

DECISION MAKING IN ENERGY:
ADVANCING TECHNICAL, ENVIRONMENTAL, AND
ECONOMIC PERSPECTIVES

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Abstract

Today, with the supply of conventional energy resources being depleted at their fastest rates and the environmental impacts of their use better understood, there is an increasing desire to develop and employ alternative energy technologies that lessen dependence on these resources and reduce environmental impact. The ability to evaluate and compare potential technologies on a level playing field based on technical, environmental, and economic performance is essential to meeting these objectives while avoiding undesirable consequences. This dissertation presents a critical assessment of the existing methods for evaluating the technical and economic performance of energy systems, and introduces a new framework for evaluating environmental performance.

The dissertation first considers the technical component of decision making. It is shown that, while all of the existing thermodynamic analysis techniques are well-established, significant subtlety is required in applying the techniques, understanding their capabilities, and interpreting their results for decision making. A detailed analysis of the production of Fischer-Tropsch liquids is used to illustrate many low-level issues associated with performing technical analysis of energy systems. These issues include the reliance on published data, empirical data, phase relationships, properties, analytical tools, and proprietary information. The analysis highlights that many of these issues are often not properly addressed in published studies and how oversights in these areas can adversely influence the decisions they inform. Following this low-level analysis, a service/carrier/resource view of the space in which energy systems operate is presented to discuss some of the considerations that are commonly not recognized when decision making across energy options. Across all levels of technical

decision making, the utility of exergy is demonstrated as an analysis tool for evaluating energy options and providing performance information for decision making.

Next, the dissertation considers the environmental component of decision making. In this consideration a new framework for evaluating environmental performance is presented. The framework utilizes the recent recognition that exergy is, in fact, a form of environmental free energy to provide a fundamental basis for valuing environmental interactions independent from their secondary impacts (e.g., global warming, photochemical smog, thermal pollution, etc.). In order to make this extension, modifications were required to the traditional representation of the environment and definition of the dead state used in technical exergy analysis. These modifications are accomplished through a combination of logical extensions and use of non-equilibrium thermodynamic principles.

The framework is comprised of two separate analysis components: (1) environmental exergy analysis and (2) anthropocentric sensitivity analysis. Environmental exergy analysis extends the principles of technical analysis to the environment in order to quantify the locations, magnitudes, and types of environmental impact—state change, alteration of natural transfers, and destruction change. Anthropocentric sensitivity analysis enables the results of environmental exergy analysis to be further interpreted for decision making, but at the expense of introducing some subjectivity into the analysis framework. One of the key attributes of the analysis framework is its ability to evaluate and compare the environmental performance of energy systems on a level playing field, regardless of the specifics of the systems (such as resources, products, by-products, sizes, or time scales).

The dissertation concludes with a discussion of the economic component of energy decision making. Recognizing the vast space of economics and energy, the discussion focuses on one of the many relevant dimensions of economic analysis—namely the influence costs and cash flow models have on the evaluation of energy systems. It is shown that the ability to accurately estimate the cost—both initial and future—of non-extant energy systems significantly influences economic performance metrics commonly used in decision making.

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Contents

Abstract	v
Acknowledgements	vii
1 Introduction	1
1.1 Motivation	1
1.2 Organization of the Dissertation	2
2 Decision Making in Energy	5
2.1 Review of Existing Analysis Techniques	6
2.1.1 Technical Performance Analysis Techniques	6
2.1.2 Economic Performance Analysis Techniques	8
2.1.3 Environmental Performance Analysis Techniques	11
2.2 Multi-Criteria Analysis for Decision Making in Energy	15
3 Evaluating Technical Performance	17
3.1 Exergy and Exergy Analysis	18
3.2 Information and Analytical Tools	20
3.3 Exergy Analysis of Natural Gas Fischer-Tropsch Plant with Co-Power Production	22
3.3.1 FT Synthesis	22
3.3.2 Developing a GTL Model	25
3.3.3 Modeled GTL Systems	32
3.3.4 Selected Results	36

3.3.5	Discussion	41
3.4	Technical Decision Making Across Energy Systems	42
3.5	Conclusion	46
4	A Thermodynamics-Based Analysis Framework for Evaluating Environmental Performance	49
4.1	Exergy as a Measure of the Potential to Drive Environmental Change	50
4.2	An Expanded Model of the Environment	57
4.3	Anthropogenic Interactions and Environmental Impact	62
4.4	Environmental Exergy Analysis	65
4.5	Interpreting the Impact Equations for Decision Making	72
4.6	Applying the Analysis Framework for Decision Making	76
4.7	Conclusion	80
5	Evaluating Economic Performance of Energy Systems	83
5.1	Estimating Costs	84
5.2	Influence of Cost Estimates and Cash Flow Models on Performance Metrics	90
5.3	Conclusion	94
6	Conclusions and Future Work	97
6.1	Future Work	99
A	Exergy and Exergy Analysis for Technical Analysis	101
A.1	Derivation of Exergy as a Measure of Maximum Work	101
A.1.1	Internal Exergy	102
A.1.2	External Exergy	107
A.1.3	Total Exergy	108
A.2	Exergy Destruction and Balances	108
A.3	Exergy Transfers	109
A.4	Energy System Performance Efficiencies	110
A.5	The Role of the Dead State	113

A.6	Radiation Exergy	114
A.7	Nuclear Exergy	118
B	Derivation of Exergy as a Form of Environmental Free Energy	121
B.1	Derivation of Helmholtz and Gibbs Free Energy	122
B.2	Derivation of Environmental Free Energy	125
C	Supplemental Material for GTL Model	131
C.1	Analytical Tool Development	131
C.2	Heat Integration and Combined Cycle Models	134
C.3	Base Case Operating Conditions	135
C.4	Additional Model Results	139
D	Environmental Analysis Framework: Example Applications	143
D.1	Application of Environmental Exergy Analysis to a Model System . .	144
D.2	Example Applications of Environmental Analysis Framework	154
D.2.1	Thermal Pollution	155
D.2.2	Photochemical Smog	158
D.2.3	Large-Scale Solar PV	162

List of Figures

3.1	Generic process flow diagram for production of liquid fuels via Fischer-Tropsch synthesis.	23
3.2	Illustrations of the four types of commercial reactors. From Spath and Dayton [51].	24
3.3	Fischer-Tropsch output distributions as predicted by the ASF model. (a) Hydrocarbon mole fraction as a function of carbon number for various chain-growth probability (CGP) values. (b) Hydrocarbon selectivity as a function of chain-growth probability.	27
3.4	Hydrocarbon product distributions from two different slurry reactors. Dots are experimental measurements, and solid lines are calculated by the double- α ASF model [55, 56]. (a) Cobalt-based catalyst, from [55]. (b) Iron-based catalyst, from [56].	29
3.5	System diagram of the GTL co-power production power plant. The acronyms stand for air separation unit (ASU), partial oxidation reformer (POX), syngas cooler (SGC), carbon dioxide separation unit (CSU), Fischer-Tropsch reactor (FTR), pressure swing adsorption (PSA), combined-cycle gas turbine (CCGT).	33
3.6	(a) Natural gas exergy distribution calculated through exergy analysis. (b) Natural gas energy distribution calculated through first-law analysis.	38
3.7	System exergy destruction distribution measured as a percentage of its total exergy destruction.	39
3.8	Fischer-Tropsch reactor outlet hydrocarbon distribution.	40

3.9	Schematic diagram illustrating the various energy transformation pathways used to provide transportation and other energy services (e.g., lighting, heating, cooling).	44
4.1	Two-reservoir system of differing thermodynamic states.	51
4.2	Three-reservoir system of different thermodynamic states.	53
4.3	(a) Driven, two-reservoir system in thermal stationary states at the same pressure, but with differing compositions. (b) Final (non-equilibrium) stationary state of the system after chemical equilibrium is reached. (c) Temperature profiles of the initial and final stationary systems.	56
4.4	Global exergy resources. From Hermann [87].	59
4.5	Model representation of the natural environment.	61
4.6	Example conversion pathways. Red arrows: upstream interactions; black arrows: downstream interactions.	63
4.7	Environmental impact drivers and terminology.	64
4.8	Model representation of the conversion of a fossil resource to electricity. Red arrows: upstream transfers; black arrows: downstream transfers; blue arrows: natural exergy transfers; black dashed lines: reservoir control boundaries.	66
4.9	Three reservoir system in communication with an anthropogenic activity. Black arrows: downstream transfers; blue arrows: natural transfers; black dashed lines: control boundaries.	73
4.10	Distribution of the drivers and types of environmental impact on an α reservoir in communication with three (hypothetical) energy systems. Exergy values are in arbitrary units (A.U.).	77
4.11	Distribution of the forms of exergy in the direct transfers to, and the state changes in, the α reservoir. The total exergy values correspond to those in Fig. 4.10. The “other” forms of exergy in the figure include radiative, nuclear, kinetic, and potential.	78

4.12	Distribution of the change in component chemical exergy in the α reservoir. The total chemical exergy changes correspond to the values shown in Fig. 4.11.	79
5.1	Example of detailed fixed-capital investment costs estimate for a coal-to-liquids facility. From [93].	88
5.2	Example of detailed O&M costs estimate for a coal-to-liquids facility. From [93].	89
5.3	Example diagram showing the results of the sensitivity analysis performed on the economic analysis of CTL facility. This “tornado” diagram illustrates how increases and decreases in individual model input parameters by 25% impact the return on investment (i.e., return on equity) in order of significance. From [93].	94
A.1	Resource in communication with the environment.	103
A.2	Diagram of a generic work-producing energy system.	109
A.3	Nucleus-bound energy of known nuclides (Ni-62 = 0). From Hermann [87].	120
B.1	Closed, rigid system in communication with a thermal reservoir with work extraction. The thermostat controls heat transfer to maintain temperature T inside the system.	122
B.2	Closed system in communication with a thermo-mechanical reservoir with work extraction. The thermostat and barostat control heat and boundary work transfers to maintain temperature T and pressure P inside the system.	124
B.3	Open system in communication with a thermodynamic reservoir. The system is comprised of two reservoirs—resource and environment. The thermostat, barostat, and chemostat control heat, boundary work, and matter transfers to maintain the environment reservoir at T_o , P_o , and $\mu_{i,o}$	126

C.1	Ethane/heptane phase envelope calculated using the cubic VLE model. Ethane composition range: 1, 0.95, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1.	133
C.2	Illustration of heat integration scheme for the GTL co-power production power plant. Acronyms stand for partial oxidation preheating (POX PH), hydrocracker preheating (HC PH), condenser (Cond.), syn-gas cooler (SGC), hydrocracker (HC), Fischer-Tropsch reactor (FTR), vapor cooler (VC), and liquid cooler (LC).	135
C.3	System diagram of the combined cycle used in the GTL co-power production power plant. Acronyms stand for high pressure superheater (HPS), intermediate pressure superheater (IPS), reheat (RH), high pressure boiler (HPB), high pressure economizer (HPE), intermediate pressure boiler (IPB), intermediate pressure economizer (IPE), low pressure superheater (LPS), input low pressure superheater (Input LPS), low pressure boiler (LPB), and low pressure economizer (LPE).	136
C.4	Combined cycle exergy destruction distribution measured as a percentage of its total exergy destruction.	139
C.5	HRSG exergy destruction distribution measured as a percentage of its total exergy destruction (top), and HRSG heat transfer profile (bottom).	141
C.6	Hydrocarbon distributions calculated using flash VLE algorithm. (a) Vapor cooler outlet hydrocarbon distribution. (b) Hydrocracker hydrocarbon distribution. Hydrocracker outlet vapor composition is not shown in the figure because it is close to zero for all components, according to the model.	142
D.1	Model system comprised of a heat engine located within in a local environment.	145
D.2	Natural and anthropogenic transfers within model system during heat engine operation. Red arrows: upstream transfers; black arrows: downstream transfers; blue arrows: natural transfers; black dashed lines: control boundaries.	146

D.3	(a) Illustration of a geothermal power plant. (b) Representation of the environmental reservoirs and interactions for analyzing the environmental impact of a geothermal power plant. Black arrows: anthropogenic transfers; blue arrows: natural transfers; black dashed lines: reservoir control boundaries.	154
D.4	Environmental reservoirs and interactions for analyzing the environmental impact of thermal pollution. Red arrows: upstream transfers; black arrows: downstream transfers; blue arrows: natural transfers; black dashed lines: reservoir control boundaries.	156
D.5	Peak ozone concentrations resulting from different initial NO_x and ROG compositions. The ROG: NO_x ratio along the line through zero is 8:1, which is common in many polluted urban areas. From Jacobson [117].	159
D.6	Diagram of L.A. Basin for illustrating the environmental conditions that promote photochemical smog formation.	160
D.7	Evolution of NO , NO_2 , and ozone mixing ratios at two locations in L.A. Basin on August 28, 1987. From Jacobson [117].	160
D.8	Environmental reservoirs and interactions for analyzing the environmental impact of photochemical smog. Red arrows: upstream transfers; black arrows: downstream transfers; blue arrows: natural transfers; black dashed lines: reservoir control boundaries.	161
D.9	Environmental reservoirs and interactions for analyzing the environmental impact of large-scale solar PV. Red arrows: upstream interactions; black arrows: downstream interactions; blue arrows: natural transfers; black dashed lines: reservoir control boundaries.	164

Chapter 1

Introduction

1.1 Motivation

The desire to quantify the performance of energy technologies has been pursued by engineers and economists since the beginning of the industrial revolution. At first, simply having a device that produced work (such as the early steam engines) was an accomplishment in itself. As the demand for energy services and competition among technologies grew, cost became the dominant performance metric. These costs included the cost to manufacture, distribute, operate, maintain, and fuel the technology. As the use of energy technologies further increased, specifically those technologies dependent on combustion, the effect of byproducts on human health was exposed. This led to the development and implementation of emissions standards as additional performance metrics.

Today, with the supply of conventional energy resources being depleted at their fastest rates and the environmental impacts of their use better understood, there is an increasing desire to develop and employ alternative energy technologies that lessen dependence on these resources and reduce environmental impact. These objectives lead to the question: Which alternative energy technologies should we pursue? In order to answer this question, the potential technologies need to be compared on a level playing field based on their technical, environmental, and economic performance.

There currently exist several well-established analysis techniques for evaluating

an energy technology’s technical and economic performance, and various analysis techniques for evaluating environmental performance. All of the existing techniques have individual merit. However, when they are employed without full understanding of their limitations, the performance information they provide can lead to decisions in energy with undesirable consequences. An example of this is the investment and policy decisions made in the U.S. over the past decade to promote the production of corn-based ethanol, which have inadvertently led to undesirable environmental and economic consequences (e.g., increased CO₂ emissions caused by land-use change [1] and higher food prices caused by supply reductions [2]).

The inadvertent consequences caused by decisions based on information provided by the existing analysis techniques—namely, those that caused the push for biofuels—motivated the assessment of the three analysis components—technical, environmental, and economic—presented in this dissertation. The hope is that the observations and proposed analysis techniques presented here can be employed to better guide future investment and policy decisions in energy.

1.2 Organization of the Dissertation

When exploring the technical, environmental, and economic analysis components of decision making in energy, it was discovered that the opportunities for advancement within these components were inversely related to their driving forces for developing and employing alternative energy technologies. This revelation is reflected in the dissertation. The environmental component, which is arguably the largest driving force for developing and employing alternative technologies, actually yielded the greatest opportunity for advancement. The technical and economic components each have established analysis bases that require significant subtlety in understanding their capabilities and interpreting their results. While many analysis techniques exist for technical and economic components, there are varying levels of restrictions concerning how they can be applied for decision making. Additionally, these restrictions are not always recognized by those that perform the analysis, especially in technical analysis. Consequently, readers will notice a distinct asymmetry in the treatment of

these components.

The path for connecting the individual components of this dissertation begins from the technical analysis of energy systems and extends these analysis principles to the environmental component of decision making. This extension leads to the development of a framework for viewing and analyzing complex environmental problems that cannot be otherwise addressed using existing methods. Economics, by virtue of its state of development and opportunities in other areas, is treated through commentary on some of the areas that become apparent in critical reading of existing studies.

Readers will additionally notice a large volume of appendices. One of the key analysis tools throughout the dissertation is exergy and the more recent recognition that it is, in fact, a form of environmental free energy. While the concept of exergy has been around for more than fifty years, it is not commonly well understood, particularly with respect to chemical exergy. For this reason, appendices are provided to aid the reader, both from the technical exergy point of view and the environmental free energy point of view, and to illustrate the application of exergy for environmental analysis. Since inclusion of these in the body of the dissertation could slow the pace of core reading, they have been moved to the appendix so that interested readers can obtain more detail.

Chapter 2 begins the body of this dissertation by discussing the roles that analysis techniques play in evaluating the performance of energy technologies and providing information for decision making. It provides a high-level review of the more prominent analysis techniques for evaluating the performance of energy technologies. The chapter concludes by discussing the utility of multi-criteria analysis based on independently evaluated technical, environmental, and economic measures of performance for decision making in energy.

Chapters 3–5 discuss the individual components that comprise multi-criteria analysis of energy technologies. Chapter 3 discusses and demonstrates the utility of exergy for evaluating and comparing the technical performance of energy technologies. The chapter identifies key constraints on the ability to perform technical systems analysis and how these constraints influence the energy options considered in decision making. Chapter 4 presents a thermodynamics-based analysis framework for evaluating the

environmental performance of energy technologies, and discusses the application and utility of the framework for decision making in energy. Chapter 5 discusses the role that cost estimates and model assumptions play in the economic analysis of energy systems and the influences they can have on economic performance metrics commonly used for decision making.

Chapter 6 brings the discussion of the individual analysis components back into the overall discussion of decision making in energy. Thoughts regarding future exploration are considered.

Chapter 2

Decision Making in Energy

Decision making in energy refers to the array of decisions made during the process of designing or selecting energy technologies, or systems, to accomplish a specified objective or set of objectives (e.g., designing a more efficient compressor, selecting a type of power plant to produce a specified amount of electricity at minimal capital cost, etc.).¹ Making informed, or reasoned, decisions in energy requires that the decision maker has information about the performance of their energy system options. The types of performance that are relevant in decision making depends on the decision maker (e.g., engineer, private investor, public utility, government agency) and the objectives of their decisions (e.g., optimize system performance, maximize return on investment, meet renewable portfolio standards, increase energy security). The relevant types of performance for decision making in energy can be broadly categorized as technical, environmental, and economic.

Analysis techniques are employed to evaluate the performance of energy systems and provide information for use in the decision-making process. Decision makers use the performance information provided by analysis techniques to compare their energy system options and make informed decisions. The performance information provided

¹The term “energy technology” is often used to refer to an individual device that accomplishes an energetic objective. In thermodynamics, the term “energy system” is used to refer to both an individual device and a set of devices that collectively accomplish an energetic objective (i.e., a system). For the sake of brevity, the term “energy system” is used in this dissertation to refer to both individual devices and systems. When necessary, the distinction is made explicit.

by analysis techniques and used by decision makers can directly affect the quality, or expected outcomes, of their decisions (e.g., incorrect information about the operating costs of a system can affect a decision maker's return on investment). In order for decision makers to make informed decisions in energy that meet their objectives, appropriate analysis techniques must be employed to provide relevant performance information about their energy system options.

The following section provides a high-level review of the more prominent, existing analysis techniques for evaluating the technical, economic, and environmental performance of energy systems. Following this review, the utility of comparing energy systems using independently evaluated measures of technical, environmental, and economic performance for decision making in energy is discussed.

2.1 Review of Existing Analysis Techniques

2.1.1 Technical Performance Analysis Techniques

The technical performance of energy systems is typically evaluated through application of thermodynamic principles and analysis techniques. The most prominent thermodynamic analysis techniques are first-law analysis, second-law analysis, and exergy analysis. The thermodynamic principles, details, and applications of these techniques are discussed and demonstrated in numerous thermodynamic texts [3–8].

First-law analysis utilizes the First Law of thermodynamics to track energy through an energy system.² It provides the ability to evaluate how well an energy system utilizes its energy inputs to produce desired energy outputs. In first-law analysis, the technical performance of an energy system is measured by comparing the energy of required inputs to the energy of desired outputs, and is typically communicated through a first-law efficiency (e.g., thermal efficiency, fuel conversion efficiency) or coefficient of performance, depending on the type of energy system. First-law performance metrics provide the ability to compare the technical performance of energy systems that use the same inputs and produce the same desired outputs.

²First-law analysis is commonly referred to as *energy analysis*.

Second-law analysis utilizes both the First and Second Laws of thermodynamics to track energy and entropy through an energy system. It provides the ability to evaluate how well an energy system performs relative to its reversible (i.e., theoretical) limit, and to quantify the locations and magnitudes of entropy generation within the system. The reversible limit of an energy system is the maximum amount of work that can be produced, or the minimum amount of work required, if the system is operated reversibly (i.e., with no entropy generation). In second-law analysis, the technical performance of an energy system is measured by comparing the reversible limit of the system to the actual amount of work produced or required, and is typically communicated through a second-law efficiency. Second-law efficiency provides a metric for comparing the technical performance of energy systems with the same architecture.³ The locations and magnitudes of entropy generation within a system provide information useful in system design and optimization, since entropy generation provides a measure of the irreversibilities (i.e., inefficiencies) within the system. By reducing entropy generation within an energy system, the system will operate closer to the theoretical limit of its architecture.

Exergy analysis tracks the flow of exergy through an energy system. Exergy is derived through the First and Second Laws and is defined as the maximum amount of work that can be produced from an energy carrier interacting with its environmental surroundings. Exergy is not conserved like energy; it can be destroyed. Exergy destruction is equivalent to lost work, and linked to entropy generation through the Gouy-Stodola Theorem: $X_{destroyed} = W_{lost} = T_o S_{gen}$, where T_o is the temperature of the environment [10]. Exergy analysis provides the ability to evaluate how well an energy system performs relative to the theoretical limits of its inputs, and to quantify a system's locations and magnitudes of lost work—exergy destruction within the system and transfers of unused exergy from the system. In exergy analysis, the technical performance of an energy system is measured by comparing the exergy of all inputs to the exergy of desired outputs, and is typically communicated through an

³The architecture of an energy system refers to the joint set of thermodynamic processes and hardware components required to define the system. It provides an idealized model of the physical embodiment of the energy system, and describes how the system could operate in the limit of theoretically realizable hardware. For more information, refer to the PhD Thesis of Miller [9].

exergy efficiency. Exergy efficiency provides a metric for comparing energy systems regardless of their architectures. The locations and magnitudes of exergy destruction and transfers of unused exergy provide information useful in system design and optimization. By decreasing exergy destruction within, and transfers of unused exergy from an energy system, the system will operate closer to the theoretical limit of its inputs.

Since all three analysis techniques are based on thermodynamics, they share some common attributes and limitations. The two main attributes of the techniques are their consistent use of control boundaries and time scales. In order to apply the analysis techniques, a control boundary for the system and a time scale for the analysis must be defined. The control boundary sets the bounds for writing the energy, entropy, and exergy balances for the system, and the time scale sets the analysis period (e.g., instantaneous or life span of the system). Defining appropriate control boundaries and time scales is essential for comparing energy systems on a level playing field. The main limitation of the techniques is their dependence on thermodynamic property and performance data. The availability of property data can affect the applicability of the analysis techniques (especially for exergy and second-law analysis since they both require entropy data), and the accuracy and range of applicability of performance data can affect the accuracy of the performance metrics they provide.

2.1.2 Economic Performance Analysis Techniques

Several analysis techniques exist for evaluating the economic performance of energy systems, with each technique providing different measures. This is due to the various interpretations of economic performance. Engineers and investors typically interpret and measure performance based on costs and economic value (i.e., investment value), whereas economists and policy makers typically interpret and measure performance based on the effect energy systems have on the economy. Despite these differences, the existing economic analysis techniques all require information about the costs of an energy system in order to quantify their respective measures of economic performance.

The costs of an energy system can be quantified through engineering cost analysis. The relevant costs of an energy system typically include the cost of equipment, operation and maintenance (O&M), fuel, capital, depreciation, and taxes. Costs can be measured in current/nominal dollars or constant/real dollars, with the difference being that current dollars do not include inflationary effects. When costs are reported in current dollars, it is often necessary to know the time at which they are incurred so that they can be properly discounted to the year in which the analysis is structured. The costs of an energy system are used as inputs to most economic analysis techniques. Therefore, it is important that they are properly valued or estimated. Bejan et al. [4] provide a detailed framework for valuing and estimating the costs of energy systems.

Engineers and investors typically use an energy system's costs to evaluate the system's investment value and provide economic performance metrics. Economic value can be evaluated through various analysis techniques. The most prominent analysis techniques are: present worth analysis, annual worth analysis, rate of return analysis, benefit-cost analysis, and payback period analysis. The economic principles and applications of these techniques are discussed and demonstrated in numerous standard Engineering Economic Analysis and Engineering Economy texts [11–16]. Each of these techniques (referred to here as engineering-economic analysis techniques) provide different measures of economic performance. The most widely used economic performance metrics for comparing the economic value energy systems are: net present value, total life cycle cost, levelized cost of energy, rate of return (internal and modified), benefit-cost ratio, and payback period (simple and discounted). A high-level review of these performance metrics and their applications in comparing the economic performance of energy systems is provided by Short et al. [17].

Economist and policy makers typically use an energy system's costs to evaluate the effects that large-scale deployment of the system has on the economy. Interactions between energy systems, energy resource consumption, and the economy are modeled by applying microeconomic and macroeconomic principles. These models are typically referred to as Energy-Economic Models. The microeconomic and macroeconomic principles used in Energy-Economic Models are discussed in numerous standard

economic texts [18–23]. The details and applications of the most widely used Energy-Economic Models are often published in journals, with *Energy Economics* and *Energy Policy* being the most common.

There are two broad modeling approaches employed in Energy-Economic Models: bottom-up and top-down. McFarland et al. [24] and Frei et al. [25] provide reviews of the differences between and applications of the two modeling approaches. Bottom-up models are typically partial equilibrium models of the energy sector that use relatively detailed descriptions of energy systems (e.g., first-law efficiency, equipment cost, O&M cost).⁴ They are typically employed to identify the least-cost mix of energy systems for meeting a final energy demand under specified energy and regulatory constraints (e.g., limited supply of natural gas, renewable portfolio standard). Bottom-up models often take energy and other prices as exogenous and can therefore overestimate the potential penetration of a system (e.g., the penetration of corn-based ethanol production could be overestimated because its influence on corn prices is not taken into account). Bottom-up models typically measure economic performance based on the effect energy systems have on the cost of energy (e.g., change in cost of electricity). Top-down models are computable general equilibrium models that use aggregated production functions to represent an energy system (e.g., capital, labor, fuel inputs).⁵ They are typically employed to evaluate the influence energy systems have on other sectors of the economy. They provide the ability to evaluate market and economy-wide feedbacks and interactions, but often by sacrificing the technology richness of bottom-up models. Top-down models typically measure economic performance based on the cross-sector price effects caused by energy systems.

The economic analysis techniques in Engineering Economic Analysis and Energy-Economic Models provide various measures of economic performance for comparing energy system alternatives. However, they provide limited insight for designing and

⁴Partial equilibrium models use an economic structure in which supply equals demand in a subset of the markets within an economy.

⁵General equilibrium models use an economic structure where supply equals demand in all markets within an economy. Supplies match demands through an equilibrium price that balances the incremental costs of producers with the willingness to pay of consumers. For more information on general equilibrium models in energy-economic modeling, refer to Weyant [26] and the reference within.

optimizing individual energy systems or technologies. Efforts have been made to combine thermodynamic principles and analysis techniques—namely exergy and exergy analysis—with economic cost analysis to provide performance information for designing and optimizing energy systems based on trade-offs between thermodynamic performance and costs. The most prominent of these analysis techniques is Thermoeconomic Analysis. Bejan et al. [4] provide a detailed review of the principles and applications of Thermoeconomic Analysis for use in energy system design and optimization.

2.1.3 Environmental Performance Analysis Techniques

Several analysis techniques have been developed for evaluating and measuring the environmental performance of energy systems. As with economic performance analysis techniques, the existing environmental analysis techniques have a range of interpretations and provide various measures of environmental performance. The most prominent analysis techniques can be categorized as being based on species, economics, or thermodynamics.

Species-based techniques measure the environmental performance of energy systems based on the amount of a particular species emitted by a system. The species of interest are typically those that have been identified as causing adverse environmental consequences. Example species include oxides of nitrogen (NO_x), sulfur dioxide, carbon dioxide, and chlorofluorocarbons (CFCs). The emission of these particular species are often monitored because of the adverse environmental consequences they can cause—photochemical smog, acid rain, global warming, and ozone depletion. Species-based techniques typically communicate an energy system’s environmental performance by the mass of a species emitted per unit of desired output (e.g., $\text{kg-CO}_2/\text{MWh}_{\text{elec.}}$).

Extensions have been made to species-based techniques for comparing a range of species on the basis of their potential to cause a common adverse environmental consequence. The most prominent of these extensions is the use of Global Warming Potentials (GWPs) by government agencies such as the U.S. Environmental Protection

Agency (EPA) and the Intergovernmental Panel on Climate Change (IPCC). GWPs provide a measure of a species' potential to cause global warming relative to that of carbon dioxide. The details of, and standard methods used to measure, GWPs are defined by the IPCC [27]. When GWPs are employed to measure an energy system's environmental performance, the results are communicated through a mass of carbon dioxide equivalent emission per unit of desired output (e.g., $\text{kg-CO}_2\text{-eq./MWh}_{\text{elec.}}$).

Economics-based techniques measure environmental performance by assigning a monetary value to the undesirable outputs from energy systems that are known to cause adverse environmental consequences. In economics, the adverse environmental consequences caused by an energy system are typically referred to as *environmental damage*, and the cost assigned to these damages are referred to as an environmental *external cost*. There are several methods employed to define what is considered environmental damage and to prescribe an environmental external cost. A detailed review of these methods is provided by Riva and Trebeschi [28]. Economists and policy makers typically use the environmental external cost of an energy system as a measure of its environmental performance. The environmental external cost of an energy system can be combined (i.e., internalized) with its internal cost to provide a measure of the system's *real cost* (where the internal cost is measured through engineering cost analysis). It is often argued that the real cost of an energy system provides a more appropriate measure of economic performance than internal cost when comparing energy system options [28, 29].

Thermodynamics-based techniques employ thermodynamic concepts to evaluate and measure the environmental performance of energy systems. The noteworthy thermodynamics-based analysis techniques are: Life Cycle Assessment (LCA), Cumulative Exergy Consumption (CEC), Cumulative Exergy Extraction from the Natural Environment (CEENE), Extended Exergy Accounting (EEA), and Emergy Analysis. All of these analysis techniques extend the control boundary of an energy system and the time scale of the analysis to include all components and processes required to support the system over its entire life (often referred to as “cradle-to-grave” analysis). The key differences between the five techniques are in how they value the inputs and outputs of a system, and how they measure environmental performance.

Life Cycle Assessment is essentially an extension of first law-analysis. It tracks the mass and energy of inputs and outputs of an energy system over its entire life (not including capital and labor). The energy of physical inputs and outputs are typically measured based on their heating value (lower or higher). LCA measures the environmental performance of an energy system through the total amount of natural resource energy required to produce a desired product, and through the total amount of emissions produced by the system. The former is typically communicated via a net energy value (e.g., $\text{LHV}_{\text{net}} = \text{LHV}_{\text{desired products}} - \text{LHV}_{\text{resource inputs}}$) or an overall first-law efficiency (e.g., $\text{LHV}_{\text{desired products}}/\text{LHV}_{\text{inputs}}$), and the later is typically communicated via the mass of emissions per unit of desired product (e.g., $\text{CO}_{2,\text{total}}/\text{MWh}_{\text{elec.}}$). The methods and applications of LCA are described by the U.S. EPA [30].

Cumulative Exergy Consumption tracks the *embodied exergy* of inputs to an energy system over its entire life (again, not including capital and labor). The embodied exergy of an input is measured by the sum of the fossil and nuclear resource exergy that went into its production (e.g., the embodied exergy of a kg of steel is the amount of fossil resource exergy consumed in during its production). CEC measures the environmental performance of energy systems through the total amount of embodied exergy required to produce a desired output (i.e., through the desired output's cumulative, or embodied, exergy content). CEC communicates environmental performance via an overall exergy efficiency, which is referred to as the *cumulative degree of perfection*. The details and applications of CEC are described by Szargut et al. [7, 31].

Cumulative Exergy Extraction from the Natural Environment extends the embodied exergy concept used in CEC to include the exergy of renewable resource inputs, such as solar radiation, wind, and geothermal exergy. CEENE measures the environmental performance of energy systems through the total amount of embodied exergy (measured through the CEC approach) and renewable exergy required to produce a desired output (i.e., through the total amount of exergy removed from the natural environment). Dewulf et al. [32] describe the details and applications of CEENE.

Extended Exergy Accounting tracks the *extended exergy content* of all inputs and outputs of an energy system over its entire life, including capital and labor. The

extended exergy content of non-capital and non-labor inputs is calculated through the embodied exergy methods used in CEC. The extended exergy content of capital is calculated by assigning an exergy value to a unit of a country's currency based on the country's gross domestic product (GDP) and the total amount of natural resource exergy consumed by the country in a given year (e.g., MJ/\$_{GDP}). The extended exergy content of labor is calculated by assigning an exergy value to a hour of work (a "man-hour") based on the total amount of natural resource exergy consumed by a person to support one hour of work (e.g., MJ/man-hour). EEA assigns an extended exergy content to an energy system's undesired outputs (e.g., emissions, waste) based on the extended exergy content of all inputs that would be required to reduce their exergy (thermo-mechanical and chemical) to zero. EEA measures the environmental performance of energy systems through the total amount of extended exergy input to a system in order to produce a desired output and reduce the exergy of undesired outputs to zero. The details and applications of EEA are described by [33–39].

Emergy Analysis tracks the *solar emergy* of all inputs to an energy system over its entire life, including capital and labor. Solar emergy is defined as the total amount of solar exergy directly or indirectly required to produce a given flow, and is measured in *solar equivalent joules* (seJ). The solar emergy of capital is calculated by assigning a solar emergy value to a unit of a country's currency based on the country's GDP and the total amount of solar exergy incident on and solar emergy consumed by the country over a given year (e.g., seJ/\$_{GDP}). The solar emergy of labor is calculated by assigning a solar emergy value to a man-hour based on the total amount of solar emergy consumed by a person to support one hour of work (e.g., seJ/man-hour). Emergy Analysis measures the environmental performance of an energy system through various metrics based on the total amount of solar emergy required to support the production of a desired output. The development, details, and applications of Emergy Analysis are described by [37, 40–42].

Emergy and EEA analysis are commonly referred to as overall performance analysis techniques because of their inclusion of capital and labor. They essentially roll all three performance components into one unit of measure—solar emergy and extended

exergy content, respectively—in order to internalize all transfers to and from a system. This is similar to the economic approach of measuring environmental damages through an environmental external cost and internalizing this cost to form the real cost of an energy system or energy product.

The various measures of environmental performance provided by the existing environmental analysis techniques can be categorized as being measures of *downstream* or *upstream* environmental impact. Downstream environmental impact refers to the environmental impact caused by the undesired outputs produced by energy systems, and upstream environmental impact refers to the environmental impact caused by the extraction and production of inputs to energy systems. Species- and economics-based techniques provide measures of the downstream environmental impact of energy systems. CEC, CEENE, and Emergy Analysis employ thermodynamic concepts to provide measures of the upstream environmental impact of energy systems. LCA employs thermodynamic concepts to measure the upstream environmental impact of energy systems, and species-based techniques to measure downstream environmental impact. EEA employs thermodynamic concepts to measure both the downstream and upstream environmental impacts of energy systems.

2.2 Multi-Criteria Analysis for Decision Making in Energy

Making informed decisions in energy requires the ability to evaluate and compare the technical, economic, and environmental performance of energy system options across the range of possible resources used (renewable and non-renewable) and outputs produced (desired and undesired) over the time scales in which energy systems operate.

Several multi-criteria analysis frameworks have been proposed by European researchers [43–46] for comparing the technical, economic, and environmental performance of energy systems using independently calculated measures of performance. The authors of the proposed frameworks suggest the use of first-law analysis and

exergy analysis for measuring technical performance, Thermoeconomic Analysis, net present value analysis, and internal rate of return analysis for measuring economic performance, and Emergy Analysis and mass-based analysis for measuring environmental performance (upstream and downstream). The only significant difference between the proposed techniques is in how they present the various performance metrics for comparing energy system options.

Multi-criteria analysis is useful for decision making in energy because it allows a decision maker to compare performance components independent from one another, and only consider those components that are relevant to meeting their decision objectives. Multi-criteria analysis is also useful because it has the ability to provide insight into possible correlations between performance components. For example, a more efficient energy system may require a larger capital investment than a less efficient system. The ability of multi-criteria analysis to provide sufficient information for decision making in energy depends on the ability of the analysis techniques employed to evaluate the individual performance components.

The individual performance components that comprise multi-criteria analysis are the topics of the next three chapters. Chapter 3 identifies key constraints on the ability of the existing thermodynamic analysis techniques to evaluate the technical performance of energy systems and demonstrates the utility of exergy and exergy analysis for decision making in energy. Chapter 4 introduces an alternative thermodynamics-based technique for evaluating the environmental performance of energy systems and discusses its application and utility for decision making. Chapter 5 discusses some of the key constraints on the existing engineering-economic analysis techniques and their influence on decision making.

Chapter 3

Evaluating Technical Performance

The existing thermodynamic analysis techniques—first-law, second-law, and exergy analysis—are all well-established techniques for evaluating the technical performance of energy systems. The thermodynamic principles of the techniques and their applications in technical energy systems analysis are discussed and demonstrated in numerous thermodynamic texts [3–8] and in thousands of publications.¹ Although each of the techniques is based on fundamental principles, only exergy analysis is capable of evaluating and comparing the technical performance of energy systems across the range of possible resources, products, and system architectures. The objective of this chapter is three fold: (1) reinforce the utility of exergy analysis for evaluating technical performance, (2) demonstrate the influence that information and analytical tools can have on the application of exergy analysis, and (3) demonstrate the utility of exergy for technical decision making.

The chapter begins with a high-level review of exergy and exergy analysis. Next, the roles that information and analytical tools play in exergy analysis are introduced. The following section uses the production of Fischer-Tropsch liquids as an example to both illustrate the influence that information and analytical tools can have on

¹Exergy and exergy analysis are often less familiar than first-law and second-law analysis. For this reason, the details of exergy and exergy analysis that are relevant in technical energy systems analysis are provided in App. A. Readers are also referred to the paper by Sciubba and Wall [47], which provides a commented review of the history and development of exergy, its various applications in energy systems analysis, and an extensive list of publications (over 2600).

technical performance analysis and to demonstrate the utility of exergy analysis for decision making. The chapter concludes by discussing the utility of exergy for decision making across energy system options.

3.1 Exergy and Exergy Analysis

Exergy is defined as the maximum amount of work that can be extracted from an *resource* relative to the *environmental surroundings* with which it interacts. The terms resource and environmental surroundings are italicized to emphasize both their importance and interdependence. A resource refers to any energy accumulation or energy flux that has the potential to do work relative to its environmental surroundings. The environmental surroundings refer to the portions of the natural environment that enable work to be extracted from a resource because it acts as a thermal, mechanical, and chemical reservoir to the resource. A resource has the ability to do work because it is out of equilibrium with its environmental surroundings. Work can theoretically be extracted from any two systems that are out of equilibrium, and the maximum amount of work is realized when they equilibrate reversibly. Exergy is an extension of this principle in which one of the systems is a resource and the other is the environmental surroundings.

Exergy is derived by applying the First and Second Laws of thermodynamics to a resource in communication with its environmental surroundings and calculating the reversible (i.e., maximum) amount of work that can be extracted as equilibrium is reached. Reversibility requires that the resource transfer heat at the environmental temperature, work at the environmental pressure, and exchange environmental species at their environmental chemical potentials. In traditional derivations of exergy, reversible interactions are realized by modeling the environmental surroundings as a large reservoir with fast internal transport such that its intensive state does not change (i.e., as a thermodynamic reservoir). A derivation of exergy that models the environmental surroundings in this manner is provided in App. A.

Exergy is useful in technical energy systems analysis because it provides an upper-bound for the amount of work that can be extracted from a resource, against which

any real use of the resource can be compared.² Since no real system is reversible, the actual amount of work extracted from a resource is always less than its exergy (i.e., its theoretical limit). The ratio of the actual amount of work produced by an energy system and the exergy input to the system is the system's *exergy efficiency*. The exergy efficiency of a system provides a measure of how well the system performs relative to the theoretical limits of its inputs. This enables different energy systems to be compared on a level playing field, regardless of their architectures, because each system is compared against an absolute theoretical limit, which is set by a system's inputs (and not their architectures, as in second-law analysis). Exergy efficiency is commonly used interchangeably with second-law efficiency, however, they are inherently different measures of performance. The distinction between exergy efficiency and other types of efficiencies commonly used in energy systems analysis is discussed in App. A.

Another inherent principle of exergy that makes it useful in technical energy systems analysis is that exergy is not conserved like energy, instead it can be destroyed. Exergy destruction is equivalent to lost work, and linked to entropy generation through the Gouy-Stodola Theorem: $X_{destroyed} = W_{lost} = T_o S_{gen}$, where T_o is the temperature of the environment [10]. In exergy analysis, exergy is tracked through an energy system to determine the locations and magnitudes of exergy destruction within the system and transfers of unused exergy from the system—both losses of potential work. Transfers of unused exergy are eventually destroyed in the environment as they naturally equilibrate, and are sometimes included in the overall exergy destruction of a system.³ The locations and magnitudes of exergy destruction and transfers of unused exergy provide insight into the performance of energy systems that can be used for making design decisions—from architecture to operating conditions—to better utilize exergy and improve system performance.

Exergy analysis provides insight into the technical performance of energy systems

²For the sake of brevity, the term work is used to represent all desired outputs produced by energy systems (e.g., work, electricity, commercial fuels, heat). When necessary, the distinction between exergetic products is made explicit.

³The impact transfers of unused exergy have on the environment is discussed in the following chapter.

that eludes first- and second-law analysis. The ability to locate inefficiencies within energy systems and compare technologies on a level playing field make exergy analysis the appropriate analysis technique for technical decision making. The modeling techniques for applying exergy analysis to evaluate the technical performance of energy systems and the methods used for defining and quantifying the exergy of resources are provided in App. A.

