Energy, Material and Emissions Flow Models of the U.S. Chemical Industry

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Abstract

Energy, Material and Emissions Flow Models of the U.S. Chemical Industry

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This study is devoted to developing methodologies to construct scaled energy, material and emission flow models of the U.S. Chemical industry. It was our objective to demonstrate a methodology that balances energy and material flow models for products produced by the Industrial Gas Manufacturing sector to U.S. production, energy use, and emissions for the industry for 1998. Such a demonstration would provide a way to extend this work to other sectors of the chemical industry, thus providing policy makers with a reliable way to assess the performance of these industries with regard to improvements in energy and material use and emissions over time. Unfortunately, the energy and material balance models currently available in the literature are not adequate to this task.

This study is intended to serve for the purpose of measuring national benefits in reduced energy and material consumption, and identification of R&D opportunities to reduce emissions. Manufacturing energy flow analysis part of this study is characterized by two types of models: an energy process-step model and an energy end-use model. An

energy process-step model shows energy inputs and outputs at each step of an industrial process, which is obtained from an engineering analysis for a typical plant in the sector. Alternatively, an energy end-use model provides basis to calibrate the energy process-step model using national data. It allocates combustible fuel and renewable energy inputs among generic end-uses including intermediate conversions through onsite power and steam generation. The material flow model represents mass inputs and outputs for an industrial process, whereas the emission flow model provides CO_2, SO_2 and NO_x emissions from both prime movers and industrial processes. However, due to the lack of sufficient material flow and energy process-step models found in the literature, it was not possible to apply the calibration methodology developed in this dissertation. Once credible quantitative models are available, the approach developed herein can be used to complete the calibration in the future.

The energy, material and emissions models are an attempt to give an overall picture of energy and raw material consumption for the purpose of industrial gas production. They also attempted to show CO_2, SO_2 and NO_x emissions as a consequence of power generation and industrial processes in this industry.

The approach to creating these models, consistent with national data, has been shown to be applicable to other industries. When used in conjunction with similar models for other years, these models can be used to identify the changes and trends in energy use along with the environmental consequences of emissions from specific industries. While this has been demonstrated for some industries, the current state of the energy and material balance models do not allow this for the Industrial Gas Manufacturing sector as a whole.

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η_9 combined cycle – steam turbine electric conversion efficiency

η_{10} combined cycle – boiler efficiency

η_{11} combined cycle waste heat recovery efficiency

η_{12} fuel fired boiler efficiency

η_{13} electric boiler efficiency

CHP combined heat and power

CIR Current Industrial Reports

EIA Energy Information Administration

EPA Environmental Protection Agency

MECS Manufacturing Energy Consumption Survey

NAICS North American Industrial Classification System

DOC Department of Commerce

DOE Department of Energy

LPG Liquefied Petroleum Gas

RSE	Relative Standard Error
Mmtc	Million metric ton carbon
PJ	Peta Joules

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DEDICATION

To my father, Mehmet Orhan Özalp

1. INTRODUCTION

Energy is called “the elemental force and medium upon which all human culture is built” (Rifkin, 2002), and “the United States and the world face an array of energy related challenges in this century” (Holdren and Baldwin, 2001). Therefore, it is important to comprehensively study and understand energy utilization in all its aspects. This dissertation provides a broad analysis of energy consumption along with the associated issues or problems for the chemical industry in general, and more specifically for industrial gas production. The models show to the extent possible energy and energy related mass inputs, outputs and environmental consequences; these models provide a useful tool to characterize industrial energy usage.

A comprehensive and consistent description of current manufacturing energy and material usage patterns along with emissions patterns can provide information on the potential effect of technological, economic and public policy changes in this energy intensive manufacturing sector. Therefore, it is important to develop energy, material and emissions flow model of the U.S. Chemical Industry.

Although energy is utilized in many sectors including the residential, commercial, industrial and transportation, the “industrial sector is the most diverse and the most challenging energy demand sector to model” (Worrell et al., 2001). Because, “data on the manufacturing sector’s energy use has been scarce, this lack of data has made energy-use analysis of industrial sector more difficult here than in the other sectors” (EIA, 1995). Therefore, the motivation of this research is to develop methodology to cope with these challenges.

The main objectives of this research are:

1. Identify the energy input patterns in the U.S. Chemical Industry and the Industrial Gas Manufacturing sector using federal databases (Sections 2.4.3. and 2.4.4),
2. Search the actual performance of the prime movers and waste heat recovery in the U.S. Chemical Industry (Sections 2.4.1., 2.4.2. and 2.4.3.),
3. Identify the fuel, steam, waste heat and electricity allocation among the end-uses in the U.S. Chemical Industry and the Industrial Gas Manufacturing sector using federal databases (Section 2.4.5.2., Figures 17 and 18),
4. Benchmark the energy end-use model of the U.S. Chemical Industry with the previous energy end-use models of the U.S. Chemical Industry (Section 2.5.2.1.),
5. Search the commercial production processes to select a representative production process for each product of the Industrial Gas Manufacturing sector (Chapter 3),
6. Identify the production levels in the Industrial Gas Manufacturing sector using federal databases (Section 1.5),
7. Identify the national scale energy, material and emissions models of manufacturing processes for the Industrial Gas Manufacturing sector based on engineering principles and assumptions (Chapters 4, 5 and 6)
8. Develop a methodology to utilize the results of the objectives 1 through 6, to calibrate the results of the objective 7 (Section 5.3),
9. Critical evaluation of databases, engineering models and the methodologies to recommend improvements (Chapter 7).

The outcome of this research will enable DOE, industry, academics and government agencies to see the macro picture of energy and material flow in the Industrial Gas Manufacturing sector. The results of this research is also of interest to policy makers since energy and material flow models "provide policy makers with information to support sustainable activities in the industrial sector" (Price and Worrell, 2005). It will also be of interest to people trying to model the rest of the chemical industry. The expectation is that the results of this research will help them to reveal what works and what does not. Similar energy, material and emissions models for a base year and recent past years can also be a key element in testing algorithms that attempt to forecast future energy, materials and emissions of manufacturing processes.

Encouragements to initiate efforts for better understanding the energy flow in the manufacturing sector have been pointed out by many government agencies. For example, a report prepared by the National Research Council gives recommendations to DOE on leveraging limited funding resources by focusing on the energy efficiencies in the manufacturing sector. In their report (National research Council, 2005), they recommend that the DOE Industrial Technologies Program address the energy saving opportunities in the energy intensive industries, which includes the Chemical Industry.

Furthermore, a report by the Congressional Research Service states that "Development and analysis of proposals on energy consumption and emission reduction require a knowledge of how energy is used -both the energy demand category e.g., space heating, lighting, process steam, trucks- and the energy sources used to supply that demand or service." (Rowberg, 1991).

Therefore the U.S. Department of Energy is interested in this research in order to pursue their fundamental goals of:

- "focusing on energy intensive industries",
- "identifying grand challenges which would dramatically improve industrial energy efficiency",
- "performing process-specific and crosscutting R&D to improve long-term energy efficiency" (DOE, 2003).

Furthermore, since "DOE partners with industry, government, and non-government organizations with the goal of significantly improving resource efficiency and competitiveness of materials and process industries", industrial energy, material and emissions flows assessments in this study will reveal the identity and quantity of the energy and material consumption in the U.S. Chemical Industry as well as consecutive emissions for heat and power by application (ADL, 2000).

Therefore, this study provides a useful macro picture of energy and material utilization, because it provides extensive specifics on energy allocation among end-uses, material consumption/emissions, and energy allocation among process-steps for the production of industrial gases.

1.1. Overview of the dissertation

In this chapter, information on energy consumption and energy related emissions from the U.S. Chemical Industry is given. Then, industry definition and characteristics of the U.S. Industrial Gas Manufacturing sector are given. Finally, energy, material and emission flow models are described along with examples.

The second chapter presents the energy end-use model for the U.S. Chemical Industry and the Industrial Gas Manufacturing sector using 1998 data. First, the concept of an energy end-use model is described and literature results are discussed to reveal the comparisons with existing energy end-use models. Then, the methodology to construct the on-site steam and power generation model, which is key part of the energy end-use model, is described. This model yields actual prime mover energy conversion and waste heat recovery efficiencies for the U.S. Chemical Industry.

The third chapter describes the production technologies for the products of the Industrial Gas Manufacturing sector. It presents manufacturing process flow diagrams for these gases along with the discussion of the representative process selection for each product.

Chapter four provides the quantitative material flow models for the products of the Industrial Gas Manufacturing sector in a national scale, whereas Chapter five combines the results of Chapter four with existing engineering models of industrial gas production processes to provide methodology to calibrate energy process-step models of the Industrial Gas Manufacturing sector products.

Chapter six gives CO_2, SO_2 and NO_x emissions from the manufacturing processes of the Industrial Gas Manufacturing sector products. It also provides CO_2, SO_2 and NO_x emissions from the prime movers of this sector during power generation.

The final chapter summarizes the results, assumptions, uncertainties, and the original contributions of the research to the field. In addition, final conclusions and recommendations are given.

The energy, material and emissions flow models for these industrial gases will provide information on a national scale, which are not provided by other currently available models. Therefore, the results of this research will provide the U.S. DOE a tool to make decisions on R&D investments by measuring the national benefits from reduced energy, material and environmentally hazardous emissions.

1.2. Energy consumption and energy related emissions in the U.S.

Trends in energy consumption in the industrial, residential, transportation and commercial sectors of the U.S. are shown in Figure 1. Energy consumption in the industrial sector has been larger than any of the other sectors over the past three decades. CO_2 emissions data in Figure 2 shows that CO_2 emissions from the industrial sector have been exceeded only by that of transportation sector since 2000.

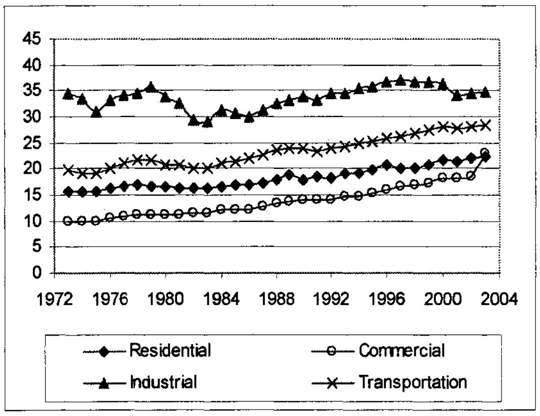

Figure 1. Energy consumption by sector, PJ *

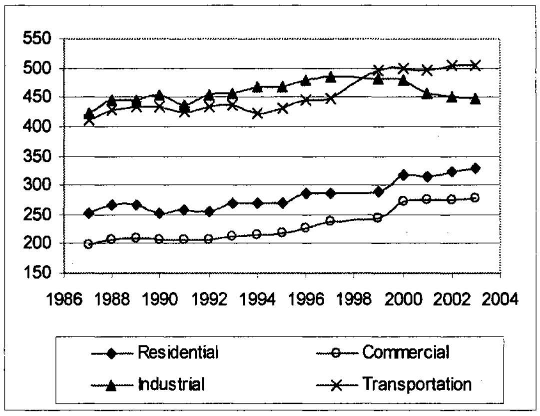

Figure 2. CO_2 emission by sector, mmtc **

* (EIA-MER, 2005)
** (EIA-Greenhouse, 1999; EIA-CO2, 2005; EIA-0573, 2001; EPA-Global warming, 2005)

The industrial sector is composed of manufacturing and non-manufacturing sectors. The manufacturing sector "consists of all facilities and equipment engaged in the mechanical, physical, chemical, or electronic transformation of materials, substances, or components into new products- assembly of component parts of products is included, except for that which is included in construction." (EIA definitions, 2005), whereas the non-manufacturing sectors include: coal mining, crops and other agriculture, oil and gas extraction, forestry, fishing, other mining, and construction sectors. A comparison between the energy consumption of manufacturing and non-manufacturing sector reveals that the non-manufacturing sector consumed about 19% of the delivered industrial energy in 1998 (EIA delivered energy consumptions, 2002). Therefore, manufacturing accounts for 81% of the energy consumed in the U.S. industrial sector.

The U.S. Energy Information Administration collects data on these following manufacturing sectors:

- Food
- Beverage and Tobacco Products
- Textile Mills
- Textile Product Mills
- Apparel
- Leather and Allied Products
- Wood Products
- Paper
- Printing and Related Support
- Petroleum
- Chemical

- Plastic and Rubber Products
- Nonmetallic Mineral Products
- Primary Metals
- Fabricated Metal Products
- Machinery
- Computer and Electronic Products
- Electrical Equipment, Appliances and Components
- Furniture and Related Products

Since this study is focusing on the Chemical Industry, a brief description of this manufacturing sector is given in the following section.

1.3. The U.S. Chemical Industry

The Chemical Industry is called the keystone in the U.S. economy because of its capacity to manufacture more than 70,000 products, which makes it the world's largest chemicals manufacturer. Within the U.S., the Chemical Industry is the second largest energy user after the Petroleum Industry. In 1998, the Chemical Industry consumed about 25% of all U.S. manufacturing energy use (EIA, 2004a). Fuel consumption of this industry not including feedstocks is shown in Figure 3, where "other" includes byproducts, steam, distillate fuel oil, coke and breeze, and fuels not listed separately (MECS-N3.2, 1998). Breeze is "the fine screenings from crushed coke. It is most often used as a fuel source in the process of agglomerating iron ore" (EIA-glossary, 2005).

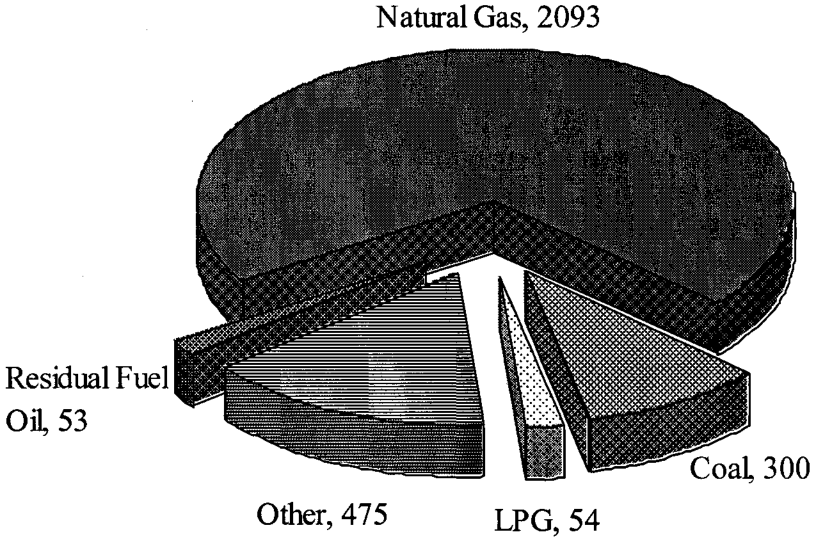

Figure 3. Fuel consumption in the U.S. Chemical Industry in 1998 as energy, PJ

The Chemical Industry is the largest consumer of natural gas in the U.S., accounting for more than 26% of the domestic total, whereas it consumed about 95% of the LPG consumed in the U.S. manufacturing industries (EIA, 2004b). Although "nearly all LPG and about one fourth of natural gas were used as feedstock." (EIA, 2004b), Figure 3 shows that a small amount of LPG is used as fuel while natural gas is the dominant fuel in the Chemical Industry. EIA's report on natural gas provides the natural gas delivery amounts from 1999 to 2003. We can refer to this source to better visualize the share of the Chemical Industry in terms of natural gas consumption in the nation. For example, the natural gas delivery amounts in 1999 are reported as follows (EIA-natural gas navigator, 2005):

- Residential deliveries: 225,198 million cubic feet,
- Commercial deliveries: 1,031,794 million cubic feet,
- Industrial deliveries: 6,564,492 million cubic feet.

This shows that the industrial sector is the largest consumer of natural gas; the Chemical Industry is the largest user of natural gas within the industrial sector.

Because of its large energy utilization capacity, material consumption, production capacity and emissions, it is important to study the U.S. Chemical Industry to identify opportunities for improved energy and raw material usage and reduced emissions.

The U.S. Chemical Industry has 56 subsectors based on the industry classifications and descriptions defined by the North American Industrial Classification System (NAICS). The NAICS was developed jointly by the U.S., Canada, and Mexico to provide new comparability in statistics about business activity across North America.

NAICS uses a 6-digit numbering system. The first two digits characterize the "sector", the third digit characterizes the "subsector", the fourth digit characterizes the "industry group", the fifth digit characterizes the "NAICS industry" and the sixth characterizes the "U.S. national industry". According to this terminology, NAICS 325 Chemicals Manufacturing is a sub-sector, whereas a 6-digit classification, NAICS 325120 Industrial Gas Manufacturing, is a U.S. national industry. The first 5-digit classification applies to all North American countries with one exception, 32522, which is only used in the U.S. Furthermore, classifications that have 6 digits are also an industry with three designations: if there is no label, they are the same for all three countries; if a "U.S." applied, it exists only for the U.S.; and if it is designated "CAN", then it applies to both the U.S. and Canada, but not Mexico. So the chemical subsector of the NAICS has seventeen 5-digit industries and thirty four 6-digit industries. Of the thirty four 6-digit industries, 8 apply to all countries (and in these cases, there is only the one 6-digit industry under the 5-digit industry); three to Canada and the U.S., with the reminder, 23, applying only in the U.S.

