can an unsustainable system be modified to become sustainable?

- **Sustainability Over Sets (S.O.S.) Definition**

  A system is sustainable over a set (S.O.S.) in the system's state-space, if the system's state trajectories initiated within the set remain within the set for all time

- **S.O.S. provides answers to above questions**

  S.O.S. defines sustainability in terms of invariant sets in the system's state-space

S.O.S. analysis of biological CSTR

- **System model**

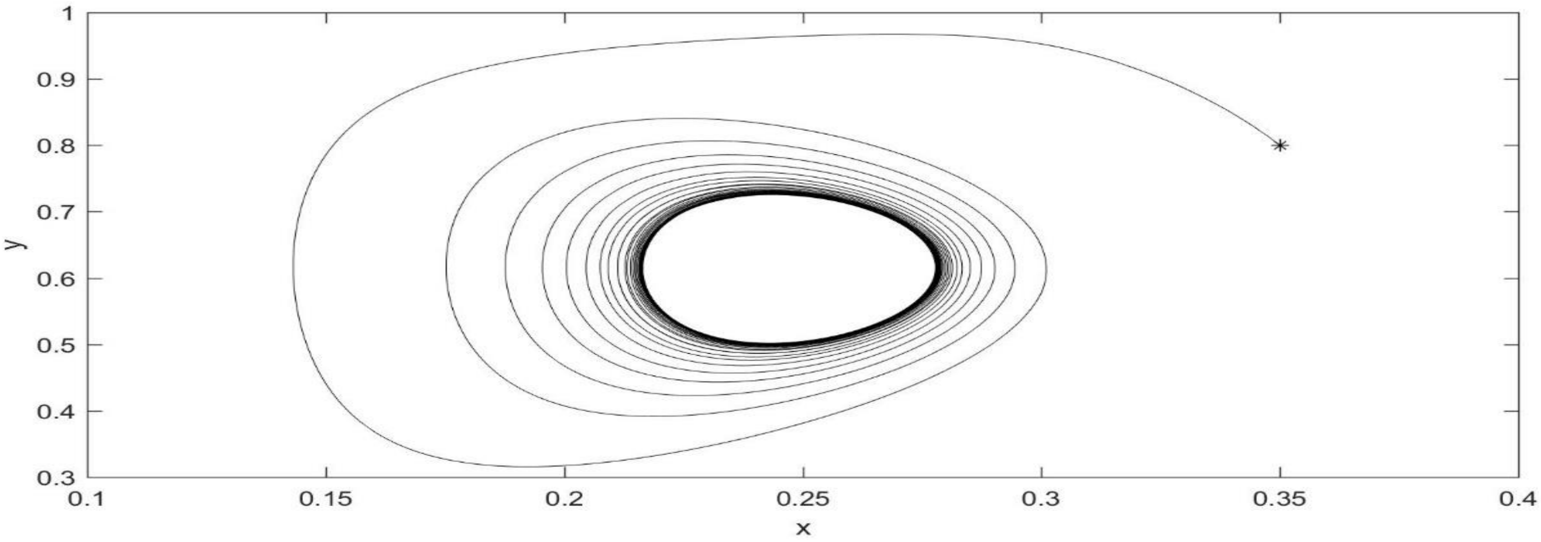
$$\begin{bmatrix} \dot{x}(t) \\ \dot{y}(t) \end{bmatrix} = \begin{bmatrix} -x(t) + Da(1+\alpha)(1-y(t))(1+\alpha-y(t))^{-1}x(t) \\ -y(t) + Da(1+\alpha)(1+\beta)(1-y(t))(1+\alpha-y(t))^{-1}(1+\beta-y(t))^{-1}x(t) \end{bmatrix}$$