3.2 Information and Analytical Tools

Technical decision making in energy requires information about the technical performances of the energy system options. The relevant technical performance information depends on the decision objectives. The objectives for technical decision making can be broken down into two broad categories: (1) system design and optimization, and (2) system comparisons and selection. In theory, exergy analysis has the ability to provide technical performance information for accomplishing both objectives. However, in practice, this ability depends on the availability of information about energy systems and the capability of analytical tools.

Applying exergy analysis to evaluate the technical performance of an energy system requires information about the system. As with decision making, the amount and type of information depends on the objectives of the analysis. The objectives of exergy analysis can be broken down into three categories: (1) calculating system overall efficiency, (2) quantifying locations and magnitudes of exergy destruction within and transfers of unused exergy from a system, and (3) optimizing system performance (i.e., maximizing system efficiency). Calculating a system's overall efficiency requires information about the system's inputs and desired outputs. Quantifying the locations and magnitudes of exergy destruction and transfers of unused exergy within a system requires information about each component's inputs and outputs (desired and non-desired) within the system. Optimizing a system's performance requires information about how the each component's inputs and outputs (desired and non-desired) vary with operating conditions. Obtaining the necessary system information for meeting these objectives can be difficult, especially when analyzing complex (e.g.,

multi-phase), new (i.e., not commercially available), or proprietary systems or components within a system.

The necessary information for meeting the various analysis objectives can be obtained from: (1) direct empirical measurement, (2) published values based on empirical measurement, (3) the use of analytical tools, and (4) published values based on information provided by analytical tools. Direct empirical measurements require that the system exists and there is access to measure the necessary information. Published values based on empirical measurements (i.e., indirect empirical measurements) require that the system had existed at one point, and the necessary information was measured and is publicly available. When the necessary system information is not available—either through direct or indirect empirical measurements—to meet the objectives of the analysis, analytical tools can be (and often are) employed to model energy systems and estimate the necessary information. For example, if the inputs to and operating conditions of a system are known, but the outputs are unknown, analytical tools can be employed to model the system and estimate its outputs. Analytic tools can be purchased from commercial software vendors (e.g., Aspen Technology, KRC Technologies) or developed in house. Thermodynamic software packages typically have an extensive property data base, but with limited transparency and flexibility (i.e., the user does not have access to the software's internals). Whereas, analytical tools developed in house typically have the opposite characteristics—transparency and flexibility, but often with limited property data. The accuracy of the information provided by analytical tools depends on the models and property data used in the analysis. Using analytical tools to calculate information about a system requires that the physical behavior of the system can be sufficiently modeled and the necessary property data is available. When using published values based on information provided by analytical tools, it is important to understand the models and property data used in the analysis.

Dependence on information and analytical tools is not exclusive to exergy analysis. In fact, the ability of all the existing thermodynamic analysis techniques to evaluate a system's technical performance depends on the availability of information about the system and the capability of analytical tools. However, second-law and exergy

analysis have an additional dependence because they both require entropy data. The following section illustrates the influence information and analytical tools can have on the application of exergy analysis.

3.3 Exergy Analysis of Natural Gas Fischer-Tropsch Plant with Co-Power Production

The analysis presented in this section was performed in collaboration with Sandia National Laboratories. The original goal of the project was to demonstrate the application and utility of exergy analysis for evaluating and comparing the technical performance of the production of alternative liquid transportation fuels from various feedstocks via Fischer-Tropsch (FT) synthesis—namely natural gas, coal, and biomass. However, during the course of the project, its scope was reduced due to the availability of information and capabilities of analytical tools. The following discussion is meant to both illustrate the influence that information and analytical tools can have on the application of exergy analysis and demonstrate the utility of technical performance information provided by exergy analysis for decision making on an individual systems basis.

The section begins by giving a high-level overview of FT synthesis. Next, the influence that information and analytical tools had on model development are discussed. The details of the modeled system are then discussed, followed by selected results of the analysis. The original report is provided in Simpson and Lutz [48].

3.3.1 FT Synthesis

Fischer-Tropsch synthesis refers to the catalytic conversion of syngas (a mixture of CO and H₂) into long-chain hydrocarbons, mostly paraffins and olefins. There are four main steps to producing liquid fuels via Fischer-Tropsch synthesis: (1) syngas generation, (2) syngas cleanup and conditioning, (3) FT synthesis, and (4) product processing and upgrading. Figure 3.1 depicts a generic process flow diagram for this process. Each step can be accomplished through a variety of energy technologies.

The appropriate technologies depend on the hydrocarbon feedstock (e.g., natural gas, coal, biomass, municipal solid waste) and the types and quantities of liquid products desired (e.g., raw naphtha and distillate liquids, or fully upgraded gasoline and diesel blending stock). For the purposes of this overview, only natural gas and raw naphtha/distillate products are considered.

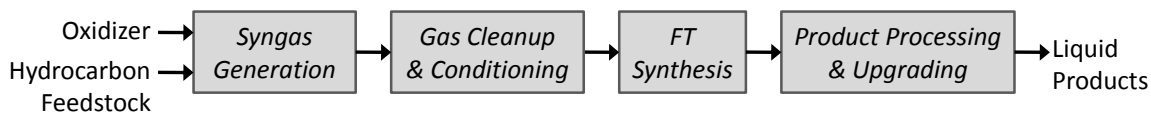


Figure 3.1: Generic process flow diagram for production of liquid fuels via Fischer-Tropsch synthesis.

Conversion of natural gas to syngas can be accomplished through several commercially available technologies. The three main technologies are steam methane reforming (SMR), partial oxidation (POX), and autothermal reforming (ATR). SMR and ATR are both catalytic processes. Wilhelm et al. [49] provide a detailed review of these technologies and their applications in gas-to-liquids (GTL) processes. Each technology has different performance characteristics and requires different auxiliary technologies (e.g., POX and ATR require air separation units). The appropriate reforming technology and the required syngas cleanup and conditioning (e.g., CO₂ separation, sulfur removal) depend on the specifics of the FT synthesis step.

Fischer-Tropsch synthesis is performed in high pressure, low temperature reactors that use either iron- or cobalt-based catalysts. There are four types of reactors used in commercial applications: circulating fluidized bed (CFB), fixed fluidized bed (FFB), multi-tubular fixed bed (MTFB), and slurry phase. Diagrams of the four reactors are shown in Fig. 3.2. CFB and FFB reactors operate between 300-350°C and 1.5-2.5 MPa and are typically referred to as high temperature Fischer-Tropsch (HTFT) reactors. MTFB and slurry reactors operate between 200-250°C and 2-3.5 MPa and are typically referred to as low temperature Fischer-Tropsch (LTFT) reactors. Commercial HTFT reactors only produce gaseous hydrocarbon products, whereas LTFT produce both liquids and gaseous hydrocarbon products. In general, HTFT reactors favor the

production of hydrocarbons suitable for making gasoline (naphtha and lighter hydrocarbons), and LTFT favor the production of hydrocarbons suitable for making diesel (distillate and heavier hydrocarbons, which are typically referred to as wax). Commercial CFB, FFB, and MTFB reactors all use iron-based catalysts, and commercial slurry reactor use either iron- or cobalt-based catalysts. Slurry reactors—both iron- and cobalt-based—are the newest generation of reactors and are expected to be used in the majority of the new commercial plants [50]. Iron-based catalysts have a higher tolerance to sulfur and require less syngas pre-treatment than cobalt-based catalysts. Reactors that use iron-based catalyst operate optimally with an input syngas H_2/CO ratio around 1, and reactors that use cobalt-based catalysts operate optimally with a ratio around 2. The main reason for the difference in H_2/CO ratios is that iron-based catalysts are water-gas-shift active, whereas cobalt-based catalysts are not. Detailed reviews of FT synthesis, commercial reactors, and catalysts are provided in [50–52].

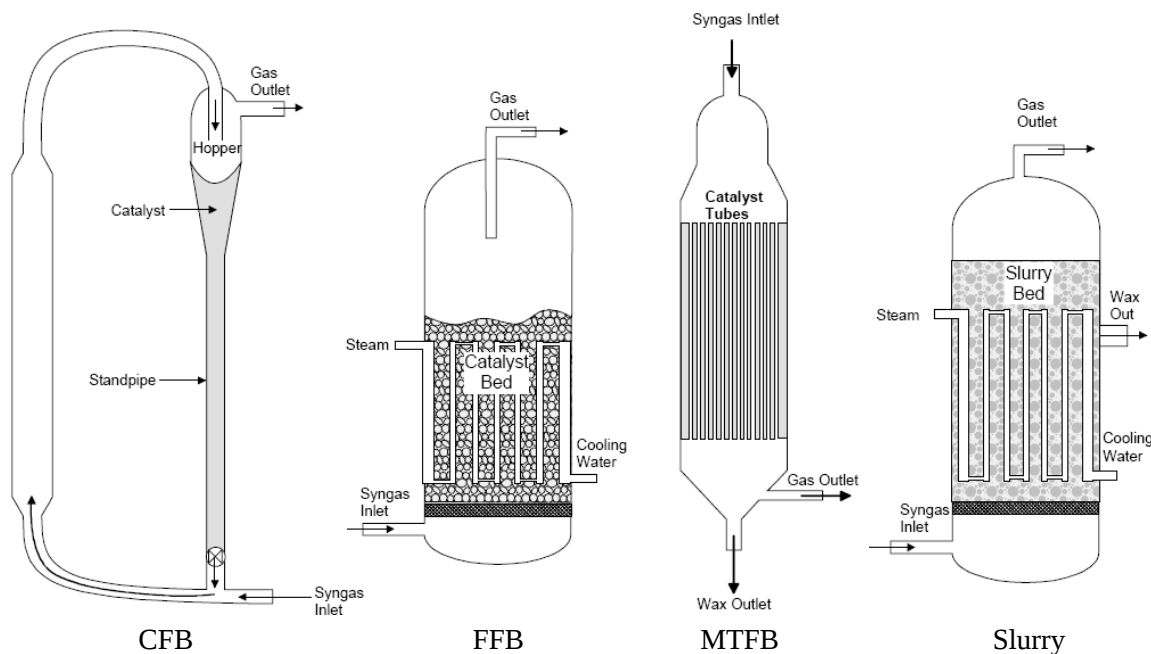


Figure 3.2: Illustrations of the four types of commercial reactors. From Spath and Dayton [51].

The amount and type of product processing and upgrading required to produce raw naphtha and distillate products depends on the temperature regime of the FT

reactor. The main requirement is that the raw liquid products are able to be transported at ambient temperatures to an existing oil refinery for further upgrading. For both HTFT and LTFT reactors, the gaseous hydrocarbon products must be condensed and any water separated. For LTFT reactors, the heavier hydrocarbons in the liquid phase (i.e., the wax) must be selectively broken-down, or “cracked”, into shorter chain hydrocarbons to obtain better flow characteristics (i.e., reduced viscosity). This is typically accomplished through commercially available catalytic hydrocracking units. The off-gases (mostly lighter hydrocarbons) produced in both processes can be recycled back to the reformer or FT reactor, combusted to produce power, or a combination of all three.

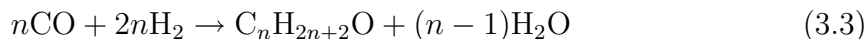
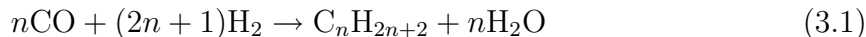
3.3.2 Developing a GTL Model

There are only three commercial GTL facilities in operation today. The first two facilities came online in the early 1990s and the most recent facility came online in 2007. The first commercial GTL facility was built and is operated by Sasol in South Africa, and is based around a slurry reactor that uses an iron-based catalyst [52]. The second facility was built and is operated by Shell in Malaysia, and is based around a MTFB reactor that uses a cobalt-based catalyst [53]. The most recent facility was built and is operated by a joint venture between Sasol and Chevron in Qatar, and is also based around a slurry reactor that uses an iron-based catalyst [54]. Information sufficient for performing exergy analysis on these systems is not publicly available. Therefore, in order to apply exergy analysis to a GTL facility, a system architecture had to be chosen and its components modeled.

The availability of information and capability of analytical tools to model FT reactors—specifically slurry reactors—and downstream processing and upgrading equipment influenced the choice of architecture and component models used in this analysis. The desire to model a slurry reactor was primarily due to their expected deployment in the majority of new FT facilities. A discussion of the advantages of slurry reactors over the other types of reactors is provided by [50, 52]. In order to illustrate how information and analytical tools influenced the analysis, an understanding of

FT chemistry and the existing methods for modeling slurry reactors and downstream processing and upgrading equipment is required.

The global reactions that describe FT synthesis are given by:



The first four global reactions describe the production of paraffins, olefins, alcohols, and methane, respectively. Reactions (3.5) and (3.6) are the water-gas-shift (WGS) and Boudouard reactions. The WGS reaction is a secondary reaction that readily occurs when iron-based catalysts are used, and the Boudouard reaction describes the deposition of carbon on the catalyst surface, which can lead to catalyst deactivation. The FT synthesis reactions are net exothermic. Heat removal is one of the major challenges for and design features of FT reactors. It is desirable to maintain a constant temperature profile within reactors in order to optimize product yield and avoid catalyst melting and deactivation. In commercial slurry reactors, heat is removed by producing steam in cooling tubes throughout the reactor. Slurry reactors are capable of operating near isothermally, which is one of their main advantages.

As with any catalytic process, the FT synthesis reactions are kinetically constrained. However, unlike SMR and ATR reactors (both catalytic), FT reactors are not well-modeled using chemical equilibrium calculations. The syngas composition from SMR and ATR reactors can be sufficiently modeled by using ideal gas property models and calculating chemical equilibrium based on input gas/steam atom population and input enthalpy and pressure (e.g., Gibbs minimization constrained by element populations). FT reactors cannot be modeled using this approach

because their output compositions deviate from that predicted by chemical equilibrium. Furthermore, slurry reactors produce products in multiple phases. Several approaches have been suggested in the literature for modeling the behavior of FT reactors and predicting output compositions and phases—all with varying dependencies on empirically-derived information.

The most basic of these approaches models FT synthesis as a stepwise chain-growth process based on ideal polymerization kinetics. The model assumes that output hydrocarbon (HC) composition is only a function of the probability that a C_n species on the catalyst surface will add another carbon and become a C_{n+1} species, rather desorb as a product [55]. The model is typically referred to as the Anderson-Schulz-Flory (ASF) model, and the probability of growth is referred to as the chain-growth probability (α). The ASF model predicts that the output HC molar composition from a FT reactor should be a straight line in semilog space, with the slope of line equal to the chain-growth probability, α . Example ASF distributions for four different α values are shown in Fig. 3.3a. Chain-growth probabilities depend on reactor type, operating conditions, and catalyst, but are typically between 0.6–0.95 for commercial reactors.

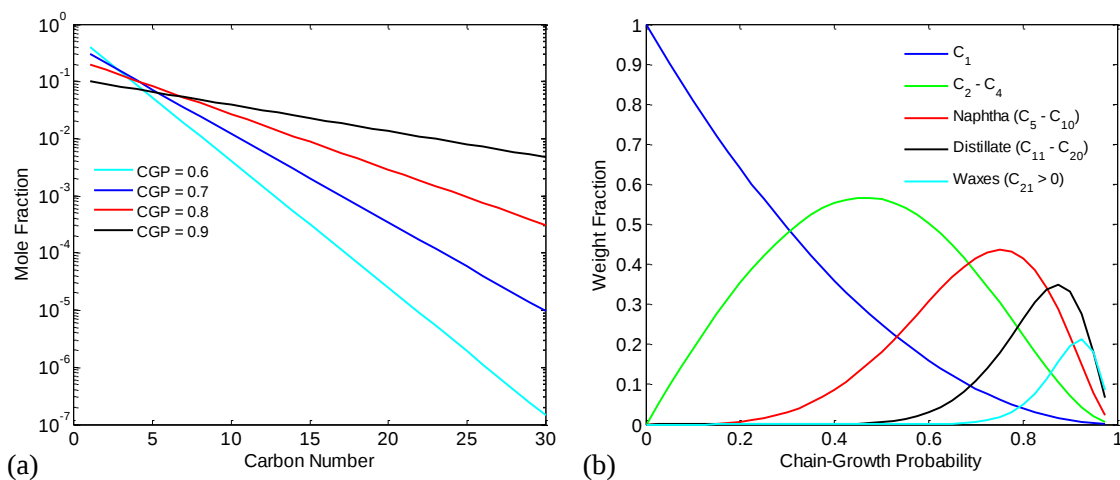


Figure 3.3: Fischer-Tropsch output distributions as predicted by the ASF model. (a) Hydrocarbon mole fraction as a function of carbon number for various chain-growth probability (CGP) values. (b) Hydrocarbon selectivity as a function of chain-growth probability.

Figure 3.3a illustrates that higher chain-growth probabilities yield hydrocarbon distributions that are weighted towards longer-chain hydrocarbons. Figure 3.3b illustrates the relationship between product selectivity and chain-growth probabilities as predicted by the ASF model.⁴ The model shows that in order to optimize distillate production it is best to use reactors/catalysts with chain-growth probabilities greater than 0.85 (typical of MTFB and slurry reactors), and to optimize naphtha production, reactors/catalysts with chain-growth probabilities between 0.7–0.8 are desirable (typical of CFB and FFB reactors).

The HC product distributions produced by real FT reactors deviate from the ideal ASF distribution. Figure 3.4 shows experimental HC product distributions from two different slurry reactors—one with a cobalt-based catalyst and the other with an iron-based catalyst. The departure is most prevalent for hydrocarbons lighter than C_3 and for hydrocarbons heavier than C_7 (although the iron-based catalyst distribution shown in the figure has a more gradual departure). The exact reasons for the observed departures are not agreed upon amongst FT researchers. For lighter hydrocarbons, the departure is commonly believed to be due to kinetic limitations [55, 56]. For heavier hydrocarbons, the most widely accepted explanation is that the mid-range olefins (C_4 – C_7) produced on the catalyst surface break-off and are then readsorbed onto another catalyst site and continue to grow in chain length before breaking-off as longer paraffins [50, 57–59]. This explanation is referred to as olefin readsorption and secondary reactions (ORSR). Another explanation is that vapor-liquid equilibrium affects the adsorption and desorption of hydrocarbons on the catalyst surface; however, this is only significant in LTFT reactors [55, 56, 60, 61]. Independent of the reason for the departures, a modified ASF model has been developed based on two chain-growth probabilities to describe the observed departure for heavier hydrocarbons [55, 56]. The HC distributions predicted by this double- α ASF model are illustrated by the black lines in Fig. 3.4.

ASF-based models can be employed to estimate the HC distribution of a reactor

⁴Product selectivity is used liberally in FT literature. It is most commonly used to specify the mass fraction of products within a specific carbon number range (e.g., the mass fraction of hydrocarbons between C_1 – C_4 relative to all hydrocarbons) or the type of species (e.g., the mass of paraffins produced relative to all other products).

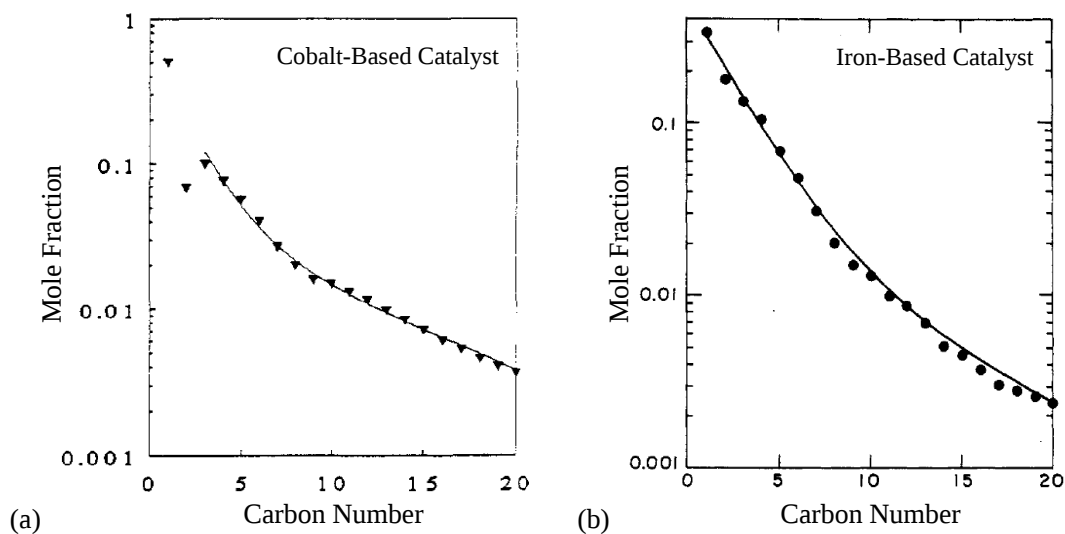


Figure 3.4: Hydrocarbon product distributions from two different slurry reactors. Dots are experimental measurements, and solid lines are calculated by the double- α ASF model [55, 56]. (a) Cobalt-based catalyst, from [55]. (b) Iron-based catalyst, from [56].

by using chain-growth probabilities estimated from empirical distributions of similar reactors. The models do not specify the types of hydrocarbons or their phases. Furthermore, they do not predict the concentrations of hydrocarbons lighter than C_3 very well (as shown in Fig. 3.4a). For a specified syngas composition and empirical chain-growth probabilities, ASF-based models can be employed in conjunction with assumptions about Eqs. (3.1)–(3.6) (e.g., only paraffins and olefins, WGS reaction is in equilibrium or inactive) and/or empirical data or fits (e.g., olefin-to-paraffin ratios) to calculate a reactor’s overall HC composition. Vapor-liquid equilibrium (VLE) models can then be employed to calculate the phases of the products. This approach was used in several studies [61–68].

Several kinetic models based on empirical data have been developed to calculate overall HC composition [57, 58, 60, 69, 70]. The reviewed kinetic models all limited the possible products to paraffins and olefins, and at most methanol, ethanol, and propanol. FT kinetic models are derived based on the observed performance of a specific reactor and catalyst—typically at laboratory scale. As a result, they are

generally not robust enough to be applied across reactor designs and catalysts. Furthermore, in order to use kinetic models, specific data about the reactor are required such as reactor geometry, gas velocity, and catalyst activity. As with ASF-based models, kinetic models do not predict the phase of the HC products. Several studies that used kinetic models to calculate overall HC composition also employed VLE models to calculate their phases [57, 58, 60, 67, 68, 71, 72].

The VLE models employed in the cited FT literature were either developed in house [57, 58, 60, 61, 64, 71, 72] or based on pre-defined models provided in Aspen Plus [62, 63, 65–68], a commercial software developed by Aspen Technology, Inc. Depending on the desired level of detail and accuracy, calculating the VLE compositions and phases of slurry reactor products can require a significant amount of empirically-derived property data. The main difficulty in calculating VLE for slurry reactor products is the treatment of non-hydrocarbon liquids and gases. The gaseous and liquid products produced by slurry reactors contain non-hydrocarbons in both phases. Some studies have even suggested the presence of a third liquid phase—an aqueous phase with trace amounts of HC liquids and gases and non-hydrocarbon gases [73–75]. VLE models based on two- and three-parameter equations of state (e.g., van der Waals, Redlich-Kwong, Soave-Redlich-Kwong, Peng-Robinson) are not capable of accurately predicting the concentrations of non-hydrocarbons species in two phases, let alone in three phases. Several VLE models based on modified three-parameter equations of state and empirical property data (e.g., K-factors, interaction coefficients) have been proposed to model the concentrations of non-hydrocarbon species in two- and three-phase mixtures [61, 72, 73, 76–78]. The empirical property data required to implement these modified VLE models (if available) is typically limited to a narrow range of temperatures, pressures, and compositions.

Another difficulty associated with modeling slurry reactors is in modeling catalyst separation. In slurry reactors, the catalyst particles are suspended in the liquid phase within the reactor. As liquid products are extracted from the reactor, so are some of the catalyst particles. Catalyst particles can be separated through the use of filters or cyclones, or by phase manipulation through a technique referred to as *near critical extraction*. However, the methods used in commercial slurry reactors are not

publicly disclosed. The majority of the published studies that model slurry reactors ignored the presence of catalyst all together. Bailes et al. [72] modeled catalyst separation through near critical extraction using a VLE model based on a modified three-parameter equation of state and empirical data from the literature. Studies performed by Bechtel Corp. [65, 66] modeled catalyst separation using ASPEN Plus and “proprietary” information provided by Syncrude Technology, Inc., a commercial catalyst provider.

The same type of empirically-derived information required to model slurry reactors is required to model downstream product processing and upgrading equipment. The amount of information depends on the desired end products—fully upgraded gasoline and diesel, or raw naphtha and distillate. Modeling the production of gasoline and diesel requires information sufficient for essential modeling an entire oil refinery, whereas modeling the production raw naphtha and distillate only requires information sufficient for modeling distillation and hydrocracking. Technical systems analysis of both product processing and upgrading options in a GTL system with a slurry reactor have been performed by Bechtel Corp. [65, 66]. The analytical tools used to model both processes were developed in Aspen Plus and based on empirical data provided by commercial vendors (both proprietary and publicly available information).⁵

The off-gases produced during product processing and upgrading can be recycled back to the reformer or FT reactor, combusted to produce power, or a combination of all three. Recycling off-gas influences the composition of the syngas entering the FT reactor until steady-state is reached. In order to model off-gas recycling, the dynamic behavior of the FT reactor and downstream processing and upgrading equipment must be able to be modeled, which requires additional information. The Bechtel study with refinery integration modeled full-recycling of the off-gases [65], and the other Bechtel study modeled a once-through reactor with the off-gases combusted in a gas turbine combined cycle to produce power [66]. Again, the analytical tools used

⁵In an email conversation with one of the researchers from Bechtel Corp. that developed their models, it was asked how they modeled aqueous liquid phases in their slurry reactor and distillation models. The researcher’s response was that they “checked a box in Aspen that did not allow for a separate aqueous phase” in their reactor model, but that they had “no empirical basis for this decision”. In their distillation model, they allowed a separate aqueous phase, but assume gas solubility is negligible.

to model both processes were developed in Aspen Plus and based on empirical data provided by commercial vendors. Two other systems analysis studies [67, 68] also modeled full-recycling of the off-gases. However, these studies do not specify how the dynamic behavior of the system was modeled.

In choosing a system architecture and developing component models to perform exergy analysis on a GTL process with a slurry reactor, the availability of empirically-derived information and the capability of analytical tools played major roles. The lack of information sufficient for implementing kinetic models to calculate the slurry reactor's output composition led to the decision to calculate product composition based on a double- α ASF model, assumptions about Eqs. (3.1)–(3.6), and empirically-based adjustments for lighter hydrocarbons. The lack of information sufficient for modeling the dynamic behavior of the slurry reactor and downstream processing and upgrading equipment led to the decision to model a once-through system with co-power production via a combined-cycle gas turbine. The lack of information sufficient for modeling an entire oil refinery led to the decision to only model the production of raw naphtha and distillate products. The lack of empirically-derived property data sufficient for implementing modified VLE models to calculate the compositions of three-phase mixture led to the decision to use standard VLE models with assumptions about the number and composition of phases. And lastly, the lack of controllability, transparency, and flexibility offered by analytical tools provided by commercial software—specifically for VLE calculations—lead to the decision to develop analytical tools in house for calculating VLE. The details of the analytical tool developed for this analysis are provided in App. C. The following subsection discusses the modeled GTL system in more detail.

3.3.3 Modeled GTL Systems

A process flow diagram of the modeled GTL system is shown in Fig. 3.5. The model can be broken-down into four stages: (1) syngas production and clean-up, (2) FT synthesis and syncrude (naphtha and distillate) recovery, (3) heat integration, and (4) combined cycle power production. The main components of the syngas production

and clean-up stage are the partial oxidation (POX) reformer with water moderation, air separation unit (ASU), syngas cooler (SGC), condenser, and carbon separation unit (CSU). The main components in the FT synthesis and syncrude recovery stage are the FT reactor (FTR), vapor cooling unit, pressure swing adsorption (PSA) unit, hydrocracker, and liquid cooling unit.

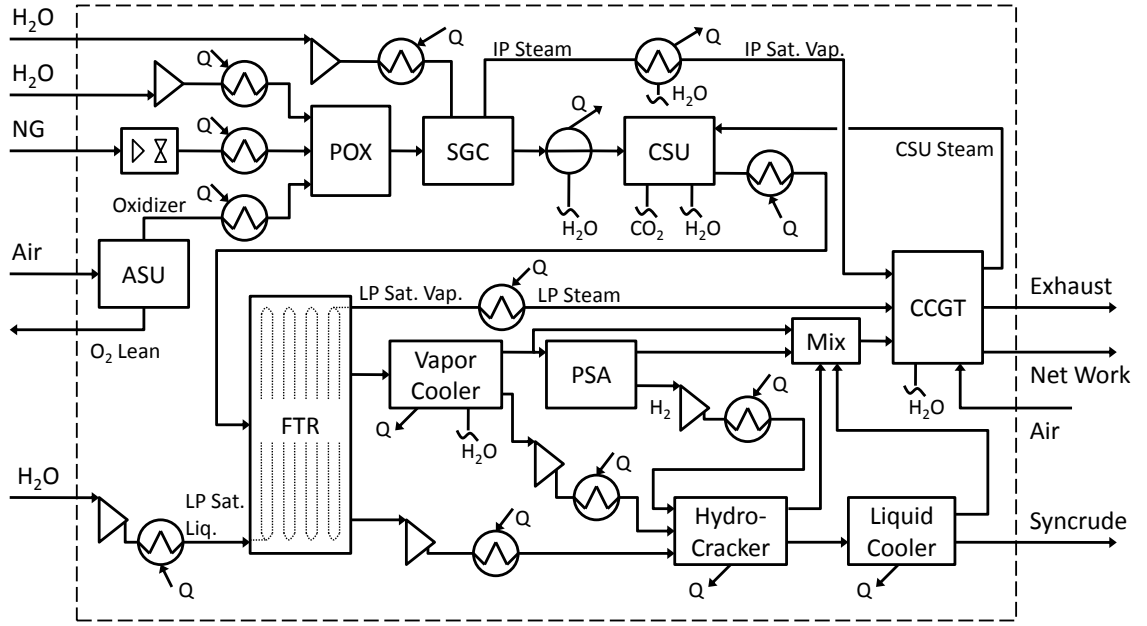


Figure 3.5: System diagram of the GTL co-power production power plant. The acronyms stand for air separation unit (ASU), partial oxidation reformer (POX), syngas cooler (SGC), carbon dioxide separation unit (CSU), Fischer-Tropsch reactor (FTR), pressure swing adsorption (PSA), combined-cycle gas turbine (CCGT).

A water-moderated POX reformer was selected for this model to provide comparisons with the reformer options modeled the Bechtel studies—an ATR in [66], and a SMR and POX reformer combination in [65]. The ASU is modeled as a black box based on the performance of commercial cryogenic air separation units [79, 80]. The input parameters to the ASU model are the inlet and outlet temperatures and pressure, O_2 separation effectiveness and product purity, and the amount of work required per kg of O_2 separated. The POX reformer model iterates on the amount of oxygen required to produce a specified outlet H_2/CO syngas ratio (set by the FT reactor model)

for a specified inlet temperature, pressure, and flow rates of natural gas and water. The inlet streams to the POX reformer are pre-heated and compressed/pumped to the specified inlet temperature and pressure. The hot syngas exiting the POX reformer is assumed to be in equilibrium. The syngas is cooled in the SGC and condenser before entering the CSU. The SGC produces intermediate-pressure steam for use in heat integration and the combined-cycle gas turbine (CCGT). The CSU is modeled as a black box based on the performance of an amine CO_2 separation process [79, 81]. The input parameters to the CSU model are the inlet and outlet temperatures and pressure, CO_2 separation effectiveness and product purity, and the amount of work and steam required per kg of CO_2 separated. Following the CSU unit, the cleaned syngas is heated to the inlet FTR temperature. The inlet pressure of the POX reactor is set based on the FTR pressure and the pressure drops in the POX reactor, SGC, condenser, CSU, and FTR pre-heater.

The FT reactor is modeled as a black box based on the operating conditions and parameters reported in literature for slurry reactors that use cobalt-based catalyst [55, 65, 66, 69, 70]. The inputs to the FT reactor model are the syngas conversion efficiency, overall product hydrocarbon distribution, outlet temperature, and pressure loss. The overall product hydrocarbon distribution is based on a double- α ASF model [56]. Methane and ethane concentrations are adjusted based on empirical data [61]. It is assumed that the WGS reaction is inactive (i.e., no CO_2 is produced inside the reactor) and that only paraffin hydrocarbons are produced (i.e., no olefins or alcohols). With these two assumptions, Eq. (3.1) and the syngas conversion efficiency provide enough information to calculate the overall outlet composition. A flash VLE calculation is then performed using the overall outlet composition to determine the compositions of the liquid and vapor streams exiting the FTR. This flash VLE calculation is performed by assuming that only hydrocarbon liquids are present in the liquid phase (i.e., no gas or water solubility and no separate aqueous phase). The FT reactor is cooled by producing low-pressure steam for use in heat integration and the CCGT.

The liquid hydrocarbon stream exiting the FT reactor is pumped and heated to the hydrocracker inlet pressure and temperature. The FT reactor vapor stream

is cooled to recover liquid FT products and separate water. The vapor cooler is modeled using a flash VLE calculation and assuming that the condensed water is pure (i.e., no gas or hydrocarbon liquid solubility) and only hydrocarbons are present in the recovered FT liquid phase (i.e., no gas or water solubility). The recovered FT liquid phase exiting the vapor cooler is pumped and heated to the hydrocracker inlet pressure and temperature. A portion of the cool vapor phase exiting the vapor cooler (lighter hydrocarbons, H_2 , CO, H_2O) is fed to a PSA unit to separate H_2 for use in the hydrocracker, and the rest is sent to the CCGT. The PSA is modeled as a black box based on commercially available units [65, 66, 79]. The input parameters to the PSA model are the inlet and outlet temperatures and pressure, H_2 separation effectiveness and product purity, and the amount of work required per kg of H_2 separated. The near pure H_2 product stream exiting the PSA unit is compressed and heated to the hydrocracker inlet pressure and temperature, and the purge gas exiting the PSA is sent to the CCGT.

The hydrocracker is modeled as a black box based on the performance of commercially available selective hydrocrackers described in [82]. The hydrocracker model uses a weighted empirical distribution for the amount of hydrocarbons heavier than C_{21} that are cracked to shorter chain hydrocarbons in the distillate range (C_{14} - C_{19}). The model calculates the amount of H_2 necessary to produce the overall outlet composition, which is met by adjusting the PSA load. A flash VLE calculation is performed to determine the compositions of the liquid and vapor streams exiting the hydrocracker. The hot liquid stream exiting the hydrocracker is cooled and expanded in the liquid cooler. The liquid phase exiting the liquid cooler is the FT syncrude (raw naphtha and distillate products), and the hot vapor stream exiting the hydrocracker is sent to the CCGT.

An important aspect of any high temperature energy system is heat integration, especially when trying to minimize exergy destruction. The heat integration scheme used in the model was chosen to minimize exergy destruction while being constrained by the system's architecture. A diagram of the heat integration scheme and a discussion of its details are provided in App. C. As shown in Fig. 3.5, the unconverted hydrocarbon vapor streams are mixed and sent to the CCGT along with the LP and

IP steam produced through heat integration. The CCGT is modeled based on the operating conditions and component performances of the GE STAG combined cycle product line [83]. A diagram of the CCGT and a discussion of its details are also provided in App. C.

3.3.4 Selected Results

The GTL model was exercised using operating conditions and parameters based on published values for commercial equipment. The values used in the analysis are discussed in App. C. Selected results from the analysis are presented here to illustrate the utility of exergy analysis for quantifying technical performance and providing performance information for technical decision making. Additional results are provided in App. C.

The exergy and first-law efficiencies of the GTL system are summarized in Table 3.1. Both the overall exergy and first-law efficiencies are approximately 58%, which is in agreement with the efficiencies calculated using the system inputs and outputs reported in Bechtel’s analysis [66]. The GTL-only efficiency provides a performance metric for the first two stages of the system—syngas production and clean-up, and FT synthesis and syncrude. On an exergy basis the GTL-only efficiency is approximately 73%, whereas on a first-law basis it is approximately 91%. This difference is primarily due to the energy content of the IP, LP, and CSU steam being higher than their exergy content. The energy content of steam does not account for its quality, or work potential, whereas its exergy does. This is one of the disadvantages of using first-law efficiencies as performance metrics for systems that use or produce heat. The CC-only efficiency provides a performance metric for the combined cycle. As with the GTL-only efficiencies, the difference between the efficiency calculated on an exergy and energy basis is due to the way in which the steam is valued. The CC-only exergy efficiency is in agreement with the efficiency values published by GE when taking into account the influence of the IP, LP, and CSU steam [83].

Exergy analysis provides the ability to determine the fate of the exergy input to a system—both on system and component levels. The only exergy input to the GTL

Efficiency	Type	Definition	Value
Overall	Exergy	$\frac{X_{SC} + W_{Net}}{X_{NG}}$	58.3 %
	First-Law	$\frac{LHV_{SC} + W_{Net}}{LHV_{NG}}$	57.8 %
GTL-Only	Exergy	$\frac{X_{SC} + X_{CC\ Gas} + X_{LP\ Steam} + X_{IP\ Steam}}{X_{NG} + X_{CSU\ Steam} + X_{Water} + W_{Input}}$	73.2 %
	First-Law	$\frac{LHV_{SC} + LHV_{CC\ Gas} + Q_{LP\ Steam} + Q_{IP\ Steam}}{LHV_{NG} + Q_{CSU\ Steam} + W_{Input}}$	91.3 %
CC-Only	Exergy	$\frac{W_{CC\ Net} + X_{CSU\ Steam}}{X_{CC\ Gas} + X_{LP\ Steam} + X_{IP\ Steam}}$	59.6 %
	First-Law	$\frac{W_{CC\ Net} + Q_{CSU\ Steam}}{LHV_{CC\ Gas} + Q_{LP\ Steam} + Q_{IP\ Steam}}$	41.7 %

Table 3.1: Summary of efficiency calculations. Variables stand for exergy (X), lower heating value (LHV), heat (Q), and work (W). Subscripts stand for syncrude (SC), natural gas (NG), combined-cycle gas ($CC\ Gas$), low-pressure steam ($LP\ Steam$), intermediate-pressure steam ($IP\ Steam$), carbon separation unit steam ($CSU\ Steam$).

system is the chemical exergy of the natural gas (water and air are modeled as having zero exergy). Figure 3.6a illustrates a break down of the natural gas exergy input to the system. The figure shows that 58% of the natural gas exergy is converted to desired product, with 43% in the syncrude and 15% as electricity. Of the remaining natural gas exergy, 40% is destroyed within the system and 2% is discharged from the system as unused exergy to the environment. The discharged exergy is transferred from the system in the exhaust and water from the combined cycle, oxygen-lean air from the ASU, CO_2 and water from the CSU, and water from the SGC condenser and vapor cooler. The ability of exergy analysis to quantify how a system uses its input exergy provides insight into the system's performance that eludes first-law analysis. First-law analysis concludes that all of the energy not contained in the syncrude and

electricity produced by the system (approximately 42%) is discharged from the system as unused energy to the environment, as shown in Fig. 3.6b. This can lead to two misconceptions: (1) that the waste energy can be harnessed and used to produce work, and (2) that the inefficiencies in the system are caused by transferring energy from the system. However, as the Fig. 3.6a shows, only 2% of the energy discharged from the system can theoretically be converted to work and the majority of the inefficiencies occur within the system due to exergy destruction.

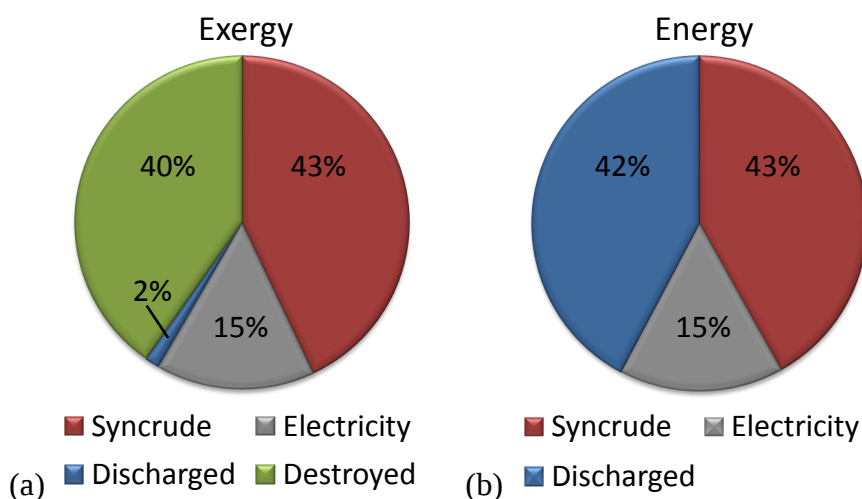


Figure 3.6: (a) Natural gas exergy distribution calculated through exergy analysis. (b) Natural gas energy distribution calculated through first-law analysis.

Figure 3.7 shows a break down of the exergy destroyed within the GTL system by component. The locations and relative magnitudes of exergy destruction within the system provide insight into the performance of the system that can be used to make design improvements. The largest amount of the exergy destruction occurs in the POX reformer. This destruction is due to mixing and unrestrained chemical reaction—both of which are inherently irreversible processes. Exergy destruction within the reformer could be reduced by removing the constraints on its outlet H_2/CO syngas ratio and inlet water flow rate, and optimizing the reformer’s exergetic performance based on water and oxygen flow rates. Removing the constraint on the outlet H_2/CO syngas ratio would require a shift reactor downstream of the POX reactor, but before the CSU, in order to adjust the ratio to that required by the FT reactor.

Although a portion of the exergy saved in the POX reactor would be destroyed in the shift reactor, this modification would most likely reduce the overall amount destroyed.