Although the NAICS 325120 Industrial Gas Manufacturing is defined as an industry and the NAICS 325 Chemicals Manufacturing as a subsector by the NAICS coding system, in this study the opposite terminology has been used. The reason is that NAICS 325 Chemical Manufacturing is referred to as "Chemical Industry" colloquially, and 325120 Industrial Gas Manufacturing is a branch of NAICS 325 Chemical Manufacturing. Therefore I considered it more appropriate to call Chemical Manufacturing as an industry and the Industrial Gas Manufacturing as a subsector. That is the terminology used throughout in this work.

NAICS codes for the subsectors of the U.S. Chemical Industry are given in Table 1.

Table 1. The Chemical Industry NAICS definitions and industry classification (Census Bureau, 2002)

NAICS code	NAICS title
325	Chemical Manufacturing
3251	Basic Chemical Manufacturing
32511	Petrochemical Manufacturing
325110	Petrochemical Manufacturing
32512	Industrial Gas Manufacturing
325120	Industrial Gas Manufacturing
32513	Synthetic Dye and Pigment Manufacturing
325131	Inorganic Dye and Pigment Manufacturing
325132	Synthetic Organic Dye and Pigment Manufacturing
32518	Other Basic Inorganic Chemical Manufacturing
325181	Alkalies and Chlorine Manufacturing
325182	Carbon Black Manufacturing
325188	All Other Basic Inorganic Chemical Manufacturing
32519	Other Basic Organic Chemical Manufacturing
325191	Gum and Wood Chemical Manufacturing
325192	Cyclic Crude and Intermediate Manufacturing
325193	Ethyl Alcohol Manufacturing
325199	All Other Basic Organic Chemical Manufacturing
3252	Resin, Synthetic Rubber, and Artificial and Synthetic Fibers and Filaments Manufacturing
32521	Resin and Synthetic Rubber Manufacturing
325211	Plastics Material and Resin Manufacturing
325212	Synthetic Rubber Manufacturing

Table 1. (Continued)

	32522		Artificial and Synthetic Fibers and Filaments Manufacturing
		325221	Cellulosic Organic Fiber Manufacturing
		325222	Noncellulosic Organic Fiber Manufacturing
3253			Pesticide, Fertilizer, and Other Agricultural Chemical Manufacturing
	32531		Fertilizer Manufacturing
		325311	Nitrogenous Fertilizer Manufacturing
		325312	Phosphatic Fertilizer Manufacturing
		325314	Fertilizer (Mixing Only) Manufacturing
	32532		Pesticide and Other Agricultural Chemical Manufacturing
		325320	Pesticide and Other Agricultural Chemical Manufacturing
3254			Pharmaceutical and Medicine Manufacturing
	32541		Pharmaceutical and Medicine Manufacturing
		325411	Medicinal and Botanical Manufacturing
		325412	Pharmaceutical Preparation Manufacturing
		325413	In-Vitro Diagnostic Substance Manufacturing
		325414	Biological Product (except Diagnostic) Manufacturing
3255			Paint, Coating, and Adhesive Manufacturing
	32551		Paint and Coating Manufacturing
		325510	Paint and Coating Manufacturing
	32552		Adhesive Manufacturing
		325520	Adhesive Manufacturing
3256			Soap, Cleaning Compound, and Toilet Preparation Manufacturing
	32561		Soap and Cleaning Compound Manufacturing
		325611	Soap and Other Detergent Manufacturing
		325612	Polish and Other Sanitation Good Manufacturing
		325613	Surface Active Agent Manufacturing
	32562		Toilet Preparation Manufacturing
		325620	Toilet Preparation Manufacturing
3259			Other Chemical Product and Preparation Manufacturing
	32591		Printing Ink Manufacturing
		325910	Printing Ink Manufacturing
	32592		Explosives Manufacturing
		325920	Explosives Manufacturing
	32599		All Other Chemical Product and Preparation Manufacturing
		325991	Custom Compounding of Purchased Resins
		325992	Photographic Film, Paper, Plate, and Chemical Manufacturing
		325998	All Other Miscellaneous Chemical Product and Preparation Manufacturing

However, national data is not available for all of these subsectors. For example, the U.S. Department of Energy's (DOE) Manufacturing Energy Consumption Survey (MECS) provides energy data only for these eleven subsectors of the U.S. Chemical Industry (MECS, 1998):

- NAICS 325110 Petrochemicals

- NAICS 325120 Industrial Gas Manufacturing
- NAICS 325181 Alkalies and Chlorine
- NAICS 325188 Other Basic Inorganic Chemicals
- NAICS 325192 Cyclic Crudes and Intermediates
- NAICS 325199 Other Basic Organic Chemicals
- NAICS 325211 Plastic Materials and Resins
- NAICS 325212 Synthetic Rubber
- NAICS 325222 Noncellulosic Organic Fibers
- NAICS 325311 Nitrogenous Fertilizers
- NAICS 325312 Phosphatic Fertilizers

Availability of further federal data on these subsectors is discussed in the next section.

1.4. Availability of the federal data on the Chemical Industry subsectors

As stated earlier, there is a federal energy database for 11 subsectors of the Chemical Industry. My search on availability of federal materials production data on these subsectors identified the NAICS 325120 Industrial Gas Manufacturing sector as the best candidate to study for the following reasons.

Materials production database provides the production amounts of each chemical by each industry. However, if the products manufactured by a particular sector are also manufactured by other sectors, then constructing a material flow model for that particular sector may miscount the material output since they are also produced by other sectors. Therefore, a subsector which produces the vast majority of the products described under its category eliminates this complication. The identification of the producer industries for each product can be found at the U.S. Department of Commerce, Bureau of Economic Analysis industry database, called “Benchmark input-output tables” (DOC, 1997). The benchmark input-output tables provides materials data for all of these listed subsectors of the Chemical Industry.

The material outputs in this database are given in terms of millions of dollars in producer’s price for each product. Although this database is given in terms of product monetary value, the production amount can be estimated by knowing the average market price for that particular product in that year. The most useful information that the benchmark input-output database offers is the products that are produced by each sector, so that we know how many different sectors produce the same chemical.

For example, if we use this database to search for the industries producing industrial gases, we find that the Industrial Gas Manufacturing sector produced about 92% of the industrial gases in the nation in 1997 as shown in Table 2.

Table 2. Industries producing industrial gases, million dollars, 1997 (DOC, 1997)

Industry	Value	% of total
Industrial Gas Manufacturing	4,791	92%
Plastics Material and Resin Manufacturing	162	3%
Other Basic Organic Chemical Manufacturing	135	3%
Petrochemicals	89	2%
Nitrogenous Fertilizer Manufacturing	26	<1%
TOTAL	**5,203**	**100%**

If the vast majority of the industrial gases were not produced by one sector, modeling material and energy flows for products that are produced by multiple industries would have been a significant challenge and may have lead to an erroneous analysis. For the purpose of this dissertation, we will consider the production of industrial gases by other industries to be negligible as the production of industrial gases is concentrated in the Industrial Gas Manufacturing sector.

If we look at petrochemicals producers in the nation as a counter example, the benchmark input-output database shows us that there are other industries that produce significant amount of petrochemicals as shown in Table 3.

Table 3. Industries producing petrochemicals, million dollars, 1997 (DOC, 1997)

Industry	Value	Percentage of total
Petrochemicals	10,702	58%
Petroleum Refineries	3,060	16%
Other Basic Organic Chemical Manufacturing	2,267	12%
Other Basic Inorganic Chemical Manufacturing	1,071	6%
Plastics Material and Resin Manufacturing	1,138	6%
Industrial Gas Manufacturing	89	<1%
Synthetic Rubber Manufacturing	30	<1%
Custom Computer Programming Services	4.2	<1%
Other	217.7	1.2%
TOTAL	**18,580**	**100%**

Table 3 shows that 58% percent of the petrochemicals produced in the U.S. in 1997 were manufactured by the Petrochemicals sector. On the other hand, 16% of the petrochemicals produced in the U.S. were manufactured by Petroleum Refineries, whereas 12% were produced by the Other Basic Organic Chemical Manufacturing sector. Even if there were no price differences between petrochemicals produced by these industries, this table shows us that the amounts of petrochemicals produced by other industries are significant which makes Petrochemicals subsector a highly challenging subsector to model.

Finally, since this study is the first attempt to model energy, material and emission flows in the U.S. Chemical Industry based on the national data, NAICS 325120 Industrial Gas Manufacturing sector is a good start. Future studies can use this dissertation as a reference to construct models for other sectors, which have more complicated relationships between the products and the industries that produce them.

The description of the U.S. Industrial Gas Manufacturing sector is given in the next section.

1.5. The U.S. Industrial Gas Manufacturing sector

According to the U.S. Census Bureau definition, NAICS 325120 Industrial Gas Manufacturing sector "comprises establishments primarily engaged in manufacturing industrial organic and inorganic gases." It is the biggest electricity consuming subsector of the U.S. Chemical Industry (EIA, 1998). In terms of total energy consumption, Industrial Gas Manufacturing sector is the sixth largest energy consuming subsector of the U.S. Chemical Industry (MECS-N3.2., 1998). Among 34 subsectors of the Chemical Industry, it is the 21st biggest chemical producer (ASM, 1998).

The products manufactured by this sector are (CIR, 1998a; CIR 1998b; CIR, 2002; ASM, 1998):

- Acetylene
- Carbon dioxide
- Nitrogen

- Oxygen
- Argon
- Hydrogen
- Fluorocarbons and all other Industrial Gas Manufacturing sector products

The U.S. Census Bureau's Current Industrial Report provides production amounts of acetylene, carbon dioxide, nitrogen, oxygen, argon and hydrogen by Industrial Gas Manufacturing sector in 1998 (CIR, 1998a). The "production" values in this database:

- For "acetylene" excludes information from railroad ships, shipyards, welding shops, and small establishments using portable generators,
- For "carbon dioxide" excludes quantities produced and consumed in plants manufacturing soda ash and urea,
- For "nitrogen" excludes amounts produced and consumed in the manufacturing of synthetic ammonia and ammonia derivatives,
- For "oxygen" excludes captive uses for consumption in the same plant,
- For "hydrogen" excludes amounts vented, used as fuel, etc., and amounts produced and consumed in the manufacturing of synthetic ammonia and methanol, but includes amounts produced for sale or interplant transfer to plants consuming this gas in the production of ammonia. Also excludes amount produced by ammonia dissociation process (cracking of ammonia). Also excludes amounts produced in petroleum refineries for captive use.

Table 4 summarizes the production of these chemicals by Industrial Gas Manufacturing sector in 1998 based on Current Industrial Reports. It should be noted that the purity levels for these gases are not reported in this database.

Table 4. Industrial Gas Manufacturing production in 1998, kg (CIR, 1998a)

Chemical	**Production**
Nitrogen	2.9×10^{10}
Oxygen	2.5×10^{10}
Carbon dioxide	1.3×10^{10}
Argon	9.1×10^{8}
Acetylene	1.4×10^{8}
Hydrogen	1.3×10^{8}
TOTAL	$\mathbf{6.8\times10^{10}}$

The values in Table 4 will be used in scaling in order to obtain national scale material flow models in Chapter 4.

Although there is national data for the production of acetylene, carbon dioxide, nitrogen, oxygen, argon and hydrogen by Industrial Gas Manufacturing sector in 1998, there is no federal data on the amount of "fluorocarbons and all other Industrial Gas Manufacturing sector products" produced. However, other U.S. Census Bureau reports, namely, other Current Industrial Reports (CIR) and Annual Survey of Manufacturers (ASM), provide data on these chemicals in terms of value of shipments (CIR, 1998b; CIR, 2002; ASM, 1998). Based on the information given in these sources, estimated fluorocarbons production in 1998 was less than 1% of the total industrial gas production. Therefore, we may conclude that the major products manufactured by the Industrial Gas Manufacturing sector are, carbon dioxide, nitrogen, oxygen, argon and hydrogen.

A concise introduction to the energy, material and emissions flow models for these products is given in the next section.

1.6. Energy, material and emissions flow models

After selecting the subsector to study based on the availability of the data, the next step is to construct energy, material and emissions flow models. Manufacturing energy flows are characterized by two types of models: an energy process-step model and an energy end-use model. The following section provides a brief introduction to energy and material process step models.

1.6.1. Energy and materials process-step models

A material flow model shows mass inputs and outputs at each step of an industrial process, whereas an energy process-step model shows energy inputs at each step of an industrial process. Numerical values for each step of a process are obtained from thermodynamic principles and engineering analysis for a typical plant in the sector. "The complex industry profile cannot be appreciated by a cursory examination of the industry as whole, rather, one should analyze the major processes used to produce the more abundant products within the industry" (Energy and Environment Analysis Inc., 1982). Therefore, studying the major manufacturing processes is the key to better understanding and establishing energy and material process step models for an industry.

Material flow models given on a national scale are very important for national benefits because: "efforts at tracking sources and flow of materials have allowed public and private sector decision makers to answer critical questions for decades," such as:

“Where were the alternate sources of supply or substitutes for strategic materials necessary to support American industry and national security,” and “What were the environmental consequences of the material and energy flows?” (National Research Council, 2004).

In this study, national scale material flow models were established for the manufacturing processes of the Industrial Gas Manufacturing sector products. Since “for the majority of chemicals, there is economic competition that forces a similarity in chemical and energy efficiency, selecting any major process is probably representative, given the modest level of precision needed” as a first step of creating a material flow model in a national scale (Jiménez-González et al., 2000). After the selection of a representative process and a cross-check for the mass balance of each process-step, material input and outputs are scaled against federal data to obtain material flows on a national scale. However, it should be noted that the industry is constantly transitioning from one technology to another, usually over a 20-30 year span. Therefore, any industry is often a mix of old and new technologies.

One of the initial and most comprehensive efforts to create material and energy flow models was developed at Drexel University for 108 different manufacturing processes (Brown et al., 1996). Drexel models were created based on data collected in 1976 and industrial process technology for that time period. As an example, the Drexel model for nitrogen and oxygen production is given in Figure 4 and Table 5.

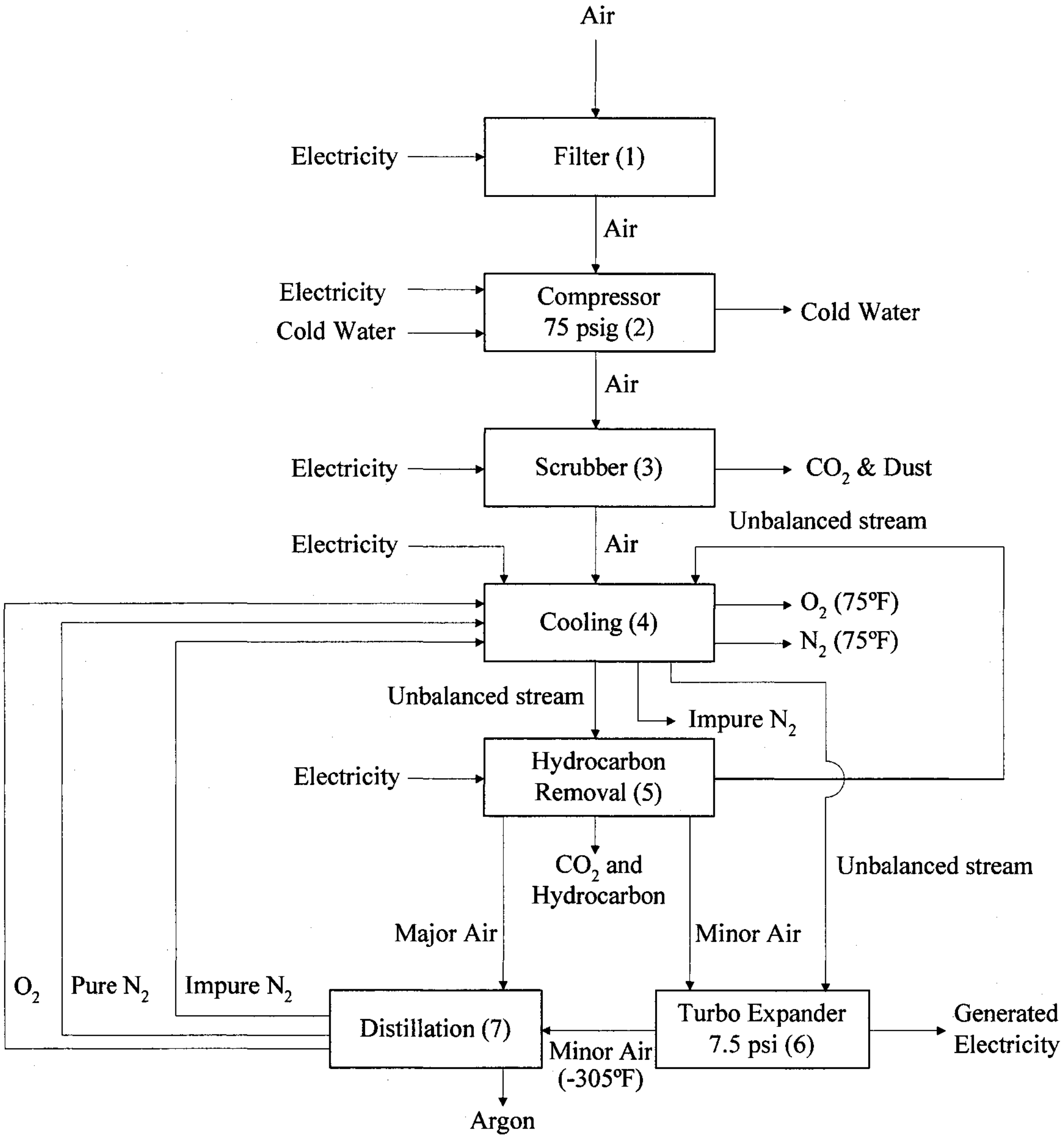

Figure 4. Nitrogen and oxygen production material and energy flow model by Drexel

Figure 4 identifies seven key process steps to manufacture nitrogen and oxygen. The primary data collected to construct Drexel models were based on plant surveys and questionnaires, whereas industrial consultants, the Annual Survey of Manufacturers data published by the Census Bureau in 1976, and other reports were used as secondary data. Input and output values for each process step in Figure 4 are given in Table 5.