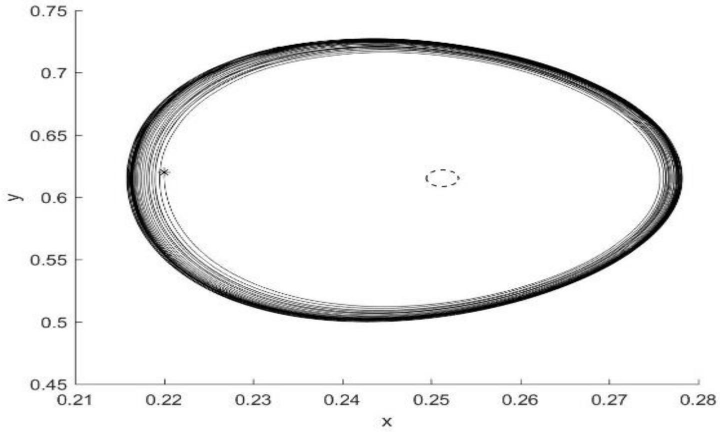
$y = 1 - SS_f{}^{-1} \in [0,1]$ represents dimensionless pollutant concentration

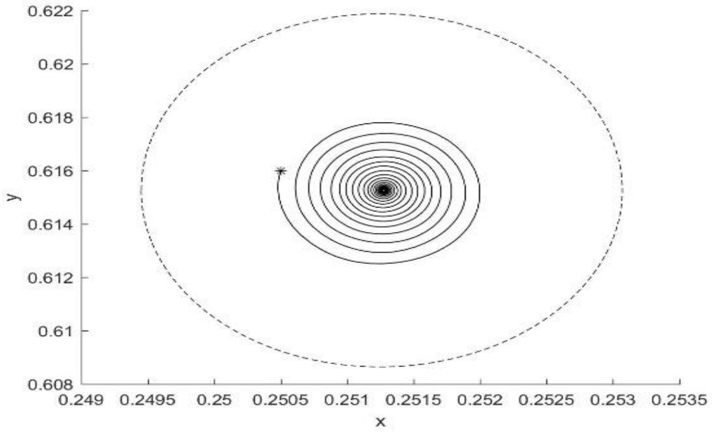
$x \in [0,\infty)$ represents the normalized microorganism concentration

Agrawal, P., Lee, C., Lim, H. C., & Ramkrishna, D. (1982). Theoretical investigations of dynamic behavior of isothermal continuous stirred tank biological reactors. Chemical Engineering Science, 37(3), 453-462.

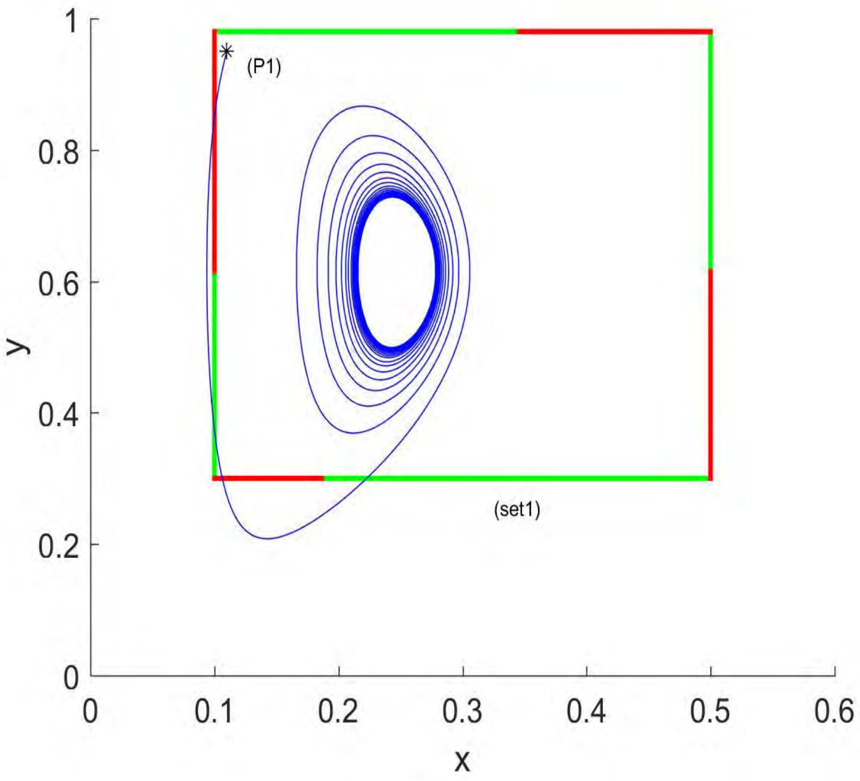
S.O.S. analysis of biological CSTR (cont’d)