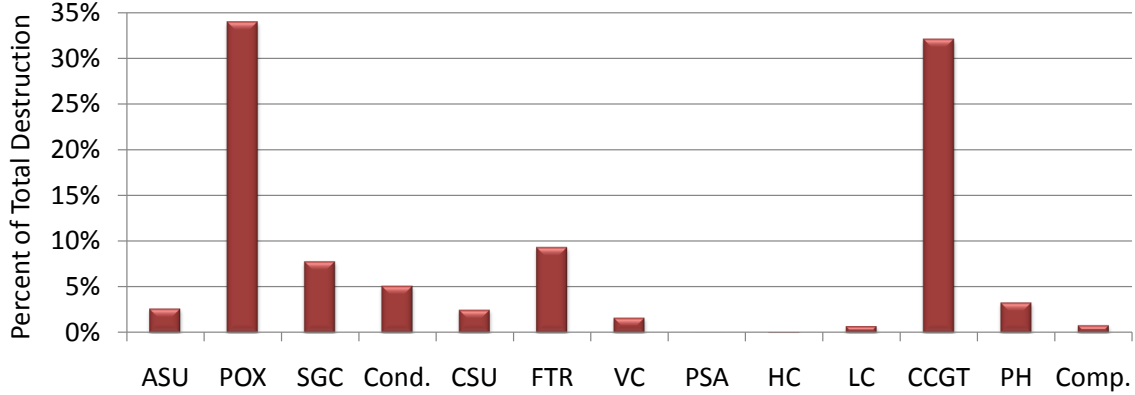


Figure 3.7: System exergy destruction distribution measured as a percentage of its total exergy destruction.

The second largest amount of exergy destruction occurs in the combined cycle. A break down and discussion of the exergy destroyed in the combined cycle is provided in App. C. The third largest amount of exergy destruction occurs in the FT reactor. The exergy destroyed in FT reactor is due to mixing, unrestrained chemical reaction, and heat transfer. Exergy destruction caused by mixing and chemical reaction is unavoidable; however, it could be reduced in the FT reactor by optimizing its operating temperature and pressure. Investigating the influence temperature and pressure had on the reactor's performance was not possible in this analysis because the empirical information used to model the reactor is only valid at the operating conditions used in the analysis. The exergy destroyed due to heat transfer could be reduced by increasing the pressure of the steam such that its saturation temperature is closer to the operating temperature of the reactor. The pressure level used in the model was chosen such that the steam produced could be integrated with the combined cycle, which has fixed pressure-levels based on GE operating specifications.

Exergy analysis also has the ability to provide information for optimizing a system's performance by performing a parametric analysis on the system's operating conditions (e.g., by varying a component's operating temperature and pressure). However, in order to perform a parametric analysis, information sufficient for modeling

the system across a range of operating conditions is required. A parametric analysis was not performed in this study because the empirical information used to model the ASU, CSU, FT reactor, and hydrocracker is only valid at the conditions they were measured, which were the conditions used in the analysis. Exercising the model outside of these conditions would not have provided accurate information sufficient for system optimization.

As discussed in the previous subsection, the FT reactor was modeled based on empirical data and its outlet phases and compositions were calculated using a (constrained) flash VLE algorithm developed in house. The results of this modeling approach are shown in Fig. 3.8. The results are in good agreement with published empirical distributions for cobalt-based slurry reactors operating at similar temperatures and pressures [55, 61, 64]. The outlet distributions for the vapor cooler and hydrocracker are provided in App. C, and are also in good agreement with published empirical distributions.

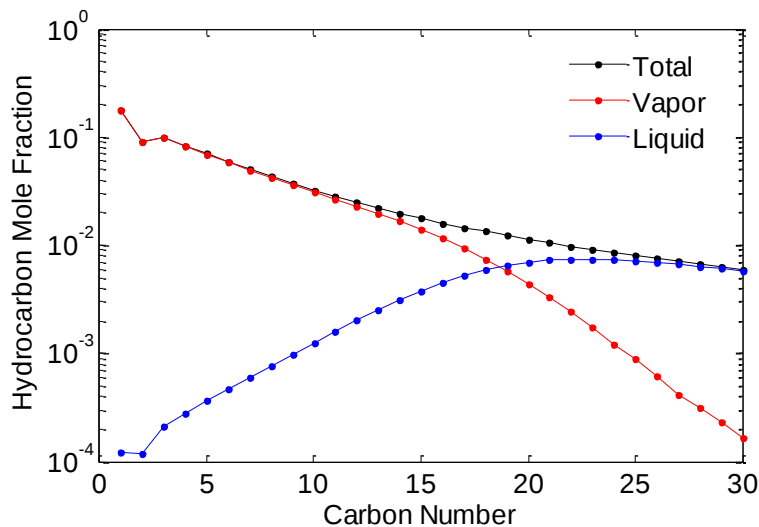


Figure 3.8: Fischer-Tropsch reactor outlet hydrocarbon distribution.

3.3.5 Discussion

The analysis presented here illustrates the influence information and analytical tools can have on the application of exergy analysis on an individual system basis. The choice of system architecture (e.g., once-through), the methods used to model individual components (e.g., black box), and the operating conditions for exercising the system model were all influenced by the availability of information and the capability of analytic tools for modeling FT slurry-reactor processes. As a result, the analysis was only able to achieve two of the three possible objectives of exergy analysis: (1) calculate system efficiency, and (2) quantify the locations and magnitudes of exergy destruction. The third objective—optimize system performance—was not attempted because of the limitations imposed by the empirical information used in the model.

The system efficiency provides a technical performance metric for how well the system accomplishes its objective—conversion of natural gas to synthetic crude oil. The locations and magnitudes of exergy destruction within the system provide technical performance information for use in system design (e.g., replace the POX reformer with an ATR). However, since the model was limited to fixed operating conditions, the analysis does not provide performance information for system optimization.

Recognizing and understanding the influence that information and analytical tools can have on the application of exergy analysis (or any thermodynamic technical analysis technique for that matter) is important when using the performance results for technical decision making. When using performance results provided by technical systems analysis for decision making on an individual system basis, the following questions should be asked:

- What is the architecture of the system (e.g., full-recycle, once-through)?
- Why was this architecture modeled (e.g., based on existing architectures, limited by information or analytical tools)?
- How were the components modeled (e.g., analytical tools, property models)?
- What information was used in the model (e.g., empirical data)?
- What operating conditions were used in exercising the model (e.g., within material limitations, within bounds of empirical data)?

Answering these questions requires information about the analysis, which can often be difficult to obtain—especially when using published studies. However, the answers to these questions are needed before the performance information should be used in technical decision making.

To illustrate the utility of answering these questions before using performance information in decision making, consider the published systems analysis studies of FT processes based on slurry reactors [62, 63, 67, 68]. All of these studies modeled the slurry reactor using ASF-based distributions in conjunction with kinetic models (based on empirical information) and assumptions about products (only paraffins) to model the hydrocarbon distribution, and predefined VLE models provided in Aspen Plus to calculate outlet phases and compositions. They all also used predefined distillation models provided in Aspen Plus to model downstream processing and upgrading. Despite the limitations imposed by the use of empirical data in the kinetic models and the fixed distributions calculated by ASF-based models, all of the studies performed parametric analysis outside of the operating conditions for which the empirical data and distributions are valid. Furthermore, all of the studies except [62], modeled full-recycle of the off-gases produced during the process—again, not taking into account the inherent limitations of their models. As a result of the models, information, analytical tools, and operating conditions used in these studies, the performance results provided by their parametric analysis are not appropriate for use in system optimization and should not be used in decision making.

3.4 Technical Decision Making Across Energy Systems

The previous section demonstrates the application of exergy analysis for evaluating the technical performance of an energy system, and discusses the utility of the performance information provided by the analysis—specifically the locations and magnitudes of exergy destruction—for decision making on an individual system basis (i.e., system design). We now take a step back to discuss technical decision making across

energy systems.

To provide a framework for having this discussion, a resource/service view of the space in which energy systems operate is proposed. Figure 3.9 illustrates this view, showing several energy transformations and transformation pathways for providing energy services. Energy transformations refer to the conversions of energy carriers from one form to another by energy systems, and transformation pathways refer to a chain of energy transformations used to provide energy services (e.g., transportation, lighting, heating, cooling) from natural resources. Natural resources refer to energy accumulations or energy fluxes that exist or occur naturally within the environment and have the ability to produce work in their surroundings (i.e., the environment). Transportation—an energy service—is explicitly shown in the figure because the pathways for providing transportation are used to illustrate the utility of exergy for evaluating and comparing different options for providing the same service. The transformations and pathways shown in the figure are meant to provide a framework for viewing the energy-system space and facilitate the discussion of technical decision making across energy systems; they are by no means meant to represent all possible energy transformations or transformation pathways.

All transformation pathways begin with natural resources and end with providing an energy service. Natural resources can be categorized as being resource fluxes or accumulations. Resource fluxes include “renewable” resources such as solar radiation, wind, hydro (e.g., tides, waves, rivers), and geothermal heat. Resource accumulations include “non-renewable” resources such as fossil fuels (e.g., crude oil, natural gas, coal) and nuclear matter, and “renewable” resources such as biomass. Energy services are provided by either work, electricity, or heat—all of which are energy carriers.

The conversion of natural resources into energy carriers can be referred to as *resource-to-carrier* transformations. Resource fluxes can be converted into energy carriers such as electricity and biomass, and/or into heat for use as an energy service. Resource accumulations (including biomass) must first be extracted from their natural locations (e.g., sub-surface reservoir, land) before they can be converted into energy carriers such as *fuels* and electricity, and/or into heat for use as an energy service.

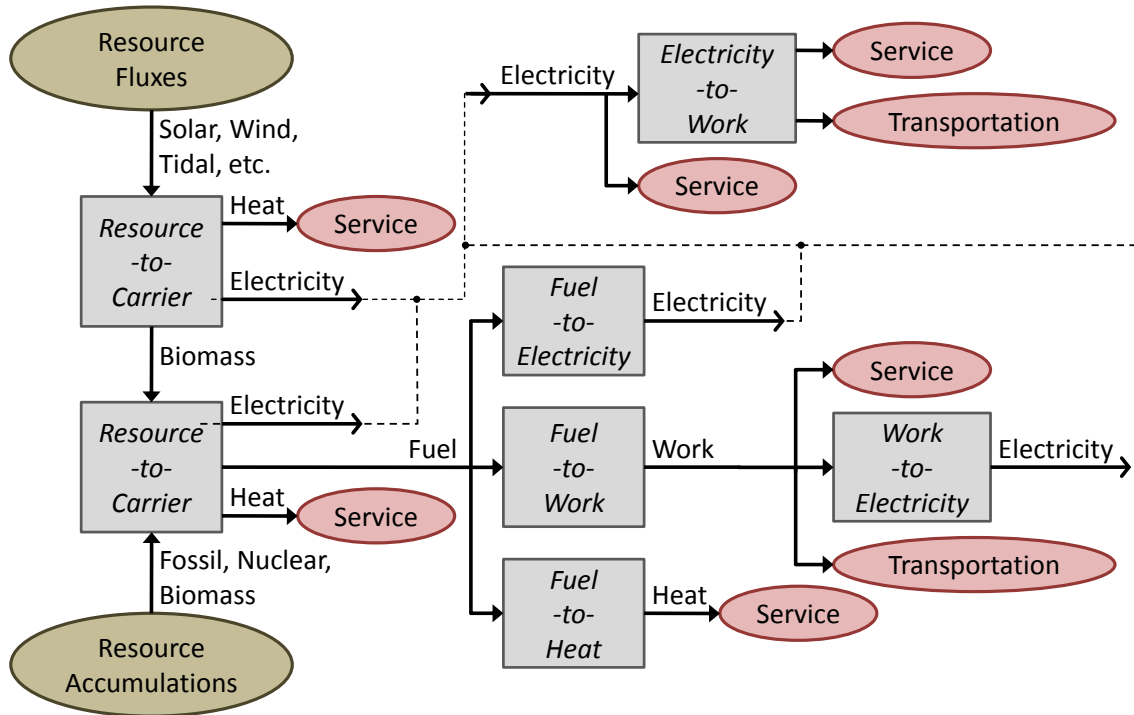


Figure 3.9: Schematic diagram illustrating the various energy transformation pathways used to provide transportation and other energy services (e.g., lighting, heating, cooling).

Fuels can be used to produce electricity, work, and/or heat. *Fuels-to-electricity* transformations refer to the direct conversion of fuels to electricity (e.g., via fuel cells), *fuel-to-work* transformations refer to the conversion of fuels to mechanical work (e.g., via engines), and *fuel-to-heat* transformations refer to the conversion of fuels to provide heat for use as an energy service (e.g., via boilers). Work produced by fuel-to-work transformations can be used to directly provide energy services (both transportation and non-transportation) or to produce electricity through *work-to-electricity* transformations (e.g., via a generator). Electricity produced from resource-to-carrier or work-to-electricity transformations can be used to directly provide energy services (e.g., lighting, heating, cooling) or to produce work through *electricity-to-work* transformations (e.g., via motors). Work produced by *electricity-to-work* transformations can be used to directly provide energy services (both transportation and non-transportation).

Viewing the space in which energy systems operate in terms of services, carriers, and resources provides insight for decision making in energy. The reason why we employ energy systems is to ultimately provide energy services. For a given energy service, decisions are made when choosing energy carriers, energy systems, and natural resources to provide the service. Even before conducting detailed, low-level technical analysis of the kind outlined in the previous sections, there is a larger set of decisions to be made: What are the energy carrier, energy system, and natural exergy resource options for providing a desired service?

Decision making across the possible energy carriers, energy systems, and natural exergy resources for providing a given service requires the ability to evaluate and compare the options on a level playing field. Exergy and exergy efficiency provide this ability. Exergy provides a common metric for valuing energy carriers and natural resources, and exergy efficiency provides a metric for comparing the technical performance of energy systems, transformations, and pathways across system architectures, energy carriers, and natural resources.

The previous section demonstrates the application of exergy analysis for evaluating (at a low-level) the technical performance of a resource-to-carrier energy transformation with specified *analysis constraints*—i.e., the conversion of natural gas to liquid transportation fuels via FT synthesis. As constraints on the analysis are removed, the boundaries on the analysis extend—allowing for other possible energy carriers, energy systems, and natural resources for providing the desired service (i.e., ground transportation). For example, removing the upstream constraint on the production of FT liquids opens up the possibility of other hydrocarbon-based resources (e.g., coal and biomass). Removing the system constraint on FT synthesis opens up the possibility for other transformation processes for producing liquid transportation fuels (e.g., biological process for producing alcohol-based fuels). Removing the downstream constraint on the production of liquid transportation fuels as the energy carrier opens up the possibility for other energy carriers (e.g., electricity, gaseous fuels), energy systems (e.g., electric motors, fuel cells), and natural resources (accumulations and fluxes). The same analysis methodology demonstrated in the previous section can be applied to evaluate and compare the technical performance of all possible energy

systems, energy transformations, and pathways—albeit with limitations imposed by information and analytical tools.

Recognizing the constraints on an analysis and why or how they are imposed is critically important for decision making across energy options. Constraints can be endogenously imposed by the desired service (e.g., ground transportation requires work as the method of providing the service) or exogenously imposed by the decision maker (e.g., liquid transportation fuels for I.C. engine-based vehicles). Both types of constraints narrow the possible energy options—resources, energy carriers, energy transformations, architectures, energy systems—available for consideration in the decision-making process. However, exogenous constraints can be removed—allowing for other energy options to be considered. Recognizing that exogenous constraints (which are often imposed without their own recognition) can be removed is essential for decision making in energy, especially for large-scale, long-time horizon energy decisions such as those for meeting future transportation needs. Viewing the space in which energy systems operate in terms of services, carriers, and resources provides insight for decision makers to ask questions about other energy options for providing a desired energy service.

3.5 Conclusion

Technical decision making in energy occurs across levels—from the high-level decisions made in choosing a method of service to the low-level decisions made in designing an energy system. At the highest levels, decisions made in choosing a method of providing a service or the natural resources to be mobilized can restrict the possible options available for consideration in decision making. In both cases, proscriptions like these are restrictive in the sense that they narrow the technical options one considers in the decision-making process, occasionally without explicit recognition of doing so. Moving down a level, proscriptions set by pre-defined architectures for providing a chosen method of service further narrow possible options for exploration.

Although analysis is often performed using first-law principles, it is important

to recognize the role of the second law for comparing systems within the same architecture. Even more important is the role of exergy for comparing options across architectures as well as up to the highest levels of decision making. The utility of exergy analysis has been demonstrated at the system level and its application at the highest levels has been discussed.

Moving down to the lowest level, the ability of thermodynamic analysis to evaluate energy systems further restrict the options available for consideration. Restrictions on the ability to perform thermodynamic analysis include reliance on published data, empirical data, phase relationships, properties, analytical tools, proprietary information, etc. All of these issues have been shown to limit the ability of technical analysis techniques to provide adequate performance information for decision making in energy.

Chapter 4

A Thermodynamics-Based Analysis Framework for Evaluating Environmental Performance

This chapter presents an analysis framework based on thermodynamic principles and analysis techniques—namely exergy and exergy analysis—for evaluating the environmental impact of energy systems. The framework utilizes the recognition that exergy is a form of environmental free energy to extend the models and techniques used in technical exergy analysis to the environment. This extension enables the locations, magnitudes, and types of environmental impact caused by energy systems—both upstream and downstream—to be quantified under a common metric amenable to comparisons.

The chapter begins with a discussion of the connection between exergy and free energy, and the ability of exergy to provide a measure of the potential to drive change in the environment. Next, an expanded model of the environment is introduced, followed by a discussion of how anthropogenic activity—energy systems in the present study—interact with and impact the environment. The following section outlines the application of environmental exergy analysis for quantifying the environmental impact of anthropogenic activity. The concept of *anthropocentric sensitivity* is then introduced, and its role in decision making is discussed. The chapter concludes with a

discussion of the application and utility of the analysis framework for decision making in energy.

4.1 Exergy as a Measure of the Potential to Drive Environmental Change

The potential for work extraction exists within all non-equilibrium systems. The maximum (i.e., reversible) amount of work that can be extracted from a non-equilibrium system under specified interaction constraints is the system's *free energy*. For example, the maximum amount of work that can be extracted from a closed system constrained to equilibrate at constant temperature and pressure is the Gibbs free energy (ΔG), and at constant temperature and volume it is the Helmholtz free energy (ΔA). Exergy is, by definition, the maximum amount of work that can be extracted from a system comprised of a resource and its environment, constrained to equilibrate at the conditions of the environment. Exergy is therefore the free energy of a resource relative to its environmental surroundings; in other words, exergy is the *environmental free energy* of a resource. A derivation of exergy similar to that of other forms of free energy is provided in App. B.

The connection between exergy and free energy is significant because of the connection between free energy and the potential to drive change. In order for a system to have free energy, the system must be out of equilibrium, and all systems that are out of equilibrium have the potential to drive change [84]. Therefore, all forms of free energy inherently measure the ability to drive change—albeit with differing interaction constraints. The free energy of a closed system can be extracted from the system as work, or if no work is extracted, change will occur within the system in the form of state change and entropy generation.

To demonstrate the connection between free energy and exergy, and the concept of exergy as a measure of the potential to drive environmental change, several model systems are considered. First, consider a two-reservoir system of differing thermodynamic states initially restrained from interaction, as shown in Fig. 4.1. The γ

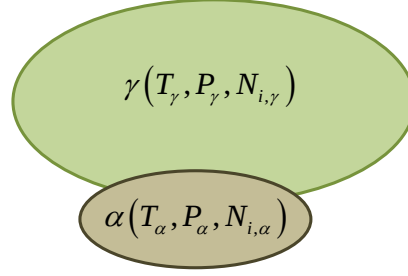


Figure 4.1: Two-reservoir system of differing thermodynamic states.

reservoir is sufficiently large with respect to the α reservoir that it can be modeled as a thermodynamic reservoir (i.e., having a fixed intensive state). Each reservoir is initially in internal equilibrium, but not in mutual equilibrium. The free energy of the joint system is measured by the maximum amount of work that can be extracted as the system equilibrates reversibly. Since the γ reservoir is large with respect to the α reservoir, the final (i.e., equilibrium) intensive state of the system is the original state of the γ reservoir. Therefore, the free energy of the system is measured as the work potential of the α reservoir relative to the γ reservoir. The free energy of this two-reservoir system is given by:

$$\begin{aligned}
 W_{max, System} &= W_{max, \alpha} \\
 &= U_\alpha + P_\gamma V_\alpha - T_\gamma S_\alpha - \sum_i \mu_{i,\gamma} N_{i,\alpha} - \sum_j \left[\sum_i \mu_{i,\gamma} \left(\frac{\nu_{ij}}{\nu_j} \right) \right] N_{j,\alpha} \quad (4.1)
 \end{aligned}$$

where all extensive properties are evaluated at the initial state of the α reservoir, all intensive properties are evaluated at the state of the γ reservoir (which is constant), subscripts i and j refer to species present and not present in the γ reservoir, respectively, and ν_j and ν_{ij} are the stoichiometric coefficients for the reaction of species. A detailed derivation of Eq. (4.1) is presented in App. B.

Equation (4.1) is equivalent to the traditional equation for internal exergy derived in App. A if the state of the γ reservoir is defined as the state of the reference environment, or dead state (i.e., if $T_\gamma = T_o$, $P_\gamma = P_o$, and $\mu_{i,\gamma} = \mu_{i,o}$ for all i). Considering the γ reservoir to be an environmental reservoir, then the α reservoir

has exergy relative to its environment, the γ reservoir. The exergy of the system is free to be extracted as work. If the reservoirs are permitted to interact without work extraction, exergy will be transferred from the α reservoir to the γ reservoir causing exergy destruction, and therefore entropy generation, to occur within the γ reservoir.¹ Exergy will continue to be transferred and destroyed until equilibrium is reached. At equilibrium, the entropy of the system is maximized, and the potential for change no longer exists. The change that occurs within the system is driven by the fact that the two reservoirs are out of equilibrium. In order for no change to occur, the α reservoir must initially be in equilibrium with the γ reservoir, and therefore not have any potential to drive change (i.e., zero exergy, or zero free energy).

Next, consider a three-reservoir system of differing thermodynamic states initially restrained from interaction, as shown in Fig. 4.2. Again, the γ reservoir is sufficiently large that it can be modeled as a thermodynamic reservoir. Each reservoir is initially in internal equilibrium, but not in mutual equilibrium. Since the final intensive state of the system is that of the γ reservoir, the free energy of the system is measured as the sum of the individual work potentials of the α and β reservoirs relative to the γ reservoir. The free energy of the system is given by:

$$W_{max, System} = W_{max, \alpha} + W_{max, \beta} \quad (4.2)$$

$$W_{max, \alpha} = U_{\alpha} + P_{\gamma}V_{\alpha} - T_{\gamma}S_{\alpha} - \sum_i \mu_{i, \gamma} N_{i, \alpha} - \sum_j \left[\sum_i \mu_{i, \gamma} \left(\frac{\nu_{ij}}{\nu_j} \right) \right] N_{j, \alpha} \quad (4.3)$$

$$W_{max, \beta} = U_{\beta} + P_{\gamma}V_{\beta} - T_{\gamma}S_{\beta} - \sum_i \mu_{i, \gamma} N_{i, \beta} - \sum_j \left[\sum_i \mu_{i, \gamma} \left(\frac{\nu_{ij}}{\nu_j} \right) \right] N_{j, \beta} \quad (4.4)$$

where, again, the intensive properties of the γ reservoir are constants.

Equations (4.3) and (4.4) are equivalent to the internal exergy of the α and β reservoirs, respectively, if the state of the γ reservoir is defined as the state of the reference environment. Considering the γ reservoir to be an environmental reservoir, then if the α and β reservoirs are permitted to interact without work extraction, exergy will

¹Exergy destruction is equivalent to lost work, and is linked to entropy generation through the Gouy-Stodola theorem: $X_{Destroyed} = W_{Lost} = T_o S_{Gen}$ [10, 85].

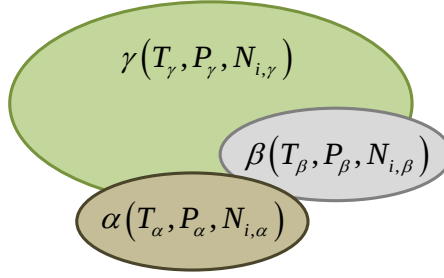


Figure 4.2: Three-reservoir system of different thermodynamic states.

be transferred between the reservoirs, causing both exergy change and destruction to occur within each reservoir. The relationship between the exergy transfers, changes, and destructions is shown through the exergy balances for the individual reservoirs and system:

$$\alpha : \delta X_{\beta \rightleftharpoons \alpha} = dX_\alpha + \delta X_{Dest.,\alpha} \quad (4.5)$$

$$\beta : \delta X_{\alpha \rightleftharpoons \beta} = dX_\beta + \delta X_{Dest.,\beta} \quad (4.6)$$

$$System : dX_{System} = dX_\alpha + dX_\beta = -\delta X_{Dest.,\alpha} - \delta X_{Dest.,\beta} \quad (4.7)$$

where $\rightleftharpoons$ represents a net transfer (e.g., $\delta X_{\beta \rightleftharpoons \alpha} \equiv \delta X_{\beta \rightarrow \alpha} - \delta X_{\alpha \rightarrow \beta}$). Equations (4.5) and (4.6) show that, at any instant, the net exergy transferred to a reservoir is equivalent to the sum of the exergy change and destruction within the reservoir. Equation (4.7) shows that the change in exergy of the system is equivalent to the sum of the exergy destruction within the reservoirs. In order for no change to occur, the α and β reservoirs must initially be in equilibrium, and therefore not have a potential to drive change relative to one another.

Both of the example systems just considered involved a thermodynamic (“infinite”) reservoir that, when considered to be an environmental reservoir, provides a reference state from which the exergy of the other reservoirs could be defined. The inherent principle of exergy as a measure of the ability to drive change is not limited to systems involving a large environmental reservoir. To illustrate this, consider the same three-reservoir system shown in Fig. 4.2, but with all reservoirs considered to be environmental reservoirs of similar size. Since the reservoirs are initially out of

equilibrium, each reservoir has the potential to drive change relative to the other reservoirs. The potential to drive change vanishes when the three reservoirs reach equilibrium. The mutual equilibrium state of the system defines a reference state from which the exergy of the individual reservoirs and system can be measured. In other words, the mutual equilibrium state is a kind of “dead state” from which no change can occur. The exergy of the composite system and individual reservoirs relative to the mutual equilibrium state—referred to here as the reference state—is given by:

$$X_{System} = X_{\alpha} + X_{\beta} + X_{\gamma} \quad (4.8)$$

$$X_{\alpha} = U_{\alpha} + P_{ref}V_{\alpha} - T_{ref}S_{\alpha} - \sum_i \mu_{i,ref}N_{i,\alpha} - \sum_j \left[\sum_i \mu_{i,ref} \left(\frac{\nu_{ij}}{\nu_j} \right) \right] N_{j,\alpha} \quad (4.9)$$

$$X_{\beta} = U_{\beta} + P_{ref}V_{\beta} - T_{ref}S_{\beta} - \sum_i \mu_{i,ref}N_{i,\beta} - \sum_j \left[\sum_i \mu_{i,ref} \left(\frac{\nu_{ij}}{\nu_j} \right) \right] N_{j,\beta} \quad (4.10)$$

$$X_{\gamma} = U_{\gamma} + P_{ref}V_{\gamma} - T_{ref}S_{\gamma} - \sum_i \mu_{i,ref}N_{i,\gamma} - \sum_j \left[\sum_i \mu_{i,ref} \left(\frac{\nu_{ij}}{\nu_j} \right) \right] N_{j,\gamma} \quad (4.11)$$

where the properties of the reference state are considered to be known (or knowable) constants.²

If the reservoirs are permitted to interact, exergy will be transferred between the reservoirs, causing both exergy change and destruction to occur within each of the reservoirs. The relationship between the exergy transfers, changes, and destructions

²Equations (4.8)–(4.11) can also be derived by considering a four-reservoir system composed of the three environmental reservoirs of similar size, and a “large” environmental reservoir that has the same state as the mutual equilibrium state of the other three reservoirs. The state of the “large” reservoir acts as a reference state from which the exergy of the composite system and other three reservoirs can be defined. Therefore, by analogy, the mutual equilibrium state of the three-reservoir system shown in Fig. 4.2 serves as a fiducial state for defining exergy.

is, again, shown through the exergy balances for the individual reservoirs and system:

$$\alpha : \delta X_{\beta \rightleftharpoons \alpha} + \delta X_{\gamma \rightleftharpoons \alpha} = dX_{\alpha} + \delta X_{Dest,\alpha} \quad (4.12)$$

$$\beta : \delta X_{\alpha \rightleftharpoons \beta} + \delta X_{\gamma \rightleftharpoons \beta} = dX_{\beta} + \delta X_{Dest,\beta} \quad (4.13)$$

$$\gamma : \delta X_{\alpha \rightleftharpoons \gamma} + \delta X_{\beta \rightleftharpoons \gamma} = dX_{\gamma} + \delta X_{Dest,\gamma} \quad (4.14)$$

$$System : dX_{System} = dX_{\alpha} + dX_{\beta} + dX_{\gamma} = -\delta X_{Dest,\alpha} - \delta X_{Dest,\beta} - \delta X_{Dest,\gamma} \quad (4.15)$$

where all exergy values are measured relative to the reference state. The above equations show that, at any instant, the net exergy transferred to a reservoir is equivalent to the sum of the exergy change and exergy destroyed within the reservoir, and the change in exergy of the system is equivalent to the sum of the exergy destroyed within all the reservoirs. In order for no change to occur within the system, the reservoirs must initially be in equilibrium, and therefore not have a potential to drive change relative to one another.

In the three isolated, multi-reservoir systems considered, the potential for change exists because the reservoirs are initially out of equilibrium. At equilibrium, the entropy of the systems is maximized (i.e., energy is maximally dispersed), and the potential for change no longer exists. The equilibrium state of isolated systems serves as a reference state from which its free energy (or exergy if the reservoirs are environmental reservoirs) can be measured.

The same methodology used to define the free energy, or exergy, of isolated, multi-reservoir systems can be extended to driven, multi-reservoir systems. To illustrate this, consider a two-reservoir system driven by heat transfer between two large thermal reservoirs, as shown in Fig. 4.3a. Energy is transferred to the system (the α and γ reservoirs) from a high-temperature thermal reservoir, and energy is transferred from the system to a low-temperature thermal reservoir. The α and γ reservoirs are initially in thermal stationary states at the same pressure, but with differing compositions. The initial stationary temperature distribution of the system is shown in Fig. 4.3c.³

³A stationary temperature $T(y)$ implies that mean heat flow is uniform; otherwise there will be an accumulation or depletion of energy within the system, which would require a time-dependent temperature profile [86].

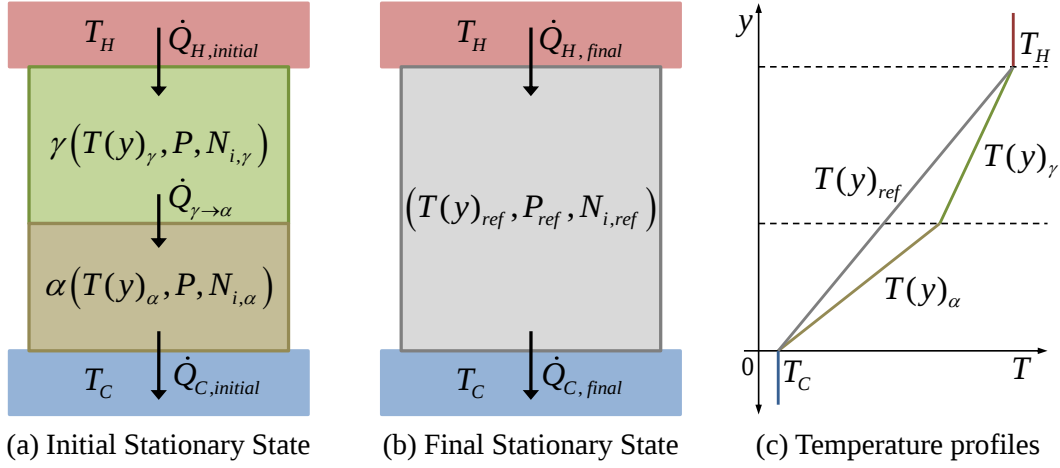


Figure 4.3: (a) Driven, two-reservoir system in thermal stationary states at the same pressure, but with differing compositions. (b) Final (non-equilibrium) stationary state of the system after chemical equilibrium is reached. (c) Temperature profiles of the initial and final stationary systems.

Since the α and γ reservoirs initially have different compositions, each reservoir has the potential to drive change relative to the other. The potential to drive change vanishes when the reservoirs reach chemical equilibrium, and a final (non-equilibrium) thermal stationary state is formed. The final state defines a reference “state” from which the free energy, or exergy, of the individual reservoirs and system can be measured—similar to the mutual equilibrium state for isolated, multi-reservoir systems.

The final, or mutual, stationary state is reached when the entropy generation rate within the system is minimized [86]. This is known as the theorem of Minimum Entropy Production, and applies to all driven systems that are in the linear regime (i.e., it is not limited to systems driven by thermal fluxes).⁴ For this system, if both the α and γ reservoirs are gaseous, and gravitational and buoyancy forces are negligible, the final state will have uniform composition and pressure with a linear temperature distribution, as shown in the Fig. 4.3c. The final stationary state for

⁴*Linear regime* refers to thermodynamic flows (e.g., heat transfer, diffusion, chemical reactions, electrical conduction) that are linear functions of their driving forces (e.g., temperature, concentration, chemical affinity, electric field). The theorem of Minimum Entropy Production is derived in a branch of thermodynamics known as non-equilibrium thermodynamics. For more information refer to the text by Kondepudi and Prigogine [86] and the references within.

the system—referred to here as the reference state—is defined by its pressure (P_{ref}), composition ($N_{i,ref}$), and temperature as a function of position ($T(y)_{ref}$). In general, the reference state for a driven, multi-reservoir system can be defined by its intensive properties as functions of position (e.g., $T_{ref} = T(\mathbf{x})$, $P_{ref} = P(\mathbf{x})$, and $\mu_{i,ref} = \mu_i(\mathbf{x})$ for all i , where $\mathbf{x}$ is a general position vector).

The concepts demonstrated in this section can be extended to analyze environmental change—both natural and anthropogenic. However, in order to extend exergy and exergy analysis to the environment, the traditional representation of the environment used in technical exergy analysis must first be expanded.⁵

4.2 An Expanded Model of the Environment

In technical exergy analysis, the environment is typically modeled based on the properties of the atmosphere—with modifications for solid mineral and liquid substances—as a large reservoir with fast internal relaxation such that its intensive state does not change (i.e., a thermodynamic reservoir)[7]. This type of reference environment simplifies exergy calculations because the final (equilibrium) intensive state of a resource and its environment is equal to the state of the reference environment. It also implies that any exergy transferred from an energy system to the environment only causes exergy destruction within the environment (i.e., no environmental state change). This traditional representation of the environment is sufficient for calculating exergy as a measure of maximum work when performing technical exergy analysis. However, in order to effectively extend the principles of exergy and exergy analysis to analyze environmental change, a more detailed representation is required. This can be accomplished by taking a macroscopic view of the natural environment.

The terrestrial environment can be broken down into three *major* environmental reservoirs: atmosphere, hydrosphere, and lithosphere. The atmosphere is a reference environment of the air (similar to the traditional atmosphere-based reference environment), the hydrosphere is a reference environment of the oceans, and the lithosphere

⁵Technical exergy analysis refers to the application of exergy analysis for quantifying the technical performance of energy systems, as discussed in Ch. 3.

is an aggregated reference environment of the earth's crust and surface water (e.g., lakes, rivers, snow pack). Depending on the specifics of the energy system and type of analysis, the major reservoirs may need to be further broken down into sub-reservoirs, or *minor* reservoirs, in order to provide a suitable representation of the environment. For example, when analyzing a power plant that uses a lake for cooling water, the lake should be broken apart from the lithosphere and modeled as a separate, finite reservoir.

The terrestrial environmental reservoirs serve as large reservoirs for resources to be converted into exergetic products (e.g., work, electricity, commercial fuels, heat).⁶ A diagram of the global exergy resources available for work production is shown in Fig. 4.4. Global exergy resources can be categorized as either exergy accumulations or exergy fluxes. The majority of the work on Earth is produced from accumulated fossil and nuclear resources.⁷ Fossil resources are the byproducts of plant and animal matter that have been converted by the Earth's natural exergy fluxes and processes into higher quality resources (e.g., crude oil, natural gas, coal). They are typically located within the lithosphere and naturally segregated from communication with the other major reservoirs. Nuclear resources are from the origin of the universe and are located within the lithosphere and hydrosphere. Both resources are typically considered non-renewable—nuclear resources because they are finite, and fossil resources because the time scales over which they are replenished are significantly longer than the anthropogenic time scales in which they are extracted and consumed. For modeling purposes, fossil and nuclear resources are represented as individual resource reservoirs located within their respective terrestrial environmental reservoirs.

The Earth's second largest accumulated resource behind nuclear matter is the thermal energy in its mantle and core, which is called crustal thermal energy in Fig. 4.4. Crustal thermal energy is derived from the decay of nuclides in the Earth's interior, the original internal energy from the gravitational collapse of the Earth, and to a lesser extent, the dissipation of tidal forces [87]. The Earth's crustal thermal energy provides a relatively constant flux of exergy through the lithosphere in the

⁶For the sake of brevity, the term work is used to represent all exergetic products.

⁷See App. A for an explanatory discussion of nuclear exergy.

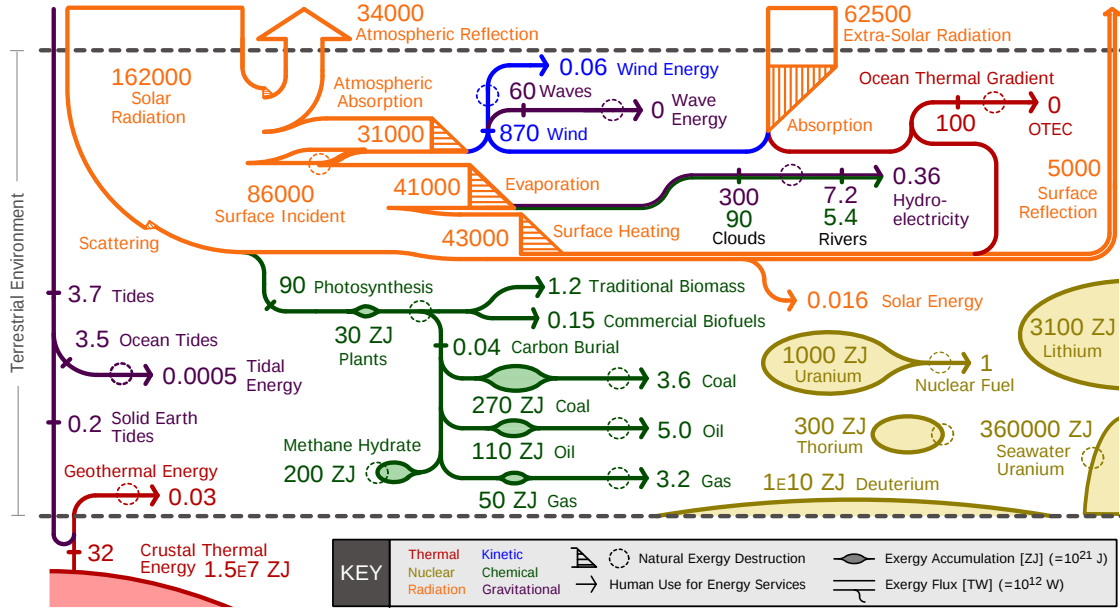


Figure 4.4: Global exergy resources. From Hermann [87].

form of heat. The quality of the heat that reaches the surface of the lithosphere is, in most cases, too low for it to be economically converted to work. Therefore, work is typically produced by intervening in the natural exergy flux deep within the lithosphere. The locations of heat extraction are commonly referred to as geothermal reservoirs. Exergy extracted from geothermal reservoirs is typically considered a renewable resource; however, this is only true when the exergy is extracted in a manner such that there is sufficient time for natural replenishment to take place. For modeling purposes, geothermal reservoirs are represented as resource reservoirs located within the lithosphere.

The Earth's largest resource flux is the relatively constant flux of solar radiation generated from fusion reactions occurring within the sun.⁸ The fusion reactions occurring within the sun are finite, however, the solar radiation produced is typically considered a renewable resource because of the relatively long life expectancy of the sun and the rapid time scales over which the fusion reactions occur. Solar radiation travels through space, which acts as a medium for transmitting radiation to the

⁸See Appendix A for an explanatory discussion of solar exergy.

Earth, as well as a sink for the Earth's re-radiation. For modeling purposes, the sun is represented as a resource reservoir and space is included as an environmental reservoir.

Other major resource fluxes shown in Fig. 4.4 include wind, tides, waves, and rivers. All of these fluxes occur within the terrestrial environmental reservoirs and are typically considered renewable resources due to the relatively short time scales over which they are regenerated. In order to model work extraction from these resource fluxes, the terrestrial environmental reservoir in which the flux is located must be broken apart into a resource reservoir and an environmental reservoir. For example, when analyzing work extraction from wind, the atmosphere must be broken apart into high and low kinetic energy reservoirs—with the high kinetic energy reservoir modeled as the resource and the low kinetic energy reservoir modeled as the environment.

The environmental and resource reservoirs can be represented graphically, as shown in Fig. 4.5.⁹ The environmental reservoirs are naturally out of equilibrium with one another, and therefore have the potential to drive change. As a result, exergy is naturally transferred between the reservoirs, driving natural state change and natural exergy destruction. These *natural interactions*, and the resulting natural changes and destructions, occur on a wide-range of time scales and magnitudes. Natural interactions enable and support life on Earth. Living organisms (e.g., animals, plants, fungus, micro-organisms) exist in all three terrestrial environmental reservoirs. For modeling purposes, living organisms are represented in their own region, referred to here as the biosphere. The pathways for natural interactions are depicted in the figure by the locations of the reservoirs. For example, the atmosphere interacts with the lithosphere, hydrosphere, biosphere, and space.

In order to measure the exergy (i.e., driving potential) of natural interactions and environmental reservoirs, an environmental reference state is required. As shown in

⁹The distinction between environmental and resource reservoirs depends on the relative sizes of the reservoirs. For example, if a small amount of air is introduced into a large fossil resource reservoir (e.g., a natural gas reservoir), the air is the resource because it has the potential to produce work relative to its fossil resource surroundings. For the sake of brevity, environmental and resource reservoirs will be referred to as environmental reservoirs. When necessary, the distinction will be made explicit.