Table 5. Input and output values of nitrogen and oxygen production process steps from Drexel model

Process step no	Description	Inlet				Outlet			
		Flow	Temp. (°F)	Mass (lb)	En. (Btu)	Flow	Temp. (°F)	Mass (lb)	En. (Btu)
1	Filter	Air	75	4.3	0	Air	75	4.3	0
		Electric	-	-	7.4	Loss	-	-	7.4
2	Compressor	Air	75	4.3	0	Air	90	4.3	15.5
		Cold H_2O	75	31.3	0	C.W.	95	31.3	626.6
		Electric	-	-	642.1	-	-	-	-
3	Scrubber	Air	90	4.3	15.5	Air	90	4.3	15.5
		Electric	-	-	14.8	CO_2	90	0.001	0
		-	-	-	-	Loss	-	-	14.8
4	Cooling	Air	90	4.3	15.5	Air	-270	4.3	-342.4
		O_2	-275	1	-70	O_2	75	1	0
		N_2	-275	0.3	-26	N_2	75	0.3	0
		Unbl. st.	-270	0.3	-24.1	Unbl. st.	-120	0.3	-13.4
		Imp. N_2	-275	2.9	-251.2	Imp. N_2	75	2.9	0
		Electric	-	-	14.8	Loss	-	-	14.8
5	Hydrocarbon Removal	Air	-270	4.3	-342.4	Maj. air	-270	2.7	-213.4
		Electric	-	-	8.1	Hyd. carb.	-270	0.001	0
		-	-	-	-	Unbl. st.	-270	0.3	-24.1
		-	-	-	-	Min.air	-270	1.3	-106
		-	-	-	-	Loss	-	-	7.4
6	Turbo Expander	Unbl. st.	-300	0.3	-13.4	Min.air	-305	1.6	-148.6
		Min. air	-270	1.3	-106	Loss	-	-	29.2
7	Distillation	Min. air	-305	1.6	-148.6	O_2	-275	1	-70
		Maj. air	-270	2.7	-213.4	N_2	-275	0.3	-26
		-	-	-	-	Ar	-275	0.02	-1.5
		-	-	-	-	Imp. N_2	-275	2.9	-251.2
		-	-	-	-	Loss	-	-	-13.3

Drexel Models have been used by government, industry and institutions since the 1980s. Due to the changes in technology, production practices, product composition, energy prices, and availability of data, Drexel models do not necessarily reflect current material and energy consumption patterns. As it is stated by Mizrahi, "the Chemical

Industry has always been exposed to many changes"(Mizrahi, 2001). What would be useful would be contemporary industrial process models that reflect new technologies and are scaled to recent data. Therefore, with such a model, with results scaled against national data, we could understand the national significance of the energy and mass flows in a manufacturing process.

The goal of this study is to identify representative manufacturing processes based on the quantitative and qualitative information given in the literature and to calibrate the process models against the most recent national data. For example, processes provided in Drexel models and other sources in the literature can be used in identifying the characteristic manufacturing processes for a particular product. Alternately, any information in literature referring to a particular technique as the "most dominantly used technique", or "most commonly applied" can be used in determining which technique would be representative.

There have been other studies to create contemporary Drexel-type material and energy flow models for other industries (Andersen and Hyman, 2001; Giraldo and Hyman, 1995; Giraldo and Hyman, 1996; Schulze, 1999; JVP, 2004; Worrell et al., 2000). However, among all manufacturing industries, creating material flow models for the U.S. Chemical Industry is the most challenging one due to its complexity. A very limited number of studies on energy and material flows in this industry have been conducted and this is one of the main motivations for analyzing this industry.

One of the major complications in dealing with the U.S. Chemical Industry or its subsectors is due to the number of products produced. For example, it is relatively straightforward to construct a material flow model for the U.S. Paper Industry by focusing on the fiber, water and chemicals associated with the recovery process. Estimating the moisture content in pulp or stock on a weight basis at each manufacturing step allows one to calculate material flows based on a unit mass of finished paper or paperboard. As for the energy flow model of paper making, tracking moisture content of the material gives the energy consumed during the paper drying process, which is a significant contributor to total energy consumption. However, for the Chemical Industry, since there are many materials involved in a process, it is more complex to track each material in a process. Another complication in dealing with the Chemical Industry is the variety of production techniques. For example, there could be several widely used production processes for one particular product. Therefore, choosing a representative manufacturing process for that product may underestimate the macro picture due to not taking other production processes into consideration. However, in order to have an overall estimation, a representative process may serve as a good starting point.

1.6.2. Energy end-use models

An energy end-use model provides the basis to scale energy process-step model based on national data. It allocates combustible fuel and renewable energy inputs among generic end-uses including intermediate conversions through onsite power and steam generation. End uses are defined as process end-uses and non-process uses. The process uses, based on standardized MECS definitions, are:

- Process heating: “The direct process end use in which energy is used to raise the temperature of substances involved in the manufacturing process. Examples are many and include the use of heat to melt scrap for electric-arc furnaces in steel-making, to separate components of crude oil in petroleum refining, to dry paint in automobile manufacturing, and to cook packaged foods. Not included are heat used for heating of buildings or for cafeteria and personal cooking" (MECS-glossary, 2005),

- Process cooling and refrigeration: "The direct process end use in which energy is used to lower the temperature of substances involved in the manufacturing process. Examples include freezing processed meats for later sale in the food industry and lowering the temperature of chemical feedstocks below ambient temperature for use in reactions in the chemical industries. Not included are uses such as air-conditioning for personal comfort and cafeteria refrigeration." (MECS-glossary, 2005),
- Machine drive: "The direct process end use in which thermal or electric energy is converted into mechanical energy. Motors are found in almost every process in manufacturing. Therefore, when motors are found in equipment that is wholly contained in another end use (such as process cooling and refrigeration), the energy is classified there rather than in machine drive." (MECS-glossary, 2005),
- Electrochemical processes: "The direct process end use in which electricity is used to cause a chemical transformation. Major uses of electrochemical process occur in the aluminum industry in which alumina is reduced to molten aluminum metal and oxygen, and in the alkalies and chlorine industry, in which brine is separated into caustic soda, chlorine, and hydrogen." (MECS-glossary, 2005),
- Other process uses.

Non-process end-uses are:

- Facility HVAC: “The direct non-process end use that includes energy use in systems that condition air in a building.” (MECS-glossary, 2005),
- Facility lighting: “The direct non-process end use that includes energy used in equipment that illuminates buildings and other areas on the establishment site.” (MECS-glossary, 2005),
- Facility support: “The direct non-process end use that includes energy used in diverse applications that are normally associated with office or building operations such as cooking in cafeterias; operation of office equipment such as personal computers and copying machines; and operation of elevators.” (MECS-glossary, 2005),
- Onsite transportation: “The direct non-process end use that includes energy used in vehicles and transportation equipment that primarily consume energy within the boundaries of the establishment. Energy used in vehicles that are found primarily offsite, such as delivery trucks, is not measured by the MECS.” (MECS-glossary, 2005),
- Other non-process uses.

The process end-uses are the focus of this dissertation. In order to calibrate an energy process-step model for an industrial process on a national scale, an energy end-use model must be constructed first so that the energy inputs to process end-uses are clearly identified.

The main federal database to construct energy end-use models is the Energy Information Administration’s (EIA) Manufacturing Energy Consumption Survey (MECS). This database provides information on how much energy is used for each end-use on a national scale in each industry. Detailed information about the quality of this database is contained in Chapter 2.

The secondary federal database to construct the energy end-use models is the Energy Information Administration's EIA-860B: Annual Electric Generator Report. This database provides information about fuel consumed, gross generation and recovered waste heat at the prime mover level of detail. This information was used to calculate actual energy conversion efficiencies of the prime movers used in the Chemical Industry, which were then used to calculate steam and waste heat allotments to end-uses. Detailed information about the quality of this database is also explained in Chapter 2.

Energy end-use models are constructed based on the data obtained from these two federal databases. A generic representation of an energy end-use model is given in Figure 5.

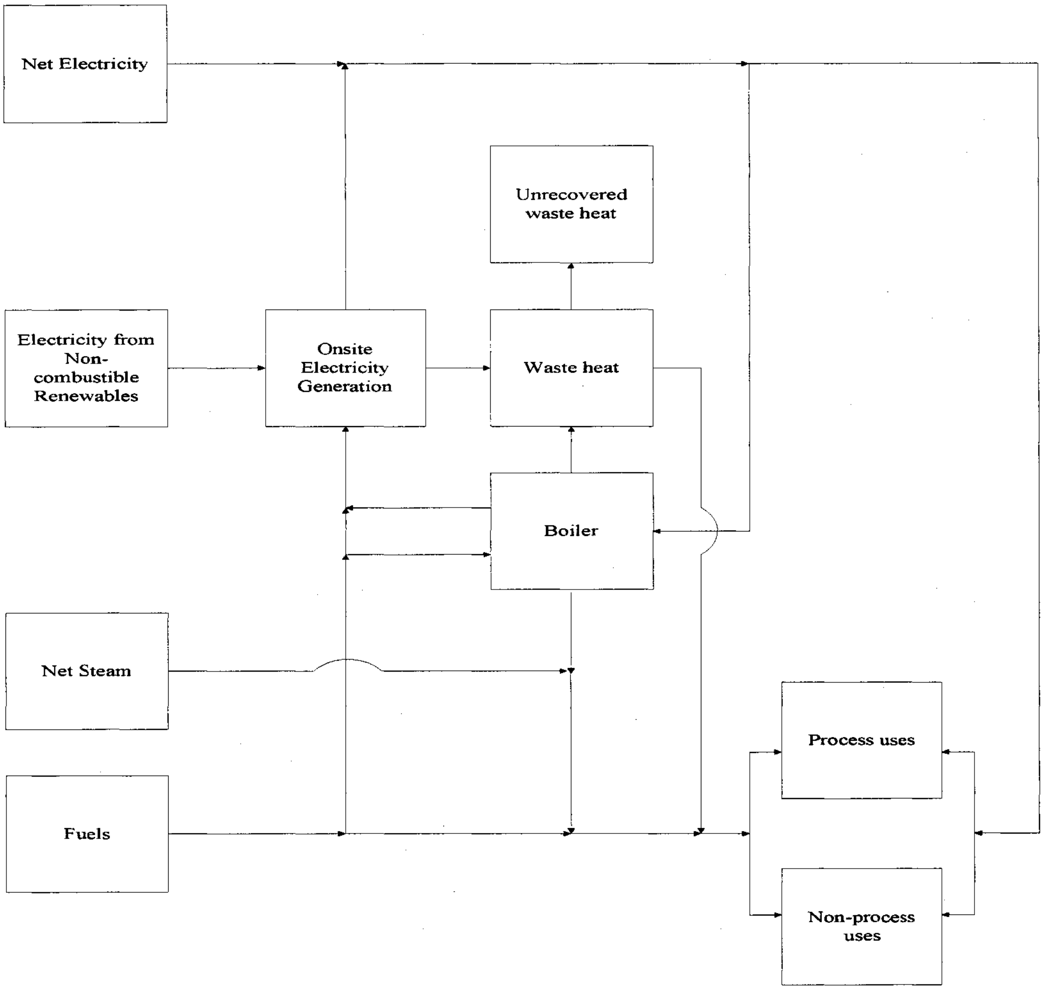

Figure 5. Generic relationship between energy and end-uses

In Figure 5, energy sources are located in the left side in the form of electricity, steam and fuels. The middle section of the figure contains onsite steam and power generation. The end-uses are located on the right side of Figure 5 as process uses and non-process usage.

The fuel input values on the left lower corner of the model are obtained from the MECS data. These fuel values combined with EIA-860B data are used in calculating the electricity conversion, and waste heat recovery of the internal combustion engines, gas turbines, steam turbines and combined cycles used in this industry. These conversion efficiencies are used to calculate the total amount of steam and waste heat that goes to end-uses. Therefore, the onsite electricity and steam generation part of the energy end-use model is a key to explain energy consumed by end-uses. Furthermore, since "part of the reason for general lack of industrial applications is the nature of the way industry uses heat", onsite steam and power generation model is very important to reveal the steam and heat utilization in this industry (Rafferty, 2003).

Electricity, fuel, steam and waste heat input to end-uses provide the key information in calibrating energy process-step model on a national scale.

1.6.3. Emissions flow model

Since energy and material consumption yield emissions, it is essential to construct an emissions flow model to have a complete understanding of a manufacturing industry. A national representation of emissions flows can help to identify targets for a national R&D effort such as those funded by the Environmental Protection Agency (EPA). Furthermore, "understanding of the environmental problems relating to energy presents a high-priority need and urgent challenge, both to allow the problems to be addressed and to ensure that the solutions are beneficial to the economy and the energy policy making activities" (Dincer, 2002).

My generic depiction of emissions flow showing the relationship between energy consumption for on-site power generation, manufacturing processes and associated emissions due to these activities is given in Figure 6.

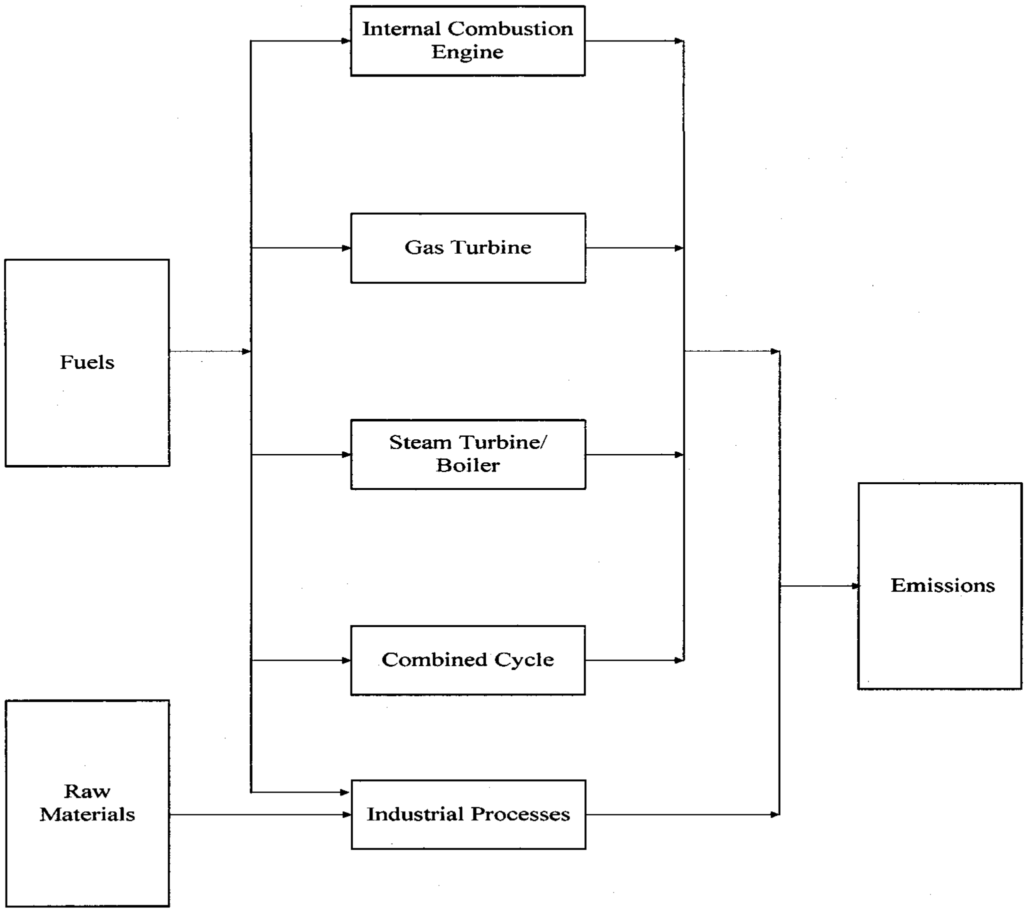

Figure 6. Generic relationship between manufacturing energy usage, industrial processes and emissions

Figure 6 combines emissions from boilers, prime movers, and industrial processes. Therefore, it provides information about the emissions in the manufacturing industry from the intermediate onsite conversions as well as the manufacturing processes. This flow model is constructed based upon national scale energy and material flow models.