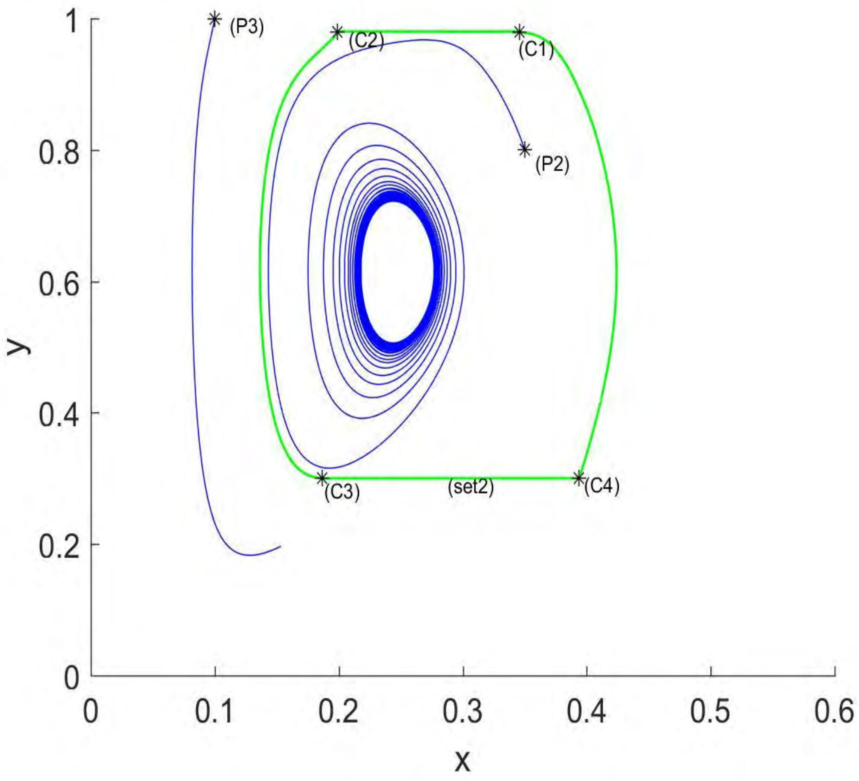






S.O.S. analysis of biological CSTR (cont'd)