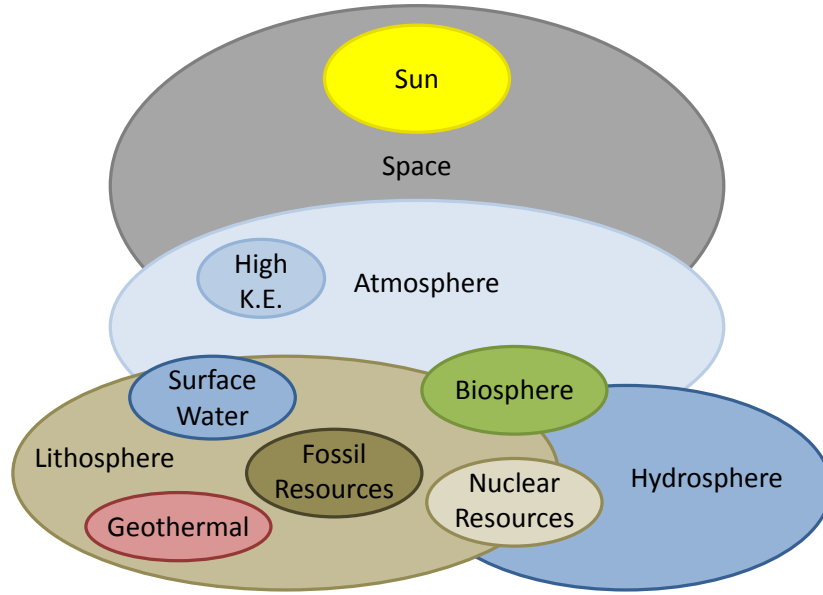


Figure 4.5: Model representation of the natural environment.

Sec. 4.1, the exergy (i.e., free energy) of multi-reservoir systems can be measured relative to either the system's mutual equilibrium state if it is isolated, or the system's mutual stationary state if it is driven. Since the Earth is a driven, multi-reservoir system, its mutual stationary state defines an environmental reference state from which the exergy of reservoirs and interactions can be measured. Any stationary state can be defined by its intensive properties as functions of position. For the purposes of environmental exergy analysis, we choose to define the environmental reference state (a stationary state) using a mean temperature (T_{ref}), pressure (P_{ref}), and chemical potential for all relevant species ($\mu_{i,ref}$). The mean intensive properties are chosen such that they correspond to the first-order moments of the intensive property distributions that define the terrestrial environment's stationary state. This choice of environmental reference state serves as a fiducial state for measuring exergy.¹⁰

¹⁰One could choose to define the environmental reference state using intensive properties as functions of position and time (assuming that, at any instant, a mutual stationary state exists). Doing so would mean that the exergy of a transfer or reservoir would depend on its location and the time of evaluation (e.g., the thermal exergy of a hot substance would increase with altitude and during night hours—both due to cooler environmental temperatures). Defining the environmental reference state using position- and time-averaged (i.e., mean) intensive properties sets an absolute reference

4.3 Anthropogenic Interactions and Environmental Impact

Human activity occurs within the natural environment in a region referred to as the *anthrosphere*. The anthrosphere is defined as the part of the natural environment physically modified by humans and used for their activities [88]. The size of the anthrosphere depends on the specifics of the activity. For example, when analyzing the extraction of natural gas from an underground reservoir, the anthrosphere extends into the lithosphere to the location of extraction within the reservoir.

There are two main pathways by which energy systems within the anthrosphere convert resources to work: (1) by cross-connecting environmental reservoirs, and (2) by intervening in natural exergy fluxes between environmental reservoirs. Both conversion pathways interact with the environment. Each pathway's environmental interactions can be broken down into *upstream* and *downstream interactions*. Upstream interactions are defined as exergy transfers to or from the anthrosphere, or alterations of natural exergy transfer within the anthrosphere, in order to extract and convert a resource to work. Downstream interactions are defined as energy transfers to or from the anthrosphere as a consequence of the conversion process.

An example of the first conversion pathway is the extraction and conversion of natural gas into electricity using air from the atmosphere and cooling water from a surface water reservoir. A diagram illustrating the environmental interactions of this example energy system is shown in Fig. 4.6a. The upstream interactions include the transfers of natural gas from the gas reservoir, air from the atmosphere, and water from the surface water reservoir. The downstream interactions include the transfers of cooling water to the surface water reservoir, and exhaust gases, heat, and noise to the atmosphere. Both upstream and downstream interactions transfer energy between the anthrosphere and connected environmental reservoirs. The electricity produced by the conversion process remains in the anthrosphere until final consumption by an electrical device.

An example of the second conversion pathway is the conversion of surface-incident

state that is independent of position and time.

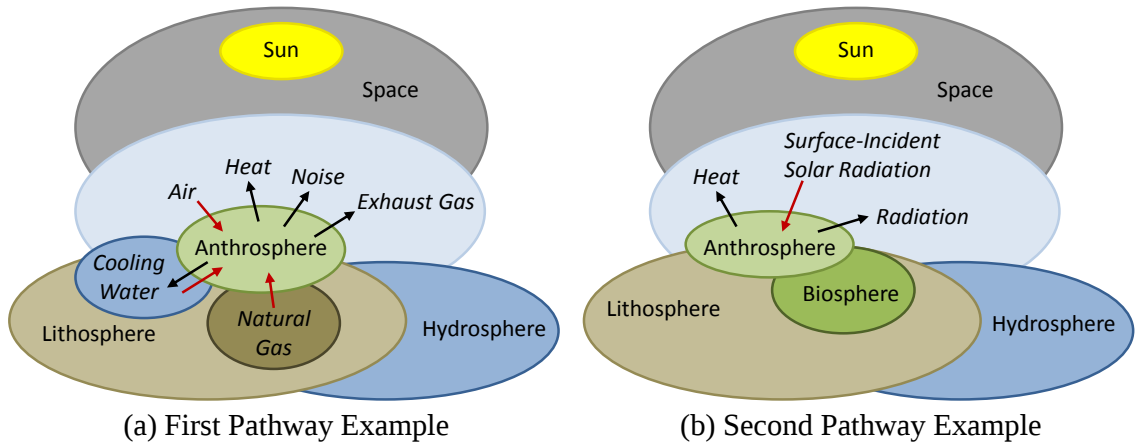


Figure 4.6: Example conversion pathways. Red arrows: upstream interactions; black arrows: downstream interactions.

solar radiation into electricity via photovoltaic (PV) cells. A diagram illustrating the environmental interactions of this example energy system is shown in Fig. 4.6b. The anthrosphere is located at the intersection of the lithosphere, biosphere, and atmosphere. The activity intervenes in the natural exergy flux of solar radiation above the lithosphere and biosphere, and as a result of the conversion process, transfers heat and radiation to the atmosphere. The surface-incident solar radiation altered within the anthrosphere is considered the upstream interaction, and the transfers of heat and radiation from the anthrosphere are the downstream interactions.

In the absence of anthropogenic activity, natural interactions would occur without disturbance—exergy would be naturally transferred between environmental reservoirs driving natural state change and natural exergy destruction within the reservoirs. The natural exergy transfers, state changes, and exergy destructions within the environmental reservoirs set a baseline from which any changes caused by anthropogenic activity can be measured. Any changes to the states of, natural exergy transfers between, or exergy destruction within the environmental reservoirs caused by anthropogenic activity is defined as *environmental impact*. This definition of environmental impact is agnostic to the consequences of the impact, and it is not limited to a specific type of impact (e.g., atmospheric state change) or consequence (e.g., global warming).

A diagram illustrating the drivers of environmental impact and the terminology

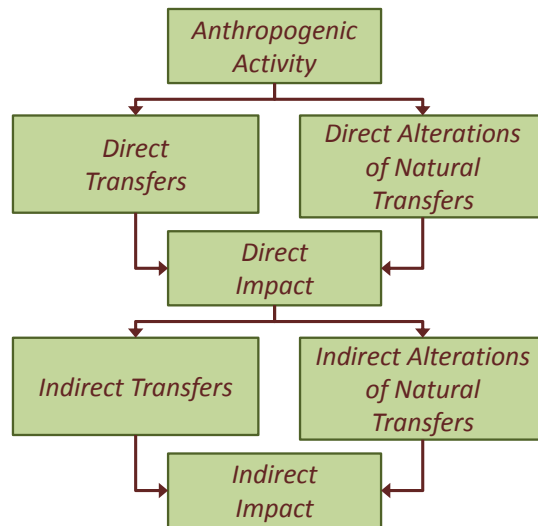


Figure 4.7: Environmental impact drivers and terminology.

used to describe environmental interactions and impacts is shown in Fig. 4.7. Environmental impact begins with anthropogenic activity. The environmental interactions of anthropogenic activity may involve upstream or downstream transfers (e.g., transfers of natural gas to the anthrosphere or emissions from the anthrosphere), which are called *direct transfers*, or upstream alterations of natural transfers (e.g., alteration of surface incident solar radiation within the anthrosphere), which are called *direct alterations of natural transfers*. Direct transfers and direct alterations of natural transfers have exergy, and therefore the potential to cause environmental impact (i.e., drive environmental change). Direct transfers impact the environmental reservoirs to or from which the transfers occur (e.g., gaseous emissions to the atmosphere impact the atmosphere; natural gas removal from an underground reservoir impacts the reservoir), and direct alterations of natural transfers impact the environmental reservoirs from which the alterations occurs (e.g., alteration of incident solar radiation from the lithosphere impacts the lithosphere). Environmental impact caused by direct transfers and direct alterations of natural transfers is referred to as *direct impact*.

Direct impact may cause alterations of natural transfers between environmental reservoirs (e.g., direct changes to the amount of CO_2 in the atmosphere may cause

alterations of natural transfers of CO_2 between the atmosphere and hydrosphere), or transfers between environmental reservoirs that did not occur prior to the anthropogenic activity (e.g., direct changes to the amount of fertilizer on the surface of the lithosphere may cause fertilizer run-off into the hydrosphere). Transfers and alterations of natural transfers caused by direct impact are called *indirect transfers* and *indirect alterations of natural transfers*, respectively. Indirect transfers and indirect alterations of natural transfers have exergy, and therefore the potential to cause environmental impact. Environmental impact caused by indirect transfers and indirect alterations of natural transfers is referred to as *indirect impact*.

The objective of any environmental analysis technique or framework is to be able to model the environmental impact of an anthropogenic activity prior to the activity actually taking place. As illustrated in Fig. 4.7, the drivers of environmental impact—defined as changes to the states of, exergy transfers between, or exergy destruction within environmental reservoirs—are the transfers and alterations of natural transfers caused by an anthropogenic activity. The potential for transfers and alterations of natural transfers to drive environmental impact is measured by their exergy (i.e., environmental free energy). As shown in the next section, the locations, magnitudes, and types of environmental impact caused by an anthropogenic activity can be quantified by applying exergy analysis to the environment.

4.4 Environmental Exergy Analysis

To demonstrate the application and utility of exergy for quantifying environmental impact, the extraction and conversion of a fossil resource into exergetic products is considered. A diagram illustrating the environmental interactions of a generic fossil resource conversion process is shown in Fig. 4.8. As shown in the figure, activities in the anthrosphere cross-connect a fossil resource reservoir located within the lithosphere to the atmosphere and a surface water reservoir. The upstream interactions include exergy transfers from the fossil resource reservoir (the fossil resource), atmosphere (air), and surface water reservoir (cooling water), and the downstream interactions include exergy transfers to the surface water reservoir (coolant return)

and atmosphere (exhaust gases, heat, noise). Both the upstream and downstream interactions are direct transfers between the anthrosphere and environmental reservoirs. Also shown in the figure are the natural exergy transfers between the environmental reservoirs.

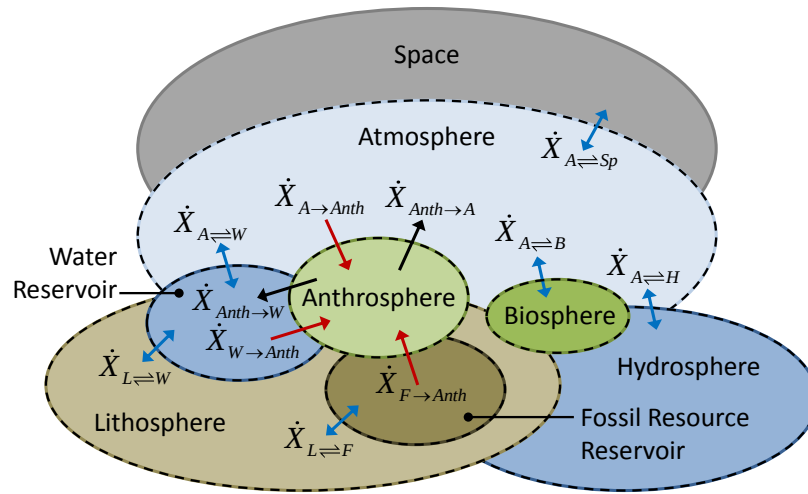


Figure 4.8: Model representation of the conversion of a fossil resource to electricity. Red arrows: upstream transfers; black arrows: downstream transfers; blue arrows: natural exergy transfers; black dashed lines: reservoir control boundaries.

The environmental reservoirs can be categorized based on their communication with the anthrosphere. Reservoirs in direct communication with the anthrosphere are referred to as α reservoirs, and reservoirs not in direct communication with the anthrosphere are referred to as β reservoirs. The α reservoirs in this example include the atmosphere, fossil resource reservoir, and surface water reservoir, and the β reservoirs include the lithosphere, biosphere, hydrosphere, and space. The control boundaries for the individual reservoirs are shown by the dashed lines in Fig. 4.8.

In the absence of anthropogenic activity, exergy would be naturally transferred between the environmental reservoirs—driving natural state change and natural exergy destruction. The relationship between the natural exergy transfers, state changes,

and destructions is shown through the exergy balances for the α and β reservoirs:

$$[\alpha_i] : \sum_j [\delta X_{\alpha_j \rightleftharpoons \alpha_i}^o] + \sum_k [\delta X_{\beta_k \rightleftharpoons \alpha_i}^o] = dX_{\alpha_i}^o + \delta X_{Dest, \alpha_i}^o \quad (4.16)$$

$$[\beta_k] : \sum_l [\delta X_{\beta_l \rightleftharpoons \beta_k}^o] + \sum_m [\delta X_{\alpha_m \rightleftharpoons \beta_k}^o] = dX_{\beta_k}^o + \delta X_{Dest, \beta_k}^o \quad (4.17)$$

where the superscript o designates values in the absence of anthropogenic activity, the indices j and k refer to α and β reservoirs in communication with reservoir α_i , and indices l and m refer to β and α reservoirs in communication with reservoir β_k .¹¹ All exergy values are measured relative to the environmental reference state discussed in Sec. 4.2. The above exergy balances show that, at any instant, the net exergy transferred to a reservoir is equivalent to the sum of the exergy change and exergy destruction within the reservoir. The equations can be interpreted as showing that the natural exergy transfers between the reservoirs are the drivers of natural state change and natural exergy destruction.

During anthropogenic activity, state change and exergy destruction is caused by both anthropogenic and natural transfers. The relationship between the natural and anthropogenic exergy transfers, state changes, and destructions is again shown through the exergy balances for the α and β reservoirs:

$$[\alpha_i] : \delta X_{Anth \rightleftharpoons \alpha_i} + \sum_j [\delta X_{\alpha_j \rightleftharpoons \alpha_i}] + \sum_k [\delta X_{\beta_k \rightleftharpoons \alpha_i}] = dX_{\alpha_i} + \delta X_{Dest, \alpha_i} \quad (4.18)$$

$$[\beta_k] : \sum_l [\delta X_{\beta_l \rightleftharpoons \beta_k}] + \sum_m [\delta X_{\alpha_m \rightleftharpoons \beta_k}] = dX_{\beta_k} + \delta X_{Dest, \beta_k} \quad (4.19)$$

As in Eqs. (4.16) and (4.17), the above equations show that, at any instant, the net exergy transferred to a reservoir is equivalent to the sum of the exergy change and exergy destruction within the reservoir. However, due to the anthropogenic

¹¹Implicit in the differential impact equations are surface and volume integrals that correspond to the control boundaries shown in Fig. 4.8. All exergy transfers are integrated over the surface of the control boundary they cross (e.g., $\delta X_{\alpha_j \rightleftharpoons \alpha_i} = \int \delta X''_{\alpha_j \rightleftharpoons \alpha_i} dS$, where X'' is exergy per surface area, and S is the surface area), and all exergy changes and destructions are integrated over the volume enclosed by the control boundary (e.g., $dX_{\alpha_i} = d(\int X'''_{\alpha_i} dV)$, $\delta X_{Dest, \alpha_i} = \int \delta X'''_{Dest, \alpha_i} dV$, where X''' is exergy per volume, and V is the volume).

transfers, the natural transfer, exergy change, and exergy destruction terms in the above equations are different from those in Eqs. (4.16) and (4.17).

The environmental impact that anthropogenic activity has on a given α reservoir can be shown by taking the difference between the exergy balances for the reservoir with anthropogenic activity and in the absence of the activity. Doing this and rearranging the equation yields:

$$\begin{aligned} \delta X_{Anth \rightarrow \alpha_i} - \delta X_{\alpha_i \rightarrow Anth} &= [dX_{\alpha_i} - dX_{\alpha_i}^o] + [\delta X_{Dest, \alpha_i} - \delta X_{Dest, \alpha_i}^o] \\ &+ \sum_j [\delta X_{\alpha_i \rightleftharpoons \alpha_j} - \delta X_{\alpha_i \rightleftharpoons \alpha_j}^o] + \sum_k [\delta X_{\alpha_i \rightleftharpoons \beta_k} - \delta X_{\alpha_i \rightleftharpoons \beta_k}^o] \end{aligned} \quad (4.20)$$

The equation shows that, at any instant during anthropogenic activity, the net exergy directly transferred to an α reservoir (upstream or downstream of the conversion process) is equivalent to the sum of the differences between the exergy change, exergy destruction, and net exergy naturally transferred from the α reservoir during the activity and in the absence of the activity. The equation can be interpreted as showing that direct transfers are the drivers of environmental impact on α reservoirs, and the types of direct impact on α reservoirs are state change, destruction change, and alterations of natural transfers.

The environmental impact that anthropogenic activity has on a given β reservoir can be shown by taking the difference between the exergy balances for the reservoir with anthropogenic activity and in the absence of the activity, and rearranging the equation. Doing this for a β reservoir in communication with an α reservoir yields:

$$\begin{aligned} \delta X_{\alpha_i \rightleftharpoons \beta_k} - \delta X_{\alpha_i \rightleftharpoons \beta_k}^o &= [dX_{\beta_k} - dX_{\beta_k}^o] + [\delta X_{Dest, \beta_k} - \delta X_{Dest, \beta_k}^o] \\ &+ \sum_l [\delta X_{\beta_k \rightleftharpoons \beta_l} - \delta X_{\beta_k \rightleftharpoons \beta_l}^o] + \sum_m [\delta X_{\beta_k \rightleftharpoons \alpha_m} - \delta X_{\beta_k \rightleftharpoons \alpha_m}^o] \end{aligned} \quad (4.21)$$

and doing this for a β reservoir not in communication with an α reservoir yields:

$$\begin{aligned} \delta X_{\beta_k \rightleftharpoons \beta_m} - \delta X_{\beta_k \rightleftharpoons \beta_m}^o &= [dX_{\beta_m} - dX_{\beta_m}^o] + [\delta X_{Dest, \beta_m} - \delta X_{Dest, \beta_m}^o] \\ &+ \sum_n [\delta X_{\beta_m \rightleftharpoons \beta_n} - \delta X_{\beta_m \rightleftharpoons \beta_n}^o] \end{aligned} \quad (4.22)$$

The above equations show that, at any instant during an anthropogenic activity, the difference between the net exergy naturally transferred to a β reservoir during the activity and in the absence of the activity is equivalent to the sum of the differences between the exergy change, exergy destruction, and net exergy naturally transferred from the β reservoir during the activity and in the absence of the activity. The equations can be interpreted as showing that alterations of natural transfers are the drivers of indirect impact on β reservoirs, and the types of impact on β reservoirs are state change, destruction change, and other alterations of natural transfers.¹²

Equations (4.20)–(4.22) can be referred to as the *differential impact equations*. They apply to any energy system categorized by the first conversion pathway—i.e., they are not limited to fossil resource conversion processes. For energy systems categorized by the second conversion pathway, the above impact equations apply for all reservoirs except for α reservoirs upstream of the conversion process. As discussed in the previous section, direct alterations of natural transfers impact the environmental reservoirs from which the alterations occur (e.g., alteration of surface-incident solar radiation from the lithosphere impacts the lithosphere). Therefore, α reservoirs upstream of the conversion process are directly impacted by the exergy altered within the anthrosphere from naturally reaching the reservoir. The differential impact equation for an α reservoir upstream of an energy system categorized by the second conversion pathway is given by:

$$\begin{aligned} \delta X_{\alpha_j \rightarrow \alpha_i} - \delta X_{\alpha_j \rightarrow \alpha_i}^o &= [dX_{\alpha_i} - dX_{\alpha_i}^o] + [\delta X_{Dest, \alpha_i} - \delta X_{Dest, \alpha_i}^o] \\ &+ [\delta X_{\alpha_i \rightarrow \alpha_j} - \delta X_{\alpha_i \rightarrow \alpha_j}^o] + \sum_k [\delta X_{\alpha_i \rightleftharpoons \alpha_k} - \delta X_{\alpha_i \rightleftharpoons \alpha_k}^o] \\ &+ \sum_l [\delta X_{\alpha_i \rightleftharpoons \beta_l} - \delta X_{\alpha_i \rightleftharpoons \beta_l}^o] \end{aligned} \quad (4.23)$$

The difference on the left hand side of this equation represents the amount of exergy altered within the anthrosphere from naturally being transferred from reservoir α_j

¹²When using Eqs. (4.21) and (4.22) to quantify the impact on β reservoirs caused by indirect transfers (i.e., transfers between environmental reservoirs that did not occur prior to the anthropogenic activity), the net exergy transferred to the reservoir in the absence of the activity is zero (i.e., $\delta X_{\alpha_i \rightleftharpoons \beta_k}^o = 0$, $\delta X_{\beta_k \rightleftharpoons \beta_m}^o = 0$).

to reservoir α_i (e.g., the amount of surface-incident solar radiation altered by PV cells from being transferred from the atmosphere, α_j , to the lithosphere, α_i). The equation shows that, at any instant during an anthropogenic activity, the exergy altered from reaching an α reservoir upstream of a conversion process is equivalent to the sum of the differences between the exergy change, exergy destruction, and net exergy naturally transferred from the reservoir during the activity and in the absence of the activity. The equation can be interpreted as showing that direct alterations of natural transfers are the drivers of environmental impact on α reservoirs upstream of a conversion process, and the types of direct impact on the reservoir are state change, destruction change, and alterations of natural transfers.

The differential impact equations provide insight into the possible locations and types of environmental impact caused by an anthropogenic activity. In order to solve for the actual locations, magnitudes, and types of environmental impact, the differential impact equations must be integrated over the interval of interest—from the start of the activity to some defined final time, which is referred to here as the *integration time*. The integration time is independent of the time of the anthropogenic activity, and can be shorter than, equal to, or longer than the time of the activity. Integration times less than the time of the activity are not of particular interest for environmental impact analysis, since the activity has not ended.

Integration is complicated by the fact that the reservoirs are coupled. For example, direct impact on an α reservoir caused by transfers from the anthrosphere can indirectly change the properties of another α reservoir, which is also being directly impacted by transfers from the anthrosphere. Coupling between reservoirs may require that the impact equations be integrated simultaneously. Integration of the impact equations is simplified, and in some cases the need for simultaneous integration is avoided, if certain model assumptions about the reservoirs and transfers can be employed. Appendix D provides an overview of some of the key modeling assumptions that can be used to simplify the analysis.

Integration of Eqs. (4.20)–(4.23) from the start of an activity to a specified integration time (t_{int}) yields:

$$X_{Anth \rightarrow \alpha_i} - X_{\alpha_i \rightarrow Anth} = [X_{\alpha_i, t_{int}} - X_{\alpha_i, t_{int}}^o] + [X_{Dest, \alpha_i} - X_{Dest, \alpha_i}^o] \\ + \sum_j [X_{\alpha_i \rightleftharpoons \alpha_j} - X_{\alpha_i \rightleftharpoons \alpha_j}^o] + \sum_k [X_{\alpha_i \rightleftharpoons \beta_k} - X_{\alpha_i \rightleftharpoons \beta_k}^o] \quad (4.24)$$

$$X_{\alpha_i \rightleftharpoons \beta_k} - X_{\alpha_i \rightleftharpoons \beta_k}^o = [X_{\beta_k, t_{int}} - X_{\beta_k, t_{int}}^o] + [X_{Dest, \beta_k} - X_{Dest, \beta_k}^o] \\ + \sum_l [X_{\beta_k \rightleftharpoons \beta_l} - X_{\beta_k \rightleftharpoons \beta_l}^o] + \sum_m [X_{\beta_k \rightleftharpoons \alpha_m} - X_{\beta_k \rightleftharpoons \alpha_m}^o] \quad (4.25)$$

$$X_{\beta_k \rightleftharpoons \beta_m} - X_{\beta_k \rightleftharpoons \beta_m}^o = [X_{\beta_m, t_{int}} - X_{\beta_m, t_{int}}^o] + [X_{Dest, \beta_m} - X_{Dest, \beta_m}^o] \\ + \sum_n [X_{\beta_m \rightleftharpoons \beta_n} - X_{\beta_m \rightleftharpoons \beta_n}^o] \quad (4.26)$$

$$X_{\alpha_j \rightarrow \alpha_i} - X_{\alpha_j \rightarrow \alpha_i}^o = [X_{\alpha_i, t_{int}} - X_{\alpha_i, t_{int}}^o] + [X_{Dest, \alpha_i} - X_{Dest, \alpha_i}^o] \\ + [X_{\alpha_i \rightarrow \alpha_j} - X_{\alpha_i \rightarrow \alpha_j}^o] + \sum_k [X_{\alpha_i \rightleftharpoons \alpha_k} - X_{\alpha_i \rightleftharpoons \alpha_k}^o] \\ + \sum_l [X_{\alpha_i \rightleftharpoons \beta_l} - X_{\alpha_i \rightleftharpoons \beta_l}^o] \quad (4.27)$$

The above equations are referred to as the (integrated) *impact equations*. In each equation, the exergetic magnitude of the drivers of impact (transfers or alterations of natural transfers) on a reservoir is equal to the sum of the types of impact within the reservoir—state change, destruction change, and alterations of natural transfers. As shown in the equations, state change is measured as the difference between the exergy of a reservoir evaluated at the end of integration (t_{int}) with anthropogenic activity and in the absence of the activity. The initial exergy of the reservoirs with and without activity cancel because they are the equal at time zero (i.e., the beginning of the integration).

The actual locations, magnitudes, and types of environmental impact caused by an anthropogenic activity depend on the form (e.g., thermal, mechanical, chemical, gravitational potential), rate, and magnitude of the direct exergy transfers and alterations, and the properties and size of the environmental reservoirs. For example, a direct transfer of thermal exergy to an environmental reservoir can cause different

impacts than a direct transfer of chemical exergy to the same reservoir at the same rate and magnitude. Or, a direct transfer of chemical exergy to a small reservoir can cause different impacts than the same direct transfer to a larger reservoir with the same properties (e.g., less state change and more destruction change).

The framework of environmental exergy analysis presented in this section is based on fundamental thermodynamic principles. The differential impact equations derived through environmental exergy analysis provide insight into the possible locations and types of environmental impact, and evaluation of the impact equations quantifies the actual locations, types, and magnitudes of environmental impact. As shown in the next section, the impact equations provide a basis for decision making.

4.5 Interpreting the Impact Equations for Decision Making

The impact equations can be interpreted as showing that in order to avoid environmental impact, all direct transfers must have zero exergy. However, it is impossible to produce work in the anthrosphere without directly transferring exergy upstream or downstream of a conversion process.¹³ Therefore, a practical objective inferred from the impact equations might be to minimize the exergy of direct transfers (regardless of the form in which the exergy is transferred) in order to minimize the overall environmental impact (regardless of the types of impact caused by the direct transfers). This approach is valid if the consequences of the types of impacts caused by an activity are all valued equally. On an exergetic basis, the types of impact are all valued equally. However, from an anthropocentric viewpoint, the types of impact are not likely to be of equal value. The *anthropocentric value* a type of impact has depends on the consequences of the impact and *anthropocentric sensitivity* to the impact.

To introduce the concepts of anthropocentric value and sensitivity, consider the anthropogenic activity shown shown in Fig. 4.9. The activity directly transfers exergy

¹³As discussed in Sec. 4.1, the potential for work extraction only exists when a system is out of equilibrium. Therefore, exergy, or free energy, must be transferred upstream or downstream of a given conversion process in order for work extraction to occur.

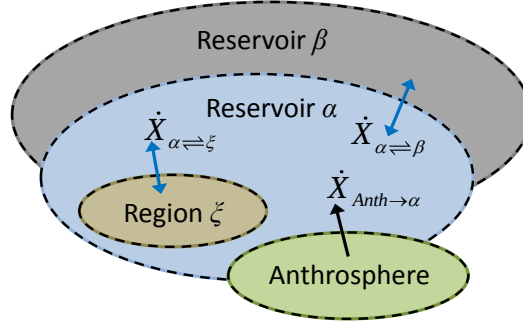


Figure 4.9: Three reservoir system in communication with an anthropogenic activity. Black arrows: downstream transfers; blue arrows: natural transfers; black dashed lines: control boundaries.

to an α reservoir that is in communication with a β reservoir and another reservoir called region ξ . The differential impact equation for the reservoirs are:

$$\begin{aligned} \delta X_{Anth \rightarrow \alpha} = & [dX_{\alpha} - dX_{\alpha}^o] + [\delta X_{Dest, \alpha} - \delta X_{Dest, \alpha}^o] \\ & + [\delta X_{\alpha \rightleftharpoons \beta} - \delta X_{\alpha \rightleftharpoons \beta}^o] + [\delta X_{\alpha \rightleftharpoons \xi} - \delta X_{\alpha \rightleftharpoons \xi}^o] \end{aligned} \quad (4.28)$$

$$\delta X_{\alpha \rightleftharpoons \xi} - \delta X_{\alpha \rightleftharpoons \xi}^o = [dX_{\xi} - dX_{\xi}^o] + [\delta X_{Dest, \xi} - \delta X_{Dest, \xi}^o] \quad (4.29)$$

$$\delta X_{\alpha \rightleftharpoons \beta} - \delta X_{\alpha \rightleftharpoons \beta}^o = [dX_{\beta} - dX_{\beta}^o] + [\delta X_{Dest, \beta} - \delta X_{Dest, \beta}^o] \quad (4.30)$$

The differential impact equations provide insight into the possible locations and types of environmental impact. To interpret the equations for decision making, an anthropocentric value for each type of impact must be assigned.

Consider the case where region ξ has been identified as being sensitive to state change, such that any state change within the region is valued as being undesirable. As shown by Eq. (4.29), the driver of impact on region ξ is the alteration of natural transfers between the region and the α reservoir, and the types of impact are state change and destruction change. With knowledge of the sensitivity to, and value of, state change within region ξ , the practical objective is to design or choose an energy system that directly transfers exergy to the α reservoir in a form that *does not* cause state change within the region. The direct exergy transfer term in Eq. (4.28) can therefore be viewed as the *control variable*, and since the driver of state change is the

alteration of natural transfers, it can be viewed as the *sensitivity constraint*.

The differential impact equations provide insight for designing or choosing an energy system that avoids causing state change within region ξ . There are two options for avoiding state change within the region: (1) directly transfer exergy in a form such that there is no alteration of natural transfers between the region and the α reservoir, or (2) directly transfer exergy in a form such that any alteration of natural transfers only cause destruction change within the region. Information is needed in order to know which forms of exergy cause alterations of natural transfers between the region and the α reservoir, and which forms only cause destruction change. If this information is known, an energy system can be designed or chosen to avoid directly transferring exergy in these forms.

In order to identify the sensitivities to a type of impact, the consequences of the impact must inherently have some value to humans—either directly or indirectly. A consequence can be valued as being negative (e.g., global warming, loss of biodiversity, adverse health affects) or positive (e.g., global warming remediation, enhanced biodiversity, beneficial health affects). Often, the sensitivities to a type of impact are not identified until after the consequences of the impact have negatively affected humans (e.g., ocean acidification, acid rain, photochemical smog, global warming). In order to avoid unintended consequences, even when the objective is to maximize positive consequences, all other types of impact should be minimized. Therefore, the practical objective for decision making is three-fold: (1) avoid direct transfers of exergy that cause environmental impact with negative consequences, (2) maximize direct transfers of exergy that cause environmental impact with positive consequences, and (3) minimize direct transfers of exergy with no known sensitivities in order to avoid unintended consequences.

Meeting the practical objective for decision making can be accomplished by: (1) controlling the magnitude, rate, and form in which exergy is directly transferred from the anthrosphere, (2) controlling the reservoir to which the direct transfers occur, or (3) a combination of both. An example of the first approach is the conversion of smog forming gases (NO_x , CO, and hydrocarbons) by a three-way catalyst to stable species (N_2 , CO_2 , and H_2O) in order to mitigate localized increases in atmospheric ozone

concentrations. An example of the second approach is carbon capture and sequestration (CCS) from stationary, fossil resource-based power plants in order to mitigate global increases in atmospheric CO₂ concentrations. An example that combines both approaches is the mitigation of thermal pollution (i.e., temperature change) in existing water reservoirs caused by cooling water from power plants. This is accomplished by using a sufficiently large water reservoir (to avoid global temperature increase) and water flow rate (to minimize return temperature and avoid local temperature increase). In each of these examples, a larger amount of exergy is destroyed within the anthrosphere in order to avoid transferring exergy in a form, or to a reservoir, that causes environmental impact with identified negative consequences.¹⁴

Anthropocentric sensitivity to a type of impact varies based on magnitude and time scale. For example, exposure to atmospheric ozone concentrations above 75 parts per billion for eight hours is known to negatively affect the human respiratory system [89]. Whereas, maintaining atmospheric CO₂ concentrations below 450 parts per million indefinitely has been identified as appropriate for avoiding dangerous global climate change [90].

Applying the concepts of anthropocentric value and sensitivity to interpret the results of environmental exergy analysis for decision making—referred to here as *anthropocentric sensitivity analysis*—introduces subjectivity into the environmental analysis framework. The anthropocentric value a type of impact has, and the threshold for which the magnitude of an impact is considered sensitive, can vary across decision makers (e.g., individuals, groups, agencies, countries). However, in the absence of anthropocentric value and sensitivity, the exergetic magnitudes of the terms in the impact equations provide limited information for decision making. It is the combination of environmental exergy analysis and anthropocentric sensitivity analysis that provide an environmental analysis framework capable of both quantifying environmental impact and providing insight for decision making.

¹⁴A more detailed discussion of photochemical smog and thermal pollution is provided in App. D.

4.6 Applying the Analysis Framework for Decision Making

To illustrate the application and utility of the analysis framework for decision making, consider the scenario where a decision maker has to choose between three different energy systems to meet a given objective (e.g., produce 1 TW of electricity for the next 30 years, or 2 million barrels of liquid transportation fuel per day for the next 20 years). The three energy systems—Systems A, B, and C—all meet the given objective, but use different resources and have different environmental interactions. In order for the decision maker to choose the energy system that best minimizes or avoids the types of impact valued as being negative, and/or maximizes those valued as being positive, the locations, magnitudes, and types of environmental impact caused by each energy system must be quantified. This can be accomplished through the application of environmental exergy analysis.

Application of environmental exergy analysis can be broken down into three steps: (1) defining control boundaries, (2) deriving the applicable form of the differential impact equations, and (3) solving the impact equations. Control boundaries must be defined for the environmental reservoirs, and for each energy system's anthrosphere. The control boundaries should be defined such that the energy systems can be compared on a level playing field, and to provide the level of detailed required for the decision. With defined control boundaries, the environmental reservoirs can be categorized based on their communication with the anthrosphere as α or β reservoirs, and the differential impact equations can be written using Eqs. (4.20)–(4.23) as a basis. The differential impact equations provide insight into the possible locations and types of environmental impact caused by each energy system. To solve for the magnitude of environmental impact, the differential impact equations must be integrated over the interval of interest. Quantifying the environmental impact of each energy system may require a significant amount of information about the properties and behavior of the anthropogenic interactions and environmental reservoirs. Appendix D provides an overview of some of the key requirements for quantifying environmental impact.

The results of environmental exergy analysis can be represented graphically for

comparison purposes. Figure 4.10 shows a distribution of the terms in the impact equation for an α reservoir in communication with the three (hypothetical) energy systems. The values shown in the figure are strictly notional. This figure shows that for each energy system, the driver of impact is a net direct transfer of exergy to the α reservoir ($X_{Anth.\rightarrow\alpha_i} - X_{\alpha_i\rightarrow Anth.} > 0$), and that the direct transfers drive state change, destruction change, and alterations of natural transfers within the reservoir. The amount of exergy directly transferred to the α reservoir is equal to the sum of the types of impact on the reservoir, which are all measured as differences in exergy. The figure shows that all three notional systems cause an increase in the exergy of the reservoir ($X_{\alpha_i,t_{int}} - X_{\alpha_i,t_{int}}^o > 0$) and the amount of exergy destroyed within the reservoir ($X_{Dest.,\alpha_i} - X_{Dest.,\alpha_i}^o > 0$), whereas the magnitudes and directions of the alterations of natural transfers vary between systems. Negative alterations of natural transfers correspond to a net decrease in the amount of exergy naturally transferred from the reservoir (e.g., $X_{\alpha_i\rightleftharpoons\alpha_j} - X_{\alpha_i\rightleftharpoons\alpha_j}^o < 0$).

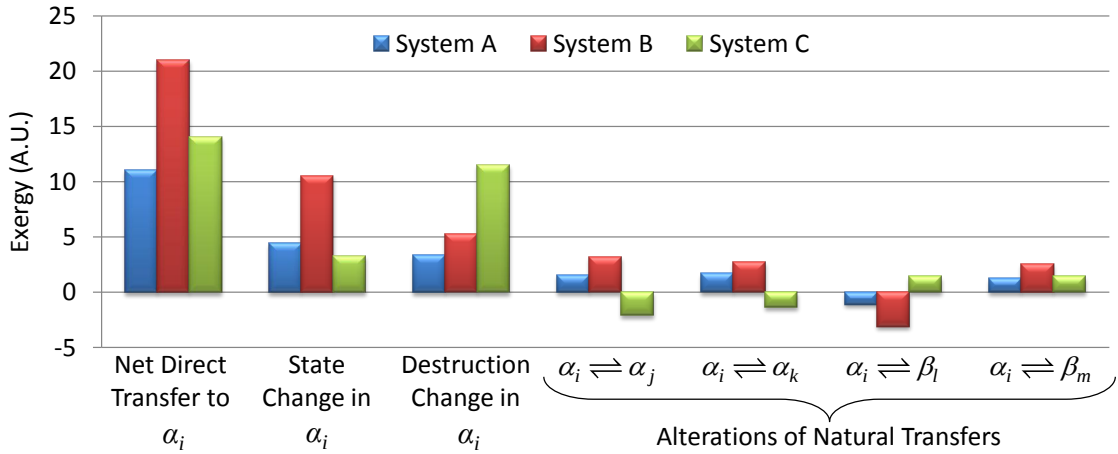


Figure 4.10: Distribution of the drivers and types of environmental impact on an α reservoir in communication with three (hypothetical) energy systems. Exergy values are in arbitrary units (A.U.).

The exergy of the drivers and types of environmental impact shown in Fig. 4.10 can be broken down by form. Figure 4.11 shows a distribution of the forms of exergy in the direct transfers to, and state change in, the α reservoir. For each energy system, the total amount of exergy transferred to, and changed in, the α reservoir is equal to

the sum of their individual forms. The values depicted in the figure are all differences in exergy, and can therefore be negative. For example, Systems A and B cause a net transfer of mechanical exergy from the α reservoir ($X_{Anth. \rightarrow \alpha_i}^M - X_{\alpha_i \rightarrow Anth.}^M < 0$, where superscript M refers to mechanical exergy) and therefore a decrease in mechanical exergy within the reservoir ($X_{\alpha_i, t_{int}}^M - X_{\alpha_i, t_{int}}^{M,o} < 0$).

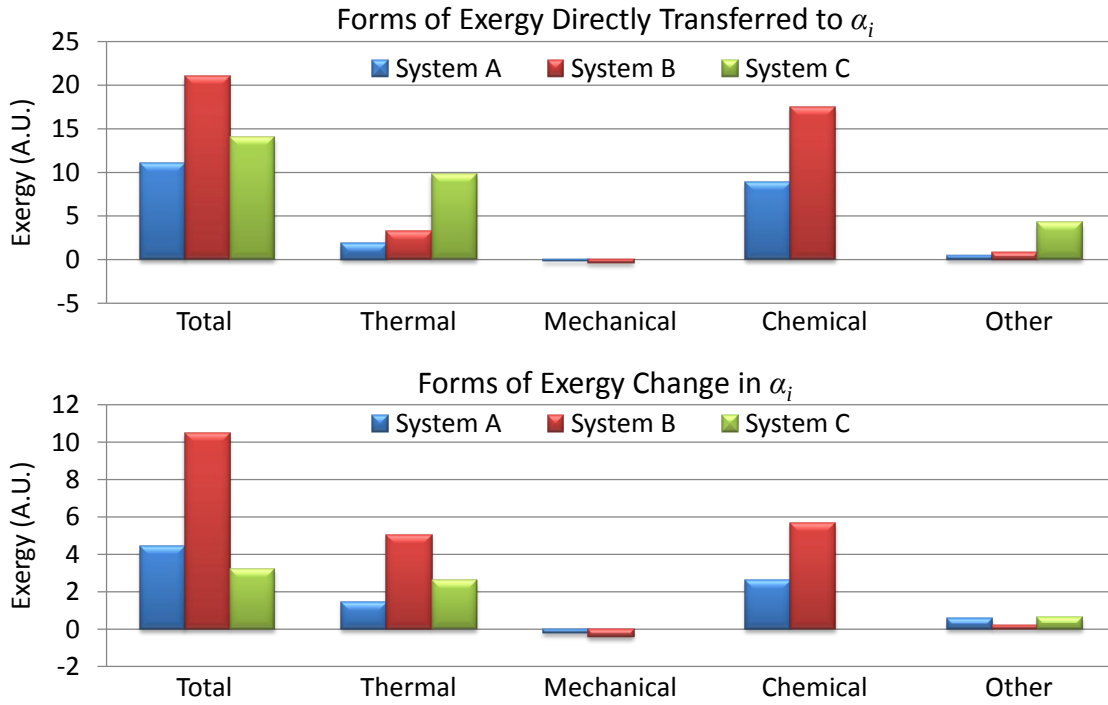


Figure 4.11: Distribution of the forms of exergy in the direct transfers to, and the state changes in, the α reservoir. The total exergy values correspond to those in Fig. 4.10. The “other” forms of exergy in the figure include radiative, nuclear, kinetic, and potential.