2. ENERGY END-USE MODELS

The main objective of this chapter is to develop models of the energy inputs and allocation of energy among specific end-uses in the Chemical Industry and the Industrial Gas Manufacturing sector, such as HVAC, machine drive, lighting etc. The energy types included in the models are: fuel, steam, waste heat and electricity. Hydrocarbons used as feedstock, e.g. natural gas to produce ethylene, methanol etc., are not included in the scope of this analysis.

"The concept of energy end-use analysis emerged in the 1970s in response to some of the failures of supply-side energy planning." (Feder, 2004). A representative energy end-use model of an industry can identify opportunities to improve energy efficiencies. It can also serve as a basis for other studies such as an energy process-step model (Andersen and Hyman, 2001; Hyman and Reed, 1995; Worrell et al., 2000; JVP, 2004; Patel, 2003), energy cost analysis and exergy analysis for manufacturing industries and other sectors (Ayres et al., 2003; Utlu and Hepbasli, 2004; Ertesvag and Mielnik, 2000; Rosen and Dincer, 2003). The approach to building energy end-use models is applicable to other industries (Ozalp and Hyman, 2005a; 2005b; 2005c; 2005d).

The energy end-use model developed in this chapter will serve as the base to calibrate national scale energy process-step models in Chapter 5 for the products of Industrial Gas Manufacturing sector.

2.1. Energy end-use models from literature

There have been a number of prior efforts to model energy end-use in manufacturing industries (Giraldo and Hyman, 1995; Andersen and Hyman, 2001; ADL, 2000; EERE, 2004, Iniyan and Sumathy, 2000). Comparison of my model with these references are given below.

The previous work that is most closely related to this dissertation was that of Giraldo and Hyman (1995) and Andersen and Hyman (2001), who used 1991 and 1994 data to construct end-use models for the paper and steel industries. These studies assume that all cogeneration was via steam topping cycle, which excludes the utilization of internal combustion engines, gas turbines, steam turbines and combined cycles. That approach ignores the details of onsite power and steam generation and hence provides an incomplete picture of the intermediate onsite energy conversions. In Giraldo and Hyman's model, there is a recirculation of recovered waste heat from the process heating end-use, which results in double counting. This problem is eliminated in Andersen and Hyman's (2001) model. These two studies use separate boiler efficiencies for each fuel rather than using a standard industrial boiler efficiency based on literature. Finally, steam distribution losses are not taken into account in Giraldo and Hyman (1995) and Andersen and Hyman (2001).

Another energy end-use modeling effort similar to my end-use model was done by Arthur D. Little Inc. (ADL) through a subcontract with the Oak Ridge National Laboratory (ORNL) for the U.S. Department of Energy, Office of Industrial Technology (ADL, 2000).

Energy end-use models provided in ADL's report were created for the U.S. Chemical Industry and other U.S. industries using 1994 MECS data combined with some assumptions (ADL, 2000). Although ADL energy end-use models are given for eight

U.S. manufacturing industries, they are not given for any of the subsectors of these industries. The ADL energy end-use model for the U.S. Chemical Industry is given in Figure 7.

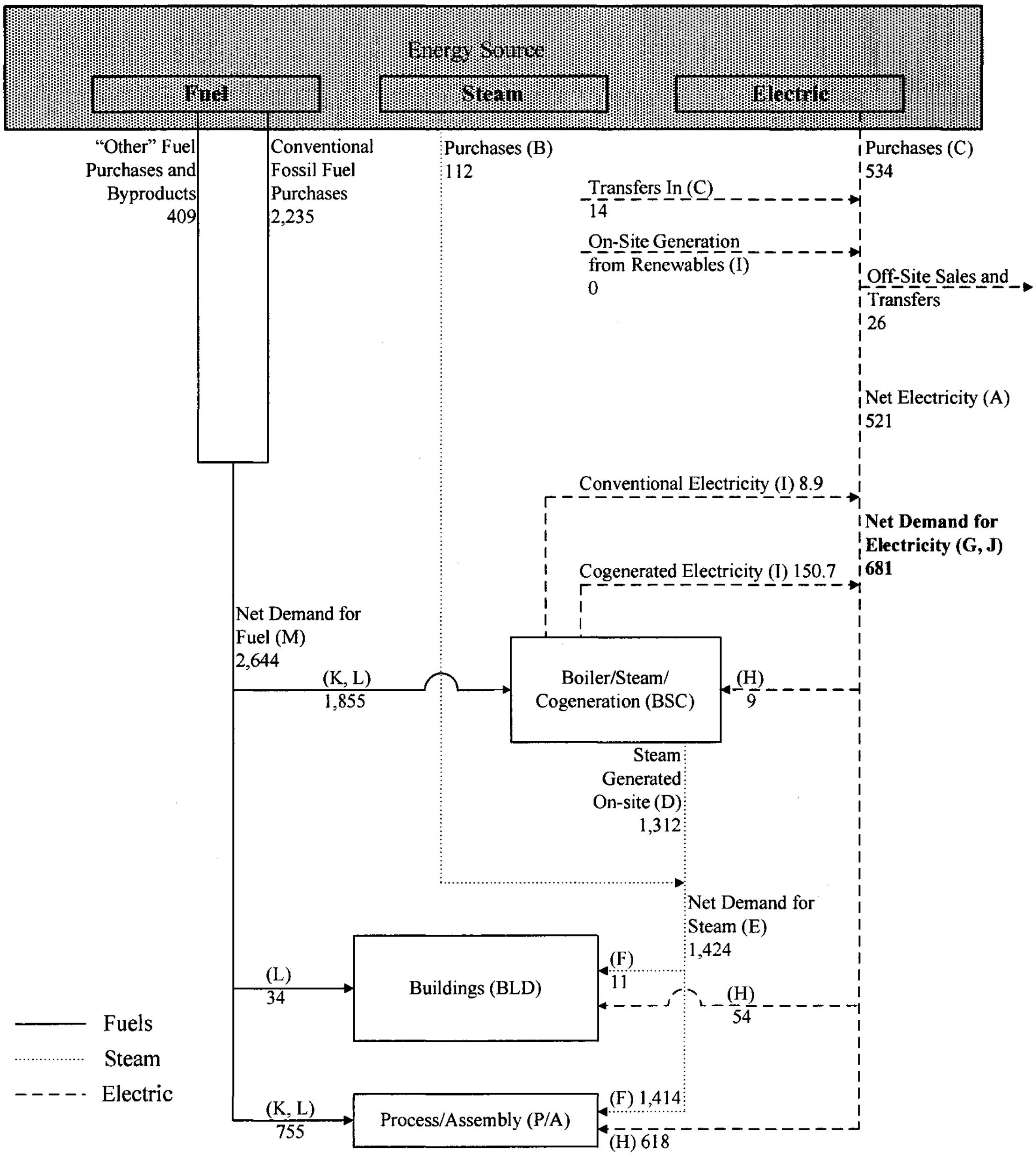

Figure 7. ADL Energy End-use Model for the U.S. Chemical Industry for 1994, TBtu

The ADL energy end-use model categorizes energy sources into three components: fuel, steam and electricity. However, it does not show the type and quantity of the fuels individually. The end-uses included in the ADL energy end-use model are grouped as: boiler/steam/cogeneration (BSC), buildings (BLD), and process/assembly (P/A). The end-uses grouped as BSC covers the onsite steam and electricity generated by boiler and cogeneration. The BLD includes:

- Facility heating, ventilation, and air conditioning,
- Facility lighting,
- Facility support,
- Onsite transportation,
- Other non-process uses.

The ADL definition of BLD corresponds to MECS "non-process end-uses". On the other hand, the P/A end-uses includes:

- Process heating,
- Process cooling and refrigeration,
- Machine drive,
- Electro-chemical processes,
- Other process use.

The ADL classification of P/A corresponds to "process end-uses" in the MECS end-use definition. The detailed components of these end-uses shown as BSC, BLD and P/A are given in a separate table in the ADL report. Therefore, the energy input to, for example, process heating is not shown on the ADL energy end-use model, but is included in the P/A. In order to see the energy inputs to each end-uses, one must refer to the separate table given as an attachment to the model.

The ADL end-use model includes the onsite steam and electricity generation, however, it does not account for waste heat created and recovered. The components of steam and electricity in the ADL model are:

- Purchases,
- Transfers,
- On-site production.

The ADL develops the energy estimates using MECS as follows:

- "Step 1: Refine MECS estimates for electricity and direct fuel",
- "Step 2: Calculate the net steam demand, i.e. purchases and on-site generation",
- "Step 3: Estimate steam use on the BLD and P/A components",
- "Step 4: Allocate unreported energy use to the BSC, BLD and P/A components".

The boiler efficiency assumption in the ADL energy end-use model is 80%. Although this assumption is made by conducting an extensive investigation on industrial boiler efficiencies, the sensitivity analysis of this assumption on their results was not made. The details of the industrial boiler efficiency analysis can be found in their report.

Although the ADL energy end-use model provides a comprehensive energy consumption analysis, energy losses are not included in their model. Finally, the uncertainty of their model is not given either.

The other study analogous to my energy end-use model are “energy footprints” by U.S. Department of Energy, Energy Efficiency and Renewable Energy (EERE), Industrial Technologies Program. These models were created by DOE for several manufacturing industries without giving any end-use models for the subsectors of industries (EERE, 2004). Energy footprints are given in the form of flow diagrams showing energy supply, demand and losses for manufacturing industries based on data and information from ADL, MECS, Pacific Northwest National Laboratory, Department of Commerce, personal communications with experts on motor-driven systems at Pacific Northwest National Laboratory, and Oak Ridge National Laboratory.

Energy footprints are given for each industry as three graphical components, starting from an overall model to more specific models. DOE’s “energy footprint” diagram for the U.S. Chemical Industry is shown in Figure 8 and is the third and the most specific model that they give.

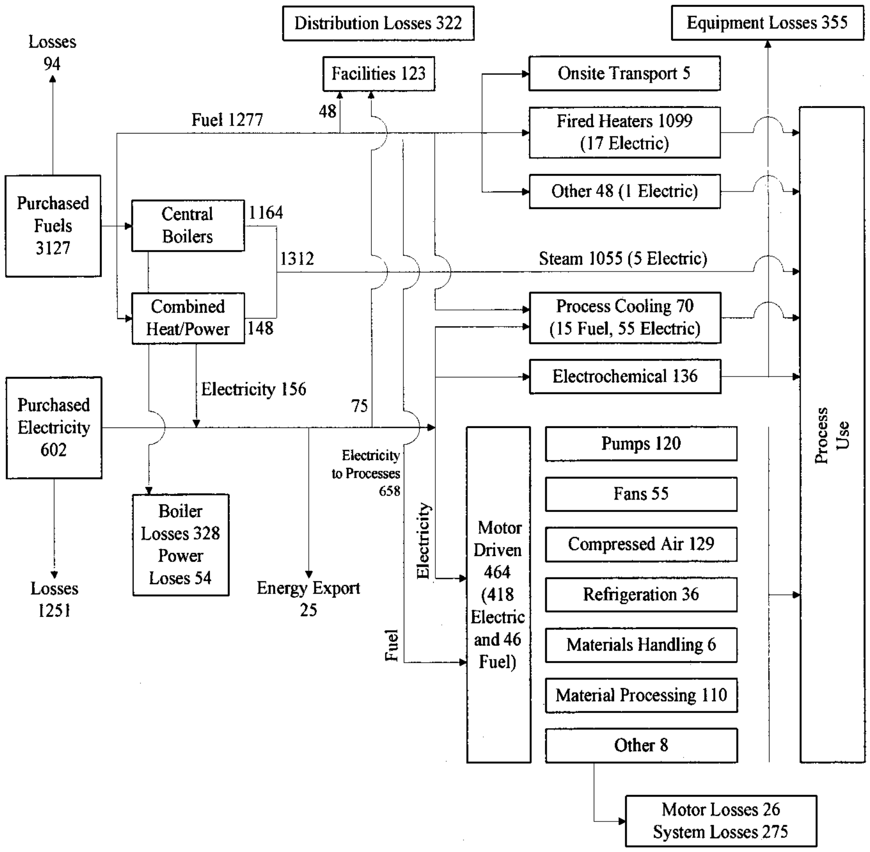

Figure 8. DOE's overall Energy Footprint for the U.S Chemical Industry for 1998, TBtu

The third and the most specific energy footprint demonstrates total energy input to generate heat and power. The model categorizes energy input into three components: fossil and biomass fuels, energy supply and utility/power plant. Although fuel input is given as a summation, the quantity of fuel types or individual fuel inputs for steam and power generation is not given.

The energy supply given in the energy footprint does not show the amount of purchased steam separately. Energy footprint provides a very detailed analysis of energy allocation among machine drive components, such as: pumps, fans, refrigeration etc. but provide no basis for these allocations. The energy footprint provides a comprehensive energy loss analysis. It estimates the motor losses and system losses associated with machine drive. In addition, it estimates the losses associated with electricity generation and transmission. Finally, it provides estimations for distribution and equipment losses, however, no documentation is provided for the basis of these loss estimates.

Although energy footprints provide a very comprehensive energy consumption and energy loss assessment, they neither include the sensitivity analysis of their assumptions on their results, nor the uncertainty of their model.

Iniyan and Sumathy (2000) is not as closely related to my model as Giraldo and Hyman (1995), Andersen and Hyman (2001), ADL (2000), and DOE's energy footprints, but it allocates energy input to end-uses to minimize cost/efficiency ratio and other factors. Iniyan and Sumathy (2000) is not limited to manufacturing sector, but allocates renewable energy sources between pumping, cooking, transportation, lighting, cooling and heating. Finally, they provide a sensitivity analysis of their model along with examination of uncertainties involved. The details of their sensitivity analysis methodology can be found at Iniyan et al. (2000).

2.2. Data sources

The primary data source used to construct energy end-use models is the Manufacturing Energy Consumption Survey (MECS) issued by the Energy Information Administration (EIA) of the U.S. Department of Energy (MECS, 1998), whereas the secondary data that was used is EIA 860B: "Annual Electric Generator Report for Non-utility."(EIA-860B, 1998).

MECS data is collected every four years. This study covers MECS database for 1998 since the data for 2002 was not released during the time frame that this study was done. The complete 2002 MECS data released in June 2005, but I use 1998 MECS data throughout.

2.2.1. Manufacturing Consumption Survey (MECS)

The main reason for choosing this database as a primary data source is because it provides data for each industry very comprehensively and the industry classification codes used in this database are being used by other federal databases on materials and emissions as well. This provides a consistency in creating energy, material and emission models for the industry of interest on a national scale. An additional constructive aspect of using this database is: “this data is derived from a single source, the double counting issue is minimized and the boundary line between industries is clear.” (ADL, 2000).

Other databases, such as those maintained by trade associations or other private databases may not put facilities that are classified as Industrial Gas Manufacturing by MECS under the same category. As a result, MECS energy inputs and/or outputs for one particular industry may differ compared to other databases because of the differences in classification of plants and industries. Besides, “inconsistent boundaries for the industry analysis and inconsistent conversion factors for the Btu equivalent of electric energy (3,412 in some studies vs. 7,000 to 11,000 in others to reflect “heat rates” for power generation in other studies) led to a confusing array of data which often displayed wide discrepancies." (ADL, 2000).

MECS includes data on fuel inputs for heat, power and electricity generation and allocation of inputs to generic end-uses. It also contains data on electricity and steam purchases/sales, and onsite electricity generation from noncombustible renewable energy sources (MECS-N13.2, 1998). This inclusive database allows one to build a model that illustrates the characteristics of an industry comprehensively.

In terms of onsite power and steam generation, MECS contains data for total on-site power generation, total CHP power, fuel input to ICE and gas turbine prime movers, and fuel and electric input to boilers.

Finally, since "no consistent data sources were found across all industrial NAICS that covered energy use by process step", the MECS remains as the only consistent and comprehensive database that provides energy consumption data for end-uses, which is the main focus of this dissertation (ADL, 2000).

2.2.1.1. Quality of the MECS survey

MECS collects completed surveys forms from a nationally representative sample of manufacturing establishments. "Returned questionnaires are examined for completeness and consistency. Inconsistent ones are reviewed by industry specialists to retrieve missing data and verify questionable items by contacting the individuals who completed the questionnaire. Collected data is edited by computer to check consistency among the data items for different parts of the MECS, and the Annual Survey of Manufacturers (another federal survey). Collected data is also checked for outliers in the distribution of individual variables. The failed records in the collected data are sent for review and then followed up by the industry specialists." (MECS, 1997). Hence, the MECS survey results go thorough rigorous quality verifications before they are published.

The methodologies used in EIA surveys "are consistent with generally accepted professional standards for all aspects of surveys, including frame development; statistical design; questionnaire design and testing; data collection; and control of sampling and non-sampling errors through non-response analysis, imputation of missing data, and development of weights, adjustments, and variance estimates, as appropriate" (EIA, 2002). Furthermore, the quality of MECS survey methodology has been acknowledged by the Office of Management and Budget under the Paperwork Reduction Act of 1995.

The estimation process of the MECS starts with establishing a population representation. It is done by weighting the data from the establishment records by "multiplying the reported values by a case-specific constant designed to inflate the data from each sample case to that portion of the population that it represents" (MECS, 1997).

There are two components in the MECS weights, namely, sampling weight and adjustment for non-response. "The sampling weight for a MECS sample case is the reciprocal of its overall probability of selection into the MECS", whereas adjustment to non-response is handled by accounting adjustment factors. "Adjustment factors were calculated by using the known energy measures of size of the respondents and the total sample" (MECS, 1997).