S.O.S. Fortification

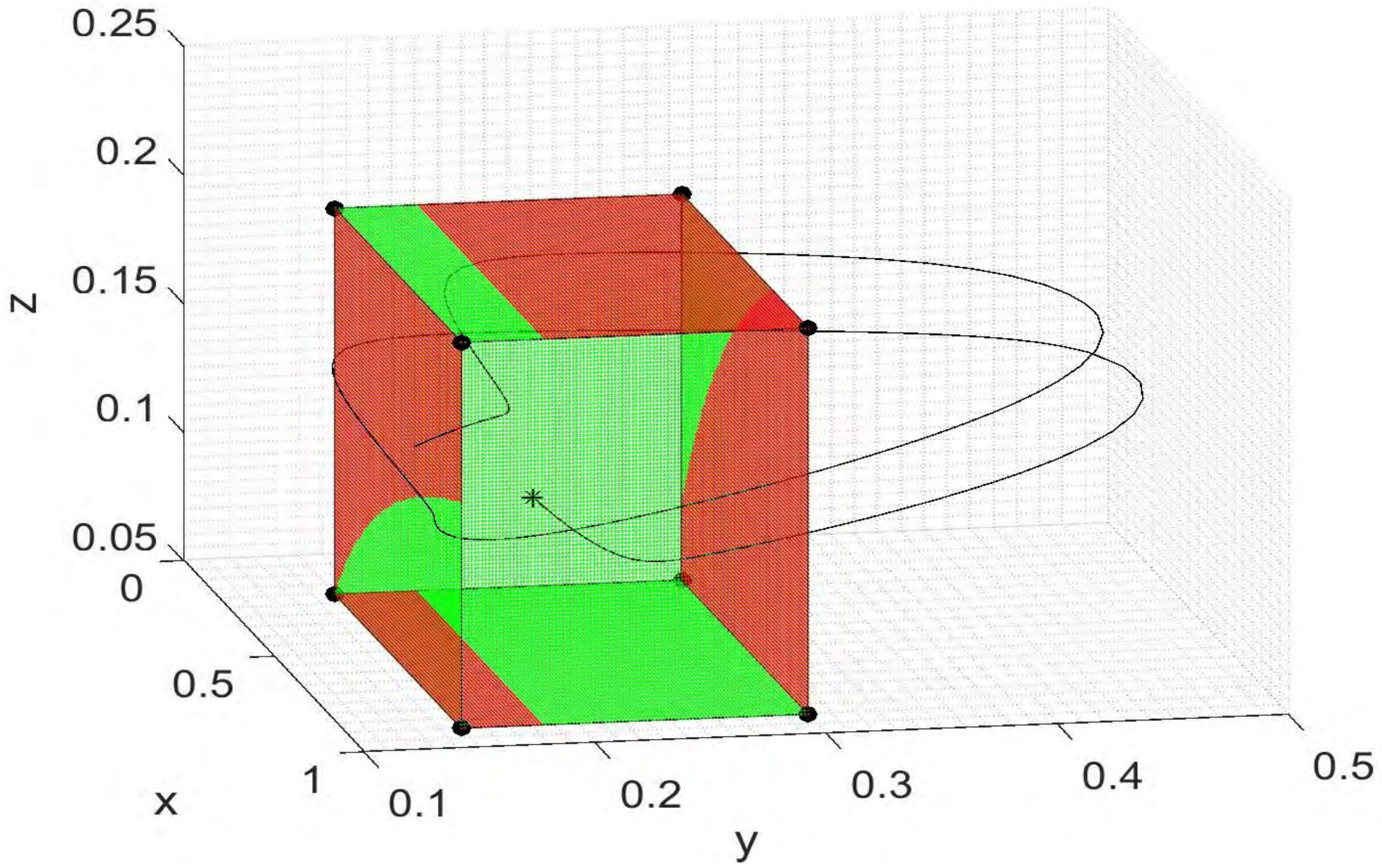
- **System model**

$$\begin{bmatrix} \dot{x} \\ \dot{y} \\ \dot{z} \end{bmatrix} = \begin{bmatrix} f_1 : (x,y,z) \to f_1(x,y,z) \triangleq \dfrac{x}{\zeta}\left(1 - x - \dfrac{y}{\beta_1 + x}\right) \\ f_2 : (x,y,z) \to f_2(x,y,z) \triangleq y\left(\dfrac{x}{\beta_1 + x} - \delta_1 - \dfrac{z}{\beta_2 + y}\right) \\ f_3 : (x,y,z) \to f_3(x,y,z) \triangleq \varepsilon z\left(\dfrac{y}{\beta_2 + y} - \delta_2\right) \end{bmatrix}$$