The chemical exergy of the drivers and types of impact on a reservoir can be further broken down by chemical components. Figure 4.12 shows a distribution of the components of chemical exergy change in the α reservoir caused by Systems A and B (in this example System C does not cause a chemical change in state). For each energy system, the total chemical exergy change is equal to the sum of the components of chemical exergy change: $(X_{\alpha_i, t_{int}}^C - X_{\alpha_i, t_{int}}^{C,o}) = \sum_k [(N_k \mu_k)_{\alpha_i, t_{int}} - (N_k \mu_k)_{\alpha_i, t_{int}}^o]$, where superscript C refers to chemical exergy, and all chemical potentials (for each species k)

are evaluated at the environmental reference temperature (T_{ref}) and pressure (P_{ref}). Negative changes correspond to a decrease in a component's exergy from what it would have naturally been at the end of integration (e.g., $(N_{O_2}\mu_{O_2})_{\alpha_i,t_{int}} - (N_{O_2}\mu_{O_2})_{\alpha_i,t_{int}}^o < 0$).

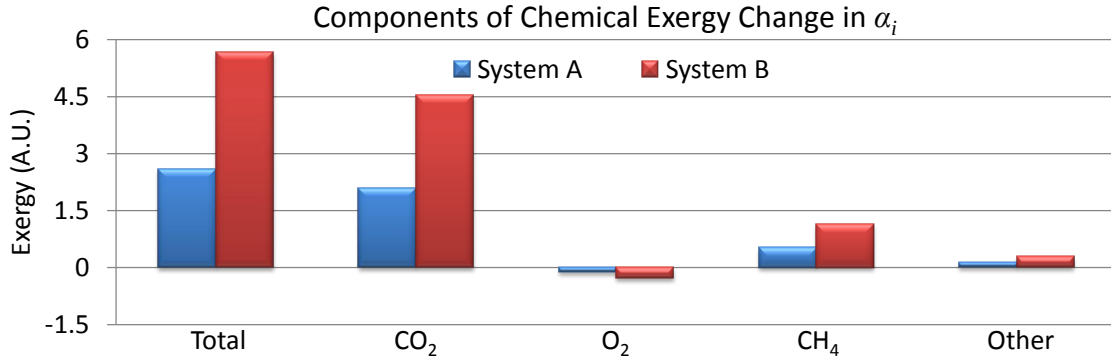


Figure 4.12: Distribution of the change in component chemical exergy in the α reservoir. The total chemical exergy changes correspond to the values shown in Fig. 4.11.

The results of environmental exergy analysis provide a basis for performing anthropocentric sensitivity analysis. The decision maker can use the results to ask questions about sensitivity and value. For example: Are there any identified sensitivities to the types and forms of impact on the α reservoir, and if so, how are they valued? With knowledge of the anthropocentric sensitivities to, and value of, the types and forms of impact caused by the three energy systems, the decision maker is able to choose the energy system that best minimizes or avoids the types of impact valued as being negative and/or maximizes those valued as being positive. Again, for example, if only the α reservoir is considered, and it is identified as only being sensitive to chemical forms of state change, with the consequences of chemical change valued as being negative, then the decision maker would choose System C since it does not cause any chemical state change (as can be seen in Fig. 4.11).

It is often the case that there are several types and forms of impact with identified sensitivities. When this occurs, the types of impact with identified sensitivities can be weighted based on their relative level of sensitivity. If the α reservoir is only sensitive to thermal and chemical forms of state change, and the reservoir is four

times as sensitive to thermal change than chemical change (with the consequences of both valued as being negative), then the decision maker would choose System A. This can be shown by using the values in Fig. 4.11. Systems A, B, and C cause a change in thermal and chemical exergy of approximately 1.5 and 2.6 A.U., 2.6 and 0 A.U., and 5.0 and 5.7 A.U., respectively. Weighting the impact values by their relative level of sensitivity, the “equivalent” impact values for Systems A, B, and C are $4 \times 1.5 + 2.6 = 8.6$, $4 \times 2.6 = 10.4$, and $4 \times 5 + 5.7 = 25.7$, respectively.¹⁵ Since the equivalent impact for System A is less than that of Systems B and C, the decision maker would choose System A.

There is also the possibility that there are no identified sensitivities to the types of impact caused by an energy system. When this is the case, the decision maker should choose the energy system that directly transfers, or alters, the least amount of exergy in order to minimize overall impact and unintended consequences. For example, if only the α reservoir is considered, and there are no identified sensitivities, the decision maker would choose System A because it directly transfers the least amount of exergy to the reservoir (as can be seen in Fig. 4.10).

4.7 Conclusion

The environmental analysis framework developed here can be broken down into two parts: first, the application of environmental exergy analysis to quantify environmental impact, and second, the application of anthropocentric sensitivity analysis to interpret the results of environmental exergy analysis for decision making. Environmental exergy analysis enables the locations, magnitudes, and types of environmental impact to be quantified. It is based on thermodynamic principles and analysis techniques, but provides limited insight for decision making. Anthropocentric sensitivity analysis enables the results of environmental exergy analysis to be interpreted for decision making, but at the expense of introducing subjectivity into the analysis framework. Together, environmental exergy analysis and anthropocentric sensitivity

¹⁵*Equivalent* impact refers to the sum of the actual impact values, measured by exergy, weighted by their relative sensitivity values. They are not measures of exergy and therefore do not have units.

analysis form an environmental analysis framework that is capable of both quantifying environmental impact and providing insight for decision making.

The analysis framework can be applied to individual energy systems to aid in system design, or to a set of energy systems to aid in system selection. In both cases, the objective is to minimize or avoid causing the types of impacts with negative consequences, and/or maximize causing those with positive consequences. One of the key attributes of the analysis framework is its ability to quantify and compare the environmental performance of energy systems on a level playing field, regardless of the specifics of the systems—resources, products, by-products, sizes, or time scales. With the increasing desire to transition from traditional, fossil resource-based energy systems to alternative, renewable-resource-based systems (e.g., from crude oil-derived transportation fuels to biofuels, or from coal-derived electricity to solar), having this ability is essential to making sound policy and investment decisions.

Chapter 5

Evaluating Economic Performance of Energy Systems

The objective of this chapter is to illustrate some of the main areas where subjectivity and uncertainty enter into the economic analysis of individual energy systems, and how they compound to influence the accuracy of performance metrics. The hope is that the observations presented here can be used to ask questions about performance metrics published in the literature before they are used as a basis for decision making in energy.

There currently exist several well-established analysis techniques for evaluating the economic performance, or value, of an energy system. The most prominent analysis techniques include present worth analysis, rate of return analysis, and equivalent annual worth analysis. The economic principles and idealized applications of these techniques are discussed and demonstrated in numerous standard Engineering Economic Analysis and Engineering Economy texts [11–16]. All of the techniques use the annual cash flows of an energy system to derive performance metrics and provide information for decision making. The most widely used economic performance metrics for measuring and comparing the economic value of energy systems include net present value, internal rate of return, and levelized cost of energy. A detailed review of these performance metrics and their applications in energy systems analysis is provided by Short et al. [17].

Engineering Economic Analysis texts typically describe the application of the various analysis techniques by assuming cash flows are known. However, when applying economic analysis techniques to non-extant energy systems, cash flows must be estimated. An energy system's cash flows include the initial costs to purchase, install, and finance the system, and the annual taxes, depreciation, returns on debt and equity, fuel costs, operating and maintenance costs, and revenues generated. The accuracy of cash flow estimates has a direct influence on the quality of the performance metrics provided by analysis techniques. When using published performance metrics for decision making in energy, it is important to understand how an energy system's cash flows were estimated.

The chapter begins by providing a high-level review of the relevant costs that should be considered in the economic analysis of an energy system, and discussing some of the cost-estimation methods used in energy economic analysis. The following section discusses how cost estimates directly influence a system's cash flows, and how the treatment of financing, taxes, and depreciation in cash flow models influence the accuracy of performance metrics. The chapter concludes by providing a “check list” of questions to aid in interpreting the results of published economic analysis.

5.1 Estimating Costs

The first step in evaluating an energy system's economic performance—regardless of the cash flow model or analysis technique—is to estimate the system's costs. The costs of an energy system are to economic analysis techniques what property data are to thermodynamic analysis techniques. As discussed in Ch. 3, the accuracy and availability of property data greatly influences the accuracy of thermodynamic analysis techniques since these data are the underpinnings of all calculations. Likewise, the accuracy of an energy system's costs has a direct effect on its cash flows, and therefore an indirect effect on the accuracy of the performance metrics provided by an analysis technique.

The process of determining an energy system's costs typically begins with estimating its *fixed-capital investment*. The fixed-capital investment represents the total

system cost assuming that the construction time is zero (i.e., overnight construction). It is commonly broken down into *direct costs* and *indirect costs*. Direct costs are often broken down further into *inside-battery-limits* (ISBL) and *outside-battery-limit* (OSBL) costs. The battery limits typically correspond to the energy system's boundary (e.g., the control boundary for the modeled GTL facility shown in Fig. 3.5). ISBL costs correspond to the installed equipment costs for all energy technologies (including supporting equipment, piping, and connections) shown in a system diagram. The OSBL costs include the costs required to build service facilities (e.g., office space, roads, waste water-treating facilities, storage facilities). Indirect costs include the costs of engineering and supervision costs, construction costs (including contractor's profit), and contingency costs. Engineering and supervision costs include the costs for developing detailed plant design, cost engineering, purchasing, scale modeling, engineering supervision, project management, etc. Contingency costs account for possible cost changes during the time frame from initial design to final operation (e.g., construction delays, design changes, increases in raw material costs, etc.). Contingencies are meant to account for uncertainties in cost estimates, and typically range between 10–30% of the the total purchased and installed equipment costs depending on the complexity, size, and uniqueness of the system [4].

The next step after estimating an energy system's fixed-capital investment costs is to account for the cost incurred during the construction time and the costs to purchase the initial raw materials for system operation before revenues are generated. These costs are commonly referred to as the start-up costs, working capital, and allowance funds during construction. The sum of these costs and the fixed-capital investment are typically referred to as the *total capital investment*. Start-up costs include labor, materials, equipment, and overhead expenses to be used only during startup time, plus the loss of income while the system is initially operating at partial capacity [4]. Working capital includes the funds required to pay for the operating expenses (e.g., raw materials, fuels, supplies, etc.) before payment is received from the sale of product(s) [91]. Allowance funds used during construction are commonly referred to as the interest during construction, and account for the time value of money during construction (i.e., the lost opportunity cost). The appropriate interest

rate for calculating the allowance funds depends on the type of financing used in the project.

The final step in estimating an energy system's costs is to determine its operation and maintenance (O&M) costs. O&M costs are typically separated into fixed and variable costs. Fixed O&M costs include the costs for operating labor, maintenance labor, maintenance materials, and administrative and support labor. Variable O&M costs depend on the *average annual system capacity factor* (CF), which determines the equivalent average number of hours of system operation per year at full load.¹ The variable O&M costs include the costs for fuel, chemicals, water, waste treatment, and emissions treatment. For energy systems that use fuel as their main energy (exergy) input, the fuel costs are typically accounted for as a separate variable operating cost.

Investment and O&M costs can be reported in current (nominal) or constant (real) dollars. Current dollars are more appropriate in energy systems analysis because taxes and depreciation are accounted for on a nominal basis. Constant dollars can be used, but this requires adjustment to cash flows in every year of the analysis. When using published economic performance metrics, it is important to make sure a consistent dollar basis was used in the analysis. Mixing real and nominal dollars can have a significant influence on performance metrics.² For the remainder of this chapter, costs are discussed in current dollars unless otherwise specified.

Since O&M costs are incurred over the life of the energy system, the initial costs must be projected into the future. This, of course, adds a level of uncertainty to already estimated costs. Fixed O&M costs are typically adjusted for inflation, and variable costs (including fuel) are typically adjusted for both inflation and cost-specific real escalation (e.g., fuel costs can be adjusted by a higher nominal escalation rate than other material costs to account for resource depletion). The methods used to account for future price changes directly influence future cash flow estimates, as will be discussed in the following section.

Estimating an energy system's investment and initial O&M costs can be a difficult and time consuming process. The most detailed economic analysis studies account for

¹Average annual system capacity factor is some times referred to as *plant availability*.

²It is not uncommon to discover that dollar bases are misused in published economic studies of energy systems (see, for example, [62, 63]).

all the costs described above, which requires site-specific information and detailed engineering designs. Even when great efforts are made to account for all relevant costs, there is still a significant amount of uncertainty. Due to the inherent uncertainty in estimating an energy system's investment and initial O&M costs, sensitivity analysis is often performed on the costs in economic analysis techniques. This provides information about how changes in cost can affect economic performance metrics, but it does not address inherent assumptions in the cash flow models use to calculate the metrics (also discussed in the next section).

There are several methods for estimating an energy system's costs. The most accurate costs estimated are obtained from direct vendor or contractor quotations. Direct quotations typically require that the equipment be off-the-shelf, and that there is an intent to purchase.³ The next most accurate method for estimating costs is through the use of engineering cost estimating databases (such as the extensive databases published by the Electric Power Research Institute (EPRI) [92]). Other cost-estimation methods, in order from most accurate to least, include equipment-specific cost estimating charts, equipment-specific scaling factors, general scaling factors, and correlations based on other costs used in the analysis (e.g., installation cost measured as a percentage of purchased cost). The details of, and methods used in, these techniques are described in numerous general and industry-specific economic analysis texts (see, for example, [4, 91]).

To provide a perspective for the amount of information required to estimate an energy system's costs, Figs. 5.1 and 5.2 show the fixed-capital investment and O&M costs for a coal-to-liquids (CTL) facility estimated by the National Energy Technology Laboratory (NETL) [93]. The costs presented in the figures are in mid-2006 dollars and were estimated using "adjusted vendor-furnished cost data" and an in-house cost estimating database. The non-fixed-capital investment cost for this facility was estimated to be \$878 million, or 24% of the \$3.65 billion in fixed-capital investment, for a construction period of five years.

³From experience, even obtaining a direct vendor quotation for a gas engine generation set (approximately 1 MW) proved to very difficult without the expressed intent to purchase.

Client: DEPARTMENT OF ENERGY Project: NETL Coal To Liquids Study - Illinois										TOTAL PLANT COST SUMMARY				Report Date: 10-Dec-06	
Case: E-Gas Design for Fischer-Tropsch (No Refinery, No Sequestration) Plant Size: 125,254 MMW/net										Estimate Type: Conceptual				Cost Base (July) 2006 : \$x1000	
50,000 FT Liquids bbl/day															
Acct No.	Item/Description	Equipment Cost	Material Cost	Labor		Bare Erected Cost \$	Eng'g CM H.O.& Fee	Contingencies		TOTAL PLANT COST \$					
				Direct	Indirect			Process	Project						
1	COAL & SORBENT HANDLING	40,655	8,404	35,203	2,464	86,727	6,938		23,416	117,081					
2	COAL-WATER SLURRY PREP & FEED	62,767	13,721	51,844	3,629	131,962	10,557		35,630	178,148					
3	FEEDWATER & MISC. BOP SYSTEMS	12,310	11,530	12,929	905	37,674	3,014		10,172	50,859					
4	GASIFIER & ACCESSORIES														
4.1	Gasifier & Auxiliaries	270,951	128,128	223,895	15,673	638,647	51,092		172,435	862,173					
4.2	Syngas Cooling	w/4.1	w/4.1	w/4.1											
4.3	ASU/Oxidant Compression	287,187	57,900	w/equip.	4,579	287,187	22,975		77,540	387,702					
4.4-4.9	Other Gasification Equipment	46,865	186,028	65,414	20,252	174,757	13,981		47,184	235,922					
	Subtotal 4	605,002		289,309		1,100,591	88,047		297,159	1,485,797					
5A	GAS CLEANUP	164,720	18,909	169,318	11,852	364,800	29,184		98,496	492,480					
5b	FISCHER-TROPSCH SYSTEMS	326,877	48,364	39,571	2,770	417,582	33,407	112,747	140,934	704,669					
6	COMBUSTION TURBINE GENERATOR														
6.1	Combustion Turbine Generator	69,575		2,445	171	72,191	5,775		19,492	97,458					
6.2-6.9	Combustion Turbine/Generator Accessories		437	387	27	851	68		230	1,149					
	Subtotal 6	69,575	437	2,832	198	73,042	5,843		19,721	98,607					
7	HRSG, DUCTING & STACK														
7.1	Heat Recovery Steam Generator	20,035		2,445	171	22,651	1,812		6,116	30,579					
7.2-7.9	HRSG Accessories, Ductwork and Stack	1,942	1,320	1,558	109	4,929	394		1,331	6,655					
	Subtotal 7	21,977	1,320	4,003	280	27,581	2,206		7,447	37,234					
8	STEAM TURBINE GENERATOR														
8.1	Steam TG & Accessories	45,258		6,037	423	51,718	4,137		13,964	69,819					
8.2-8.9	Turbine Plant Auxiliaries & Steam Piping	12,080	1,195	9,025	632	22,933	1,835		6,192	30,959					
	Subtotal 8	57,339	1,195	15,062	1,054	74,651	5,972		20,156	100,778					
9	COOLING WATER SYSTEM	13,603	9,129	12,852	900	36,484	2,919		9,851	49,254					
10	ASH/SPENT SORBENT HANDLING SYS	47,228	26,435	44,694	3,129	121,486	9,719		32,801	164,006					
11	ACCESSORY ELECTRIC PLANT	12,858	6,162	15,567	1,090	35,676	2,854		9,633	48,163					
12	INSTRUMENTATION & CONTROL	19,899	3,238	16,063	1,124	40,324	3,226		10,888	54,438					
13	IMPROVEMENTS TO SITE	6,302	3,998	14,961	1,047	26,308	2,105		7,103	35,515					
14	BUILDINGS & STRUCTURES		8,918	14,464	1,012	24,395	1,952		6,587	32,933					
	TOTAL COST	\$1,461,113	\$347,788	\$738,673	\$51,707	\$2,599,281	\$207,943	\$112,747	\$729,993	\$3,649,964					

Figure 5.1: Example of detailed fixed-capital investment costs estimate for a coal-to-liquids facility. From [93].

INITIAL & ANNUAL O&M EXPENSES				Cost Base (July)	2006
Illinois 50,000 BPD CTL Plant (Analysis 1-1)		12/12/2006		Heat Rate-net(Btu/kWh):	N/A
				MWe-net:	125.254
				Capacity Factor: (%):	85.0
OPERATING & MAINTENANCE LABOR					
<u>Operating Labor</u>					
Operating Labor Rate(base):		34.78	\$/hour		
Operating Labor Burden:		30.00	% of base		
Labor O-H Charge Rate:		25.00	% of labor		
Operating Labor Requirements(O.J.)per Shift:		<u>1 unit/mod.</u>	<u>Total Plant</u>		
Skilled Operator		4	16		
Operator		20	80		
Foreman		4	16		
Lab Tech's, etc.		<u>8</u>	32		
TOTAL-O.J.'s		36	144		
				Annual Cost	
				\$	
Annual Operating Labor Cost(calc'd)					\$57,034,748
Maintenance Labor Cost(calc'd)					\$77,978,439
Administrative & Support Labor(calc'd)					\$14,258,687
Maintenance Material Cost(calc'd)					\$51,985,626
TOTAL FIXED OPERATING COSTS					\$201,257,499
VARIABLE OPERATING COSTS					
<u>Consumables</u>		<u>Consumption</u>		<u>Unit Cost</u>	<u>Initial Cost</u>
		<u>Initial</u>	<u>/Day</u>		
Water(/1000 gallons)		0	21,400	1.20	\$0
Chemicals					
MU & WT Chem.(lbs)		227,904	32,556	0.19	\$42,588
Carbon (Mercury Removal) (lb.)		217,712	392	0.90	\$195,941
COS Catalyst (lb)		494,800	272	0.91	\$450,268
Selexol Solution (gal.)		445,320	100	14.40	\$6,412,608
MDEA Solution (lb)		0	0	0.89	\$0
Zinc Oxide		494,800	60	0.20	\$98,960
Ammonia (28% NH3) ton		0	0	228.00	\$0
Subtotal Chemicals					\$7,200,365
Other					
Supplemental Fuel(MBtu)		0	0	0.00	\$0
SCR Catalyst Replacement		w equip	0	9,480	\$0
Emission Penalties		0	0	0.00	\$0
Subtotal Other					\$0
Waste Disposal					
Spent Mercury Catalyst (lb.)		0	392	0.38	\$0
Flyash (ton)		0	0	18.00	\$0
Bottom Ash(ton)		0	2,470	18.00	\$0
Subtotal Solid Waste Disposal					\$0
By-products & Emissions					
Sulfur(tons)		0	612	-25.00	\$0
Power Production, MWh		0	3,006	-35.00	\$0
Subtotal By-Products					\$0
TOTAL VARIABLE OPERATING COSTS					(\$13,056,882)
FUEL (tons)		0	24,533	33.33	\$0
					\$253,662,383

Figure 5.2: Example of detailed O&M costs estimate for a coal-to-liquids facility. From [93].

To illustrate how plant design and cost-estimation methods can influence an energy system's costs, Table 5.1 provides a comparison between the the fixed-capital investment cost estimated in the NETL study to that of other published cost estimates for CTL facilities of similar size, but with differing plant designs [94, 95]. The costs shown in the table are adjusted to mid-2006 dollars from their individual base years using an nominal cost escalation rate of 5% (the NETL estimates are the first entry). It should also be noted that even adjusting costs for inflation and real escalation to provide direct comparison adds uncertainty through the choice of rates. The range in cost estimates illustrate the inherent uncertainty of detailed cost estimates of the type shown in Figs. 5.1 and 5.2. These uncertainties carry over to influence cash flow analysis and therefore performance metrics.

Coal Feed Rate (tons/day)	FT Liquids (bbl/day)	Net Elec. (MW)	Fixed-Capital Investment (\$M)	FCI / FTL (\$ / bbl/day)	Year Adjusted From	Ref.
24,500	49,990	124	3,650	73,015	2006	[93]
18,575	47,440	-54	5,321	112,165	1994	[94]
20,257	50,000	-50	5,196	103,923	1996	[95]
20,257	50,000	1,000	5,299	105,976	1996	[95]

Table 5.1: Comparisons of published estimates of the fixed-capital investment cost of similar CTL facilities. All costs are adjusted from the year they were reported in to mid-2006 dollars (to be consistent with the NETL estimates, which is the first entry) using a nominal cost escalation rate of 5%. Acronyms stand for barrels (bbl), fixed-capital investment (FCI), and Fischer-Tropsch liquids (FTL).

5.2 Influence of Cost Estimates and Cash Flow Models on Performance Metrics

Detailed economic analysis of an energy system requires the analysis of each year of the system's life, taking into account investment costs, O&M costs, taxes, depreciation, returns on equity, and interest on debt. This requires the application of cash flow

models. There are two broad categories of cash flow models: (1) models that specify a return on equity and calculate the revenue requirements for each year, and (2) models that specify a selling price for each unit of product and calculate the return on equity and net present value (NPV). The first category is commonly referred to as a *revenue requirement* (RR) model, and the second is commonly referred to as a *discounted cash flow* (DCF) model. Both categories of model require as inputs the interest on debt, annual tax rates, a depreciation schedule, annual O&M costs, and the investment costs (and their timing). Therefore, the accuracy of O&M costs and their estimated projections, as well as the accuracy of the investment costs and their timing, have a direct influence on an energy system’s cash flows.

Revenue requirement models use a specified return on equity to calculate the revenues required in each year to cover the annual O&M costs and carrying charges (i.e., taxes, interest on debt, depreciation, and the specified return on equity). The annual revenue required can be used to calculate the required selling prices of products (i.e., cost of energy) for that year, and the sum of the present values of the annual revenues required can be levelized to calculate the system’s levelized cost of energy (LCOE). The required selling price of products for a given year represents the “break-even” selling price for that year, and the levelized cost of energy represents the average break-even price over the life of the system. RR models are typically used by regulated investor-owned utilities because they have a specified rate of return they are allowed to earn. The most commonly used RR model is that specified by EPRI’s Technical Assessment Guide (TAG) [92].

Direct cash flow models, on the other hand, use a specified, required selling price of products to calculate a return on equity (also called the return on investment). The initial and projected selling prices of products have to be estimated, similar to O&M costs, which adds subjectivity and uncertainty to the analysis. DCF models are typically used by independent power producers that operate in competitive markets because the rate of return provides a measure of the “break-even” return for investors. A commonly used DCF model is the NETL Power Systems Financial Model (PSFM) [96]. The principles of DCF models are discussed in detail by Stermole [97] (traditional Engineering Economic texts typically provide simplified discussions).

The main difference between the TAG RR model and DCF models is in how repayment of investment costs and depreciation are accounted for over the life of the energy system. The TAG RR method charges each year of the useful life (N) of a system with a book depreciation charge equal to $1/N$ of the total-capital investment corresponding to the interest on debt and return on equity required on the non-book depreciated portion of the total capital investment and operating expenses over the system's book life. Tax depreciation is accounted for independent of book depreciation, and is done so according to the IRS depreciation schedule specified by the Modified Accelerated Cost Recovery System (MACRS). This method leads to a series of declining values to pay back the total capital investment, which is referred to as the *capital recovery cost*. The accounting method used in the TAG RR model is not typically practiced outside of energy system economic analysis [98]. A detailed and commented application of the TAG RR model to a natural gas combined cycle plant is provided by Bejan et al. [4].

In contrast to the TAG method, DCF models treat the debt portion of the total capital investment as a constant payment (in current dollars) comprised of interest and principle—similar to the repayment of a home mortgage. The equity portion of the total capital investment is simply treated as a negative cash flow at the time of the investment. Unlike the TAG RR model, DCF models account for tax and book depreciation using the same method, which is specified by the developer/user of the model.

Recognizing the differences between the TAG RR model and DCF models is important when using their performance results for decision making for two main reasons: (1) the additional model input of the selling price of products in DCF models adds subjectivity and uncertainty to its performance results, and (2) the subjectivity in the choice of depreciation schedule in DCF models can influence the performance metrics it provides. For example, if all other model inputs are the same in two DCF models (costs, selling prices, taxes, financing percentages, interest on debt, etc.), but different depreciation schedules are used, the models will yield different after-tax cash flows, and therefore different returns on equity. The use of the IRS-specified MACRS depreciation schedule is the most attractive legally acceptable schedule for investments,

whereas straight-line depreciation is the least attractive schedule. This is because the MACRS schedule allows for larger tax deductions earlier in the depreciation life, which is economically more attractive as a result of the time value of money. For more information on the influence of depreciation schedules and their effect on economic performance metrics, refer to texts [13, 14]. Despite the inherent attributes of using accelerated depreciation schedules, straight-line depreciation schedules are often used in economic analysis of energy systems (see, for example, [63, 93, 99]).

DCF models can be developed with the flexibility to specify the return on equity and then calculate the required revenues, which can then be used to calculate the system's levelized cost of energy (LCOE), or average required selling price of products. This approach is commonly used to compare with the LCOE calculated by the TAG RR method. However, since the two models inherently use different methods for repayment of the equity portion of the system's initial investment costs (and possibly depreciation schedules), it does not actually provide a level comparison—only an approximate comparison. This is important to recognize when comparing performance results across the types of models.

As mentioned in the previous section, sensitivity analysis can be, and often is, applied in economic analysis studies—regardless of the cash-flow model. Figure 5.3 shows the sensitivity analysis performed in the NTEL CTL study. The figure illustrates the influence changes in individual costs, selling price estimates, and other model parameters have on the return on equity (the base case return on equity was calculated to be 19.8% in the study). This type of one-way sensitivity is common in economic analysis of energy systems. However, it does not provide insight into the influence that cash flow assumptions (e.g., depreciation schedule, cost and selling price escalation techniques) have on calculated performance metrics. The most complete economic analysis should include a probabilistic sensitivity analysis on both model inputs and cash flow assumptions (see, for example, the GTL study by Ogugbue et al. [100]).

The combination of the inherent uncertainty and subjectivity of cost estimates, and in cash flow models, can have a significant influence on estimated performance metrics. For example, the NETL study estimated a required selling price of FT liquids

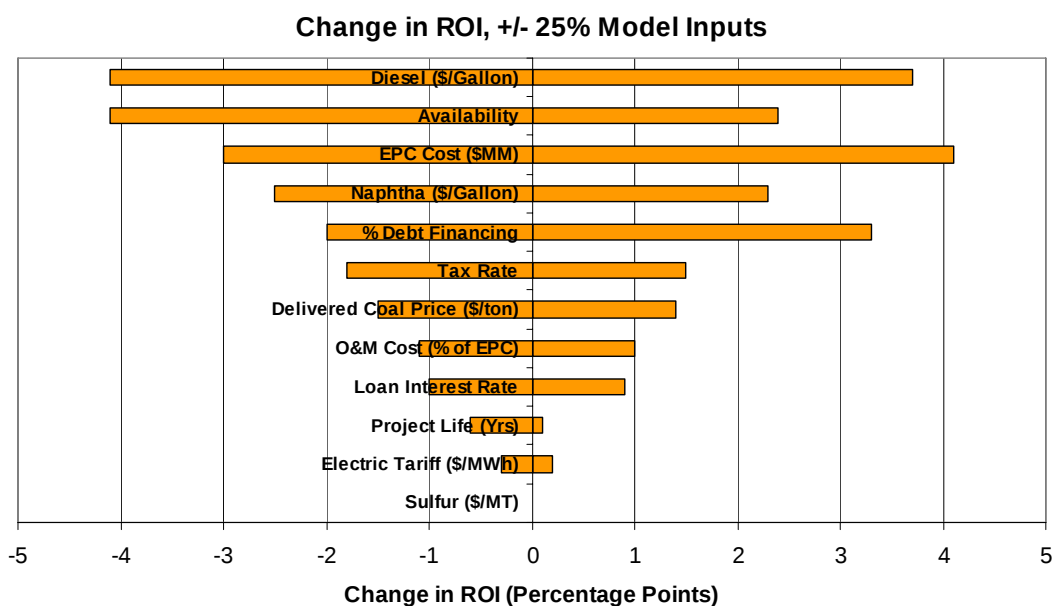


Figure 5.3: Example diagram showing the results of the sensitivity analysis performed on the economic analysis of CTL facility. This “tornado” diagram illustrates how increases and decreases in individual model input parameters by 25% impact the return on investment (i.e., return on equity) in order of significance. From [93].

of \$43 per barrel in mid-2006 dollars to provide a return on equity of 12%. Whereas, economic analysis of two different CTL facility designs presented in [95] estimated a required selling prices for FT liquids between \$35–46 per barrel in mid-1996 dollars to provide the same return on equity, 12%. Adjusting these costs for a nominal escalation rate of 5% yields a required selling price between \$57–75 dollars per barrel in mid-2006 dollars, a significant difference.

5.3 Conclusion

The discussion in this chapter focused on the low-level, detailed economic analysis of energy systems. The objective was to bring to the forefront some of the details of economic analysis techniques that are commonly overlooked, or simply not discussed, in the literature. Of course, the level of detail required in an economic analysis of energy systems depends on the decision objectives that the performance results are

meant to inform. However, as analysis is performed at higher, more aggregated levels, the assumptions, uncertainties, and subjectivity associated with low-level, detailed analysis are only compounded further.

When using published analysis results of energy systems—regardless of the level of the analysis—it is important to ask the following questions:

- How were investment and O&M costs estimated (e.g., vender quotations, published literature, scaling factors, etc.)?
- How were O&M costs projected (e.g., escalation, inflation)?
- What costs were included in these estimates (e.g., total capital investment or just fixed-capital investment)?

When detailed analysis results are considered, additional questions should be asked:

- How was repayment on the debt and equity portions of investment costs discounted (e.g., DCF method, TAG RR method)?
- What type of depreciation schedule was used (e.g., straight-line, MACRS)?
- How were the selling prices of products estimated and projected?

Answering these questions requires information about the analysis, which can often be difficult to obtain because the assumptions and models used in published economic studies are not always transparent (see, for example, [62, 63, 95]). However, the answers to these question are needed before the performance information should be used in decision making.

Chapter 6

Conclusions and Future Work

There is currently an increasing desire to develop and employ alternative energy technologies that lessen dependence on conventional energy resources and reduce environmental impact. The ability to evaluate and compare potential technologies on a level playing field is of critical importance to meeting these objectives while avoiding inadvertent, undesirable consequences. This dissertation presents the results of a critical assessment of the existing methods for evaluating three performance components that are essential to decision making across energy options—technical, environmental, and economic. During the course of this assessment, there appeared to be a significant opportunity for advancement within the environmental component of decision making. This discovery led to the development of a framework for describing and evaluating the environmental implications of energy systems, or more generally, anthropogenic activity. The assessment also proves fertile in addressing some key aspects of existing technical and economic analysis techniques that restrict their ability and application in decision making—albeit with varying levels of consideration.

The dissertation first considers the technical component of decision making. It is shown that while all of the existing thermodynamic analysis techniques are well-established, significant subtlety is required in applying the techniques, understanding their capabilities, and interpreting their results for decision making. A detailed analysis of the production of Fischer-Tropsch liquids is used to illustrate many of the low-level issues associated with performing technical analysis. These issues include the

reliance on published data, empirical data, phase relationships, properties, analytical tools, and proprietary information. The analysis highlights that many of these issues are often not properly addressed in published studies and how oversights in these areas can influence the decisions they inform. All of these issues are shown to restrict the ability of thermodynamic analysis techniques to provide adequate performance information for decision making, especially for non-extant technologies. Following this low-level analysis, a service/carrier/resource view of the space in which energy systems operate is presented to discuss some of the considerations that are commonly not recognized when decision making across energy options. These issues include predefined methods of services, predefined conversion pathways, and predefined architectures within a transformation or pathway. These issues act as proscriptions, restricting the number of possible energy options one considers in decision making, often without recognition of doing so. Across all levels of technical decision making, the utility of exergy as an analysis tool for evaluating energy options and providing performance information for decision making is discussed.

Next the dissertation considers the environmental component of decision making. In this consideration a new framework for evaluating environmental performance is presented. The framework utilizes the recent recognition that exergy is, in fact, a form of environmental free energy to provide a fundamental basis for valuing environmental interactions independent from their secondary impacts (e.g., global warming, photochemical smog, thermal pollution, etc.). In order to make this extension, the traditional representation of the environment and definition of the dead state needed to be revised. This was accomplished through a combination of logical extensions and use of non-equilibrium thermodynamic principles.

The framework is comprised of two separate analysis components: (1) environmental exergy analysis and (2) anthropocentric sensitivity analysis. Environmental exergy analysis extends the principles of technical analysis to the environment in order to quantify the locations, magnitudes, and types of environmental impact—state change, alteration of natural transfers, and destruction change. Anthropocentric sensitivity analysis enables the results of environmental exergy analysis to be further interpreted for decision making, but at the expense of introducing some subjectivity

into the analysis framework.

One of the key attributes of the analysis framework is its ability to evaluate and compare the environmental performance of energy systems on a level playing field, regardless of the specifics of the systems—resources, products, by-products, sizes, or time scales. With the increasing desire to transition from traditional, fossil resource-based energy systems to alternative, renewable-resource-based systems (e.g., from crude oil-derived transportation fuels to biofuels, or from coal-derived electricity to solar), having this ability is essential to evaluating potential options and making sound policy and investment decisions.

The dissertation concludes with a discussion of the economic component of decision making. Recognizing the vast space of economics and energy, the discussion focuses on one of the many relevant dimensions of economic analysis—namely the influence costs and cash flow models have on the evaluation of energy systems. It is shown that the ability to accurately estimate the cost—both initial and future—of non-extant energy systems significantly influences economic performance metrics. Recognizing the restrictions imposed by cost information and the influence cost estimation techniques have on performance metrics is critically important when using the performance information to guide decision making in energy.

6.1 Future Work

While a framework has been established for describing and evaluating the environmental implications of energy systems, future work is needed to investigate and understand the interplay between exergy and anthropocentric sensitivity. This thesis asserts that the two should remain separate, but future research is needed to confirm this assertion. A detailed application of the framework to the environmental examples described in this dissertation would also be a significant next step. One comparison, in particular, that would be of immediate interest is between the use of land for biofuels vs. solar electricity (solid state or solar thermal). Directly comparing these two energy options using the environmental analysis framework could provide critical insight for planning future energy systems.

The ability to remedy some of the issues that plague low-level technical analysis—namely properties and phase relationships—has been problematic for decades. With the increasing complexity of energy systems, there has been a noticeable shift to commercial software programs for performing technical analysis. This dependence is often at the sacrifice of technical understanding of the systems being modeled. An area of future work could be to investigate the trade-offs between useability and transparency in commercial software.

Efforts are currently underway to investigate several key areas of energy-economic models. These areas include understanding better the feedbacks within the energy sector as well as across economic sectors, and providing more transparent methods of technological representation across bottom-up and top-down models. The results of these efforts are critically important to modeling the economic consequences of decisions in energy.

Appendix A

Exergy and Exergy Analysis for Technical Analysis

This appendix presents a derivation of exergy and a discussion on exergy-related topics relevant for technical energy systems analysis. First, a derivation of internal and external exergy is presented, and the application of exergy to energy systems analysis is demonstrated. Next, the exergy associated with various energy transfers relevant in energy systems are defined, followed by a discussion of performance metrics commonly used in technical energy systems analysis. The appendix concludes with a discussion on the role of the dead state, and the evaluation of radiation and nuclear exergy.

A.1 Derivation of Exergy as a Measure of Maximum Work

Exergy is defined as the maximum amount of work that can be extracted from a resource relative to the environmental surroundings with which it interacts. A resource is defined as any energy accumulation or energy flux that has the potential to produce work relative to its environmental surroundings. The environmental surroundings are defined as the portions of the natural environment that enable work to be extracted

from a resource because they act as a thermal, mechanical, and chemical reservoir to the resource. The maximum amount of work is realized when the resource is reversibly brought into equilibrium with its environmental surroundings. The exergy of a resource can be broken down into various forms. The relevant forms of exergy for energy systems analysis include: thermal, mechanical, chemical, kinetic, potential, radiation, and nuclear. The thermal, mechanical, and chemical exergy of a resource are commonly referred to as its internal exergy, and the kinetic and gravitational potential exergy of a resource are commonly referred to as its external exergy. Presented in this section is a derivation of internal and external exergy.¹

A.1.1 Internal Exergy

The internal exergy of a resource is the maximum amount of work that can be extracted from a resource as it reversibly reaches thermal, mechanical, and chemical equilibrium with the environmental surroundings with which it interacts. Reversibility requires that the resource must transfer heat at the environmental temperature, boundary work at the environmental pressure, and environmental species at their environmental chemical potentials. In technical exergy analysis, reversible interactions can be realized by modeling the environmental surroundings as a single reservoir that is sufficiently large and has sufficiently fast transport that its intensive state does not change during equilibration (i.e., the environmental temperature, pressure, and composition are fixed). An illustration of a resource in communication with the environment is shown in Fig. A.1.

As shown in the figure, there are three types of transfers between the resource and the environment: boundary work (δW_b), heat (δQ), and environmental species (δN_i). Boundary work is transferred at the environmental pressure (P_o), heat at the environmental temperature (T_o), and environmental species at their environmental chemical potentials ($\mu_{i,o}$). The maximum amount of work that can be extracted from the resource relative to the environment is derived by applying the First and Second Laws of thermodynamics to the control boundary around the resource. The

¹The derivation of internal exergy is based on lecture notes from ME370B: Energy Systems II, at Stanford University, by Professor Chris Edwards.