Measured standard errors of the survey are provided by the MECS, which can be utilized to assess the reliability of estimates and to define the confidence interval for the estimates. Relative standard errors (RSE) enable data users to assess the reliability and limitations of the estimates produced by the sample (EIA, 2003). Table 6 provides the EIA interpretation of reliability of their estimates based on the relative standard errors.

Table 6. Interpretation of reliability of estimates based on RSE (EIA, 2003)

Estimate with an RSE of:	**Conclusion**
<10%	Estimate is generally reliable
Between 10% and 30%	Estimate may be reliable
Between 30% and 50%	Estimate should be used with caution
>50%	Estimate should be considered too unreliable

EIA withholds data with greater than 50% relative standard error to maintain the quality of the database. The withheld data are denoted by letter "Q". Further information on the availability and quality of the data can be found in Freeman et al. (1997).

2.2.1.2. Data gaps in the MECS

Although MECS database provides very comprehensive and detailed good quality data, it has several gaps that need to be addressed. Besides, it should also be recognized that "since MECS contains much of the data required to conduct the energy flow assessment, it may appear to be a simple task to compile the data, nonetheless, it is important to note that there are several issues and discrepancies with the MECS data." (ADL, 2000). Therefore, to fully understand the efforts required to construct industrial energy flow by using MECS database, the gaps involved in this database must be exposed.

The major gaps in the MECS data can be listed as follows:

- Steam use by component and application is not reported,
- Steam allocation to end-uses is not reported,
- Waste heat recovery is not reported,
- Recovered waste heat allocation to end-uses is not reported,
- On-site electricity generation by component is not reported,
- Allocation of the "other fuels" among components or applications or end-uses is not reported,
- Some data is withheld to protect company name or proprietary information.

2.2.1.3. Dealing with the data gaps in the MECS

Due to the lack of some information in the MECS data, a refinement needed to be applied, such as; search for an additional federal data source which uses same industrial classification codes, and/or do separate calculations and estimates. The measures taken in this dissertation in order to overcome the gaps in the MECS data are:

- Unreported "steam use by component and application" was resolved by using additional federal data, called EIA 860B,
- Unreported "steam allocation to end-uses" was determined by assuming the ratio of steam allocation among the end-uses is the same ratio as the total fuel allocation among the end-uses,
- Unreported "recovered waste heat" was determined from additional federal data, called EIA 860B,

- Unreported "recovered waste heat allocation to end-uses" was determined by assuming the ratio of recovered waste heat allocation among the end-uses is the same ratio as the total fuel allocation among the end-uses,
- Unreported "on-site electricity generation by component" was determined by the discovery of the additional federal data, called EIA 860B,
- Unreported allocation of "other fuels" among onsite power and steam generation and end-uses was determined by referring to EIA 860B data for total fuel input to onsite steam and power generation. Not reported allocation of "other fuels" among the generic end-uses was done by using the same method as the steam and recovered waste heat allocation,
- Withheld data were calculated by extrapolating the MECS data published for earlier years and checking the row and column totals.

2.2.2. Energy Information Administration 860B data

The secondary database that was used in this project is another Energy Information Administration database called EIA 860B: Annual Electric Generator Report – Non-utility (EIA, 1998). This database provides the actual performance of non-utility power plants. Therefore, it does not contain statistical analysis, such as estimation of error due to sampling etc. as the MECS does.

The EIA-860B data files were published annually from 1998 through 2000. They include detailed information about all non-utility plants whose capacities are at least 1MW. Among the provided information in this database, of particular interest to this project are NAICS code, prime mover (including whether or not the prime mover is part of a combined cycle), fuel consumed, gross generation, and net useful thermal energy for each combined heat and power (CHP) mode (EIA, 1998).

As an Energy Information Administration database, EIA 860B database also provides the quality associated with all other EIA databases by the acknowledgement of the Office of Management and Budget under the Paperwork Reduction Act of 1995.

2.2.2.1. Data gaps and challenges using EIA 860B database

Although EIA 860B database provides very comprehensive and detailed good quality data that also fills some of the gaps in the MECS database, it still has several gaps and challenges in utilizing it that must be addressed.

There are many issues making the utilization of EIA 860B database highly challenging. First of all, EIA 860B database contains actual performance data of each prime mover. Therefore, there are multiple entries for each facility that has multiple prime movers. These entries cannot simply be added, because some of the prime movers are cogenerated, and there is separate data giving the amount of recovered waste heat from those prime movers. Furthermore, although some facilities have only one type of prime mover, e.g. steam turbine, they have multiple steam turbines which are named or given an ID number separately. Some of these prime movers may or may not recover waste heat. In a spreadsheet, these must be clearly shown to avoid double counting or not even counting at all. Therefore, sorting cannot simply be made based upon “only the type of prime mover” or any other single parameter.

Even more complicated, some facilities have more than one type of prime mover, e.g. both steam turbine and gas turbine, or steam turbine, gas turbine and internal combustion engine. The entries for these prime movers have to be examined separately, based on the same argument for one prime mover facilities. For example, some of these multiple prime movers are cogenerated, whereas some of them are not. Furthermore, some of the prime movers are part of a combined cycle, whereas some of them are not. The prime movers that are a part of a combined cycle cannot be analyzed separately: the energy input/output and recovered waste heat –if it exists- must be analyzed together as a combined cycle. EIA 860B database states all of this information clearly, e.g. if a prime mover is part of a combined cycle, or if there is cogeneration.

Therefore, in order to examine the actual energy inputs, electricity outputs, and recovered waste heat associated with each prime mover, all entries for each facility must be sorted such that:

- Energy input to each prime mover must be clearly stated,
- Electricity output from each prime mover must be stated clearly,
- Prime movers that recover the waste heat must be stated clearly,
- Prime movers which are part of a combined cycle must be stated clearly.

Although some of this sorting and summation can be done via either Microsoft Excel or Microsoft Access, the majority of the sorting still needs to be done manually because it requires judgment. Considering the thousands of facility entries of, e.g. Chemical Industry, this kind of sorting requires high concentration. In order to utilize EIA 860B correctly, this sorting is unavoidable. Without very carefully examining the available information in this database and without developing a very carefully designed methodology, EIA 860B database cannot yield meaningful information. This might be the fundamental reason for not seeing any actual performance analysis on energy conversion efficiencies of the manufacturing sector.

Although sorting and organizing the EIA 860B data provides a very clear picture of the actual energy inputs and outputs in a manufacturing industry, it is still not ready to be used for the calculation of conversion efficiencies. The reason is that EIA 860B energy input to steam turbines is given as an input to the boiler. Thus, to calculate the energy conversion efficiencies, an assumption on boiler efficiency has to be made.

The details of how to extract and sort EIA 860B data is discussed by Ozalp and Hyman (2005e).

2.2.2.2. Dealing with the gaps in EIA 860B

The only one gap in the EIA 860B database based on the needs of this project was the energy input into the steam turbines. The information provided in 860B is the energy input into the "boiler". Therefore, in order to determine the energy input to steam turbines, a boiler efficiency assumption had to be made.

Since it is difficult to develop an accurate boiler efficiency value that applies to all situations, some assumptions were made by including the parameters that primarily influence the boiler efficiency:

- It was assumed that boiler efficiency does not depend on whether or not the prime mover is part of a combined cycle,
- It was assumed that boiler efficiency does not depend on whether or not waste heat is recovered,

- Differences between the fuel-fired boiler efficiencies due to the type of fuel burned, boiler vintage, maintenance, boiler configuration (e.g. shop-assembled or field-erected; fire tube or water tube; existence of heat recovery equipment or economizers; pressure of steam raised, condensate return lines, set-point or feedback control loops), operating schedules and the age of the boiler are neglected,
- All fuel-fired boiler efficiencies in this industry are the same and equal to 80%.

Regarding the effects of boiler differences on the boiler performance, Tsirulnikov et al. states that although differences between the boilers may have impact on the boiler performance, “historically, however, there has been no net effect on boiler performance that would be considered extreme.” (Tsirulnikov et al., 2003).

The 80% boiler efficiency assumption was made based upon the industrial boiler efficiency values reported in literature (ADL, 2000; EERE, 2004; Marrero, 2002; Showers, 2002; EPA-CHP, 2005). Within these studies, the most comprehensive investigation on industrial boiler efficiencies were made by Showers (2002) and ADL (2000).

ADL estimated the average industrial boiler efficiency by making a very comprehensive private industrial databases search. The list of these private industrial databases can be found in ADL (2000). Based on their search on these sources, ADL concludes that “a vast number of boiler studies have been reported, however, the majority of such documents reported on boiler use in a single plant or provided an illustrative example. Unfortunately, current information on average boiler efficiencies is sparse and no comprehensive database exists from which to calculate boiler efficiencies."

The sources reporting industrial boiler efficiency state that parameters such as the size of the boiler and the hours that it operates may have an impact on the boiler efficiency. The reason for that is because the large boilers tend to be more efficient than the small boilers which operate one or two shifts a day.

The other parameter on the boiler efficiency is the "boiler configuration." It is stated in ADL report that "boiler manufacturers are able to provide efficiencies for shop-assembled boilers, but many of the industrial boilers are field-erected, which are often designed by an architectural and engineering firm to meet the specific needs of the client that will dictate how much waste heat recovery can be economically justified. These specifications may include items as steam pressure, fuel type, quality, sulfur content, acid dew point, annual operating hours, and value of energy."

EPA catalog of combined heat and power technologies states that in their analysis: "fuel used to produce useful heat is calculated assuming typical boiler efficiency, usually 80%" (EPA-CHP, 2005). However, they do not provide any reference source or information as a basis for making this assumption.

Showers (2002) includes information which was collected over several years by testing boiler operating efficiency at about thirty different industrial plants which have multiple operating boilers. Showers addressed the five common myths about industrial boiler system operations. The results of this article can be summarized as:

- Boilers do not necessarily operate most efficiently at full load,

- Effect of radiation losses on efficiency varies with boiler load, and in some cases, it is not so minor that it can be ignored,
- Although "for a multiple-burner boiler, adding one burner at a time is the preferred method," it is not necessarily the most efficient method to operate the boiler,
- Similar air and temperature conditions, regardless of fuel, do not necessarily result in with similar efficiency,
- "It is totally untrue that the boiler selection does not affect the plant's overall efficiency."

These arguments show how difficult it is to make an average boiler efficiency assumption due to the effects of variations in parameters on the boiler efficiency. However, a sensitivity analysis of boiler efficiency can help to reveal the effects of an assumption on the results. For example, in my study, the sensitivity analysis on the results showed that a 30% change in the boiler efficiency creates only a 4% change in the prime mover efficiency. Therefore, the boiler efficiency assumption made in this dissertation does not have a major effect on the prime mover efficiency.

2.2.3. Differences between the MECS and EIA 860B databases

Fundamental differences between MECS and EIA-860B databases are:

- MECS only publishes aggregate data for industries, not for individual facilities as 860B does,

- MECS applies sophisticated statistical analysis tools to raw survey data and applies several quality and proprietary nondisclosure criteria before publishing the results, whereas 860B consists of the raw data submitted by each facility,
- EIA 860B database must be sorted and organized to obtain its own aggregate values before it is used, while MECS database does not need any sorting,
- MECS database is available for the years 1991, 1994, 1998 and 2002, whereas EIA 860B is available only from 1998 through 2000.

The differences between the MECS and EIA 860B databases in terms of their usage in energy end-use models are:

- MECS is used to identify energy inputs to manufacturing processes and to allocate them among end-uses, whereas EIA 860B is used to identify energy inputs to prime movers to calculate energy conversion efficiencies,
- MECS is used to classify electricity purchase, electricity sales, electricity from renewable energy sources and electricity from onsite power generation, whereas EIA 860B is used to model onsite electricity generation at prime mover level,
- MECS is used to demonstrate net (purchased-sold) steam, whereas EIA 860B is used to model onsite steam generation for onsite power generation,
- MECS is used to construct main structure of the energy end-use model, whereas EIA 860B is used to construct "onsite steam and power generation" part of the energy end-use model.

Table 7 compares the total onsite power generation values given in the MECS and 860B data for the U.S. Chemical Industry in 1998.

Table 7. Comparison of MECS and 860B 1998 data for the U.S. Chemical Industry, PJ

Database	Onsite power generation
MECS	165
860B	170
MECS/860B ratio	0.96

Since the differences between the two data sets are very small, these two data sources can be treated as interchangeably in the remainder of this dissertation.

2.2.4. Other data sources

The other data sources on energy are given in Table 8 with their description, comparison with the MECS database and their applicability to this study.

Table 8. Other data sources and their applicability

Data source	Applicability
The DOE Industrial Assessment Database	**Description:** "The Industrial Assessment Center (IAC) database contains assessments of small and medium size industrial facilities. Faculty and students from accredited engineering schools and universities perform the assessments. The IAC database includes annual production and energy use for each facility that has been assessed since 1981. For some facilities, the annual production of solid, liquid and gaseous wastes has also been reported. The database currently contains information collected from virtually every state within the continental U.S. representing over 9,700 industrial site visits. Data from the Industrial Assessments performed under the DOE's IAC program are contained in two separate databases. The first file contains assessment specific data whereas the second file contains recommendation specific information." (DOE Ind. Assess. Database website). **Conclusion:** This database is limited to small and medium size industrial facilities, whereas the size of the MECS database includes "15,500 establishments drawn from a sample frame representing 97-98% of the manufacturing payroll" (MECS website). This database provides electricity demand, fuel oil, natural gas, coal, wood, and paper input as energy, whereas the MECS provides the information given in this database but also more type of fuel inputs, cogeneration, renewable energy, steam purchased, electricity sold, electricity purchased etc. Furthermore, the MECS database divides the energy inputs as "feedstock" and "non-feedstock", whereas this database does not. In addition, this database does not provide end-use information. Finally, the MECS database is organized such that you can access to each industry and subsector directly, whereas in this database you need to download their Microsoft Access files and then need to sort by industries, and then sort by subsectors. Therefore, this database is not as comprehensive as the MECS

Table 8. (Continued)

Chem-Intell Chemical Man. Plants	**Description:** Chemical Intelligence Services (Chem-Intell), a division of Reed Telepublishing Ltd. "Chem-Intell provides comprehensive information on over 36,000 existing or planned manufacturing plants, as well as trade and production figures for organic and inorganic chemicals such as petrochemicals, agrochemicals, plastics and rubbers, synthetic fibers, pulp and paper, mineral processing and oil refining. It includes information on manufacturer capacities, processes, feedstocks, quantities and value of import/export chemicals, as well as press releases, company reports, market and industrial surveys. The data is updated monthly. Trade information is available from 1973 and production information is available from 1981. The source of the data is chemical manufacturers and government agencies. It provides records from 18,000 companies in 160 countries." (EPA website for Global LCI Directory-Other Sources of LCI data). **Conclusion:** This database is posted in EPA's Global LCI directory as other sources of LCI data. It provides data on individual plants. The database shows the products manufactured in a particular plant, the feedstock and the process used to produce that particular product. Since it provides the process name, this database provides very useful information on actual commercially dominant processes. However, considering that there are records from 18,000 companies, even if each company produce only one product, it means that 18,000 entries must be separately examined to find what percent of each technology is used for the production of each product. Since the data sheets are not given in the form of Microsoft Excel or Access, they can not be sorted based on process. Therefore, for each industrial gases, or whichever chemicals are of the interest, a manual access to each sheet and an a manual record of processes for each chemical must be done. This could be done by a survey company or government to find the actual share of the commercial technologies in the market. Furthermore, this database neither contains any information on the type of fuel, steam or electricity consumption for the production of a product, nor on onsite steam or electricity generation of the plants. Finally, it does not classify the plants using the NAICS codes. Therefore, this database does not provide the comprehensive energy consumption data that MECS gives and it does not provide all information that fits the scope of this dissertation.
Annual Energy Review Database	**Description:** The source of this database is U.S. DOE, EIA. The purpose of this data collection is "annual summary of the U.S. energy statistics." "The Annual Energy Review Database (AERDB) provides automated access to data in the Annual Energy Review, the EIA's comprehensive annual summary of U.S. energy statistics. The AERDB is updated annually to reflect the most recent publication. Production, consumption, import, export, stock, and price data are shown for the primary energy sources: coal, electricity, natural gas, nuclear, and petroleum. The petroleum data are further disaggregated to show supply and disposition of crude oil, motor gasoline, distillate fuel oil, residual fuel oil, jet fuel, liquefied petroleum gases, and other petroleum products. Data are also presented by energy source for the principal consuming sectors: residential, commercial, industrial, transportation, and electric utility. Data on domestic oil and gas resource development activities are included, as well as petroleum production, consumption, stock, and nuclear generation data for selected foreign countries. Values are shown for most data series from 1949 forward." (EPA website for Global LCI Directory-Other Sources of LCI data, and EIA Annual Energy Review website). **Conclusion:** This database provides energy inputs for industrial, commercial, residential, and transportation sectors in the same level of detail as the MECS does except for the subsectors of the industrial sector. The industrial sector energy inputs given in this database are taken from the MECS but without including the subsector database. Since the focus of this dissertation is Industrial Gas Manufacturing sector, the Annual Energy Review database is not useful.