x, y, and z represent prey, predator and top predator populations respectively

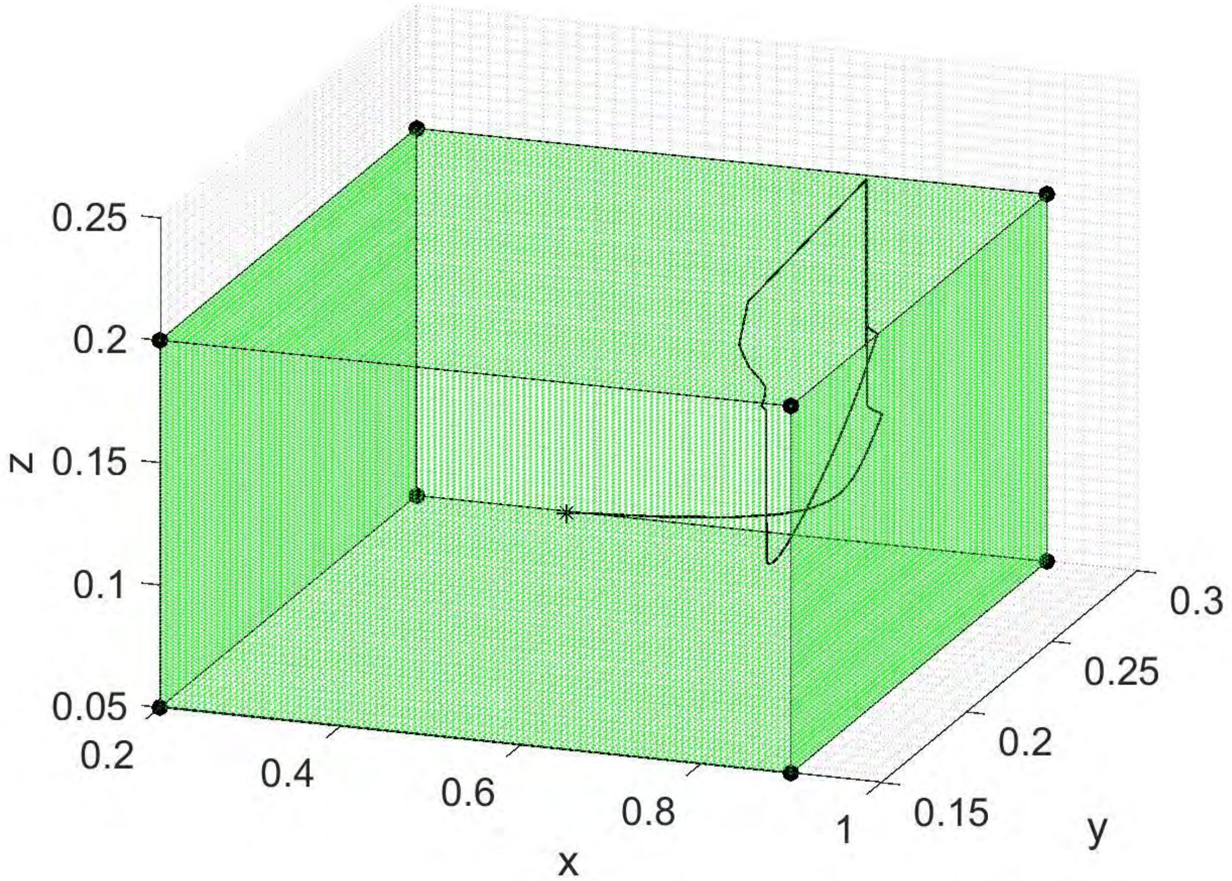
Duarte, J., Januário, C., & Martins, N. (2008). Chaos in ecology: the topological entropy of a tritrophic food chain model. *Discrete Dynamics in Nature and Society*, *2008*.

S.O.S. Fortification (Cont’d)