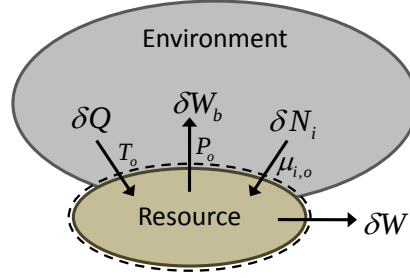


Figure A.1: Resource in communication with the environment.

differential expressions of the First and Second Laws for the resource are:

$$dU = \delta Q - \delta W_b + \sum_i h_{i,o} \delta N_i - \delta W \quad (\text{A.1})$$

$$dS = \frac{\delta Q}{T_o} + \sum_i s_{i,o} \delta N_i + \delta S_{gen} \quad (\text{A.2})$$

Combining Eqs. (A.1) and (A.2) and employing the definition of boundary work, $\delta W_b = P_o dV$, yields an expression for the differential work extracted from the resource.

$$\delta W = -dU - P_o dV + T_o dS + \sum_i (h_{i,o} - T_o s_{i,o}) \delta N_i - T_o \delta S_{gen} \quad (\text{A.3})$$

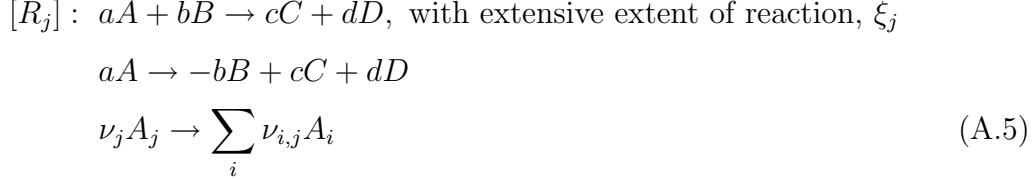
The maximum amount of work is realized when the interactions occur reversibly (i.e., no entropy generation). Therefore, the expression for the maximum differential amount of work that can be extracted from the resource is:

$$\delta W_{max} = -dU - P_o dV + T_o dS + \sum_i \mu_{i,o} \delta N_i \quad (\text{A.4})$$

Internal exergy is defined as the integral of Eq. (A.4) from the resource state to the state of the environment, called the *dead state*². In order to perform this integration, the inexact differential for the transfer of species must be converted to an exact differential. This can be accomplished by considering the reversible transformation

²The dead state is discussed in more detail in Sec. A.5

of all non-environmental species (j) present in the resource to environmental species (i) through the following reaction:



where ν_j is the stoichiometric coefficient for the non-environmental species (j) in the resource, and $\nu_{i,j}$ is the stoichiometric coefficient for the environmental species used or created by the transformation of non-environmental species (j) to environmental species (i). The species balances for environmental species (i) and non-environmental species (j) are:

$$dN_i = \delta N_i + \sum_j \nu_{i,j} d\xi_j \tag{A.6}$$

$$dN_j = -\nu_j d\xi_j \tag{A.7}$$

Combining Eqs. (A.6) and (A.7) through the differential extent of reaction yields an exact differential expression for the moles of environmental species transferred (i):

$$\delta N_i = dN_i + \sum_j (\nu_{i,j}/\nu_j) dN_j \tag{A.8}$$

Combining the above expression and Eq. (A.4) yields an exact differential equation for the maximum amount of work:

$$\delta W_{max} = -dU - P_o dV + T_o dS + \sum_i \mu_{i,o} dN_i + \sum_i \mu_{i,o} \sum_j (\nu_{i,j}/\nu_j) dN_j \tag{A.9}$$

The state of the environment enters the maximum work calculation through the fixed, intensive environmental parameters T_o , P_o , and $\mu_{i,o}$. Since the right-hand side of Eq. (A.9) is an exact function, the integral is independent of the path chosen. The internal exergy can be calculated by integrating Eq. (A.9) along two paths: (1) from

the resource state (RS) to the environmental temperature and pressure, called the *thermo-mechanical dead state* (TM DS), while at fixed resource composition (i.e., no diffusion or reaction permitted), and (2) from the thermo-mechanical dead state to the dead state (DS), while at the fixed environmental temperature and pressure.

$$\begin{aligned}
X_{int} \equiv & \int_{RS}^{TM \ DS} (-dU - P_o dV + T_o dS) \Big|_{\substack{\text{Fixed Comp.} \\ \text{No Reaction}}} \\
& + \int_{TM \ DS}^{DS} \left(-dU - P_o dV + T_o dS + \sum_i \mu_{i,o} dN_i \right. \\
& \left. + \sum_i \mu_{i,o} \sum_j (\nu_{i,j}/\nu_j) dN_j \right) \Big|_{\substack{T=T_o \\ P=P_o}}
\end{aligned} \tag{A.10}$$

The first integral in the above equation is defined as the *thermo-mechanical exergy*, X_{TM} , and the second integral is defined as the *chemical exergy*, X_C . The internal exergy of a resource is then:

$$X_{int} = X_{TM} + X_C \tag{A.11}$$

Integration of the first integral yields the thermo-mechanical exergy:

$$X_{TM} = (U + P_o V - T_o S) - (U_{TM} + P_o V_{TM} - T_o S_{TM}) \tag{A.12}$$

All properties are evaluated at the extensive composition of the resource ($\{N_k\}$), where subscript k represents both environmental (i) and non-environmental (j) species present in the resource. The terms in the first set of brackets are evaluated at the resource intensive state (T, P), and are defined as the *Availability Function* of the resource, A . The terms in the second set of brackets are evaluated at the environmental temperature and pressure (T_o, P_o), and are the Gibbs Function of the resource at the thermo-mechanical dead state, G_{TM} . The thermo-mechanical exergy simplifies to:

$$X_{TM} = A - G_{TM} \tag{A.13}$$

The thermo-mechanical exergy is therefore the difference between the Availability of the resource at the resource state and the Gibbs energy of the resource at the temperature and pressure of the environment.

Integration of the second integral in Eq. (A.18) yields the chemical exergy:

$$X_C = (U_{TM} + P_o V_{TM} - T_o S_{TM}) - (U_o + P_o V_o - T_o S_o) - \sum_i \mu_{i,o} (N_i - N_{i,o}) - \sum_i \mu_{i,o} \sum_j (\nu_{i,j} / \nu_j) (N_j - N_{j,o}) \quad (\text{A.14})$$

The terms in the first set of brackets are again the Gibbs Function of the resource at the thermo-mechanical dead state, G_{TM} . The terms in the second set of brackets are evaluated at the environmental temperature (T_o) and pressure (P_o) and extensive state ($\{N_{i,o}\}$). In the first summation, the chemical potential of each environmental species (i) present in the resource, evaluated at the environmental intensive state (T_o, P_o), is multiplied by the difference between the moles of environmental species (i) in the resource (N_i) and in the environment ($N_{i,o}$). The extensive state of the environment ($\{N_{i,o}\}$) is unknown; however, the extensive properties in the second set of brackets cancel with the extensive properties of the environment the first summation. In the second summation, the moles of non-environmental species (j) present in the environment ($\{N_{j,o}\}$) are zero. The chemical exergy therefore simplifies to:

$$X_C = G_{TM} - \sum_i \mu_{i,o} N_i - \sum_j \left[\sum_i \mu_{i,o} (\nu_{i,j} / \nu_j) \right] N_j \quad (\text{A.15})$$

The first summation is the diffusive work potential of environmental species (i) present in the resource, and the second summation is the reactive and diffusive work potential of non-environmental species present in the resource. Defining the two summations as:

$$G_o = \sum_i \mu_{i,o} N_i + \sum_j \left[\sum_i \mu_{i,o} (\nu_{i,j} / \nu_j) \right] N_j \quad (\text{A.16})$$

then the chemical exergy simplifies to:

$$X_C = G_{TM} - G_o \quad (\text{A.17})$$

The chemical exergy is therefore the difference between the chemical potential (i.e., Gibbs Function) of the resource at the thermo-mechanical dead state before and after it has reacted and diffused to become part of the environment (all at T_o and P_o).

The internal exergy of a resource is the sum of the thermo-mechanical and chemical exergy of the resource:

$$\begin{aligned} X_{int} &= X_{TM} + X_C = (A - G_{TM}) + (G_{TM} - G_o) = A - G_o \\ &= (U + P_o V - T_o S) - \sum_i \mu_{i,o} N_i - \sum_j \left[\sum_i \mu_{i,o} (\nu_{i,j} / \nu_j) \right] N_j \end{aligned} \quad (\text{A.18})$$

The internal exergy is therefore the difference between the Availability of the resource at the extensive resource state $(T, P, \{N_k\})$ and the chemical potential of the resource after it has reacted and diffused at the thermo-mechanical dead state (T_o, P_o) to become part of the environment.

A.1.2 External Exergy

A resource has external exergy as a result of its velocity relative to the reference environment and height within the reference environment. The maximum amount of work that can be extracted from a resource's velocity is the difference between the kinetic energy of the resource evaluated at the velocity of the resource and the velocity of the reference environment, and is called the kinetic exergy. The maximum amount of work that can be extracted from a resource's height is the difference between the potential energy of the resource evaluated at the height of the resource and the height of the environment, and is called gravitational potential exergy. The external exergy of a resource is the sum of kinetic and gravitational potential exergy:

$$X_{ext} = X_{KE} + X_{PE} = \frac{m}{2} (v - v_o)^2 + mg(z - z_o) \quad (\text{A.19})$$

where m is the mass of the resource, g is the gravitational constant, v and v_o are the velocities of the resource and environment, and z and z_o are the heights of the resource and environment, respectively. If the environmental velocity and height are defined to be zero, then the kinetic and potential exergy of a resource are equivalent to its kinetic and potential energy, respectively.

A.1.3 Total Exergy

The total exergy of a resource is the sum of the individual forms of exergy:

$$\begin{aligned}
 X &= X_{int} + X_{ext} + X_{other} = A - G_o + X_{KE} + X_{PE} + X_{other} \\
 &= (U + P_o V - T_o S) - \sum_i \mu_{i,o} N_i - \sum_j \left[\sum_i \mu_{i,o} (\nu_{i,j} / \nu_j) \right] N_j \\
 &\quad + \frac{m}{2} (v - v_o)^2 + mg(z - z_o) + X_{other}
 \end{aligned} \tag{A.20}$$

The “other” forms of exergy that are relevant for energy systems analysis include radiation and nuclear exergy. However, due to the intrinsic difficulties in defining radiation and nuclear exergy, they are discussed in separate sections at the end of this appendix.

A.2 Exergy Destruction and Balances

Exergy is similar to energy in that it cannot be produced; however, exergy is unlike energy in that it can be destroyed. Exergy destruction represents lost potential to do work. Tracking the flow of exergy through an energy system enables the locations and magnitudes of exergy destructions, or losses of potential work, to be determined. A diagram illustrating the exergy flows to and from a generic work-producing energy system is shown in Fig. A.2.

The differential exergy balance for the system shown in the figure is:

$$dX_{system} = \delta X_{input} - \delta X_{discharged} - \delta W - \delta X_{destroyed} \tag{A.21}$$

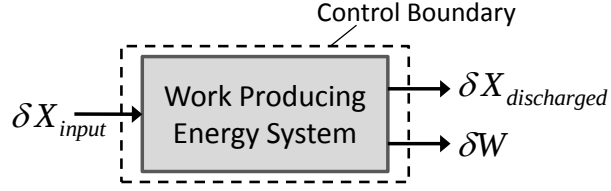


Figure A.2: Diagram of a generic work-producing energy system.

The equation shows that the change in exergy of the system is equal to the difference between the exergy input to the system and the sum of the exergy output from the system and the exergy destroyed within the system. The exergy balance for any energy system can be written as:

$$dX_{system} = \sum \delta X_{inputs} - \sum \delta X_{outputs} - \delta X_{destroyed} \quad (A.22)$$

The above equation can be rearranged to show that the exergy destroyed within an energy system is equal to the difference between the exergy input to the system and sum of the exergy output from and accumulated within the system. Exergy destruction is the result of irreversibilities in the system and is equivalent to the product of the entropy generated within the system and the environmental temperature, $\delta X_{destroyed} = T_o \delta S_{generated}$. The relationship between exergy destruction (i.e., lost work) and entropy generation is commonly referred to as the Gouy-Stodola theorem [10, 85].

A.3 Exergy Transfers

Table A.1 provides a list of common energy transfers to and from energy systems and their associated exergy values. As shown in the table, the exergy value of reversible work (i.e., shaft work and electricity) is equivalent to its energy value. The exergy of compression and/or expansion work for moving a boundary is a function of the initial pressure of the boundary and the change in volume of the resource evaluated at its initial state and the thermo-mechanical dead state. The exergy of heat is equivalent to the product of the energy of the heat and the Carnot Fraction, which

provides a measure of the quality, or work potential, of the heat. The exergy of matter transfers is commonly referred to as *flow exergy* and can be calculated by using the standard definition of exergy and correcting for the flow exergy of the resource—defined as $(P - P_o)\bar{v}$, where $\bar{v}$ is the molar specific volume. By utilizing the definition of enthalpy, $H = U + PV$, the flow exergy of a resource can also be calculated by the following equation:

$$X_{flow} = (H - T_o S) - G_o + X_{ext} + X_{other} \quad (\text{A.23})$$

Transfer Type	Exergy Value
Reversible Work	δW
Boundary Work	$(P - P_o)dV$
Heat	$\delta Q \left(1 - \frac{T_o}{T}\right)^*$
Matter	$(\bar{x} - (P - P_o)\bar{v})\delta N^{**}$

$$^* \left(1 - \frac{T_o}{T}\right) \equiv \text{Carnot Fraction}$$

$$^{**} \bar{x} = X / N \equiv \text{Molar Exergy}, \bar{v} = V / N \equiv \text{Specific Volume}.$$

Table A.1: Exergy values for common transfers.

A.4 Energy System Performance Efficiencies

The efficiency of an energy system is commonly used to communicate its technical performance. Table A.2 provides a list of commonly used efficiencies for quantifying the technical performance of work producing energy systems. The first three efficiencies—thermal, first law, and utilization—are based strictly on the First Law of thermodynamics, and the last two efficiencies—second law, and exergy—are based on both the First and Second Laws of thermodynamics. Understanding the meanings

and appropriate applications of the individual efficiencies is essential to effectively employing them for decision making in energy.

Efficiency Type	Equation
Thermal	$\eta_{Th} = \frac{W_{Out}}{Q_{Input}}$
First Law (Fuel Conversion)	$\eta_I = \frac{W_{Out}}{m_{Fuel\ Input} \cdot HV_{Fuel}}$
Utilization (Combined Heat Power)	$\eta_{CHP} = \frac{W_{Out} + Q_{Out}}{m_{Fuel\ Input} \cdot HV_{Fuel}}$
Second Law	$\eta_{II} = \frac{W_{Out}}{W_{Out, Rev}}$
Exergy	$\eta_{Ex} = \frac{W_{Out}}{X_{Input}}$

Table A.2: Commonly used efficiency metrics for work producing energy systems.

As shown in the table, thermal efficiency is defined as the ratio of the work produced by an energy system and the energy content of the heat input to the system. Thermal efficiency provides a measure of how well an energy system converts input heat energy to work. As such, thermal efficiency is only applicable to heat engines. However, since the heat input to the system is measured by its energy content, thermal efficiency neglects to account for the quality, or work potential, of the heat input to the system.

First-law (a.k.a., fuel conversion) efficiency is defined as the ratio of the work produced by an energy system to the energy content of the fuel input to the system, as measured by the fuel's heating value (HV)—either lower or higher (LHV , HHV). The heating value of a fuel is a measure of the heat transferred from a fuel as it undergoes complete combustion under standard conditions (typically 25°C and 1 atm).

Therefore, first-law efficiency inherently measures the performance of an energy system relative to that of a heat engine. Despite its inherent connection to heat engines, first-law efficiencies are often used to measure the performance of non-heat-engine energy systems (e.g., piston engines, gas turbines).

Utilization efficiency is an extension to first-law efficiency for systems that produce both work and heat, and is often called the combined heat and power (CHP) efficiency. Utilization efficiency is defined as the ratio of the sum of work and heat produced by an energy system to the heating value of the fuel input to the system. Similar to thermal efficiency, utilization efficiency does not account for the quality of the produced heat, and similar to first-law efficiency, it attempts measure the performance of an energy system relative to that of a heat engine.

Thermal, first-law, and utilization efficiencies are all based strictly on the First Law, and provide measures of how well an energy system transforms energy inputs to energy products (i.e., work and heat). They do not provide a measure of how well a system performs relative to a theoretical limit. Furthermore, since not all energy has the same work potential (e.g., heat at 300 K vs. heat at 400 K) first-law-based efficiencies are not capable of cross-comparing energy systems the use different resources or produce different outputs, both of which are essential for decision making in energy.

Second-law and exergy efficiencies are based on both the First and Second Laws of thermodynamics and provide theoretical limits for the performance of energy systems. Second-law efficiency is defined as the ratio of the work produced by an energy system to the amount of work that could be produced if all components operated reversibly; it provides a measure of how well an energy system performs relative to the theoretical limit of the system. Exergy efficiency is the ratio of the work produced by an energy system to the exergy input to the system. It provides a measure of how well an energy system performs relative to the theoretical limit of the resources input to the system.

Second-law and exergy efficiencies inherently provide different measures of performance; however, they are often used interchangeably. The two efficiencies are different because exergy efficiency is independent of the architecture of the system,

whereas second-law efficiency requires a defined architecture (i.e., energy system design). Exergy efficiency enables different energy systems to be compared on an even playing field regardless of architecture because each system is compared against an absolute theoretical limit, which is set by the system's inputs. Second law efficiency is limited to comparing energy systems within the same architecture class because the theoretical limit is that of the architecture, and not the inputs to the systems. Exergy efficiency is sometimes called the *rational* efficiency because it provides a measure of how well a resource is used to produce desired exergetic produces (e.g., work, electricity, commercial fuels, heat).

A.5 The Role of the Dead State

In order to calculate the exergy of a resource, the thermodynamic states of the resource and the environmental surroundings must be known before and after equilibration. Since the environmental surroundings are, in theory, suppose to represent the natural environment, model representations of the natural environment are employed. Model representations of the natural environment are typically referred to as the *reference environment*, and the state of the reference environment is typically referred to as the *reference state* or the *dead state*. The dead state is defined to have zero work potential (i.e., zero exergy) and serves as a datum from which the maximum work potential, or exergy, of a resource can be calculated. The dead state is typically defined by an environmental temperature (T_o), pressure (P_o), velocity (v_o), position (z_o), and composition ($\{x_{i,o}\}$), which are chosen such that every chemical element in the resource has a chemical species in the dead state that is assigned to have zero exergy.

In technical exergy analysis, the reference environment is traditionally modeled based on the properties of the atmosphere—with modifications for solid mineral and liquid substances—as a large reservoir with fast internal relaxation such that its intensive state does not change as a result of equilibration with a resource or interaction with an energy system [7]. This type of reference environment simplifies exergy calculations because the final (equilibrium) state of a resource and its environment is

equal to the state of the reference environment. The fixed dead state associated with the traditional reference environment is sufficient for calculating exergy as a measure of maximum work when performing technical exergy analysis on systems involving thermal (e.g., geothermal), mechanical, chemical (e.g., fossil resources), kinetic (e.g., wind), or potential (e.g., hydro) energy resources. However, in order to perform technical exergy analysis on systems involving radiation or nuclear resources, the traditional dead state must be modified—as is discussed in the following sections.³

A.6 Radiation Exergy

Defining the exergy of radiation is difficult because there is no equilibrium environment, or dead state, of radiation from which to measure a departure from equilibrium. Therefore, the exergy of radiation is typically defined relative to the radiation properties of a blackbody at the environmental temperature (T_o), which is assigned to have zero exergy. There are several commonly used definitions for the exergy of radiation that use this approach [3, 101–104]. Discussions on the validity, merits, and applications of the most prominent definitions of radiation exergy can be found in [3, 105–107].

The most commonly employed definition for the exergy of blackbody radiation (BR) was first presented by Petela [103], and is given by the following equation:

$$X_{BR} = aVT^4 \left(1 - \frac{4T_o}{3T} + \frac{1}{3} \left(\frac{T_o}{T} \right)^4 \right) = U \left(1 - \frac{4T_o}{3T} + \frac{1}{3} \left(\frac{T_o}{T} \right)^4 \right) \quad (\text{A.24})$$

where a is a universal constant given by:

$$a = \frac{8\pi^5 k^4}{15h^5 c^3} = 7.565 \cdot 10^{-16} \text{ Jm}^{-3}\text{K}^{-4} \quad (\text{A.25})$$

and U is the energy of blackbody radiation. Equation (A.24) does not depend on the emissivity of the environment and may also be applied to grey surfaces if its

³Refer to Ch. 4 for a discussion of defining an appropriate reference environment for performing environmental exergy analysis.

emissivity does not depend on wavelength [108]. The above equation for the exergy of black body radiation can be derived by two methods. The first method is by considering a deformable, perfectly reflective enclosure of blackbody radiation at a specified volume and temperature (V, T) ⁴ and calculating the maximum boundary work that can be extracted from the the enclosure as it reversibly expands to the environmental temperature (T_o) and corresponding radiation pressure.^{5,6} The second method is by considering two blackbody surfaces at temperature (T) and the environmental temperature, and calculating the maximum work that can be extracted from the flux of radiation between the two surfaces via a reversible heat engine. The resulting equation for the exergy of blackbody radiation measures the maximum work potential of radiation at a specified temperature relative to blackbody radiation at the environmental temperature.

Equation (A.24) is often employed to quantify the exergy of solar radiation because the spectral composition of solar radiation in space closely resembles that of a blackbody at approximately 5780 K. Using the above equation and an environmental temperature of 298 K, the ratio of the exergy to energy (X/U) of solar radiation is approximately 0.93. The spectral composition of solar radiation that reaches the surface of the Earth departs slightly from that of a blackbody due to selective frequency absorption in the atmosphere and the influence of diffuse radiation, which together reduce the exergy of solar radiation at the Earth's surface. The change in exergy due to natural changes in spectral composition is small relative to isotropic blackbody radiation, decreasing by 1–2.5% from solar zenith angles 0° – 75.5° [109]. The energy in diffuse solar radiation is often modeled, or described, by using the radiation properties of a blackbody at a lower temperature than the sun, called the characteristic

⁴Photons have zero rest mass, therefore only two intensive properties are required to define the state.

⁵Radiation pressure is defined by the temperature of the radiation, $P = aT^4/3$. At T_o , the radiation pressure is orders of magnitude less than the traditional environmental pressure, P_o , which is typically 1 bar or atmosphere.

⁶Since photons have zero rest mass, their chemical potential is zero. For a reversible expansion process, the Gibbs-Duhem relation reduces to $SdT = VdP$, which means that only one intensive property can be varied independently [3]. In this derivation, temperature is the independent variable.

temperature. It has been shown that diffuse solar radiation has a characteristic temperature of 1600 K, which corresponds to an exergy-to-energy ratio of approximately 0.75 [110]. The fractions of direct and diffuse solar radiation incident on a conversion system (thermal or photovoltaic) are typically weighted by their respective exergy-to-energy ratios and added together to quantify the total exergy input to the conversion system.

The derivations for the exergy of blackbody radiation require that equilibrium can exist between the radiation and its emitting matter [104]. Radiation from a non-blackbody has an arbitrary spectral composition that is inherently out of equilibrium with its emitting matter, and therefore requires a different exergy derivation from that of isotropic blackbody radiation. The most commonly employed definition for the exergy of arbitrary spectrum radiation (ASR), or non-blackbody radiation (NBR), is derived by Wright et al. [104], and is given by the following equation:

$$X_{ASR} = U_{ASR} - T_o \left(\frac{4}{3} a^{1/4} V^{1/4} U_{ASR}^{3/4} \right) + \frac{a}{3} V T_o^4 \quad (\text{A.26})$$

The above equation is derived by considering isotropic non-blackbody radiation in an evacuated, perfectly reflecting enclosure, which keeps the radiation from equilibrating to blackbody radiation. The non-blackbody radiation must interact with matter (e.g., a work-producing device) in order to be absorbed and used to produce work. Upon contact with an absorbing material, the non-blackbody radiation equilibrates to blackbody radiation with the same energy, but with higher entropy. This unavoidable conversion process is inherently irreversible. The exergy of blackbody radiation emitted by the absorbing material is then calculated using the equation for the exergy of blackbody radiation provided above. Therefore, the above equation for the exergy of non-blackbody radiation is derived through a two-stage process: first, the inherently irreversible conversion of non-blackbody radiation at a specified temperature (T) to blackbody radiation at the same temperature, and second, the conversion of blackbody radiation at the same specified temperature (T) to the blackbody radiation at the environmental temperature (T_o).

The two most commonly used definitions for the exergy of blackbody and non-blackbody radiation measure the maximum amount of work that can be extracted from radiation at specified temperature (T) relative to blackbody radiation at the environmental temperature (T_o). Inherent to both derivations is a theoretical process, or architecture. This implies that the above equations are not actually definitions for the maximum work potential (i.e., exergy) of radiation relative to an environmental reservoir, but instead, they are second-law constrained definitions for the maximum amount of work that can be extracted from radiation at specified temperature relative to radiation at environmental temperature. Furthermore, the derivation for the exergy of radiation with an arbitrary spectrum composition involves an irreversible process, which violates the fundamental principle of exergy as the maximum (i.e., reversible) work potential of a resource relative to the environment.

The traditional definitions of solar exergy circumvent defining a dead state for radiation by defining blackbody radiation at the environmental temperature (T_o) as having zero exergy. This means that radiation, or re-radiation, from a work producing device at the environmental temperature does not have the potential to do work. However, this is certainly not the case when one considers the work potential between radiation at the environmental temperature and radiation at the temperature of deep space. In order to define the exergy of radiation, it is proposed that a more appropriate dead state for radiation is that of radiation in deep space, which can be modeled as blackbody radiation at approximately 3 K. Deep space provides a more appropriate reference environmental reservoir for radiation because the ultimate fate of all radiation that is not absorbed by matter in the terrestrial environment is deep space. Although terrestrial solar exergy conversion systems do not directly contact or reradiate to deep space, they could be designed to collect solar exergy during day light hours and then reradiate unused exergy during night hours at a wavelength such that the radiation is not absorbed by the night sky before entering space. Inefficiencies would be incurred in real systems as a result of solar exergy conversion and storage, but the reference reservoir of deep space provides a more appropriate upper limit on the maximum amount of work that can be extracted from the natural resource flux of solar exergy.

For the purposes of the work presented in this dissertation, the exergy of radiation is quantified using the above definitions for the exergy of blackbody and non-blackbody radiation with a deep space-based dead state temperature of 3 K. Using a reference temperature for deep space of 3 K, the exergy-to-energy ratio for blackbody radiation of the sun is approximately 0.999, and the exergy-to-energy ratio of blackbody radiation at the environmental temperature of 298 K is approximately 0.987. This approach does not eliminate the issue of intrinsic irreversibilities for non-blackbody radiation conversion; however, it does provide a more appropriate measure for the absolute maximum amount of work that can be extracted from radiation that is more in line with the inherent principles of exergy—that is, a resource’s maximum work potential is measured relative to the environmental surroundings, which includes space. More research is required in the field of radiation thermodynamics to better understand the behavior and quantify the exergy of both blackbody and non-blackbody radiation.

A.7 Nuclear Exergy

The exergy of nuclear matter is traditionally defined based on the change in potential energy associated with the strong and weak nuclear forces during a specified nuclear reaction pathway [87, 111]. As nuclides undergo exothermic nuclear reactions, the potential energy is reduced due to the strong and weak forces, forming products with less rest mass than the reactants. This difference in mass is directly proportional to the energy released, which is described by Einstein’s mass and energy equivalence, $e = mc^2$. The exergy of nuclear matter is typically approximated as the energy equivalent of the mass defect between the products and reactants of a specified nuclear reaction, not including the neutrino energy [87], through the following equation:

$$X_{Nuclear} \approx \frac{(\sum m_{k,p} - \sum m_{k,r}) c^2}{\sum m_{k,r}} \quad (\text{A.27})$$

where c is the speed of light, and the summations are over all reactants, r , and products, p , of the specified nuclear reaction. The reaction products are chosen such

that they cannot be further utilized in known nuclear reactions. This approximation neglects the influence that both the change in entropy from reactants to products and the diffusion of products to their environmental concentrations has on the work potential of the nuclear matter. However, the energy released during known nuclear reactions is orders of magnitude greater than the entropy change and work potential of product diffusion [87].

The above definition for nuclear exergy is not defined relative to a standard reference state of nuclides similar to how chemical exergy is defined relative to chemical species in the traditional reference state. Defining a traditional reference state for nuclear matter is difficult because nuclear reactions do not conserve species and they produce and/or require excess subatomic particles during reaction. The definition of nuclear exergy shown in Eq. (A.27) avoids these issues by defining the exergy relative to the products of nuclear reactions for nuclides used in current or proposed nuclear cycles. The naturally occurring nuclides used in current and proposed nuclear cycles include: U-235, U-238, Th-232, H-2, Li-6, and Li-7. Nuclear reactions in stars involve a wider range of nuclides [112], but current technology is not able to reproduce such reactions. Nuclides have specific bound energies following a curve rising on either side of the atoms in the iron family of the periodic table as shown in Fig. A.3 [87, 113]. The most stable nuclide, Ni-62, is defined to have zero bound energy. Atoms heavier than Ni-62 can undergo fission to lighter atoms (e.g., U-235 to products about the mass number 95 and 135), while atoms lighter than Ni-62 can undergo fusion to heavier atoms (e.g., Li-7 and H-2 to He-4). The products of fission and fusion reactions are defined as the “reference” species, and are used in the mass defect difference calculation to approximate the exergy of the nuclear reactants.

The traditional definition of nuclear exergy yields exergy-to-energy ratios indistinguishable from unity for current and proposed nuclear reactions. This is because the energy released by nuclear reactions is effectively entropy free due to the extreme temperature of the products of nuclear reactions, approximately $650 \cdot 10^6$ K for a typical fission reaction [87]. The traditional definition of nuclear exergy provides a measure of the practical work potential of nuclides that is useful in energy systems analysis. However, since it is not defined relative to an equilibrium dead state, it is

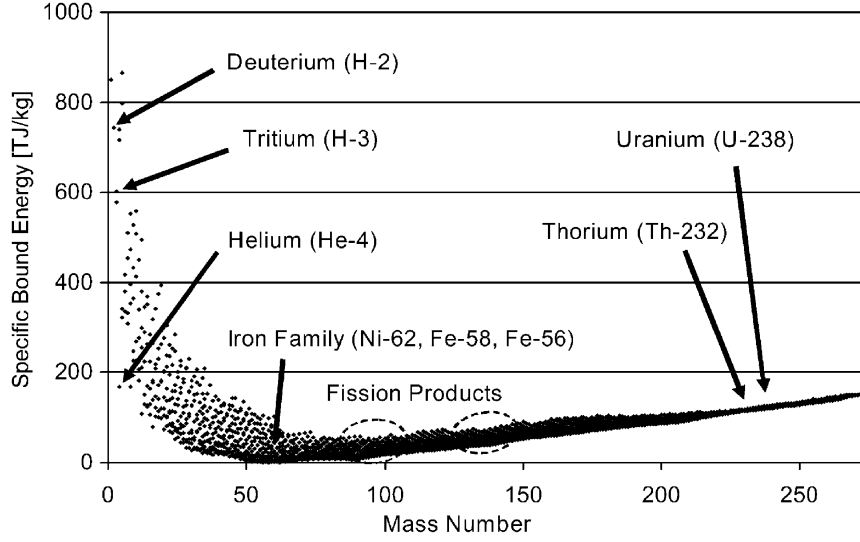


Figure A.3: Nucleus-bound energy of known nuclides ($\text{Ni-62} = 0$). From Hermann [87].

not a measure of the departure from equilibrium of nuclear matter. A possible alternative approach for defining an equilibrium dead state would be to measure the work potential of all nuclides relative to that of the most stable atom, Ni-62. However, it can be argued that this is a less useful measure of the work potential since current technology is far from being able to harness the energy equivalent of the mass defect between common nuclides and Ni-62. Furthermore, it does not address the issue of non-conservation of species and subatomic particles. For the purposes of this work, the traditional definition of nuclear exergy provided in Eq. (A.27) is employed.

Appendix B

Derivation of Exergy as a Form of Environmental Free Energy

This appendix presents an alternative derivation of exergy similar to the derivations of two common forms of free energy—Helmholtz and Gibbs—in order to introduce the concept that exergy is a form of free energy. All forms of free energy measure the maximum (i.e., reversible) amount of work that can be extracted from a non-equilibrium system constrained to equilibrate under specified interaction constraints—constant temperature and volume for Helmholtz free energy, and constant temperature and pressure for Gibbs free energy. Exergy is, by definition, the maximum amount of work that can be extracted from a system comprised of a resource and its environment, constrained to equilibrate at the conditions of the environment. Therefore, exergy is the free energy of a resource relative to its environmental surroundings; in other words, exergy is the *environmental free energy* of a resource. Recognition that exergy is a form of environmental free energy enables exergy to be used as a measure of the potential to drive environmental change, which is discussed and demonstrated in Ch. 4.¹

¹The derivation of Helmholtz and Gibbs free energy is based on lecture notes from ME370B: Energy Systems II, at Stanford University, by Professor Chris Edwards.

B.1 Derivation of Helmholtz and Gibbs Free Energy

Consider a closed system of fixed volume and temperature that is initially separated into two regions by a partition, with substances A and B on either side of the partition. The individual regions are initially in internal equilibrium and at the same temperature, but not in mechanical or chemical equilibrium. The volume of the system is held constant by a rigid container, and the temperature of the system is held constant through heat transfer with an external thermal reservoir controlled by a thermostat. Since the system is initially out of equilibrium, there exists a driving potential that can theoretically be extracted as work. A diagram of this closed, rigid system in communication with a thermal reservoir with work extraction is shown in Fig. B.1.

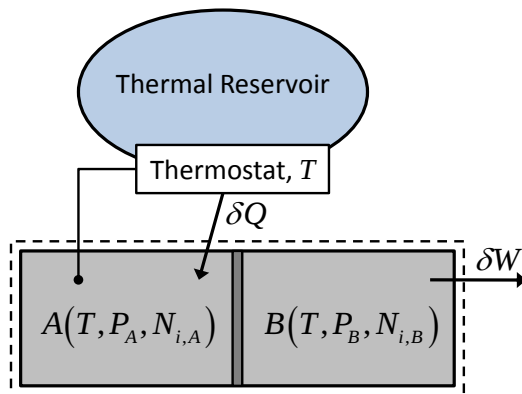


Figure B.1: Closed, rigid system in communication with a thermal reservoir with work extraction. The thermostat controls heat transfer to maintain temperature T inside the system.

The maximum amount of work that can be extracted from the system is derived by applying the First and Second Laws of thermodynamics to control boundary around the system. The differential expressions of the First and Second Laws for the system

are:

$$dU = \delta Q - \delta W \quad (\text{B.1})$$

$$dS = \frac{\delta Q}{T} + \delta S_{gen} \quad (\text{B.2})$$

Combining Eqs. (B.1) and (B.2) yields an expression for the differential amount of work extracted from the system.

$$\delta W = -dU + TdS - T\delta S_{gen} \quad (\text{B.3})$$

The maximum amount of work is realized when interactions between the regions occur reversibly (i.e., no entropy generation). Therefore, the expression for the maximum differential amount of work that can be extracted from the system is:

$$\delta W_{max} = -dU + TdS = -d(U - TS)_{\substack{T=const. \\ V=const.}} = -dA \quad (\text{B.4})$$

As shown in the above equation, the maximum differential amount of work that can be extracted from a closed, isothermal, isochoric system is equal to the differential change in the Helmholtz function of the system. The total maximum amount of work that can be extracted from the system is calculated by integrating Eq. (B.4) from the initial state to the final equilibrium state of the system. This yields:

$$W_{max} = -\Delta A = (A_{initial} - A_{EQ}) \quad (\text{B.5})$$

The above equation shows that the maximum amount of work that can be extracted from a closed, isothermal, isochoric system is equal to the change in the Helmholtz function from the initial state to the final state of the system. The equation can be interpreted as showing that the change in Helmholtz function for a closed, isothermal, isochoric system between its initial state and final equilibrium state is *free* to be extracted as work. For this reason, the maximum amount of work that can be extracted from a non-equilibrium system constrained to equilibrate at constant temperature and volume is called the Helmholtz free energy (ΔA) of the system.

Next, consider a closed system separated into two regions similar to the system shown in Fig. B.1, except now the system is of fixed pressure and temperature. The individual regions are initially in internal equilibrium and at the same temperature and pressure; however, the system is not in chemical equilibrium. The temperature and pressure of the system are held constant through heat and boundary work transfers with an external thermo-mechanical reservoir controlled by a thermostat and barostat, respectively. A diagram of this closed system in communication with a thermo-mechanical reservoir with work extraction is shown in Fig. B.2.

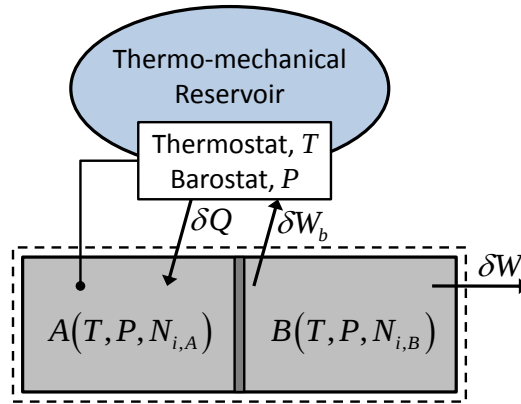


Figure B.2: Closed system in communication with a thermo-mechanical reservoir with work extraction. The thermostat and barostat control heat and boundary work transfers to maintain temperature T and pressure P inside the system.

Just as with the first system, the maximum amount of work that can be extracted from the system shown in Fig. B.2 is derived by combining the First and Second Laws and setting the entropy generation to zero. The maximum differential amount of work that can be extracted from the system is:

$$\delta W_{max} = -dU - PdV + TdS = -(U + PV - TS)_{\substack{T=const. \\ P=const.}} = -dG \quad (\text{B.6})$$

As shown in the above equation, the maximum differential amount of work that can be extracted from a closed, isothermal, isobaric system is equal to the differential change in the Gibbs function of the system. The maximum work is calculated by integrating

Eq. (B.4) from the initial state to the final equilibrium state of the system.

$$W_{max} = -\Delta G = (G_{initial} - G_{EQ}) \quad (\text{B.7})$$

The above equation shows that the maximum amount of work that can be extracted from a closed, isothermal, isobaric system is equal to the change in the Gibbs function from the initial state to the final state of the system. In other words, the change in Gibbs function for a closed, isothermal, isobaric system between its initial state and final equilibrium state is *free* to be extracted as work. For this reason, the maximum amount of work that can be extracted from a non-equilibrium system constrained to equilibrate at constant temperature and pressure is called the Gibbs free energy (ΔG) of the system.

The two example systems demonstrate that a closed system initially out of equilibrium has the potential to produce work, and the maximum amount of work that can be extracted depends on the interaction constraints. The same approach used to derive Helmholtz and Gibbs free energy can be applied to other closed systems with different interaction constraints. It can be shown that the maximum amount of work that can be extracted from a closed system constrained to equilibrate at constant entropy and volume is its change in internal energy (ΔU), and at constant entropy and pressure it is its change in enthalpy (ΔH). Therefore, for closed, isentropic, isochoric systems, the change in internal energy is a form of free energy, and for closed, isentropic, isobaric systems, the change in enthalpy is a form of free energy.

B.2 Derivation of Environmental Free Energy

The previous section applied the First and Second Laws to calculate the free energy, or maximum work potential, of closed systems constrained to equilibrate under specified interaction conditions. The same approach can be applied to calculate the free energy of open systems. To illustrate this, consider an open system in communication with a thermodynamic reservoir. The system is comprised of two reservoirs, “resource” and “environment”. Each reservoir is initially in internal equilibrium, but

not in mutual equilibrium. The environment reservoir is in communication with an external thermodynamic reservoir controlled by a thermostat, barostat, and a series of selective chemostats—one for each environmental species (i). The thermostat, barostat, and chemostats control heat, boundary work, and matter transfers to maintain the environment reservoir at its initial thermodynamic state— T_o , P_o , and $\mu_{i,o}$. Since the reservoirs are initially out of equilibrium, there exists a driving potential that can theoretically be extracted as work. The maximum amount of work that can be extracted from the system is realized as it equilibrates reversibly. The final state of the system is equal to the environment reservoir state. A diagram of this open system in communication with a thermodynamic reservoir with work extraction is shown in Fig. B.3.

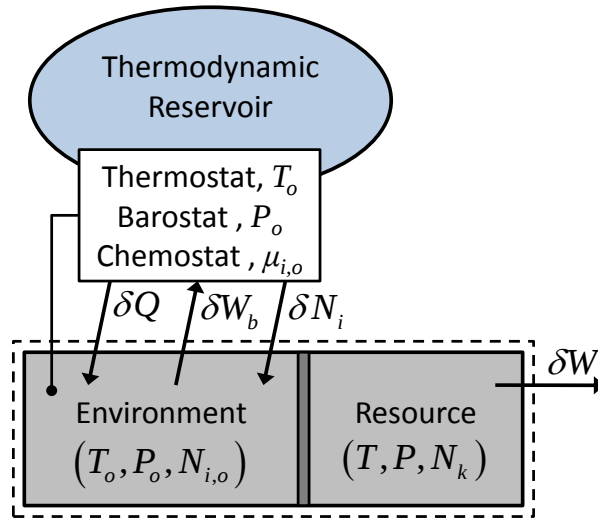


Figure B.3: Open system in communication with a thermodynamic reservoir. The system is comprised of two reservoirs—resource and environment. The thermostat, barostat, and chemostat control heat, boundary work, and matter transfers to maintain the environment reservoir at T_o , P_o , and $\mu_{i,o}$.

The maximum amount of work that can be extracted from the system is derived by applying the First and Second Laws to the control boundary around the system.

The differential expressions of the First and Second Laws for the system are:

$$dU = \delta Q - \delta W_b + \sum_i h_{i,o} \delta N_i - \delta W \quad (\text{B.8})$$

$$dS = \frac{\delta Q}{T_o} + \sum_i s_{i,o} \delta N_i + \delta S_{gen} \quad (\text{B.9})$$

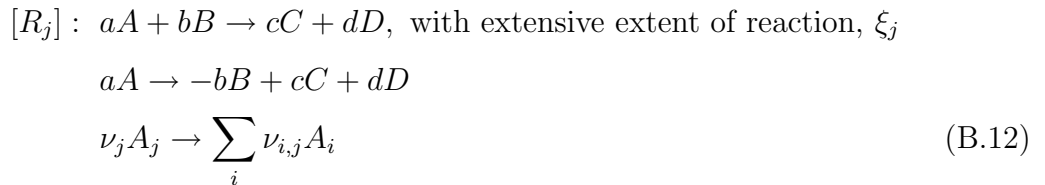
Combining Eqs. (B.8) and (B.9) and employing the definition of boundary work, $P_o dV$, yields an expression for the differential work extracted from the system.

$$\delta W = -dU - P_o dV + T_o dS + \sum_i (h_{i,o} - T_o s_{i,o}) \delta N_i - T_o \delta S_{gen} \quad (\text{B.10})$$

The maximum amount of work is realized when the interactions between the reservoirs occur reversibly (i.e., no entropy generation). Therefore, the expression for the maximum differential amount of work that can be extracted from the system is:

$$\delta W_{max} = -dU - P_o dV + T_o dS + \sum_i \mu_{i,o} \delta N_i \quad (\text{B.11})$$

The maximum work is calculated by integrating Eq. (B.11) from the initial state of the system to the mutual equilibrium state of the two reservoirs, which is equal to the state of the environment reservoir since it is maintained constant. In order to perform this integration, the inexact differential for the transfer of moles must be converted to an exact differential. This can be accomplished by considering the reversible transformation of all non-environment reservoir species (j) present in the resource reservoir to species present in the environment reservoir (i) through the following reaction:



where ν_j is the stoichiometric coefficient for the non-environment reservoir species

(j) present in the resource reservoir, and $\nu_{i,j}$ is the stoichiometric coefficient for the environment reservoir species (i) used or created by the transformation of non-environment reservoir species (j). The species balances for environment reservoir species (i) and non-environment reservoir species (j) are:

$$dN_i = \delta N_i + \sum_j \nu_{i,j} d\xi_j \quad (\text{B.13})$$

$$dN_j = -\nu_j d\xi_j \quad (\text{B.14})$$

Combining Eqs. (B.13) and (B.14) through the differential extent of reaction yields an exact differential expression for the moles of environment reservoir species (i):

$$\delta N_i = dN_i + \sum_j (\nu_{i,j}/\nu_j) dN_j \quad (\text{B.15})$$

Combining the above expression and Eq. (B.11) yields an exact differential equation for the maximum amount of work:

$$\delta W_{max} = -dU - P_o dV + T_o dS + \sum_i \mu_{i,o} dN_i + \sum_i \mu_{i,o} \sum_j (\nu_{i,j}/\nu_j) dN_j \quad (\text{B.16})$$

Integration of the above equation from the initial state of the system to the state of the state of environment reservoir yields an expression for the maximum amount of work that can be extracted from the system.

$$W_{max} = (U + P_o V - T_o S) - \sum_i \mu_{i,o} N_i - \sum_j \left[\sum_i \mu_{i,o} (\nu_{i,j}/\nu_j) \right] N_j \quad (\text{B.17})$$

Equation (B.17) was derived by applying the same approach used to derive Helmholtz and Gibbs free energy, and represents the free energy of an open system comprised of two reservoirs in communication with a thermodynamic reservoir that maintains the state of one of the reservoirs constant. The equation is equivalent to the equation of internal exergy derived in App. A. Therefore, the free energy of a system comprised of a resource and environment reservoir constrained to equilibrate at the state of the

environment is equal to the exergy of the resource. In other words, the exergy of a resource can be viewed as a form of *environmental free energy*.