Table 8. (Continued)

EIOLCA	**Description:** Economic Input-Output Life Cycle Assessment (EIOLCA) provides estimated fuel consumptions as a summation of feedstock and non-feedstock, without separating them. The database is based upon U.S. Department of Commerce's 1997 Industry Benchmark database. It also uses "1992 commodity/commodity input/output (IO) matrix of the U.S. economy as developed by the U.S. Department of Commerce" (source: What are the data sources for the eiolca.net software?: http://www.eiolca.net/methods.html). "The benchmark accounts show how industries interact at the detailed level; specifically, they show how approximately 500 industries provide input to, and use output from, each other to produce gross domestic product. These accounts provide detailed information on the flows of the goods and services that make up the production processes of industries." (DOC Benchmark overview and uses website). Therefore this database is created by converting the benchmark input-output database, which is an economic database given in terms of value shipments in U.S. dollars, into energy consumption. **Conclusion:** This database is not applicable to the scope of this dissertation. First of all it is given for 1997. Secondly, it does not distinguish energy as feedstock and non-feedstock. Furthermore, the reliability of this database compared to MECS is very poor, because the fuel consumption values provided in EIOLCA "are calculated from commodity purchases and average 1992 prices" (EIOLCA website). So, they take the average fuel price in 1992 and by knowing how much money spent on each commodity based on Department of Commerce data, they calculate how much fuel consumption that value corresponds to. Since the price of products variation in a year usually fluctuates, the values presented in this database includes uncertainty. However, the uncertainty analysis of their database is not given, whereas MECS provides the uncertainty involved in the MECS database. This database is based on Department of Commerce data, which in turn is derived from a Census Bureau database. Census Bureau conducts MECS survey for Energy Information Administration. So, by using the Industry Benchmark database, EIOLCA is basically using secondary database, because the primary energy database is the MECS. So instead of using the secondary database, it makes more sense to use the primary database, which is MECS, to avoid more uncertainties. Therefore, this database is not useful for the scope of this dissertation.
North American Chemical Processing Database (NACP)	**Description:** This private database "Coverage in the Chemical Processing industry consists of a phone verified database of 4,478 operational plants in North America with over 25,600 unique decision making contacts with over 31,000 functional management responsibilities." (NACPD website). **Conclusion:** This database defines each industry with a unique coding system. Therefore, there may be no correspondence to their classification in MECS database classification or another database classification. They provide information on primary and secondary fuel consumption and contact information of the plant staff. This database does not provide end-use data, and it is a private database, which is not accessible to others who would like to duplicate my research or would like to apply my methodology to other sectors. Therefore, since one of the objectives of this dissertation is to create an energy end-use model and since the results of this dissertation should be able to duplicated by others, this database is not useful.

Table 8. (Continued)

Major Industrial Plant database (MIP)	**Description:** Major Industrial Plant Database (MIPD)is a private database. "The 17,000 key energy-intensive plants in MIPD represent 90% of the natural gas consumed by the industrial sector. This database features a detailed breakdown of information essential to identifying new business prospects, including: ▪ Plant name, location, address, plant manager name, phone, fax, ▪ What the plant produces, SIC code/name, number of employees, ▪ Hours of production, capacity utilization, dollar value of shipments, ▪ Electric utility, use, demand, and price, ▪ If plant cogenerates, by what percentage, ▪ Gas utility, demand, and usage, ▪ Breakdown of all fuel usage by type: boiler, furnace, feedstock, ▪ Steam demand, pressure and temperature, ▪ Number and rating of boilers, including primary and secondary fuels, ▪ Directly connect pipelines, and pipelines within 20 miles, Plant longitude and latitude. Over 86 data elements on each plant provide a complete hydrocarbon and electricity consumption profile. And MIPD is as accurate as it is useful, because it's continuously updated via telephone surveys. In addition, daily, weekly, and monthly edit checks help ensure the accuracy of every data element." (MIPD website). **Conclusion:** First of all, this database is not accessible to public, therefore a study done by using this database can not be duplicated by others unless they also have access to this database. Besides, this database is created based upon phone call survey, whereas MECS database is created based upon government enforced mandatory survey, which goes through rigorous statistical analysis and check of consistency by industry experts. Therefore, the quality of this database is not as high as the MECS database. Although this database uses the same industrial classification code as MECS does, it does not provide allocation of energy to end-uses. Since one of the objectives of this dissertation is to create an energy end-use model, this database is not useful.
Trade association databases	**Description:** Trade associations collect, analyze and disseminate data on industry activities. **Conclusion:** The data and the survey and the analytical techniques used in trade association databases may not be compatible with those used by the U.S. Census Bureau. In particular, trade associations collect data on the activities of its members, who may not necessarily classified under the same NAICS code. Even if they are, they may not be statistically valid random sample of the industry. To be more precise: The plants that are considered under the "Industrial Gas Manufacturing sector" according to the MECS may not be considered "Industrial Gas Manufacturing sector" plants according to these databases. For instance, since industrial gases are inorganic gases, some of the plants that are put under "Industrial Gas Manufacturing sector" in the MECS database might be put under the category of "Inorganic Chemicals sector" in these databases because industrial gases are inorganic gases. Finally, since trade association databases include inputs only from the members and they are accessible only by members, whereas government database is collected from nationally representative sample plants and then statistically analyzed before published which is open to public. Therefore, governmental industrial database provides not only the most comprehensive, but also the most reliable database.

The list of other data sources can be extended further as not all of the investigated data sources were included here for the purpose of being brief. However, my search on examining and comparing the quality of the MECS database with other databases in terms of consistency, comprehension and statistically rigorous analysis techniques concluded that MECS is the best existing national energy end-use database for manufacturing industries.

2.3. Methodology

Constructing an energy end-use model includes creating two tables: energy utilization and end-use. The energy utilization table gives the type of fuels used, whereas the end-use table provides allocation of these fuels to end-uses. The primary federal data to construct these tables is the MECS.

2.3.1. Energy utilization table

Data to construct energy utilization table is obtained from the following five different MECS tables:

MECS Table N5.1: Selected Byproducts in Fuel Consumption

MECS Table N3.2: Fuel Consumption

MECS Table N11.3: Quantity of Purchased Electricity, Natural Gas, and Steam

MECS Table N13.1: Electricity: Components of Net Demand

MECS Table N13.2: Electricity Components of Onsite Generation

Some of the data in these tables are withheld by MECS to avoid disclosing data for individual establishments, and they are denoted by W. Also, the numerical values less than 0.5 PJ are indicated by *. Contribution of these values are included in higher level totals. In addition, some of the values in these MECS tables are denoted by Q. This represents the data withheld because the relative standard error is greater than 50%.

2.3.1.1. Energy utilization table of the U.S. Chemical Industry

See Table 9 for the energy utilization table of the U.S. Chemical Industry, constructed using the MECS tables listed earlier. The values presented in Table 9 include the sampling uncertainties of the MECS data and the numbers centered in the table are column totals within each MECS table.

As it is seen in Table 9, the values that have the highest uncertainty are "electricity purchase" with a 9% uncertainty. On the other hand, the "transfer in" values has 5% uncertainty. The rest of the values in Table 9 have uncertainties between 1% and 4%. The meaning of these uncertainty numbers and how they were got from the MECS data is given in the following section.

Table 9. Inputs for heat, power and electricity generation in NAICS 325 in 1998, PJ

MECS Source	Energy Form	Chemical Industry NAICS 325
Table N3.2.	**Total**	**3908 ± 82**
	Net Electricity	609 ± 13
	Residual Fuel Oil	53 ± 1.7
	Distillate Fuel Oil	9 ± 0.4
	Natural Gas	2093 ± 57
	LPG and NGL	54 ± 2
	Coal	300 ± 7
	Coke and Breeze	2 ± 0.1
	Other	789 ± 28
Table N5.1.	**Total Byproducts**	**464 ± 7**
	Blast Furnace/Coke Oven Gases	0
	Waste Gas	439 ± 3
	Petroleum Coke	4 ± 0.04
	Pulping Liquor or Black Liquor	0
	Wood Chips, Bark	Q
	Waste Oils, Tars and Waste Materials	11 ± 0.2
Table N13.1.	**Net Demand for Electricity**	**774 ± 30**
	Purchases	614 ± 57
	Transfers In	21 ± 1
	Total Onsite Generation	165 ± 6
	Sales and/or Transfers Offsite	26 ± 1
Table N13.2.	**Total Onsite Generation**	**165 ± 3**
	Cogeneration	156 ± 2
	Renewable Energy *(excluding Wood and Other Biomass)*	*
	Other	8 ± 0.1
Table N11.3.	**Steam purchased**	204 ± 4

2.3.1.1.1. Calculation of Generalized Relative Standard Error

MECS provides Relative Standard Error (RSE) column factors and row factors for each table. An example MECS table is given in Table 10 from a MECS report on the quality of the data (MECS, 1997). It should be noted that not all of the industries/subsectors and energy types are included in this table to be brief as the purpose of this example is to show how to calculate RSE based on the methodology given in the MECS manual.

Table 10. Total first use of energy for all purposes

Industry	**Residual Fuel Oil (1000 bbl)**	**Natural Gas (billion cu ft)**	**LPG (1000 bbl)**	**Coal (1000 short tons)**	**RSE row factors**
RSE column factors:	**1.2**	**0.6**	**1.1**	**1.2**	
Total United States					
Paper Industry	27,444	558	1,334	13,812	**3.6**
Pulp Mills	3,583	21	W	W	**13.5**
Paper Mills	14,942	264	476	476	**5.5**
Paperboard Mills	7,914	194	119	119	**2.9**
Chemical Industry	17,457	2,495	435,926	13,239	**6.4**
Nitrogenous Fertilizers	0	589	4	0	**14.0**
Plastic Materials	542	234	89,084	875	**9.1**
Synthetic Rubber	W	53	6,899	190	**26.2**

MECS gives a methodology to calculate approximate standard error for the Chemical Industry as an example (MECS, 1997, pg. 437):

- RSE column factor (Natural Gas) = 0.6
- RSE row factor for the Chemical Industry = 6.4
- Approximate RSE (Chemical Industry, Natural Gas) = 6.4 x 0.6 = 3.8%
- Approximate Standard Error (Chemical Industry, Natural Gas)

  = 0.038 x 2,495 billion cubic feet = 95 billion cubic feet.

The steps to calculate the 95% confidence range (that range which includes the true value of the estimate with 95% confidence) is also given in the MECS manual (MECS, 1997):

- Multiply the standard error by 1.96,
- Subtract the results of Step 1 from the given estimate to determine the lower bound of the range,

- Add the result of Step 1 to the given estimate to determine the upper bound of the range.

The uncertainty of the MECS values were calculated based on this methodology. Therefore, the values in Table 9 and other MECS tables in this dissertation represent 95% confidence interval.

2.3.1.2. Energy utilization table of the U.S. Industrial Gas Manufacturing sector

The energy utilization table of the U.S. Industrial Gas Manufacturing sector was constructed using the MECS tables listed earlier, and it is given in Table 11. The values presented in this table include the sampling uncertainties of the MECS data with 95% confidence interval and the numbers centered in the table are column totals within each MECS table.

Table 11. Inputs for heat, power and electricity generation in NAICS 325120 in 1998, PJ

MECS Source	Energy Form	Industrial Gas Manufacturing NAICS 325120
Table N3.2.	**Total**	**193 ± 8**
	Net Electricity	117 ± 5
	Residual Fuel Oil	0
	Distillate Fuel Oil	*
	Natural Gas	66 ± 4
	LPG and NGL	*
	Coal	0
	Coke and Breeze	0
	Other	9
Table N5.1.	**Total Byproducts**	**1**
	Blast Furnace/Coke Oven Gases	0
	Waste Gas	1
	Petroleum Coke	0
	Pulping Liquor or Black Liquor	0
	Wood Chips, Bark	0
	Waste Oils, Tars and Waste Materials	0
Table N13.1.	**Net Demand for Electricity**	**119 ± 3**
	Purchases	113 ± 7
	Transfers In	Q
	Total Onsite Generation	2
	Sales and/or Transfers Offsite	0
Table N13.2.	**Total Onsite Generation**	**2**
	Cogeneration	2
	Renewable Energy *(excluding Wood and Other Biomass)*	0
	Other	Q
Table N11.3.	**Steam purchased**	**6 ± 0.2**

As it is seen in Table 11, the values that have the highest uncertainty are "electricity purchase", and "natural gas" consumption with a 6% uncertainty. On the other hand, the "total energy consumption" and the "net electricity consumption" values have about 4% uncertainty, whereas "net demand for electricity" has about 3%. The rest of the values in Table 10 have either zero or very small uncertainties.

2.3.2. End-use data table

The construction of the energy end-use table requires the utilization of these MECS tables:

MECS Table N6.2: End Uses of Fuel Consumption

MECS Table N6.4: End Uses of Fuel Consumption

Although these MECS tables have the same title, there are two differences between them. First, Table N6.2 includes "net electricity" whereas Table N6.4 gives "net demand for electricity". "Net demand for electricity" is the total amount of electricity used. "Net electricity" is the sum of the purchases, transfers in, and generation of electricity from noncombustible renewable sources, minus electricity sold and transferred out. It does not include onsite electricity generation from combustible fuels because that energy has already been included as fuel input such as coal.

Net electricity = Electricity (purchases – sales) + Electricity from noncombustible renewables (1)

Second, Table N6.2 has an additional column for "Other" which includes net steam (the sum of purchases, generation from renewables, and net transfers) and other energy that respondents of the MECS survey indicated was used to produce heat and power.

Other = Byproducts + Steam (purchases – sales) + Steam from noncombustible renewables + Fuels not listed separately (2)

where the "Byproducts" component is disaggregated in MECS table N5.1. Also, MECS Table N13.1 shows the components of the "Net demand for electricity." If we use the terms "purchases" and "sales" to include electricity transfer transactions, then we can write that

Net Demand for Electricity = Electricity (purchases – sales) + Total onsite generation (3)

The net steam is defined analogous to the "net electricity" definition in equation (1), i.e.

Net Steam = Steam (purchases – sales) + Steam from noncombustible renewables (4)

The "transfers in" are also included in purchases. Then, substitution of equation (4) into equation (2) results in

Other = Byproducts + Net Steam + Fuels not listed separately (5)

Since I account for boiler efficiency when producing steam onsite from combustible energy forms but assume that "net steam" goes directly to end-uses, the above equation can be rewritten as

Other = Other energy sources except net steam + Net steam (6)

where

Other energy sources except net steam = Byproducts + Fuels not listed separately (7)

The MECS definition of the conventional electricity generation item in these MECS tables is: electricity generation via gas turbines or piston engines, not via steam turbines.

2.3.2.1. End-use data table of the U.S. Chemical Industry

End-use data table for the U.S. Chemical Industry was constructed using the MECS tables listed earlier, and it is given in Table 12. The values presented in this table includes the uncertainty of the MECS data and the numbers centered in the table are column totals within each MECS table.

Table 12. End-use data for NAICS 325 in 1998, extracted from MECS Tables N6.2 and N6.4, PJ

	Total	Net Electricity	Residual Fuel Oil	Distillate Oil and Diesel Fuel	Natural Gas	LPG	Coal (excluding Coal Coke and Breeze)	Other	Net Demand for Electricity
TOTAL FUEL CONSUMPTION	3908 ± NA	609 ± 31	53 ± 2	9 ± 0.6	2093 ± 79	54 ± 2	300 ± NA	790 ± NA	774 ± 33
INDIRECT USES (Boiler Fuel)	--	3 ± 0.2	32 ± 1.6	4 ± 0.3	1040 ± 41	15 ± 0.7	284 ± NA	--	5 ± 0.2
DIRECT USES (Total Process Uses)	--	34 ± 23	20 ± 0.8	2 ± 0.1	915 ± 30	37 ± 1	3 ± 0.05	--	685 ± 26
Process heating	--	16 ± 0.6	20 ± 0.7	1 ± 0.1	833 ± 24	36 ± 1.2	3 ± 0.05	--	18 ± 0.6
Process cool.&refr.	--	43 ± 0.9	0	*	12 ± 0.2	*	*	--	58 ± 1.2
Machine drive	--	382 ± 23	*	1 ± 0.1	36 ± 1.7	*	*	--	460 ± 25
Electrochem. process	--	92 ± 1.4	--	--	--	--	--	--	149 ± 1.9
Other process use	--	1 ± 0.1	0	*	34 ± 2.3	1 ± 0.1	0	--	1 ± 0.1
DIRECT USES (Tot. Non-proc. Use)	--	69 ± 3.3	1 ± 0.04	3 ± 0.2	133 ± 5	2 ± 0.1	12 ± 0.2	--	80 ± 3
Facility HVAC	--	36 ± 3	*	*	34 ± 2	*	*	--	42 ± 0.4
Facility lighting	--	25 ± 0.3	--	--	--	--	--	--	30 ± 0.4
Facility support	--	6 ± 0.3	*	*	4 ± 0.2	*	0	--	8 ± 0.4
Onsite transportation	--	*	--	2 ± 0.2	*	2 ± 0.1	--	--	*
Conventional el. gen.	--	--	*	*	92 ± 1.2	*	12 ± 0.1	--	--
Other non-process use	--	*	*	*	2 ± 0.1	0	0	--	*
END-USE (N.R)	800 ± NA	3 ± 0.6	*	*	5 ± 0.7	*	*	790 ± NA	3 ± 0.5

NA: Not available, NR: Not reported.