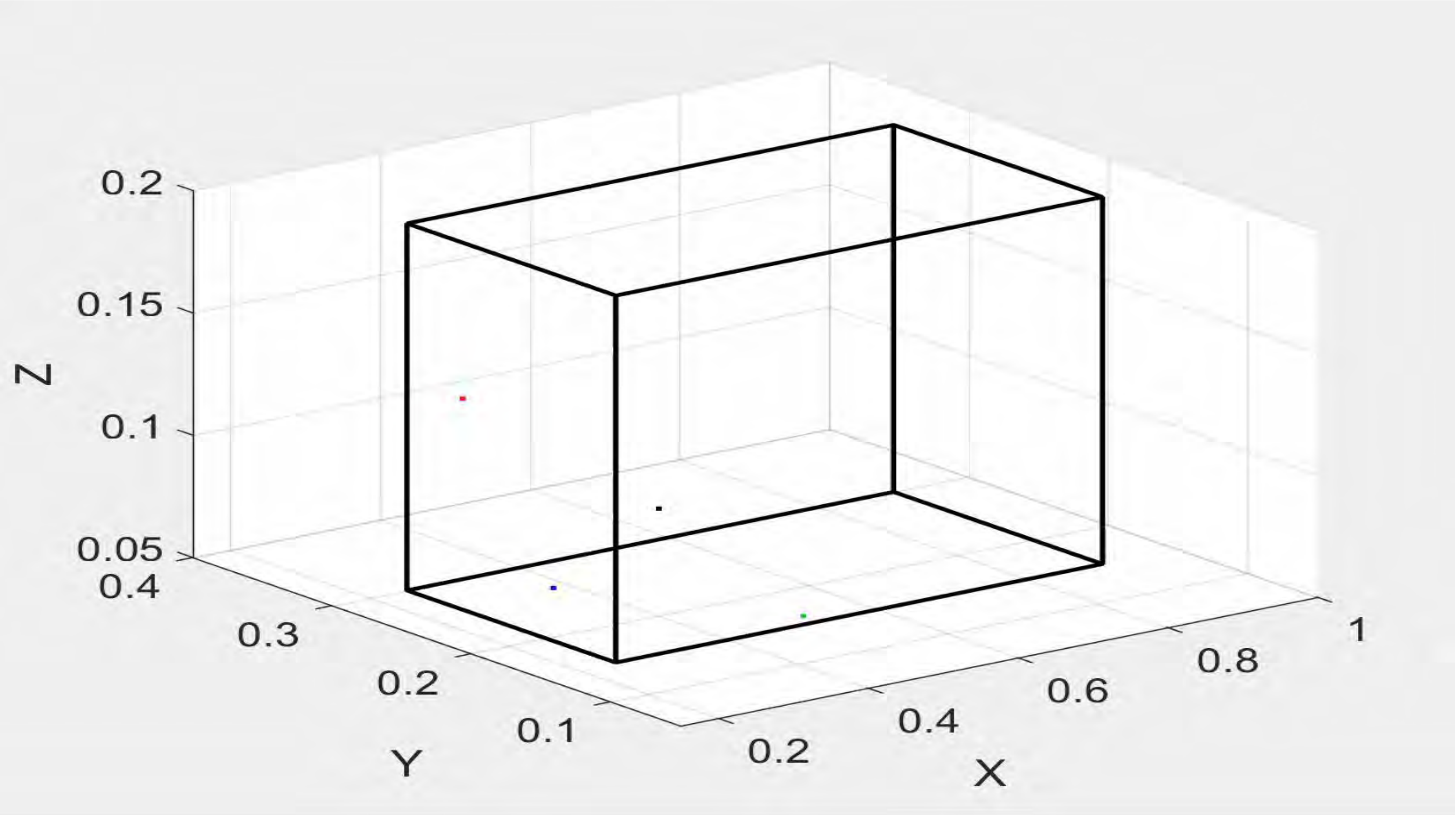


$$S \triangleq \left\{ \begin{bmatrix} x & y & z \end{bmatrix}^{\mathrm{T}} \in \mathbb{R}^3 : \ 0.2 \le x \le 0.9 \,, \ 0.15 \le y \le 0.3 \ , \ 0.05 \le z \le 0.2 \right\}$$

S.O.S. Fortification (Cont'd)



$$S \triangleq \left\{ \begin{bmatrix} x & y & z \end{bmatrix}^T \in \mathbb{R}^3 : \; 0.2 \le x \le 0.9 \, , \; 0.15 \le y \le 0.3 \; , \; 0.05 \le z \le 0.2 \right\}$$


Z
0.2
0.15
0.1
0.05
Y
0.4
0.3
0.2
0.1
X
0.2
0.4
0.6
0.8
1

Some Suggestions

- Do not have visions for the future, shape the future
- Become the mother Euryfaessa, that will give birth to the ideas needed to:

1. Move Humanity past Prometheus' Burning Paradigm, and the Climate Change Tautology
2. Create a new industry structure that utilizes hybrid energy resources, both renewable (e.g. solar, tide, wind), and fossil, by applying "Green Engineering" principles

- Embrace/Advance Chemical Engineering, , do not abandon it
- Do not get over-fascinated with Computer Science
- Embrace a spirit of Innovation that does not encourage thinking out of the box, but rather does not even contemplate a box

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Thank You George!
Ευχαριστώ Γιώργο!

Happy Birthday!
Ευτυχισμένα Γενέθλια!

Σιδερένιος!