Appendix C

Supplemental Material for GTL Model

This appendix provides supplemental material for the exergy analysis presented in Sec. 3.3. As discussed in the section, the analysis was performed in collaboration with Sandia National Laboratories (SNL) under a Laboratory Directed Research and Development (LDRD) grant. The original report is provided in Simpson and Lutz [48].

C.1 Analytical Tool Development

The analysis was performed using MATLAB—a commercial programming software package. Ideal gas properties and chemical equilibrium were calculated using SCT Cantera—a free thermodynamic software developed by researchers at the Global Climate and Energy Project at Stanford University. SCT Cantera is a modified version of Cantera—a free thermodynamic software developed by researchers at California Institute of Technology—that is better suited for tracking state points in technical energy systems analysis. SCT Cantera was designed specifically for use in MATLAB, whereas Cantera can be used in other programming languages such as C++ and Python.¹

¹Both SCT Cantera and standard Cantera can be downloaded for free from sourceforge.net.

Nearly all of the published energy systems analysis of Fischer-Tropsch (FT) processes were performed using Aspen Plus [62, 63, 65–68]. Aspen Plus is a commercial process flow simulator that is widely used in the petroleum and chemical processing industries. The decision not to use Aspen Plus was due to concerns about the controllability, accuracy, and transparency of its thermodynamic property data and vapor-liquid equilibrium (VLE) algorithms, as well as its high licensing cost. Using SCT Cantera in MATLAB provided complete control over the thermodynamic property data and VLE algorithms. Furthermore, since SCT Cantera is free and MATLAB is widely used in national laboratories and academia, the models and tools developed for the project can be more easily shared and used by other researchers, which was one of the goals of the LDRD.

In order to use SCT Cantera to model the FT reactor and downstream processing and upgrading components, the ability to calculate the thermodynamic properties of liquid mixtures and perform VLE calculations needed to be developed. Liquid properties were calculated using a generalized cubic equation of state (EOS) described in the text by Smith, Van Ness, and Abbott [114]. The generalized cubic EOS is capable of implementing either the van der Waals (VDW), Redlich-Kwong (RK), Soave-Redlich-Kwong (SRK), or Peng-Robinson (PR) equations of state. The VDW and RK equations of state are two-parameter equations that only require the critical temperature and pressure for all species, whereas SRK and PR are three-parameter equations that require the critical temperature and pressure and acentric factor for all species. The critical temperatures and pressures and acentric factors for the species used in this analysis were taken from the Design Institute for Physical Properties Research (DIPPR) thermophysical property data base [115].

Vapor-liquid equilibrium for multi-component mixtures occurs when the chemical potential of each component is equal in all phases. A method for performing VLE calculations was developed based on a standard Newton-Raphson (NR) numerical method. In the analysis, component chemical potentials were calculated using the PR EOS and a real fluid mixture model with linear mixing rules and binary interaction coefficients assumed to be zero. The VLE algorithms developed for the

project are able to perform bubble, dew, and flash calculations, and are not limited to FT analysis. An example of the VLE bubble and dew algorithms applied to ethane/heptanes mixtures is shown in Figure C.1. For a given overall composition, the VLE algorithms are able to predict the mixtures phase envelope, critical point, and max condentherm and max condenbar. Knowing the location of a mixture's phase envelope in temperature and pressure space is useful for determining when a mixture is in a two-phase region. When a mixture is in a two-phase region at a given temperature and pressure (i.e., within the phase envelope), a flash VLE algorithm can be used to calculate the composition of each phase. The analysis implemented the VLE algorithms to calculate the outlet phases and compositions of the FT reactor and downstream processing and upgrading components.

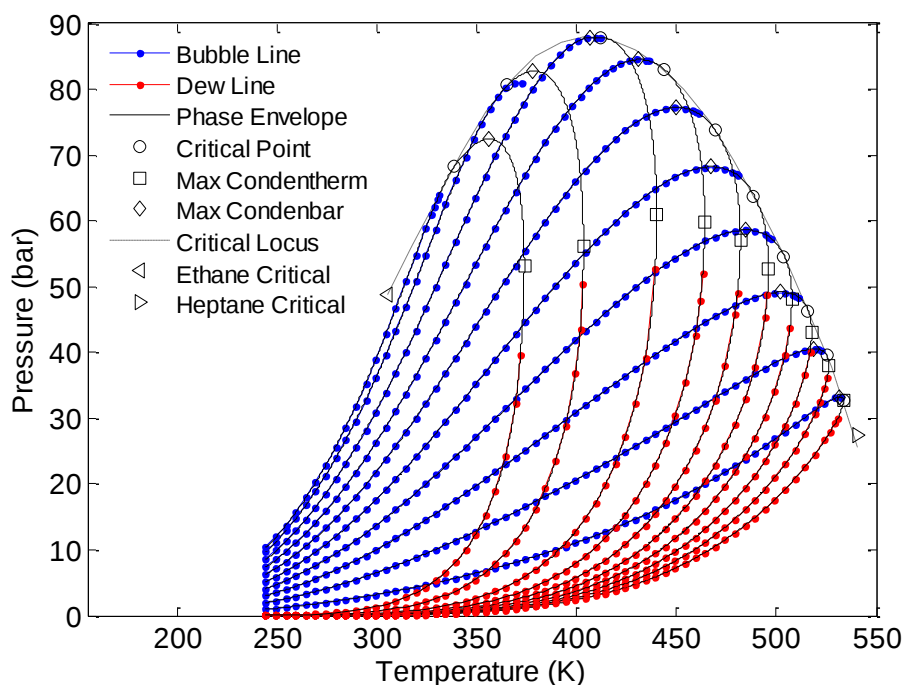


Figure C.1: Ethane/heptane phase envelope calculated using the cubic VLE model. Ethane composition range: 1, 0.95, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1.

C.2 Heat Integration and Combined Cycle Models

A diagram of the heat integration scheme used in the GTL model is shown in Fig. C.2. The heat integration scheme was chosen to minimize exergy destruction while being constrained by the system’s architecture. Two separate steam cycles—low pressure (LP) and intermediate pressure (IP)—are used to accomplish the required heat integration. The pressure levels of the steam cycles are set by the combined cycle. The mass flow of the IP steam is determined by the pinch temperature in the syngas cooler (SGC). The IP steam exiting the SGC is used to first preheat the hydrocracker streams, then the FT reactor inlet stream, followed by the partial oxidation (POX) reactor inlet streams. The saturated vapor exiting the POX O₂ pre-heater is sent to the combined cycle. The LP steam mass flow is determined by the heat available in the vapor and liquid coolers (VC, LC) in order to maximize the amount of saturated liquid produced. The FT reactor is cooled by boiling and slightly super heating the LP steam. The LP steam exiting the FT reactor is heated further in the hydrocracker (HC) before being sent to the combined cycle. All of the heat exchange components are modeled as having realistic pressure drops and minimum pinch temperatures.

A diagram of the combined cycle power production stage is shown in Fig. C.3. The main components of the combined cycle are the gas turbine (GT), three-pressure heat recovery steam generator (HRSG) with reheat, and three-pressure steam turbine (ST). The combined cycle is modeled based on the operating conditions and component parameters of the GE STAG combined cycle product line [83]. The GT is modeled based on a GE F-series gas turbine. The GT exhaust gas is cooled in the three-pressure HRSG before being transferred to the environment. The heat integration scheme used in the HRSG is based on GE specifications. The outputs from the combined cycle are the net shaft work, HRSG exhaust, steam bled from the LP ST for the CSU, and waste water from the vacuum condenser.

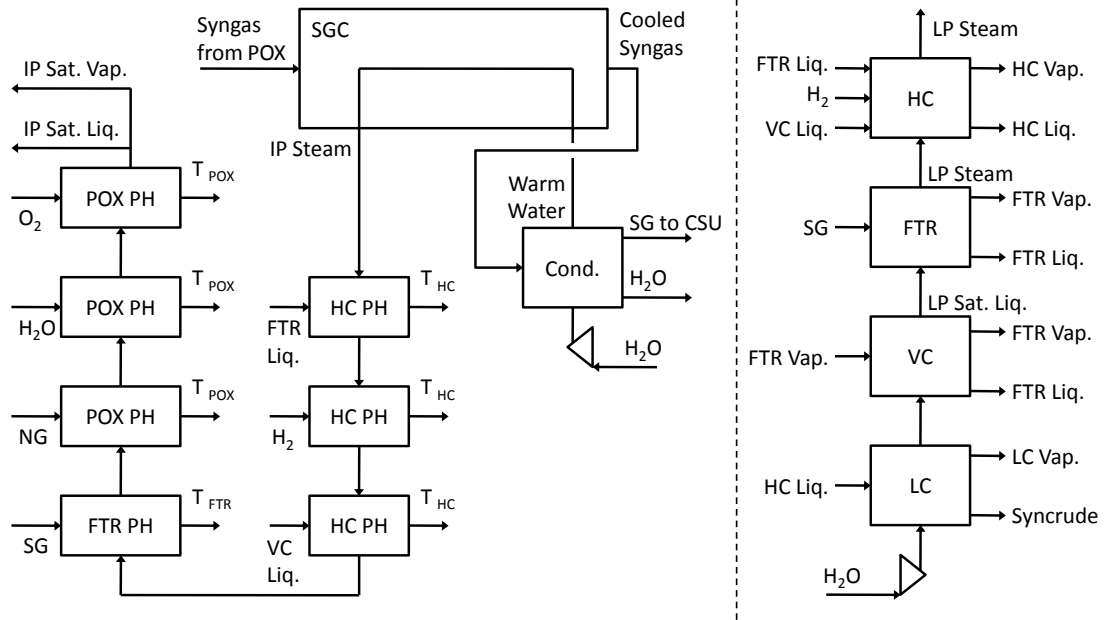


Figure C.2: Illustration of heat integration scheme for the GTL co-power production power plant. Acronyms stand for partial oxidation preheating (POX PH), hydrocracker preheating (HC PH), condenser (Cond.), syngas cooler (SGC), hydrocracker (HC), Fischer-Tropsch reactor (FTR), vapor cooler (VC), and liquid cooler (LC).

C.3 Base Case Operating Conditions

The GTL model was exercised using the operating conditions and parameters shown in Tables C.1 and C.2. The FT reactor is modeled as a black box based on the operating conditions and parameters reported in literature for slurry reactors that use cobalt-based catalysts [55, 65, 66, 69, 70]. The inputs to the FT reactor model are the syngas conversion efficiency (χ_{H_2+CO}), overall product hydrocarbon distribution, outlet temperature, and pressure drop. The overall product hydrocarbon distribution is calculated using a double- α ASF model [56], and the α values and carbon-break number used in the model are based on empirical distributions [55, 116]. The outlet conditions of the vapor cooler (VC) and liquid cooler (LC) are based on the conditions reported in study by Bechtel Corp. [65]. The hydrocracker is modeled as a black box based on the operating conditions and distributions [65, 66, 82].

The air separation unit (ASU), carbon separation unit (CSU), and pressure swing

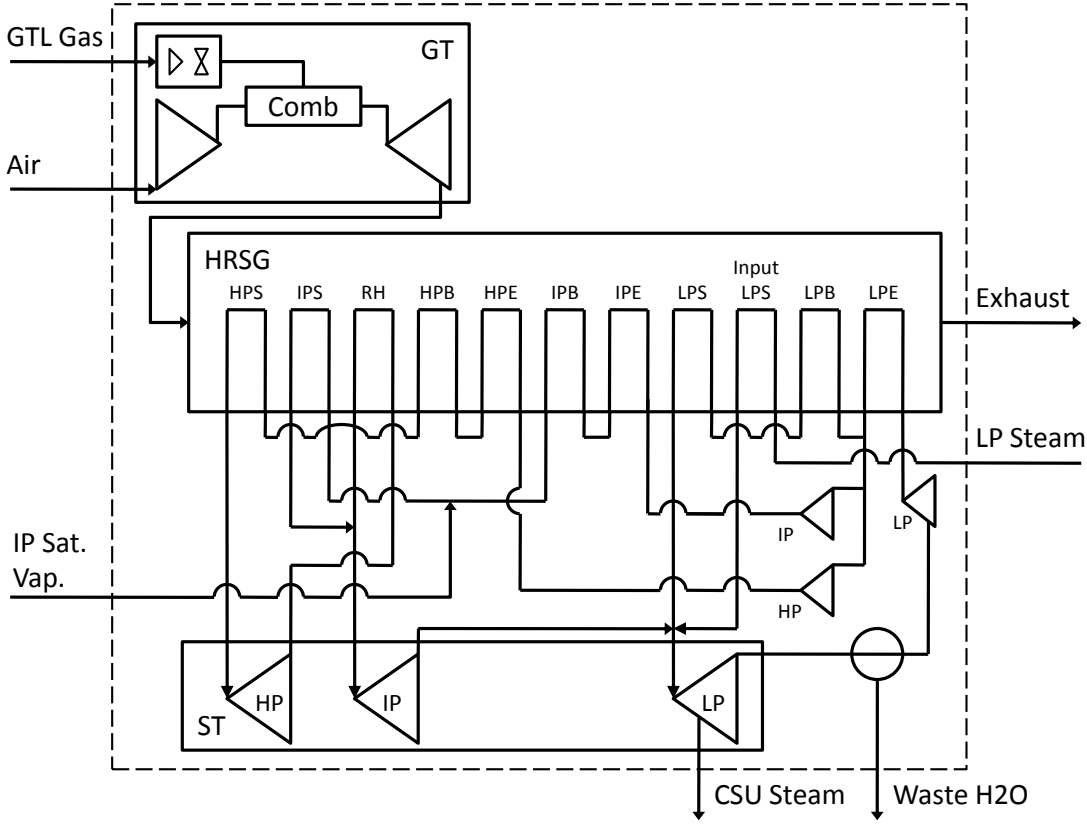


Figure C.3: System diagram of the combined cycle used in the GTL co-power production power plant. Acronyms stand for high pressure superheater (HPS), intermediate pressure superheater (IPS), reheat (RH), high pressure boiler (HPB), high pressure economizer (HPE), intermediate pressure boiler (IPB), intermediate pressure economizer (IPE), low pressure superheater (LPS), input low pressure superheater (Input LPS), low pressure boiler (LPB), and low pressure economizer (LPE).

adsorption unit (PSA) are all modeled as black boxes. The inputs to models are inlet and outlet temperatures and pressures, product stream purity, separation effectiveness, and work per kg of product species. The CSU model has an additional input defining the amount of steam per kg of CO_2 separated and its pressure. Product stream purity is defined as the mole fraction of the product species in the product stream (O_2 for the ASU, CO_2 for the CSU, and H_2 for the PSA), and separation effectiveness is defined as the to the percentage (by mass) of the product species in the inlet stream that is separated to the product stream [81]. The operating conditions

and parameters for the ASU are based on values reported in [79, 80], and those for the CSU are based on values reported in [79, 81], and those for the PSA are based on values reported in [65, 66, 79]. All efficiency values (η) are polytropic efficiencies.

<u>Dead State</u>			<u>POX</u>			<u>VC</u>		
T_o	293.15	K	T_{Inlet}	450	K	T_{Outlet}	300	K
P_o	1	atm	P_{Loss}	2	%	P_{Loss}	2	%
N_2	77.07	% v/v	H_2O/C Ratio	1	---	<u>PSA</u>		
O_2	20.49	% v/v	<u>ASU</u>			T_{H_2}	300	K
H_2O	1.5	% v/v	T_{Inlet}	T_o	K	$P_{H_2 Loss}$	5	%
Ar	0.9	% v/v	P_{Inlet}	P_o	atm	T_{SG}	300	K
CO_2	380	ppm	T_{O_2}	T_o	K	$P_{SG Loss}$	5	%
<u>Natural Gas</u>			$P_{Liquid O_2}$	170	kPa	Work	3	MJ/kg H_2
T_{Inlet}	T_o	K	T_{Waste}	T_o	K	Purity	99.99	%
P_{Inlet}	P_o	atm	P_{Waste}	P_o	atm	Effectiveness	75	%
CH_4	90.7	% v/v	Purity	95	%	<u>HC</u>		
C_2H_6	3.6	% v/v	Effectiveness	95	%	T_{Inlet}		
C_3H_8	1.9	% v/v	$\eta_{O_2 Pump Poly}$	90	%	P_{Inlet}	650	K
CO_2	1	% v/v	Work	792	kJ/kg $LiqO_2$	T_{Outlet}	80	bar
N_2	1.8	% v/v	<u>CSU</u>			P_{Loss}	650	K
O_2	1	% v/v	T_{Inlet}	310	K		5	%
<u>FTR</u>			T_{CO_2}	T_o	K	<u>LC</u>		
T_{Inlet}	500	K	P_{CO_2}	P_o	atm	T_{Outlet}	T_o	K
P_{Inlet}	25	bar	T_{SG}	305	K	P_{Outlet}	3.5	bar
T_{Outlet}	500	K	$P_{SG Loss}$	3	%	<u>Components</u>		
P_{Loss}	1	%	Purity	99.9	%	$\eta_{Comp Poly}$	85	%
α_1	0.8	---	Effectiveness	99.5	%	$\eta_{Pump Poly}$	90	%
α_2	0.95	---	Work	100	kJ/kg CO_2	$N_{NG Comp Stages}$	2	---
$C_{n Break}$	10	---	Steam	3	MJ/kg CO_2	ϵ_{HE}	90	%
H_2/CO Ratio	2	---	P_{Steam}	3.5	bar	$P_{HE Loss}$	2	%
χ_{H_2+CO}	80	%						

Table C.1: Base case operating conditions and parameters for syngas production/clean-up, FT synthesis, and syncrude recover stages. Acronyms stand for Fischer-Tropsch reactor (FTR), partial oxidation reactor (POX), air separation unit (ASU), carbon separation unit (CSU), vapor cooler (VC), pressure swing adsorption unit (PSA), hydrocracker (HC), and liquid cooler (LC). Greek letters stand for efficiency (η), heat exchange effectiveness (ϵ), and syngas conversion efficiency (χ_{H_2+CO}).

<u>Gas Turbine</u>			<u>HRSG</u>		
$T_{\text{Comb Outlet}}$	1600	K	$P_{\text{Gas Outlet}}$	1	atm
P_{Ratio}	15.5	---	$P_{\text{Gas Loss}}$	2	%
$P_{\text{Comb Loss}}$	5	%	$P_{\text{H}_2\text{O Loss}}$	8	%
$\eta_{\text{Comp Poly}}$	86	%	$\Delta T_{\text{HRSG Outlet Min}}$	20	K
$\eta_{\text{Turb Poly}}$	92	%	$T_{\text{HPS Max}}$	815	K
<u>Heat Integration</u>			T_{Pinch}	10	K
$T_{\text{SGC Pinch}}$	20	K	<u>Steam Cycle</u>		
$T_{\text{SGC H}_2\text{O Outlet}}$	815	K	P_{HPS}	150	bar
$P_{\text{SGC H}_2\text{O Loss}}$	2	%	P_{IPS}	45	bar
$P_{\text{Cond H}_2\text{O Loss}}$	1	%	P_{LPS}	10	bar
$P_{\text{IP PH Loss per Component}}$	5	%	$P_{\text{Cond Outlet}}$	6.8	kPa
$P_{\text{FTR H}_2\text{O Loss}}$	2	%	$P_{\text{Cond Loss}}$	8	%
$\Delta T_{\text{FTR H}_2\text{O Outlet Min}}$	10	K	$\text{LP Turb Outlet Quality}$	0.9	---
$P_{\text{HC H}_2\text{O Loss}}$	1	%	$m_{\text{LP H}_2\text{O}} / m_{\text{HRSG H}_2\text{O}}$	0.2	---
$P_{\text{LC H}_2\text{O Loss}}$	1	%	$m_{\text{HP H}_2\text{O}} / m_{\text{IP H}_2\text{O}}$	0.9	---
$\Delta T_{\text{LC H}_2\text{O Outlet Min}}$	10	K	$\eta_{\text{Turb Poly}}$	75	%
$P_{\text{VC H}_2\text{O Loss}}$	2	%	$\eta_{\text{Pump Poly}}$	85	%
$\Delta T_{\text{VC H}_2\text{O Outlet Min}}$	10	K	ϵ_{HRSG}	90	%

Table C.2: Base case operating conditions and parameters for the combined cycle and heat integration. Greek letters stand for efficiency (η) and heat exchange effectiveness (ϵ).

C.4 Additional Model Results

Referring back to Fig. 3.7, the second largest amount of exergy destruction occurs in the combined cycle. Figure C.4 shows the exergy destruction break-down within the combined cycle. The majority of the exergy destruction occurs in the combustor. The exergy destroyed in the combustor is due to mixing and unrestrained chemical reaction. The amount of exergy destroyed in the combustor could be reduced by increasing the equivalence ratio (decreasing the air flow rate) to raise its outlet temperature; however, the combustor outlet gas would need to be cooled to approximately 1600 K due to material limitations in the turbine, resulting in exergy destruction in the heat exchange process. The next two largest locations of exergy destruction occur in the LP steam turbine and the condenser. The LP steam turbine destroys more exergy than the other two steam turbines because it has a larger mass flow and pressure ratio. The condenser destroys a significant amount of exergy because it is modeled as an air cooled condenser. The heated air is not used in the system and its exergy is therefore destroyed when transferred back to the environment.

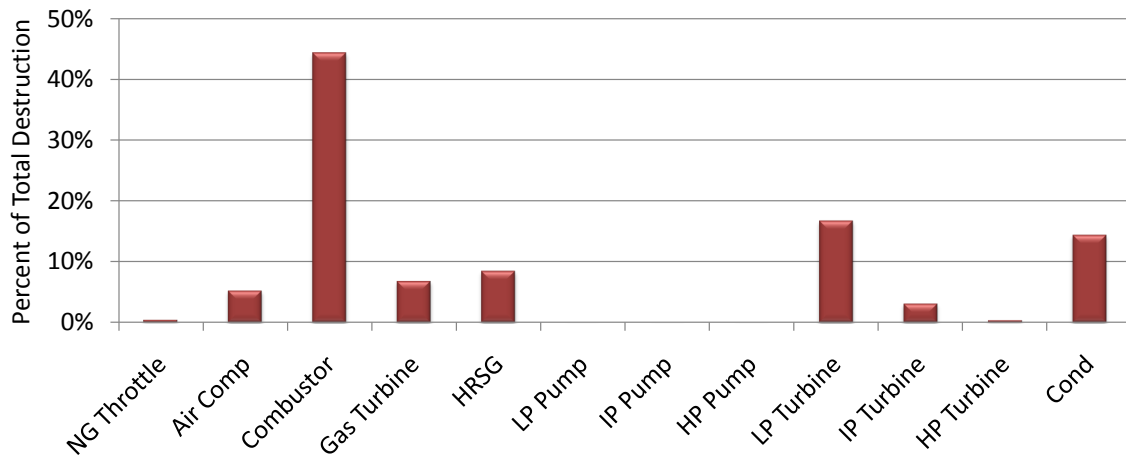


Figure C.4: Combined cycle exergy destruction distribution measured as a percentage of its total exergy destruction.

The third largest amount of exergy destruction occurs in the HRSG. Figure C.5 shows the exergy destruction break-down and heat transfer profile within the HRSG. Comparing Fig. C.5a and C.5b illustrates that the amount of exergy destroyed in

a heat recovery stage is directly proportional to the inlet and outlet temperature differences and amount of heat transferred in the stage. The HP and IP super heating, HP boiling, and the HP and LP economizing stages destroy the most exergy in the HRSG. The exergy destroyed in the HP and IP super heating stages could be reduced by heating the steam to temperatures closer to the gas temperature, reducing the HRSG inlet gas temperature, and/or increasing the number of heat transfer stages. Heating the steam to higher temperatures is difficult due to material limitations and costs. Commercial superheating boilers are limited to maximum steam temperatures of about 550°C. Reducing the HRSG inlet gas temperature can be accomplished by increasing the GT pressure ratio, expanding the GT to vacuum conditions, or reducing the combustor outlet temperature. Increasing the number of heat transfer stages and optimizing their location within the HRSG would reduce the amount of exergy destroyed; however, it would increase the cost and complexity of the system. The exergy destroyed in the HP boiler could be minimized by better matching the pressure level of the HP loop with the slope of the exhaust gas temperature profile in order to minimize the pinch temperature. The exergy destroyed in the HP economizer could be reduced by increasing the number of heat transfer stages and optimizing their location. The exergy destroyed in the LP economizer cannot be reduced by increasing the number of heat transfer stages because it occurs at the lowest temperature.

As discussed in Sec. 3.3, the vapor cooler is modeled using a flash VLE calculation and assuming that the condensed water is pure (i.e., no gas or hydrocarbon liquid solubility) and only hydrocarbons are present in the recovered FT liquid phase (i.e., no gas or water solubility). The hydrocracker model uses a weighted empirical distribution for the amount of hydrocarbons heavier than C_{21} that are cracked to shorter chain hydrocarbons in the distillate range (C_{14} - C_{19}). A flash VLE calculation is performed to determine the compositions of the hydrocarbon liquid and vapor streams exiting the hydrocracker. The model assumes that only hydrocarbons are present in the liquid phase (i.e., no gas solubility). The hot liquid stream exiting the hydrocracker is cooled and expanded in the liquid cooler. There was no need for a flash VLE calculation on the outputs from the liquid cooler because there was only a liquid phase (according to the PR EOS model used in the analysis). The results of

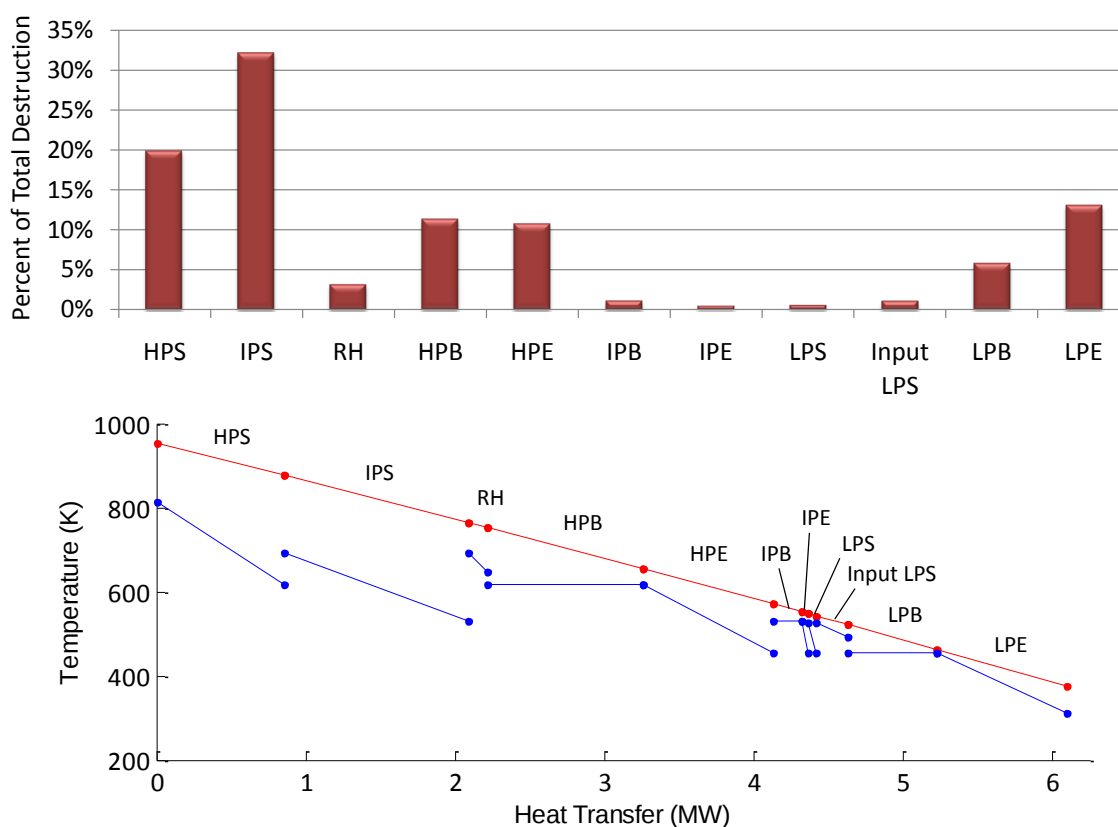


Figure C.5: HRSG exergy destruction distribution measured as a percentage of its total exergy destruction (top), and HRSG heat transfer profile (bottom).

these modeling approaches are shown in Figure C.6. The vapor cooler outlet hydrocarbon distribution is in good agreement with published empirical distributions [116], and the hydrocracker distributions are in good agreement with published empirical distributions [82].

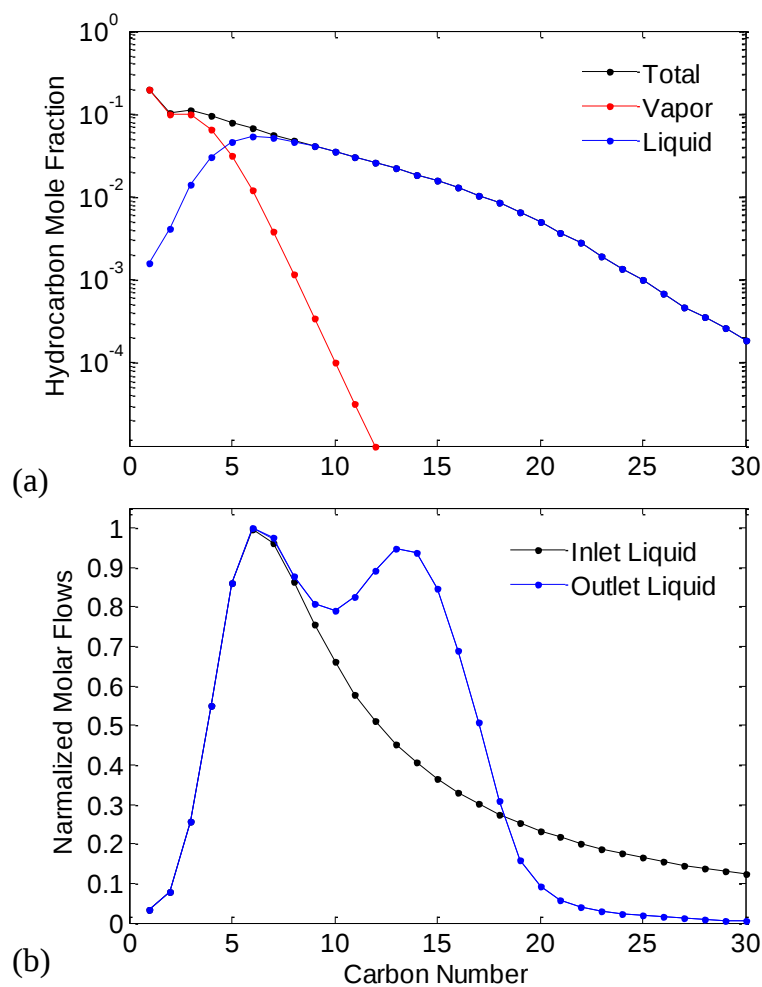


Figure C.6: Hydrocarbon distributions calculated using flash VLE algorithm. (a) Vapor cooler outlet hydrocarbon distribution. (b) Hydrocracker hydrocarbon distribution. Hydrocracker outlet vapor composition is not shown in the figure because it is close to zero for all components, according to the model.

Appendix D

Environmental Analysis Framework: Example Applications

Chapter 4 presents an analysis framework for evaluating the environmental impact of energy systems and providing insight for decision making. The components of the environmental analysis framework—environmental exergy analysis and anthropocentric sensitivity analysis—are developed using general examples, and the application and utility of the framework for decision making is discussed using notional examples. In this appendix, we apply the analysis framework to several, less-general energy systems to demonstrate its ability to quantify environmental impact and provide insight for decision making. The first section applies environmental exergy analysis to a well-defined model system to demonstrate its application and introduce some of the key assumptions that can be employed to simplify the analysis. The next section applies the analysis framework to several existing and proposed (future) energy systems to demonstrate its utility for decision making.

D.1 Application of Environmental Exergy Analysis to a Model System

To demonstrate the application of environmental exergy analysis for quantifying the locations, magnitudes, and types of environmental impact caused by an anthropogenic activity, a small-scale energy system operating within a well-defined, local environment is analyzed first. The purpose of applying environmental exergy analysis to a well-defined environment is to introduce and gain comfort with the techniques and models used to quantify environmental impact before applying environmental exergy analysis to the natural environment—a complex system. The techniques and models used to quantify the environmental impact this small-scale energy system has on its local environment are easily extended to large-scale energy systems operating within the natural environment, as is shown at the end of this section.

A diagram of the model system considered here is shown in Fig. D.1. The energy system is an insulated heat engine, and the local environment is comprised of a hot copper block, an open water tank, a rigid, closed laboratory, and a large reservoir called the “surroundings”. The heat engine cross-connects the copper block and water tank, which are both located within the laboratory. The initial states of the environmental reservoirs are specified in the figure. The composition of the laboratory and surroundings is engineering air with an initial relative humidity of 50%, and the water in the tank is pure (i.e., no dissolved air). The surroundings are considered a thermodynamic reservoir, and each environmental reservoir is in local thermodynamic equilibrium.

The natural and anthropogenic energy transfers within the model system during heat engine operation are shown in Fig. D.2. Natural transfers are the result of the environmental reservoirs being out of equilibrium, and anthropogenic transfers are caused by the operation of the heat engine. The natural transfers considered in this analysis include the transfers of heat from the copper block to the laboratory, heat and matter from the water tank to the laboratory, and heat from the laboratory to the surroundings. The anthropogenic transfers considered in this analysis include the upstream transfers of heat to the heat engine and the downstream transfers of water

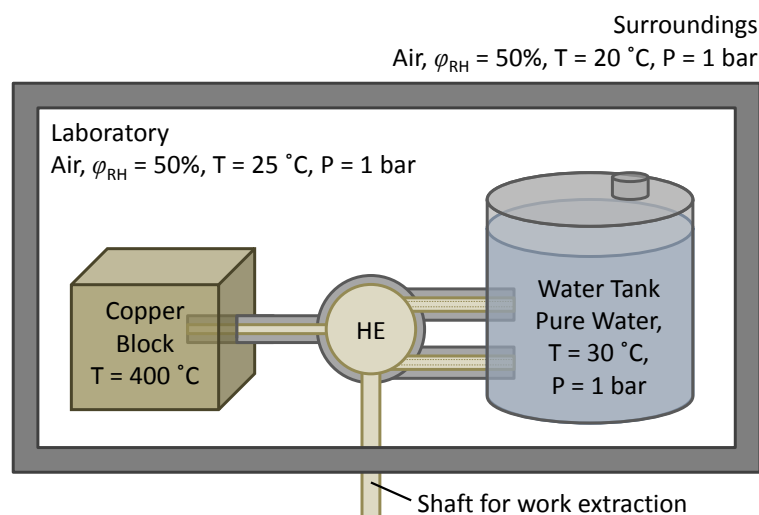


Figure D.1: Model system comprised of a heat engine located within in a local environment.

between the water tank and heat engine.¹ Implied by the limited number of transfers shown in the figure, are the assumptions that the heat engine is perfectly insulated, the laboratory is perfectly rigid and closed, the water in the water tank is remains pure, and there is no axial heat conduction through the pipes connecting the heat engine and water tank.

To measure the exergy of the transfers and individual reservoirs, an appropriate reference state must be chosen. As discussed in Ch. 4, the reference state should be chosen such that it represents the mutual equilibrium state for isolated systems, or the mutual stationary state for driven systems. For this isolated model system, the mutual equilibrium state is equal to the state of the surroundings—since it is modeled as a thermodynamic (“infinite”) reservoir. Therefore, the state of the surroundings serves as a reference state from which the exergy (i.e., driving potential) of the transfers and reservoirs can be measured.² The reference state is defined by a reference temperature

¹Strictly speaking, the engine is a “heat-matter” engine because the resource is heat but entropy is rejected to the environment in the form of matter. A true heat engine uses heat as both the resource and means of entropy rejection.

²Only the reservoirs shown in the Fig. D.1 are considered in this analysis. If the model system was considered to be within the terrestrial environment, a more appropriate reference state would be the mutual stationary state of the terrestrial environment. Refer to Ch. 4 for a discussion on reference state selection and modeling.

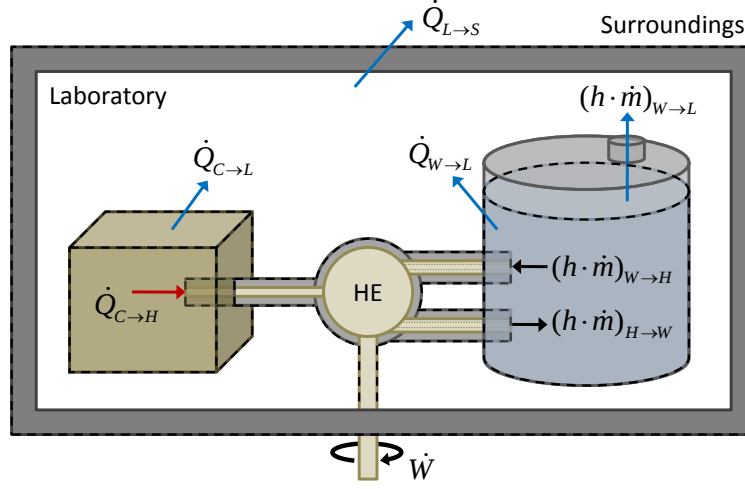


Figure D.2: Natural and anthropogenic transfers within model system during heat engine operation. Red arrows: upstream transfers; black arrows: downstream transfers; blue arrows: natural transfers; black dashed lines: control boundaries.

(T_{ref}), pressure (P_{ref}), and chemical potentials for all relevant species in the system ($\mu_{i,ref}$).³

The general form of the differential impact equations derived in Ch. 4, Eqs. (4.20)–(4.23), can be applied to the model system to quantify the impact the heat engine (H) has on the local environment. In this model system, the copper block (C) and water tank (W) are α reservoirs, and the laboratory (L) and surroundings (S) are β reservoirs. Using Eq. (4.20), the differential impact equations for the copper block and water tank are given by:

$$\delta X_{C \rightarrow H} = -[dX_C - dX_C^o] - [\delta X_{Dest,C} - \delta X_{Dest,C}^o] - [\delta X_{C \rightarrow L} - \delta X_{C \rightarrow L}^o] \quad (D.1)$$

$$\delta X_{H \rightleftharpoons W} = [dX_W - dX_W^o] + [\delta X_{Dest,W} - \delta X_{Dest,W}^o] + [\delta X_{W \rightarrow L} - \delta X_{W \rightarrow L}^o] \quad (D.2)$$

and using Eqs. (4.21) and (4.22), the differential impact equations for the laboratory

³Since copper is not present in the surroundings, a reference state for copper must be defined in order to quantify its chemical exergy. An appropriate chemical reference state for copper would be that of solid copper, which would mean that the copper block only has thermo-mechanical exergy.

and surroundings are given by:

$$[\delta X_{C \rightarrow L} - \delta X_{C \rightarrow L}^o] + [\delta X_{W \rightarrow L} - \delta X_{W \rightarrow L}^o] = [dX_L - dX_L^o] \\ + [\delta X_{Dest,L} - \delta X_{Dest,L}^o] + [\delta X_{L \rightarrow S} - \delta X_{L \rightarrow S}^o] \quad (D.3)$$

$$[\delta X_{L \rightarrow S} - \delta X_{L \rightarrow S}^o] = [dX_S - dX_S^o] + [\delta X_{Dest,S} - \delta X_{Dest,S}^o] \quad (D.4)$$

Implicit in the differential impact equations are surface and volume integrals that correspond to the control boundaries shown in Fig. D.2. All exergy transfers are integrated over the surface of the control boundary they cross (e.g., $\delta X_{C \rightarrow H} = \int \delta X''_{C \rightarrow H} dS$, where X'' is exergy per surface area, and S is the surface area), and all exergy changes and destructions are integrated over the volume enclosed by the control boundary (e.g., $dX_C = d(\int X'''_C dV)$, $\delta X_{Dest,C} = \delta(\int X'''_{Dest,C} dV)$, where X''' is exergy per volume, and V is the volume).

The differential impact equations provide insight into the possible locations and types of environmental impact caused by the heat engine (i.e., the anthropogenic activity). In order to solve for the actual locations, types, and magnitudes of environmental impact, the differential impact equations must be integrated over the interval of interest—from the start of the activity to some defined final time, which is referred to here as the *integration time* ($t_{integration}$). The integration time is independent of the time of the anthropogenic activity ($t_{activity}$), and can be shorter than, equal to, or longer than the time of the activity. Integration times less than the time of the activity are not of particular interest for environmental impact analysis, since the activity has not ended. The difference between the integration time and the time of the activity is referred to here as the *post-activity interval* ($\tau_{post-activity} \equiv t_{integration} - t_{activity}$).