In Table 12, the value that has the highest uncertainty is "Net electricity - not reported end-use" with about 18% uncertainty. The second and third highest uncertainties are "Natural Gas – not reported end-use" and "Net demand for electricity – not reported end-use", with uncertainties of 17% and 14%, respectively. The rest of the values in this table have uncertainties less than 9%.

2.3.2.2. End-use data table of the U.S. Industrial Gas Manufacturing sector

End-use data table for the U.S. Industrial Gas Manufacturing sector was constructed using the MECS tables listed earlier, and it is given in Table 13. The values presented in this table includes the uncertainty of the MECS data and the numbers centered in the table are column totals within each MECS table.

In Table 13, the value that has the highest uncertainty is "Total net electricity consumption" with about 13% uncertainty. The second highest uncertainty is "Net electricity" consumption for machine drive, which is about 10%. The rest of the values in Table 13 have uncertainties which are less than 10%.

Table 13. End-use data for NAICS 325120 in 1998, extracted from MECS Tables N6.2 and N6.4, PJ

	Total	Net Electricity	Residual Fuel Oil	Distillate Oil and Diesel Fuel	Natural Gas	LPG	Coal (excluding Coal Coke and Breeze)	Other	Net Demand for Electricity
TOTAL FUEL CONSUMPTION	193 ± NA	117 ± 15	0	*	66 ± 5	*	0	9 ± NA	19 ± 14
INDIRECT USES (Boiler Fuel)	-	*	0	*	27 ± 3	*	0	-	*
DIRECT USES (Total Process Uses)	-	114 ± 10	0	*	37 ± 2	*	0	-	16 ± 10
Process heating	-	1 ± 0.1	0	0	22 ± 1	*	0	-	1 ± 0.1
Process cool.&refrig.	-	3 ± 0.3	0	0	0	0	0	-	3 ± 0.3
Machine drive	-	108 ± 13	0	*	15 ± 1	*	0	-	110 ± 13
Electrochem. process	-	1 ± 0.04	-	-	-	-	-	-	1 ± 0.04
Other process use	-	*	0	0	*	0	0	-	*
DIRECT USES (Tot. Non-proc. Use)	-	3 ± 0.3	0	*	2 ± 0.1	*	0	-	4 ± 0.4
Facility HVAC	-	2 ± 0.5	0	*	*	*	0	-	2 ± 0.4
Facility lighting	-	1 ± 0.03	-	-	-	-	-	-	2 ± 0.1
Facility support	-	*	0	0	2 ± 0.03	*	0	-	*
Onsite transportation	-	0	-	*	0	*	-	-	0
Conventional el. gen.	-	-	0	*	*	0	0	-	-
Other non-process use	-	*	0	0	0	0	0	-	*
END-USE (N.R.)	9 ± NA	*	0	0	0	0	0	9 ± NA	*

NA: Not available, NR: Not reported

2.3.3. Filling in the missing values in the tables

Before constructing the energy end-use models, the missing parts in Tables 9-13 must be filled in. The key steps and assumptions in dealing with missing MECS data in these tables are given below.

2.3.3.1. Filling in the missing values in the tables for the Chemical Industry

In Table 9, there is one missing value denoted by Q: "Wood Chips, Bark". In order to make the column total to be 464 PJ, this withheld value should be 10 PJ. On the other hand, there is one value denoted by *: Renewable Energy *(excluding Wood and Other Biomass)*. This value should be rounded off to 1 PJ in order to make the column total 165 PJ. These steps complete the missing values in Table 9. Now we can fill in the missing values in Table 12.

There is no withheld value in Table 12. However, there is 800 PJ end-use not reported, 790 of which is "Other" fuels.

$$\text{Other} = 790\ \text{PJ} \tag{8}$$

From equation (5), we know that "Other" is summation of "Byproducts", "Net steam", and "Fuels not listed separately". If we assume that the "Fuels not listed separately" is zero, then since byproducts from Table 9 is 464 PJ, we find that net steam is 326 PJ as shown in equation (9):

$$\text{Other} = \text{Byproducts} + \text{Net Steam} + \text{Fuels not listed separately}$$

$$790\ \text{PJ} = 464\ \text{PJ} + \text{Net Steam} + 0$$

$$\text{Net Steam} = 326\ \text{PJ} \tag{9}$$

It should be noted that the "purchased steam" in Table 9 is 204 PJ. This suggests that "steam transferred in" is 122 PJ. Since chemical plants have high requirement for steam, we can assume that the steam sale is zero. Therefore, since the "purchase", "transfer in", "sale" and "transfer off" for steam is not given at the level of detail as it is given for electricity by MECS, equation (9) provides us some of this missing information.

Since all of the net steam directly goes to end-uses, the rest of the 790 PJ remains as "Other Energy Sources Except Net Steam", which equals to 464 PJ. However, we do not know the distribution of this 464 PJ among the boiler and end-uses. This information can be obtained as follows:

MECS total fuel input for boiler and conventional electricity generation given in Table 12 by excluding the "Other" fuels = 32 + 4 + 1133 + 15 + 296

= 1480 PJ (10)

EIA 860B total fuel input for boiler and conventional electricity generation

= 1833 PJ (11)

It should be noted here that 2 PJ "Coke and breeze" consumption reported in MECS Table N3.2. is not separately reported in MECS tables N6.2. and N6.4. It is more likely that MECS database included this value in the "Other" fuels in MECS Table 6.2. with a 1 PJ round off difference (790 PJ in Table N6.2. – 789 PJ in Table N3.2. = 1 PJ), or neglected due to its small contribution in the total.

The difference between the EIA 860B total boiler input and MECS total boiler input is 353 PJ (1833 PJ - 1480 PJ = 353 PJ). Therefore, this shows that the excluded "Other" in equation (10) must be 353 PJ. This means that 353 PJ of the "Other Energy Sources Except Net Steam" directly go to the boiler and conventional electricity generation. However, we do not know the distribution of 353 PJ between the boiler and conventional electricity generation. If we look at this allocation for all of the fuels given in Table 12, we see that:

"The total fuel goes to the boiler is 1375 PJ, whereas total fuel goes to conventional electricity consumption is 104 PJ."

Therefore the ratio between the boiler and the conventional electricity generation is 13:1. If we allocate 353 PJ according to this ratio, then 25 PJ goes to the conventional electricity generation, whereas 328 PJ goes to the boiler.

Next step is to find the "Other Energy Sources Except Net Steam" go to the end-uses.

Other = goes to the boiler and the conventional electricity generation + goes to the end-uses (12)

464 PJ = 353 PJ + goes to the end-uses (13)

Although equation (13) gives that "Other Energy Sources Except Net Steam" go to the end-uses is 111 PJ, we do not know the allocation of this amount among the end-uses. This allocation can be done by using the same total fuel consumption ratios among end-uses from Table 12. This resolves the "Not reported end-uses" problem for the "Other" fuels in Table 12.

The other "Not reported end-uses" in Table 12 belongs to the "Net electricity" column. If we check the sub column total for the "Non-process uses", we see that that 2 PJ is missing. In order to make this subcolumn total to be 69 PJ, 2 PJ of the 3 PJ "not reported end-use" can be allocated to that sub column. The allocation can be made using the distribution ratio of 67 PJ sub column total among HVAC, Lighting and Support. We can see that the distribution of this 67 PJ is: HVAC = 54%, Facility Lighting = 37% and

Facility Support = 9%. If we apply these ratios to distribute 2 PJ, then about 1 PJ goes into HVAC, and 1 PJ goes into Facility Lighting. This makes the column total to be 69 PJ. Now we can allocate the left 1 PJ "Not reported end use" value among the "Total process uses" of the "Net electricity" column. We see that the "Machine Drive" has the biggest electricity consumption among the process end-uses. So, we can add this 1 PJ of "Not reported end-use" electricity to "Machine Drive". This makes a less than 1% change in the "Machine drive" electricity consumption.

Next, we can allocate the 5 PJ of not reported natural gas end-use value among the process and non-process uses in that column. We can follow the same logic described for the allocation of net electricity not reported end-use above. This leads us to allocate 1 PJ to "Conventional Electricity Generation" and 4 PJ into "Process Heating". This manipulation creates less than 1% change in the natural gas consumption of "process heating".

Finally, the 3 PJ of "Not reported end uses" of "Net demand for electricity" column can distributed among the "Machine Drive", and "Electro-chemical processes", 2 PJ and 1 PJ, respectively.

The conversion of the missing values in Table 12 is completed by converting all asterisks to zero. The adjusted MECS end-use data for the Chemical Industry is given in Table 14.

Table 14. Adjusted end-use data for NAICS 325 for 1998, PJ

	Total	Net Electricity	Residual Fuel Oil	Distillate Oil and Diesel Fuel	Natural Gas	LPG	Coal (excluding Coal Coke and Breeze)	Other	Net Demand for Electricity
TOTAL FUEL CONSUMPTION	3902 ± NA	607 ± 31	52 ± 2	8 ± 0.6	2092 ± 79	54 ± 2	299 ± NA	790* ± NA	774 ± 33
INDIRECT USES (Boiler Fuel)	--	3 ± 0.2	32 ± 1.6	4 ± 0.3	1040 ± 41	15 ± 0.7	284 ± NA	328 ± NA	5 ± 0.2
DIRECT USES (Total Process Uses)	--	535 ± 23	20 ± 0.8	2 ± 0.1	919 ± 30	37 ± 1	3 ± 0.1	97 ± NA	689 ± 26
Process heating	--	16 ± 0.6	20 ± 0.7	1 ± 0.1	837 ± 24	36 ± 1.2	3 ± 0.1	88 ± NA	18 ± 0.6
Process cool.&refr.	--	43 ± 0.9	0	0	12 ± 0.2	0	0	1 ± NA	58 ± 1.2
Machine drive	--	383 ± 23	0	1 ± 0.1	36 ± 1.7	0	0	4 ± NA	462 ± 25
Electrochem. process	--	92 ± 1.4	0	0	0	0	0	4 ± NA	150 ± 1.9
Other process use	--	1 ± 0.1	0	0	34 ± 2.3	1 ± 0.1	0	0	1 ± 0.1
DIRECT USES (Total Non-proc. Use)	--	69 ± 3.3	0	2 ± 0.2	133 ± 5	2 ± 0.1	12 ± 0.2	39 ± NA	80 ± 3
Facility HVAC	--	37 ± 3	0	0	34 ± 2	0	0	11 ± NA	42 ± 0.4
Facility lighting	--	26 ± 0.3	0	0	0	0	0	1	30 ± 0.4
Facility support	--	6 ± 0.3	0	0	4 ± 0.2	0	0	1	8 ± 0.4
Onsite transportation	--	0	0	2 ± 0.2	0	2 ± 0.1	0	1	0
Conventional el. gen.	--	0	0	0	93 ± 1.2	0	12 ± 0.1	25 ± NA	0
Other non-process use	--	0	0	0	2 ± 0.1	0	0	0	0
END-USE (N.R.)	336	0	0	0	0	0	0	326 ± NA	0

NA: Not available, NR: Not reported.

* 790 PJ = 353 PJ (to the boiler and conventional electricity generation) + 326 PJ (net steam to end-uses) + 111 PJ (to end-uses) as discussed in equations (9) through (13). Since the net steam in the end-use model is distributed separately from the fuel inputs, allocation of the net steam among the end-uses is not shown in Table 14.

Allocation of 111 PJ was made based on the total fuel ratio among the end-uses given in Table 12, e.g.

- Total fuel consumption for process uses = 20 + 2 + 919 + 37 +3 = 981 PJ

i) Process heating accounts for 91% of this total,

ii) Process cooling and refrigerating accounts for 1% of this total,

iii) Machine Drive accounts for 4% of this total,

iv) Electro-chemical processes account for 4% of this total,

v) Other process uses account for 0% of this total.

- Total fuel consumption for non-process uses = 2 + 133 + 2 + 12 = 149 PJ

  i) HVAC accounts for 23% of this total,

  ii) Facility lighting accounts for 0% of this total,

  iii) Facility support accounts for 3% of this total,

  iv) Onsite transport accounts for 3% of this total,

  v) Conventional electricity generation accounts for 71% of this total,

  vi) Other non-process uses account for 0% of this total.

The process and non-process uses consume 1130 PJ fuel, 87% of which goes to process uses and 13% to non-process uses. If we allocate 111 PJ according to this ratio, then, 97 PJ goes to the process uses, whereas 14 PJ goes to non-process uses. As for the allocation within the process and non-process uses, the ratios given above can be used. Therefore, 88 PJ goes to process heating, 4 PJ goes to machine drive, 4 PJ goes to electro-chemical processes, and 1 PJ goes to the process cooling and refrigerating. As for the distribution among the non-process uses, we found earlier that the "Other" fuel consumption for the conventional electricity generation is 25 PJ and it is not part of 14 PJ non-process fuel use is allocated among the HVAC, facility lighting, facility support, onsite transportation and other non-process uses. Hence, if we exclude conventional electricity generation, the ratios among the remaining non-process uses are:

- 77% HVAC,
- 0% facility lighting,
- 9% facility support,
- 9% onsite transportation,
- 4% other non-process uses.

According to these ratios, 11 PJ goes to HVAC, 1 PJ goes to facility support, and 1 PJ goes to facility lighting. If we check the ratio of conventional electricity among the non-process uses now, we see that it is 64%, which is 7% smaller than the ratio initially given for total fuel consumption for conventional electricity generation.

2.3.3.2. Filling in the missing values in the tables for the Industrial Gas Manufacturing

The withheld data in Table 11 for "Transfers in", and "Other onsite generation" are denoted by Q. These can be calculated by checking the column balance. The other missing values in Table 11 are *, which are converted to zero. This completes filling in the missing values in Table 11.

The next step is to fix the missing values in Table 13. First, the "Net Electricity" and "Net Demand for Electricity" columns for "Process uses" do not balance. The missing 1 PJ of electricity consumption in both columns can be attributed to "Machine Drive" as it is the biggest electricity consumer among the direct process uses category. This 1 PJ correction creates less that 1% difference in the actual reported "Machine Drive" electricity consumption. There is 9 PJ "Not reported end-use" value for "Other" fuels. This can be distributed among the boiler and the end-use by using the total fuel distribution ratio. The conversion of the missing values in Table 13 is completed by converting all asterisks to zero. The adjusted MECS end-use data for the Industrial Gas Manufacturing sector is given in Table 15.

Table 15. Adjusted end-use data for NAICS 325120 in 1998, PJ

	Total	Net Electricity	Residual Fuel Oil	Distillate Oil and Diesel Fuel	Natural Gas	LPG	Coal (excluding Coal Coke and Breeze)	Other	Net Demand for Electricity
TOTAL FUEL CONSUMPTION	193 ± NA	117 ± 15	0	0	66 ± 5	0	0	9* ± NA	120 ± 14
INDIRECT USES (Boiler Fuel)	-	0	0	0	27 ± 3	0	0	1 ± NA	0
DIRECT USES (Total Process Uses)	-	114 ± 10	0	0	37 ± 2	0	0	0	116 ± 10
Process heating	-	1 ± 0.1	0	0	22 ± 1	0	0	0	1 ± 0.1
Process cool.& refrig.	-	3 ± 0.3	0	0	0	0	0	0	3 ± 0.3
Machine drive	-	109 ± 13	0	0	15 ± 1	0	0	0	111 ± 13
Electrochem. process	-	1 ± 0.04	0	0	0	0	0	0	1 ± 0.04
Other process use	-	0	0	0	0	0	0	0	0
DIRECT USES (Total Non-proc. Use)	-	3 ± 0.3	0	0	2 ± 0.1	0	0	0	4 ± 0.4
Facility HVAC	-	2 ± 0.5	0	0	0	0	0	0	2 ± 0.4
Facility lighting	-	1 ± 0.03	0	0	0	0	0	0	2 ± 0.1
Facility support	-	0	0	0	2 ± 0.03	0	0	0	0
Onsite transportation	-	0	0	0	0	0	0	0	0
Conventional el. gen.	-	0	0	0	0	0	0	0	0
Other non-process use	-	0	0	0	0	0	0	0	0
END-USE (N.R.)	0	0	0	0	0	0	0	8	0

NA: Not available, NR: Not reported.

* 9 PJ = 1 PJ (to the boiler and conventional electricity generation) + 8 PJ (net steam to end-uses) from equation (5). Since the net steam in the end-use model distributed separately from the fuel inputs, allocation of the net steam among the end-uses is not shown in Table 15.

Allocation of net steam among end-uses was made based on the total fuel ratio among the end-uses, e.g.

- Total fuel consumption for process uses = 37 PJ
  - i) Process heating accounts for 59% of this total,
  - ii) Process cooling and refrigerating accounts for 0% of this total,
  - iii) Machine Drive accounts for 41% of this total,
  - iv) Electro-chemical processes account for 0% of this total,
  - v) Other process uses account for 0% of this total.
- Total fuel consumption for non-process uses = 2 PJ
  - i) HVAC accounts for 0% of this total,
  - ii) Facility lighting accounts for 0% of this total,
  - iii) Facility support accounts for 100% of this total,
  - iv) Onsite transport accounts for 0% of this total,
  - v) Conventional electricity generation accounts for 0% of this total,
  - vi) Other non-process uses account for 0% of this total.