Integration is complicated by the fact that the reservoirs are coupled. For example, during heat engine operation, increases in the temperature of the water tank can cause changes to the composition of the laboratory (e.g., increasing its relative humidity), which can affect the laboratory's natural heat transfer with the copper block and surroundings. Coupling between reservoirs may require that the impact equations be simultaneously integrated. Integration of the impact equations is simplified, and in some cases the need for simultaneous integration is avoided, if certain

Reservoir Classification	Integration Time	Models and Assumptions in the Limits of Classification
Reservoir Size relative to Transfer Size	$t_{integration} > 0$	Large $\rightarrow$ Negligible State Change
Reservoir Relaxation Rate relative to Transfer Rate	$t_{integration} > 0$	Fast $\rightarrow$ Negligible Inhomogeneities
Reservoir Relaxation Time relative to $\tau_{post-activity}$	$\tau_{post-activity} > 0$	Short $\rightarrow$ Negligible Inhomogeneity

Table D.1: Reservoir classifications, applicable integration times, and relevant model assumptions.

model assumptions about the reservoirs and transfers can be employed.

Table D.1 gives three possible reservoir classifications, the integration times for which they apply, and the models and assumptions that can be employed in the limits of the each classification. As shown in the table, for any anthropogenic activity, regardless of integration time, two reservoir classifications can be made: (1) the reservoir size relative to the size of a transfer (referred to as the “reservoir size”), and (2) the reservoir relaxation rate relative to the transfer rate (referred to as the “reservoir relaxation rate”). Reservoir size is measured as the ratio of the extensive exergy of a reservoir relative to the amount of exergy transferred to or from the reservoir. It can be measured based on overall exergy (e.g., $X_C/X_{C \rightarrow H}$), or an individual form of exergy (e.g., $X_C^T/X_{C \rightarrow H}^T$, where superscript T indicates thermal exergy). Reservoir relaxation rate is measured as a ratio of the exergy destruction rate within a reservoir relative to the rate at which exergy is transferred to or from the reservoir. It can also be measured based on overall exergy (e.g., $\dot{X}_{Dest.,C}/\dot{X}_{C \rightarrow H}$), or an individual form of exergy (e.g., $\dot{X}_{Dest.,C}^T/\dot{X}_{C \rightarrow H}^T$).

Reservoir size provides insight into the relative magnitude of state change caused by a transfer or alteration, and reservoir relaxation rate provides insight into the inhomogeneities caused by a transfer or alteration during activity. If a reservoir is

sufficiently large relative to the amount of exergy directly or indirectly transferred to the reservoir, then state change can be modeled as being negligible when solving the impact equations (e.g., the atmosphere is large relative to the emissions from a single power plant over a one-year time period such that state change can be modeled as negligible). If a reservoir's relaxation rate (i.e., equilibration rate) is sufficiently fast relative to the rate at which exergy is transferred to or from the reservoir, then inhomogeneities caused by the transfer can be modeled as being negligible when solving the impact equations (e.g., the atmosphere has a fast relaxation rate relative to the rate at which heat is transferred from a single power plant such that any inhomogeneities caused by the heat transfer can be modeled as negligible).

For reservoirs not classified as having a sufficiently fast relaxation rate, inhomogeneities will exist within the reservoir at the end of the activity. When inhomogeneities exist within a reservoir at the end of activity, and the integration time is longer than the time of the activity, a third reservoir classification can be made: the reservoir relaxation time relative to the post-activity interval (referred to as the “reservoir relaxation time”). Reservoir relaxation time is measured as the ratio of the time required for homogeneity to be reached within a reservoir relative to the post-activity interval. The time required for homogeneity to be reached within a reservoir can be measured by an appropriate relaxation (diffusion) time constant for the reservoir being analyzed (e.g., for reservoirs with temperature gradients at the end of activity, an appropriate measure of the time required for homogeneity to be reached would be the square of the characteristic length for the reservoir divided by the reservoir's thermal diffusivity). Reservoir relaxation time provides insight into the inhomogeneity of a reservoir at the end of integration. If the time required for homogeneity to be reached within a reservoir is sufficiently short relative to the post-activity interval, then any inhomogeneities caused during an activity can be modeled as being negligible when solving the impact equations.

To illustrate the application of the three possible reservoir classifications, the following classifications are employed: the copper block is a *large* and *fast* reservoir, the water tank is a *small* and *slow* reservoir with a *long* relaxation time, the laboratory is a *small* and *slow* reservoir with a *short* relaxation time, and the surroundings is

a *large* and *fast* reservoir. The assumptions implied by these reservoir classifications are in addition to the assumptions discussed in the beginning of this section (closed laboratory, insulated heat engine, etc.). It is assumed that the heat engine operates for an extended period of time and that all exergy transfers to and from the heat engine are known over this time period. The impact that the heat engine has on the local environment is of interest after the activity ends (i.e., $\tau_{Post-Activity} > 0$).

The classification that the copper block is a large and fast reservoir, and the assumption that exergy is extracted from the center of the block (as shown in Fig. D.2), enable its differential impact equation, Eq. (D.1), to be simplified to:

$$dX_{C \rightarrow H} \approx [\delta X_{Dest,C} - \delta X_{Dest,C}^o] \quad (D.5)$$

This simplification is possible because the large classification implies that overall state change is negligible and the fast classification implies that inhomogeneities are negligible. Together, they imply that the block's boundary temperature can be modeled as being constant, which means that alterations of natural transfers are negligible. With these assumptions, the copper block is an isolated reservoir, and its impact equation can be integrated independent of the others impact equations. The direct impact the heat engine has on the copper block can be quantified by integrating the above equation from its initial state prior to the activity (t_0) to the integration time (t_{int}), with $\tau_{Post-Activity} > 0$. Doing this yields the (integrated) *impact equation* for the copper block:

$$X_{C \rightarrow H} \approx [X_{Dest,C} - X_{Dest,C}^o] \quad (D.6)$$

This equation shows that the exergy transferred from the copper block to the heat engine only causes a change in the amount of exergy that would have naturally been destroyed in the block (i.e., it causes destruction change within the block). Had the copper block been modeled as a large and *slow* reservoir, its control boundary should be broken apart into multiple control boundaries—a small volume that captures local state change, local inhomogeneities, and local destruction change, and a large volume that capture the remaining destruction change (but with no state change or

inhomogeneities).

The reservoir classifications that the water tank and laboratory are both small reservoirs requires that their differential impact equations be simultaneously integrated because the natural interaction between the reservoirs is a function of their states (i.e., the reservoirs are coupled). This requires information about how their states change over the integration time. If this information is known, then their (integrated) impact equations are given by:

$$[X_{H \rightarrow W} - X_{W \rightarrow H}] = [X_{W, \tau_{int}} - X_{W, \tau_{int}}^o] + [X_{Dest, W} - X_{Dest, W}^o] + [X_{W \rightarrow L} - X_{W \rightarrow L}^o] \quad (D.7)$$

$$[X_{W \rightarrow L} - X_{W \rightarrow L}^o] = [X_{L, \tau_{int}} - X_{L, \tau_{int}}^o] + [X_{Dest, L} - X_{Dest, L}^o] + [X_{L \rightarrow S} - X_{L \rightarrow S}^o] \quad (D.8)$$

The classification that the water tank is a slow reservoir with a long relaxation time implies that inhomogeneities exist at the integration time. Therefore, to solve for the final exergy of the water reservoir, integration must be done over its volume (e.g., $X_{W, \tau_{int}} = \int X''' dV$, where X''' is the exergy per volume). The classification that the laboratory is a slow reservoir with a short relaxation time implies that inhomogeneities are caused during the activity, but no longer exist at the integration time. The above impact equations show that the exergy transferred from the heat engine causes state change, destruction change, and alterations of natural transfers within the water tank and laboratory.

The reservoir classifications that the surroundings is a large and fast reservoir enable its differential impact equation, Eq. (D.4), to be simplified to:

$$[\delta X_{L \rightarrow S} - \delta X_{L \rightarrow S}^o] \approx [\delta X_{Dest, S} - \delta X_{Dest, S}^o] \quad (D.9)$$

This simplification is possible because the large and fast classifications imply that both state change and inhomogeneities are negligible. Integrating this equation over

the integration time yields the impact equation for the surroundings

$$[X_{L \rightarrow S} - X_{L \rightarrow S}^o] \approx [X_{Dest, S} - X_{Dest, S}^o] \quad (D.10)$$

which shows that the heat engine only causes destruction change within the surroundings. As with the copper block, if the surroundings had been modeled as a large and slow reservoir, its control boundary should be broken apart into multiple control boundaries, or regions.

The models and assumptions used to evaluate the environmental impact the heat engine has on its local environment are commonplace when evaluating the technical performance of energy systems. For example, reactors are commonly modeled as adiabatic when the heat transferred from the reactor is small relative to the reactor's energy flux, or transfers are commonly modeled as being homogenous when the influence of inhomogeneities on a transfer's state are small. These engineering models and assumptions can be applied outside of an energy system's control boundary, as illustrated through the analysis of this laboratory-scale system. To illustrate their application to a large-scale energy system operating within natural environment, a geothermal power plant is considered. A diagram of a generic geothermal power plant is shown in Fig. D.3a. The geothermal power plant and its environmental reservoirs shown in the figure are analogous to the heat engine and its local environment—the power plant is analogous to the heat engine, the geothermal reservoir to the copper block, the surface water reservoir to the water tank, the atmosphere to the laboratory, and space to the surroundings.

Figure D.3b illustrates the anthropogenic and natural interactions that occur during operation of the power plant. The general form of the differential impact equations, Eqs. (4.20)–(4.23), can be applied to quantify the power plant's environmental impact. The differential impact equations can be written by considering the geothermal reservoir (G), surface water reservoir (W), and atmosphere (A) as α reservoirs, and by considering lithosphere (L), biosphere (B), hydrosphere (H), and space (Sp) as β reservoirs. Without employing any assumptions about the environmental reservoirs,

the differential impact equations for α reservoirs are given by:

$$\begin{aligned}\delta X_{Anth \rightarrow G} - \delta X_{G \rightarrow Anth} &= [dX_G - dX_G^o] + [\delta X_{Dest,G} - \delta X_{Dest,G}^o] \\ &+ [\delta X_{G \rightleftharpoons L} - \delta X_{G \rightleftharpoons L}^o]\end{aligned}\quad (D.11)$$

$$\begin{aligned}\delta X_{Anth \rightarrow W} - \delta X_{W \rightarrow Anth} &= [dX_W - dX_W^o] + [\delta X_{Dest,W} - \delta X_{Dest,W}^o] \\ &+ [\delta X_{W \rightleftharpoons A} - \delta X_{W \rightleftharpoons A}^o] + [\delta X_{W \rightleftharpoons L} - \delta X_{W \rightleftharpoons L}^o]\end{aligned}\quad (D.12)$$

$$\begin{aligned}\delta X_{Anth \rightarrow A} - \delta X_{A \rightarrow Anth} &= [dX_A - dX_A^o] + [\delta X_{Dest,A} - \delta X_{Dest,A}^o] \\ &+ [\delta X_{A \rightleftharpoons W} - \delta X_{A \rightleftharpoons W}^o] + [\delta X_{A \rightleftharpoons L} - \delta X_{A \rightleftharpoons L}^o] \\ &+ [\delta X_{A \rightleftharpoons B} - \delta X_{A \rightleftharpoons B}^o] + [\delta X_{A \rightleftharpoons H} - \delta X_{A \rightleftharpoons H}^o] \\ &+ [\delta X_{A \rightleftharpoons Sp} - \delta X_{A \rightleftharpoons Sp}^o]\end{aligned}\quad (D.13)$$

$$\begin{aligned}\delta X_{Anth \rightarrow L} - \delta X_{L \rightarrow Anth} &= [dX_L - dX_L^o] + [\delta X_{Dest,L} - \delta X_{Dest,L}^o] \\ &+ [\delta X_{L \rightleftharpoons G} - \delta X_{L \rightleftharpoons G}^o] + [\delta X_{L \rightleftharpoons W} - \delta X_{L \rightleftharpoons W}^o] \\ &+ [\delta X_{L \rightleftharpoons A} - \delta X_{L \rightleftharpoons A}^o] + [\delta X_{L \rightleftharpoons H} - \delta X_{L \rightleftharpoons H}^o]\end{aligned}\quad (D.14)$$

and the differential impact equations for the β reservoirs are given by:

$$\begin{aligned}\delta X_{A \rightleftharpoons B} - \delta X_{A \rightleftharpoons B}^o &= [dX_B - dX_B^o] + [\delta X_{Dest,B} - \delta X_{Dest,B}^o] \\ &+ [\delta X_{B \rightleftharpoons L} - \delta X_{B \rightleftharpoons L}^o] + [\delta X_{B \rightleftharpoons H} - \delta X_{B \rightleftharpoons H}^o]\end{aligned}\quad (D.15)$$

$$\begin{aligned}\delta X_{A \rightleftharpoons H} - \delta X_{A \rightleftharpoons H}^o &= [dX_H - dX_H^o] + [\delta X_{Dest,H} - \delta X_{Dest,H}^o] \\ &+ [\delta X_{H \rightleftharpoons L} - \delta X_{H \rightleftharpoons L}^o] + [\delta X_{H \rightleftharpoons B} - \delta X_{H \rightleftharpoons B}^o]\end{aligned}\quad (D.16)$$

$$\begin{aligned}\delta X_{A \rightleftharpoons L} - \delta X_{A \rightleftharpoons L}^o &= [dX_L - dX_L^o] + [\delta X_{Dest,L} - \delta X_{Dest,L}^o] \\ &+ [\delta X_{L \rightleftharpoons H} - \delta X_{L \rightleftharpoons H}^o] + [\delta X_{L \rightleftharpoons B} - \delta X_{L \rightleftharpoons B}^o] \\ &+ [\delta X_{L \rightleftharpoons W} - \delta X_{L \rightleftharpoons W}^o]\end{aligned}\quad (D.17)$$

$$\delta X_{A \rightleftharpoons Sp} - \delta X_{A \rightleftharpoons Sp}^o = [dX_{Sp} - dX_{Sp}^o] + [\delta X_{Dest,Sp} - \delta X_{Dest,Sp}^o]\quad (D.18)$$

The differential impact equations provide insight into all possible locations and types of environmental impact caused by a geothermal power plant. Engineering models and assumptions can be employed to simplify the analysis. The appropriate

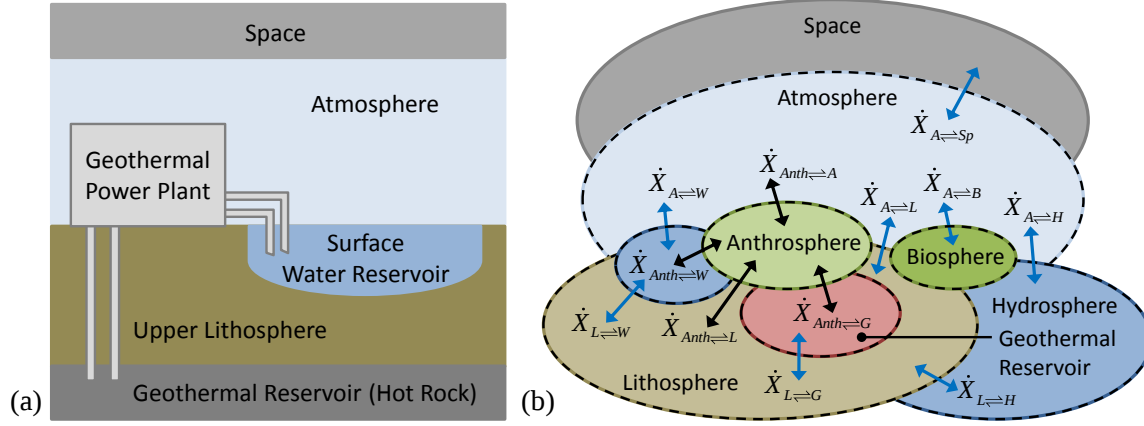


Figure D.3: (a) Illustration of a geothermal power plant. (b) Representation of the environmental reservoirs and interactions for analyzing the environmental impact of a geothermal power plant. Black arrows: anthropogenic transfers; blue arrows: natural transfers; black dashed lines: reservoir control boundaries.

models and assumptions depend on the size and location of the power plant and environmental reservoirs, and the time scale and objectives of the analysis. For example, if a single power plant located in the middle of a desert is considered, then its indirect impact on the hydrosphere and space could be modeled as negligible. If this power plant uses large geothermal and water reservoirs, then each reservoir's state change and alterations of natural transfers could be modeled as negligible. There are a wide-range of modeling assumptions that could be employed to simplify the analysis of this system. The benefit of first writing the differential impact equations without making any assumptions is that they provide insight into all possible locations and types of environmental impact, against which any simplification can be compared. In other words, all assumptions are explicitly shown.

D.2 Example Applications of Environmental Analysis Framework

In this section, we apply the environmental analysis framework to three energy systems with differing environmental interactions to demonstrate its utility for decision

making. The first two examples demonstrate the framework's ability to explain and validate design decisions employed by existing energy systems for mitigating environmental impacts with negative consequences. The last example demonstrates the framework's ability to provide insight for designing future, large-scale energy systems to avoid causing environmental impacts with potentially negative consequences.

D.2.1 Thermal Pollution

Thermal pollution refers to the degradation of water quality in an existing water reservoir by anthropogenic activity that causes a change in the reservoir's temperature. It typically refers to increases in temperature, however, it can also be used to refer to decreases in temperature. A common cause of thermal pollution is the use of water from an existing reservoir as a coolant in a power plant. Thermal pollution is an environmental concern because of the negative consequences it has on living organisms within the reservoir. Living organisms are sensitive to temperature and composition changes, which are direct and indirect consequences of thermal pollution, respectively.

The environmental analysis framework can be applied to analyze the impact of thermal pollution, and provide insight for avoiding its negative consequences. To illustrate this, a generic power plant that uses an existing water reservoir as a heat sink is considered. A diagram illustrating the environmental reservoirs and interactions of this anthropogenic activity is shown in Fig. D.4. The anthropogenic activity directly interacts with the water reservoir—transferring water from the reservoir at its ambient temperature, and transferring water back to the reservoir at a higher-than-ambient temperature. Living organisms are aggregately represented by the biosphere, which naturally interacts with the water reservoir and lithosphere.

The differential impact equations for the water reservoir and biosphere are given

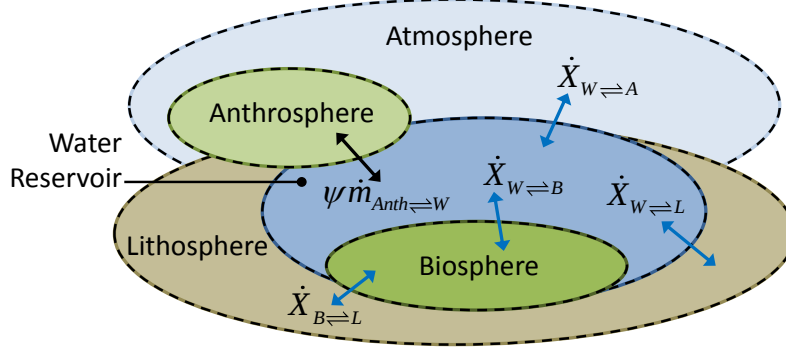


Figure D.4: Environmental reservoirs and interactions for analyzing the environmental impact of thermal pollution. Red arrows: upstream transfers; black arrows: downstream transfers; blue arrows: natural transfers; black dashed lines: reservoir control boundaries.

by:

$$\begin{aligned} \delta X_{Anth \rightarrow W} - \delta X_{W \rightarrow Anth} &= [dX_W - dX_W^o] + [\delta X_{Dest,W} - \delta X_{Dest,W}^o] \\ &\quad + [\delta X_{W \rightleftharpoons L} - \delta X_{W \rightleftharpoons L}^o] + [\delta X_{W \rightleftharpoons A} - \delta X_{W \rightleftharpoons A}^o] \\ &\quad + [\delta X_{W \rightleftharpoons B} - \delta X_{W \rightleftharpoons B}^o] \end{aligned} \quad (D.19)$$

$$\begin{aligned} \delta X_{W \rightleftharpoons B} - \delta X_{W \rightleftharpoons B}^o &= [dX_B - dX_B^o] + [\delta X_{Dest,B} - \delta X_{Dest,B}^o] \\ &\quad + [\delta X_{B \rightleftharpoons L} - \delta X_{B \rightleftharpoons L}^o] \end{aligned} \quad (D.20)$$

The direct impact equation for the water reservoir shows that the net exergy directly transferred to the water reservoir drives state change, destruction change, and alterations of natural transfers between the reservoir and the lithosphere, atmosphere, and biosphere. The indirect impact equation for the biosphere shows that the alteration of natural transfers between the biosphere and water reservoir drives state change, destruction change, and alterations of natural transfers between the biosphere and lithosphere.

The direct transfers between the anthrosphere and water reservoir indirectly impact the biosphere by altering its natural transfers with the water reservoir. The direct transfer of return water can cause local and global temperature increases within the

water reservoir, which increase the temperature of its natural transfers with the biosphere. Increases to the temperature of the water reservoir can increase the transfer of oxygen from the reservoir to the atmosphere, which decreases the oxygen concentration within the reservoir, and therefore the oxygen concentration in its natural transfers with the biosphere. Since the biosphere has been identified as being sensitive to both temperature and concentration change, it is desirable to avoid causing temperature increases within the water reservoir.

The impact equations provide insight for managing the direct transfer of return water to avoid causing temperature increases that are detrimental to the biosphere. For this example, the water reservoir's state change term in Eq. (D.19) can be treated as the sensitivity constraint, the downstream direct transfer term in the equation is the control variable. The sensitivity constraint can be specified by a maximum allowable temperature increase (local and/or global) within the water reservoir, and serves as an environmental design constraint for the power plant. The design objective is to directly transfer exergy in a manner such that the sensitivity constraint is not violated.

Assuming that the power plant requires a fixed rate of heat removal (for steady state operation), then the change in temperature between the water transferred to and from the reservoir is only a function of the water's mass flow rate (assuming the water is incompressible). Local temperature increases can be mitigated by two design approaches: (1) having a sufficiently large water flow rate such that the water's temperature increase is sufficiently small, and/or (2) distributing the return water over a sufficiently large region within the water reservoir such that the exergy transfer rate is matched to the reservoir relaxation rate (i.e., adjusting the direct transfer such that the reservoir can be categorized as having a fast relaxation rate). The first approach decreases the temperature of the return water (and therefore its intensive thermal exergy), but at the expense of increasing the pumping work and exergy destruction within the anthrosphere, and possibly increasing the extensive exergy of the return water (depending on the contribution of kinetic exergy). The second approach shifts the types of impact caused by the direct transfer—trading local state change for destruction change—but does not alter the exergy directly transferred

(intensive or extensive).

With a fixed rate of heat removal from the power plant, global temperature increase depends on the water reservoir's size, its natural interactions, and the time scale of operation. Global temperature increase can also be managed by two design approaches: (1) choosing a sufficiently large reservoir such that the total energy transferred to the reservoir over the time of operation is small relative to the thermal capacity of the reservoir, and/or (2) choosing a reservoir with sufficient heat transfer to the atmosphere and lithosphere such that energy accumulation is negligible. By managing global and local temperature increases within the water reservoir, its oxygen concentration is indirectly managed since it is a function of the reservoir's temperature.

The design approaches inferred from the direct impact equation explain and validate the actual design solutions employed by power plants that use existing water reservoirs as a heat sink. In practice, thermal pollution is typically avoided by using sufficiently large water reservoirs and flow rates to avoid causing "hot spots" within the reservoir (i.e., thermal inhomogeneities).

D.2.2 Photochemical Smog

Photochemical smog is formed by the chemical and photochemical reactions of NO, NO₂, oxygen, ozone, and reactive organic gases (ROGs, total organic gases exclusive of methane) in the atmosphere [117]. Photochemical smog is a concern because the ozone produced by the smog-forming reactions can be detrimental to human health. Exposure to ozone concentrations above 60 ppb causes human respiratory and eye irritation [118], and long-term exposure has been shown to increase risk of death from respiratory illness [119, 120]. The amount of ozone formed in a given region depends on the initial composition of NO_x and ROGs present in the region, as well as the region's meteorology. Figure D.5 shows a plot of how peak ozone concentrations vary with initial compositions of NO_x and ROGs.

Photochemical smog is especially prevalent in urban areas and is primarily caused by the emissions of NO_x and ROGs from vehicles and power plants. The meteorology

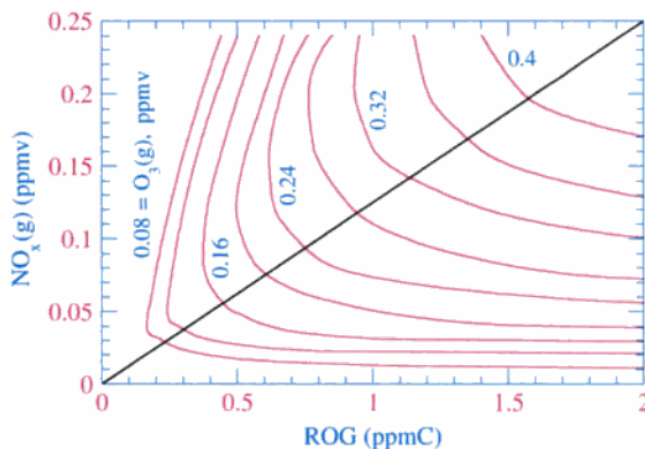


Figure D.5: Peak ozone concentrations resulting from different initial NO_x and ROG compositions. The ROG: NO_x ratio along the line through zero is 8:1, which is common in many polluted urban areas. From Jacobson [117].

and dense concentration of vehicles in the Los Angeles Basin promote the formation of photochemical smog. The Basin's meteorology that promotes photochemical smog formation is the frequent formation of an inversion layer, which acts as a cap that essentially prohibits matter transfer with the upper atmosphere. Photochemical smog is most prevalent on days in which an inversion layer exists and there is little or no wind activity (onshore or offshore). When this occurs, an *inversion region* is created around the Basin that essentially prohibits matter transfer with the surrounding atmosphere. Figure D.6 shows a diagram of the L.A. Basin when an inversion region exists.

Emissions of NO_x and ROG from anthropogenic activity—namely I.C. engine-based transportation—are trapped within the region where they chemically and photochemically react causing elevated ozone concentrations. Inversion regions typically only exist for a day, but can last up to several days. A diagram of the evolution of NO_x and ozone concentrations during one day at two locations—central Los Angeles and San Bernardino—is shown in Fig. D.7. The figure shows that NO_x concentrations increase during the morning, and decrease during the afternoon. The morning increase is primarily due to vehicle emissions during the morning commute, and the afternoon decrease is due to chemical and photochemical reducing reactions, which

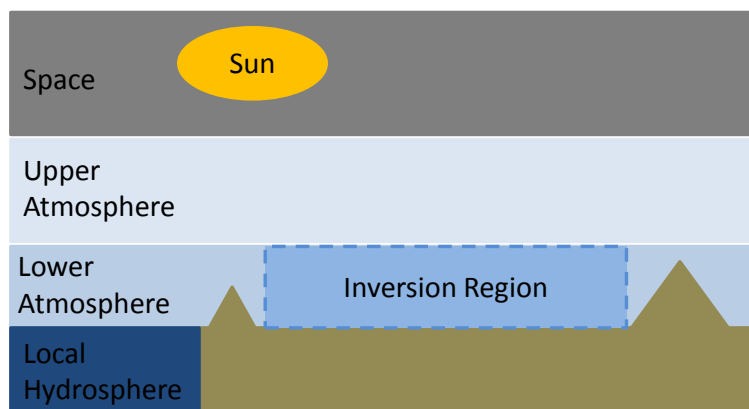


Figure D.6: Diagram of L.A. Basin for illustrating the environmental conditions that promote photochemical smog formation.

form ozone. The figure shows that ozone concentrations are above 60 ppb for an extended period of time in both regions during the day the data were collected.

The environmental analysis framework can be applied to analyze the formation of photochemical smog, and explain the techniques used in practice to avoid its negative consequences. A diagram illustrating the environmental reservoirs and interactions that promote the formation of photochemical smog is shown in Fig. D.8. In this example, the anthropogenic activity is I.C. engine-based transportation, and the biosphere's interactions is human breathing.

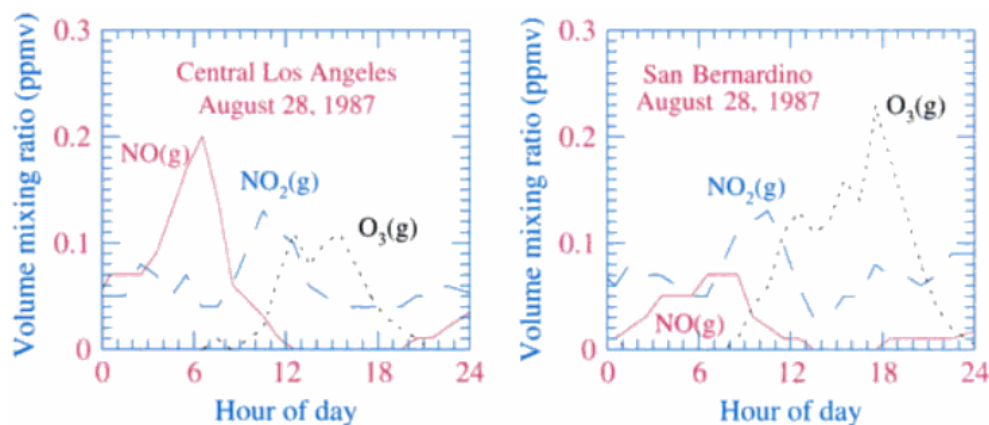


Figure D.7: Evolution of NO, NO₂, and ozone mixing ratios at two locations in L.A. Basin on August 28, 1987. From Jacobson [117].

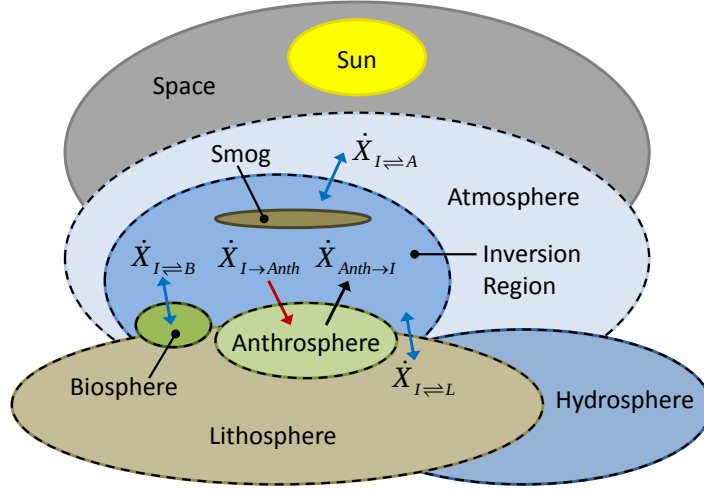


Figure D.8: Environmental reservoirs and interactions for analyzing the environmental impact of photochemical smog. Red arrows: upstream transfers; black arrows: downstream transfers; blue arrows: natural transfers; black dashed lines: reservoir control boundaries.

The differential impact equations for the inversion region and biosphere are given by:

$$\begin{aligned} \delta X_{Anth \rightarrow I} - \delta X_{I \rightarrow Anth} = & [dX_I - dX_I^o] + [\delta X_{Dest,I} - \delta X_{Dest,I}^o] \\ & + [\delta X_{I \rightleftharpoons A} - \delta X_{I \rightleftharpoons A}^o] + [\delta X_{I \rightleftharpoons L} - \delta X_{I \rightleftharpoons L}^o] \\ & + [\delta X_{I \rightleftharpoons B} - \delta X_{I \rightleftharpoons B}^o] \end{aligned} \quad (D.21)$$

$$\delta X_{I \rightleftharpoons B} - \delta X_{I \rightleftharpoons B}^o = [dX_B - dX_B^o] + [\delta X_{Dest,B} - \delta X_{Dest,B}^o] \quad (D.22)$$

The direct impact equation for the inversion region shows that the net exergy directly transferred to the inversion region drives state change, destruction change, and alterations of natural transfers with the atmosphere, lithosphere, and biosphere. The indirect impact equation for the biosphere shows that the alteration of natural transfers between the biosphere and inversion region drive state change and destruction change within the biosphere.

The direct transfers between the anthrosphere and inversion region indirectly impact the biosphere by altering its transfers with the region. Since the biosphere

has been identified as being sensitive to transfers of ozone, it is desirable to avoid direct transfers that cause an increase in the ozone concentration in the inversion region—namely transfers of NO_x and ROGs. For this example, the inversion region’s state change term in Eq. (D.21) can be treated as the sensitivity constraint, and the downstream direct transfer term in the equation is the design variable. The sensitivity constraint can be specified by a maximum allowable concentration of ozone within the inversion region over a specified amount of time. An example sensitivity constraint could be the Air Quality Index developed by the U.S. Environmental Protection Agency, which classifies eight-hour-average ozone concentrations between 85-104 ppb as “unhealthy for sensitive group”, between 105-124 ppb as “unhealthy”, and between 125-400 ppb as “very unhealthy” [89]. The design objective is to avoid directly transferring NO_x and ROGs in an amount and at a rate that would violate the sensitivity constraint.

In practice, this is accomplished by reducing the amount of NO_x and ROGs in a vehicle’s exhaust through the use of a three-way catalyst, which converts NO_x , ROGs, and CO to stable N_2 , CO_2 , and H_2O . The reactions that take place within a three-way catalytic converter are (net) exothermic. This design approach reduces the chemical exergy of exhaust, but at the expense of increasing its thermal exergy and increasing the amount of exergy destroyed within the anthrosphere. By shifting the form in which exergy is directly transferred to the inversion region—from chemical to thermal—the type of impact is shifted from chemical state change with a high anthropocentric sensitivity to destruction change (due to thermal dissipation) with a low anthropocentric sensitivity.

D.2.3 Large-Scale Solar PV

The Earth’s largest resource flux is the relatively constant flux of solar radiation generated by the sun. A potential—not necessarily practical or realistic—solution for meeting the world’s energy demand would be to utilize this natural exergy flux through the large-scale deployment of photovoltaic (PV) solar cells. To analyze the environmental impact of such an endeavor, the following (hypothetical) project is

considered: Meet the world's energy demand in year 2100 using only PV solar cells, assuming there are 9 billion people with an average energy consumption of 10 kW per person.⁴ A potential solution for producing 90 TW of electricity using only PV solar cells would be to cover 1% of the Earth's surface with solar cells with an average exergy efficiency of approximately 10%. This would produce approximately 90 TW of electricity from the 860 TW of solar radiation incident on the solar cells, or 1% of the 86,000 TW of total surface incident solar radiation (as shown in Fig. 4.4). The remaining 770 TW of exergy must be either destroyed in the PV cells or transferred to the environment as unused exergy.

The environmental interactions of this anthropogenic activity can be broken down into upstream and downstream interactions. Upstream of the conversion process, 860 TW of solar radiation is altered by the solar cells. Assuming that the solar cells are located above the lithosphere, then 860 TW of exergy is prevented from reaching the lithosphere. Downstream of the conversion process, the unused portion of the 770 TW not converted to electricity must be transferred to the environment. Assuming that 40% is destroyed within the solar cells, then the remaining 60%, approximately 460 TW, must be transferred to the environment. To put this value into perspective, referring back to the global exergy resources diagram shown in Fig. 4.4, 460 TW is on the order of magnitude of the exergy in wind and ocean thermal gradients, an order of magnitude greater than the exergy of clouds and the natural flux of crustal thermal energy, and two orders of magnitude greater than the exergy of rivers and tides.

The environmental analysis framework can be applied to analyze the environmental impact of the upstream and downstream interactions and provide insight for system design. Figure D.9 illustrates of the environmental reservoirs and interactions for this activity, with the assumptions that the solar cells are located above the lithosphere and all unused exergy is directly transferred to the atmosphere. The direct alteration of surface incident radiation within the anthrosphere is depicted as the upstream interaction, however, as discussed in Ch. 4, direct alterations of natural transfers have a direct impact on the reservoirs from which they are altered—the

⁴Average consumption in the U.S. in 2008 was 14.4 kW per person [121].

lithosphere in this example. Whereas, the direct transfer of unused exergy from the anthrosphere has a direct impact on the atmosphere.

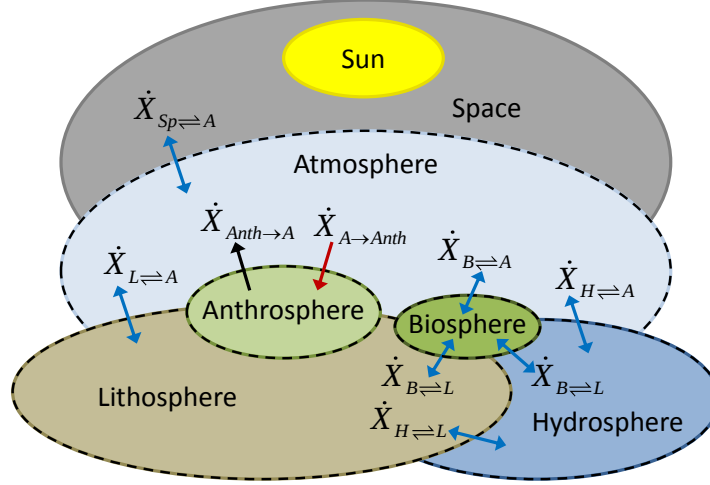


Figure D.9: Environmental reservoirs and interactions for analyzing the environmental impact of large-scale solar PV. Red arrows: upstream interactions; black arrows: downstream interactions; blue arrows: natural transfers; black dashed lines: reservoir control boundaries.

The direct impact the alteration of surface incident radiation has on the lithosphere, upstream of the conversion process, is given by the following instantaneous impact equation:

$$\begin{aligned} \dot{X}_{A \rightarrow L} - \dot{X}_{A \rightarrow L}^o &= \left[\frac{dX_L}{dt} - \frac{dX_L^o}{dt} \right] + \left[\dot{X}_{Dest,L} - \dot{X}_{Dest,L}^o \right] \\ &+ \left[\dot{X}_{L \rightarrow A} - \dot{X}_{L \rightarrow A}^o \right] + \left[\dot{X}_{L \rightleftharpoons H} - \dot{X}_{L \rightleftharpoons H}^o \right] + \left[\dot{X}_{L \rightleftharpoons B} - \dot{X}_{L \rightleftharpoons B}^o \right] \end{aligned} \quad (D.23)$$

The difference on the left hand side of this equation is equal to the opposite of the amount of incident solar radiation altered within the anthrosphere (-860 TW). Therefore, the driver of direct impact on the lithosphere can be viewed as a removal of 860 TW of exergy from the lithosphere. The types of impact on the lithosphere are state change, destruction change, and alterations of natural transfer to the atmosphere and with the hydrosphere. Assuming that 10% of the incident surface radiation is naturally transferred back to the atmosphere, then the alteration of natural transfer

term between the lithosphere and atmosphere on the right hand side of the equation is equal to -86 TW.

The atmosphere is impacted by the direct transfer of unused exergy and the alteration of natural transfer between it and the lithosphere. This can be shown by the instantaneous impact equation for the atmosphere:

$$\begin{aligned} \dot{X}_{Anth \rightarrow A} + \left[\dot{X}_{L \rightarrow A} - \dot{X}_{L \rightarrow A}^o \right] = & \left[\frac{dX_A}{dt} - \frac{dX_A^o}{dt} \right] + \left[\dot{X}_{Dest,A} - \dot{X}_{Dest,A}^o \right] \\ & + \left[\dot{X}_{A \rightarrow L} - \dot{X}_{A \rightarrow L}^o \right] + \left[\dot{X}_{A \rightleftharpoons H} - \dot{X}_{A \rightleftharpoons H}^o \right] + \left[\dot{X}_{A \rightleftharpoons Sp} - \dot{X}_{A \rightleftharpoons Sp}^o \right] \\ & + \left[\dot{X}_{A \rightleftharpoons B} - \dot{X}_{A \rightleftharpoons B}^o \right] \end{aligned} \quad (D.24)$$

The direct transfer term on the left hand side of this impact equation is equal to the 460 TW of unused exergy transferred from the anthrosphere, and the direct alteration of natural transfer term is equal to the exergy indirectly altered from naturally being transferred from the lithosphere (-86 TW). The alteration of natural transfer term between atmosphere and lithosphere on the right hand side is equal to zero, since it is the driver of impact on the lithosphere.⁵ Therefore, the drivers of impact on the atmosphere drive state change, destruction change, and alterations of natural transfers with the hydrosphere and space.

The instantaneous impact equations provide a framework for asking questions about sensitivity and determining how to manage the alterations of natural exergy transfers caused by this system. Downstream of the conversion we should ask: Are there any sensitivities associated with preventing 860 TW from reaching the lithosphere? Upstream of the conversion process we should ask: Are there any sensitivities associated with directly transferring 460 TW of exergy to the atmosphere? The answers to these questions provide information for how to manage these interactions.

For example, if transferring 460 TW of thermal exergy to the atmosphere causes thermal plumes (i.e., local state change) that adversely affect the local biosphere, then a possible design solution would be to adjust the direct transfer such that its transfer rate is better matched to the atmosphere's relaxation rate (i.e., adjusting the transfer

⁵Otherwise, there would be double counting.

such that atmosphere can be categorized as having a fast relaxation rate). Two approaches could be implemented to accomplish this: (1) reduce the temperature of the direct transfer by using cooling water from another reservoir, or (2) distribute the PV cells over a sufficiently large region. The first approach reduces the thermal exergy transferred to the atmosphere by increasing the rate of exergy destruction within the anthrosphere (due to heat transfer) and shifting the location of where the unused exergy is transferred (to the water reservoir). The second approach shifts the types of impact caused by the direct transfer—trading local state change for destruction change—but does not alter the exergy directly transferred. Both approaches could be implemented to avoid causing local state change in the atmosphere, but they do not address the potential for global state change caused by energy accumulation. In the thermal pollution example considered in the beginning of this section, one potential approach for avoiding global state change was to choose a sufficiently large reservoir. However, for transfers on the hundreds of terawatts scale, the question becomes: Are any of the terrestrial environmental reservoirs large enough to avoid causing global state change? If the answer to this question is no, then a possible design solution would be to transfer all unused exergy off of the terrestrial environmental reservoir. This could theoretically be accomplished by re-radiating unused exergy at a wavelength such that it passes through the atmosphere and into space.

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