The process and non-process uses consume 39 PJ fuel, 95% of which goes to process uses, whereas 5% goes to non-process uses.

2.3.4. Building the end-use models

The following sections describe the details of constructing the end-use models given in Figures 19 and 22.

2.3.4.1. Fuel inputs in the model

The input values of residual fuel oil, distillate fuel oil, natural gas, LPG and NGL, coal, and coke and breeze from Tables 9 and 10 are located in the lower left corner of Figures 19 and 22.

From equation (5), we know that "Other" fuels include net steam. Since the "Net steam" is modeled separately, "Other energy sources except net steam" is located in the lower left corner of Figures 19 and 22.

2.3.4.2. Allocation of fuels and electricity to end-uses

Tables 14 and 15 provide allocations of fuels and electricity to end-uses. Electricity allocation among the end-uses are located on the right side of the process and non-process uses column, whereas fuel allocation among the end-uses are located on the left side.

2.3.4.3. Allocation of net steam to end-uses

Net steam was calculated from equation (5) and for the Chemical Industry it was found as 326 PJ in equation (9). By using the equation (5) and the same assumption of "Fuels not listed separately" is zero, the net steam for Industrial Gas Manufacturing is found as:

$$\text{Net Steam} = 8 \text{ PJ} \qquad (14)$$

The net steam is located in the left column of Figures 19 and 22. The allocation of the net steam to end-uses is made based on the fuel distribution ratios given in section

2.3.3.1. for the Chemical Industry, and in section 2.3.3.2. for the Industrial Gas Manufacturing sector.

2.3.4.4. Offsite electricity

The acquisition and disposition of electricity is presented in the upper left corner of Figures 19 and 22 as purchased electricity, electricity sold and electricity from noncombustible renewables. These values are taken from Tables 9 and 10 and they do not include onsite power generation from combustible fuels.

2.3.4.5. Steam loss

Steam distribution losses due to heat transfer, ineffective steam traps, leaks etc. varies from 20% to 40% (Bhatt, 2000; Petek and Glavic, 1996; Hooper and Gillette, 2002). In my energy end-use model, I assume an average 30% steam loss during distribution.

2.3.4.6. Onsite steam and power generation

Onsite steam and power generation is a key part of the energy end-use model. There are significant energy efficiency and carbon emissions reduction potential from on-site combined heat and power (CHP) in the manufacturing sector (Khrushsh et al., 1999). Detailed models of current industrial onsite power and steam generation activities can serve as valuable base cases to project future benefits of programs and policies designed to encourage expansion of this activity. The credibility and value of such models would be greatly enhanced if they could be scaled to agree with national data. While detailed engineering models of CHP exist, they typically deal with a specific installation or technology, and are much too detailed to be scaled against macro data available at the national level (Zheng and Furmisky, 2003). On the other hand, several models scaled against the macro data assume that all on-site CHP was via the steam turbine topping cycle and/or utilize conversion and waste heat recovery efficiencies based on typical values appearing in the literature rather than actual data (Giraldo and Hyman, 1995; Andersen and Hyman, 2001; ADL, 2000; EERE, 2004).

The onsite power and steam generation model presented in this dissertation have six different modes based on the most common technologies used in the Chemical Industry. Four modes involve both electricity generation and heat production and two modes represents steam generation with no associated electricity generation.

Each mode is described by energy balance equations according to the first law of thermodynamics and efficiency equations including, as needed, boiler efficiency, turbine efficiency, internal combustion engine efficiency, and waste heat recovery efficiency.

The six modes of power and steam production are:

1. Internal combustion engine (ICE) with heat recovery
2. Gas turbine with heat recovery
3. Steam turbine with heat recovery
4. Combined cycle
5. Steam generation in fuel fired boiler
6. Steam generation in electric boiler

2.3.4.6.1. Internal combustion engine with heat recovery

This mode represents onsite electricity generation via an internal combustion engine with waste heat recovery. The graphical depiction of this mode is given in Figure 9, which provides the conversion efficiency and energy balance relationships for this mode as four equations containing seven unknowns,

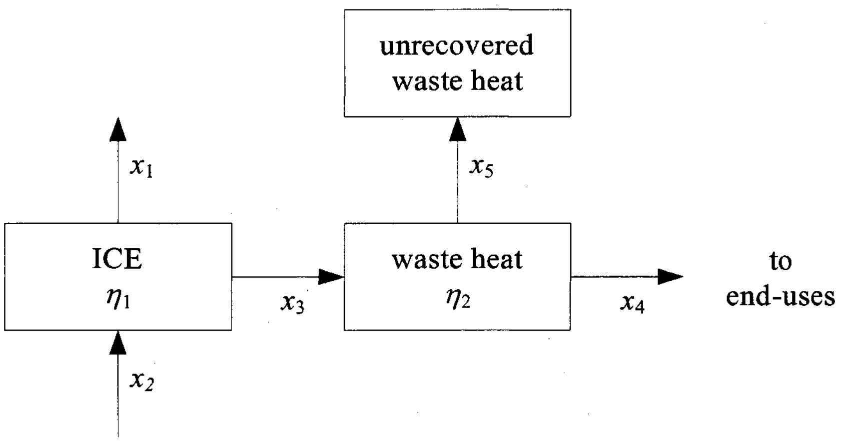

Figure 9. Internal combustion engine with heat recovery

$$x_1 = \eta_1 x_2 \tag{15}$$

$$x_2 = x_1 + x_3 \tag{16}$$

$$x_4 = \eta_2 x_3 \tag{17}$$

$$x_3 = x_4 + x_5 \tag{18}$$

Note that the special case of no waste heat recovery can be modeled by setting $\eta_2 = 0$.

2.3.4.6.2. Gas turbine with heat recovery

The second mode, shown in Figure 10, consists of onsite electricity generation by a gas turbine with recovery of the waste heat. The conversion efficiency and first law equations for this mode provides the following four equations with seven unknowns,

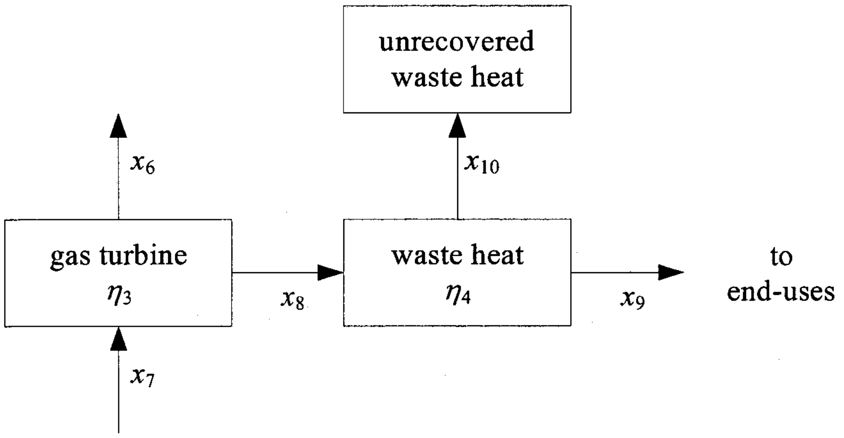

Figure 10. Gas turbine with heat recovery

$$x_6 = \eta_3 x_7 \tag{19}$$

$$x_7 = x_6 + x_8 \tag{20}$$

$$x_9 = \eta_4 x_8 \tag{21}$$

$$x_8 = x_9 + x_{10} \tag{22}$$

Note that the special case of no waste heat recovery can be modeled by setting $\eta_4 = 0$.

2.3.4.6.3. Steam turbine with heat recovery

This mode represents onsite electricity generation by a steam turbine with waste heat recovery. The model for mode 3 is shown in Figure 11. It consists of the following six equations containing ten unknowns,

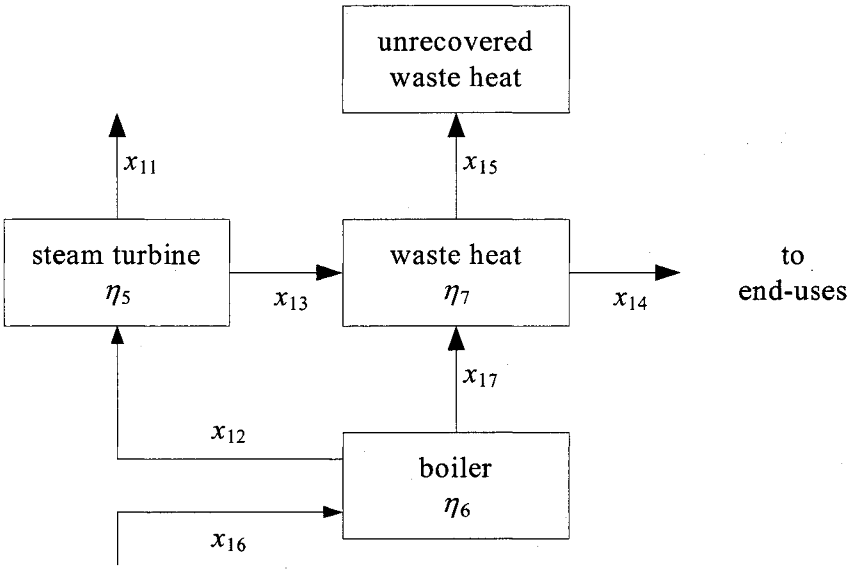

Figure 11. Steam turbine with heat recovery

$$x_{11} = \eta_5 x_{12} \tag{23}$$

$$x_{12} = x_{11} + x_{13} \tag{24}$$

$$x_{12} = \eta_6 x_{16} \tag{25}$$

$$x_{16} = x_{12} + x_{17} \tag{26}$$

$$x_{14} = \eta_7 (x_{13} + x_{17}) \tag{27}$$

$$x_{13} + x_{17} = x_{14} + x_{15} \tag{28}$$

Note that the special case of no waste heat recovery can be modeled by setting $\eta_7 = 0$.

2.3.4.6.4. Combined cycle

As shown in Figure 12 and equations (29) – (36), the model for the combined cycle mode consists of eight equations and 14 unknowns. In a combined cycle, the exhaust gasses from the gas turbine are sent to a heat recovery steam generator that provides input to the steam turbine. To maintain consistency with the way I model the other modes, I depict the heat recovery steam generator as a boiler with supplementary fuel input.

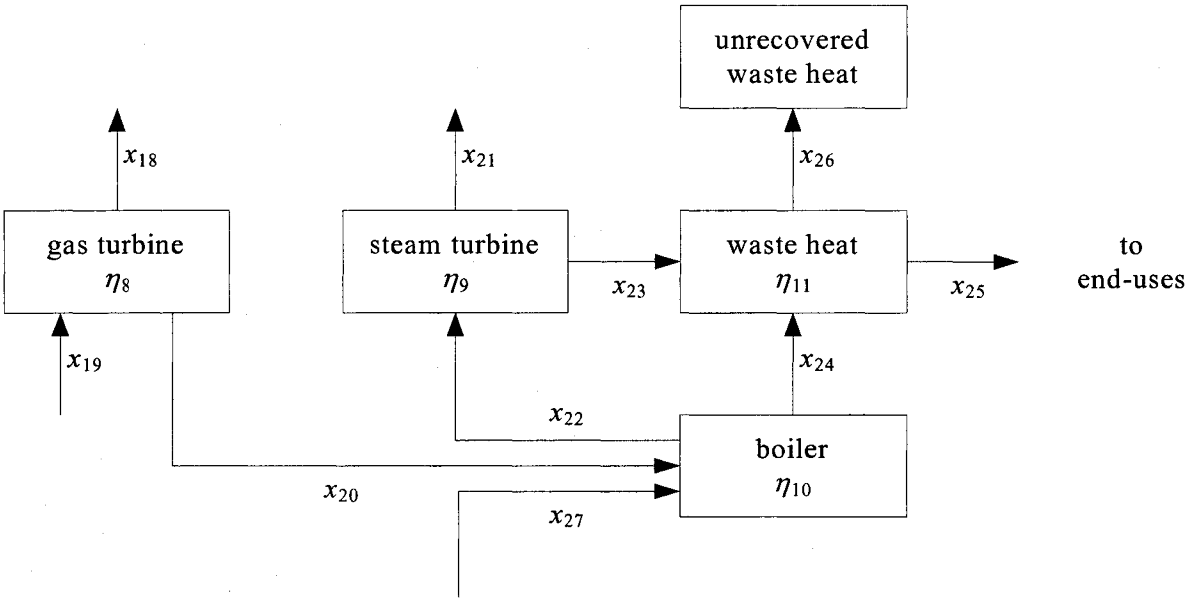

Figure 12. Combined cycle

$$x_{18} = \eta_8 x_{19} \tag{29}$$

$$x_{19} = x_{18} + x_{20} \tag{30}$$

$$x_{21} = \eta_9 x_{22} \tag{31}$$

$$x_{22} = x_{21} + x_{23} \tag{32}$$

$$x_{22} = \eta_{10}(x_{20} + x_{27}) \tag{33}$$

$$x_{20} + x_{27} = x_{22} + x_{24} \tag{34}$$

$$x_{25} = \eta_{11}(x_{23} + x_{24}) \tag{35}$$

$$x_{23} + x_{24} = x_{25} + x_{26} \tag{36}$$

2.3.4.6.5. Steam generation in fuel fired boiler

This mode represents onsite steam generation in a fuel-fired boiler. There is no electricity generation associated with this mode as the boiler is used only to produce steam. My model for this mode is shown in Figure 13 and represented by equations (37) and (38) containing four unknowns.

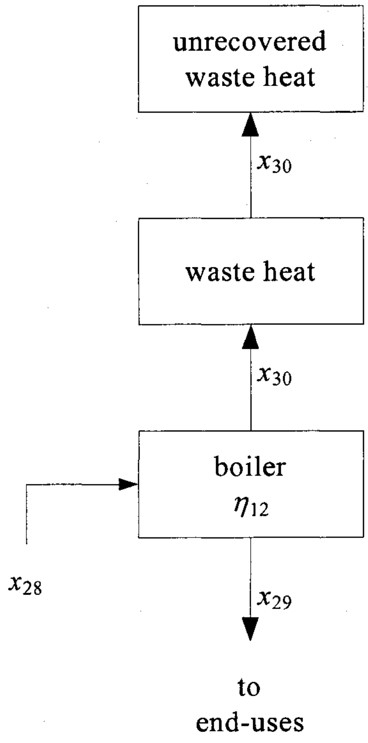

Figure 13. Steam generation in fuel fired boiler

$$x_{29} = \eta_{12} x_{28} \tag{37}$$

$$x_{28} = x_{29} + x_{30} \tag{38}$$

2.3.4.6.6. Steam generation in electric boiler

The sixth mode represents steam generation in an electric boiler. The difference between mode 5 and mode 6 is that the boiler has fuel as the input in mode 5, whereas the boiler in mode 6 uses electricity to boil water. The graphical depiction of mode 6 is given in Figure 14.

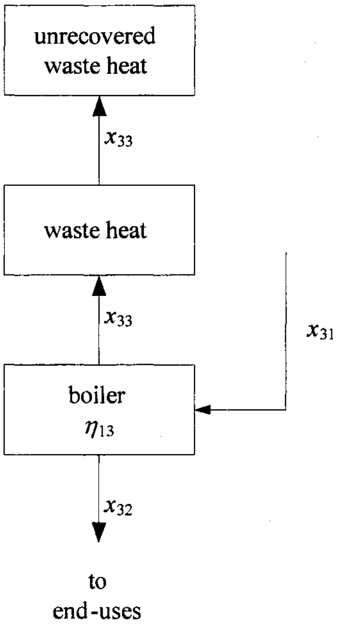

Figure 14. Steam generation in electric boiler

This mode gives the following two equations and four unknowns,

$$x_{32} = \eta_{13} x_{31} \tag{39}$$

$$x_{32} + x_{33} = x_{31} \tag{40}$$

2.3.4.7. Boiler efficiencies

In preparation for solving the governing equations for the six modes, a boiler efficiency assumption must be made as it is not provided in EIA 860B. As it was explained in section 2.2.2.2., I assumed that:

- All fuel-fired boiler efficiencies are the same and equal to a value found in the literature (ADL, 2000; EERE, 2004; Showers, 2002; Marrero et al., 2002), i.e. $\eta_6 = \eta_{10} = \eta_{12} = 0.8$,
- I furthered assumed 100% efficiency for the electric boilers, i.e. $\eta_{13} = 1.0$, since "the heating elements of electric water heaters, and the efficiency of all resistance heaters is 100 percent as they convert all electric energy they consume into heat" (Cengel and Boles, 4th edition, pg. 253).

2.4. Results

2.4.1. Prime mover electric conversion efficiencies

EIA 860B provides data for energy input and gross generation for each prime mover in each facility, which enabled me to calculate prime mover electric conversion efficiencies. For steam turbines though, I had to modify the energy input value to account for the 80% boiler efficiencies. I assumed that the efficiencies do not depend on whether or not the prime movers are used as a part of a combined cycle system. Thus for the gas turbine efficiency I set $\eta_3 = \eta_8$, and for the steam turbine efficiency I set $\eta_5 = \eta_9$. I calculated the electric conversion efficiencies for each prime mover type from (Onovwiona and Ugursal, 2005)

$$\eta_{\text{electric}} = \frac{\sum \text{gross generation}}{\sum \text{energy input to prime mover}} \tag{41}$$

where the summation is taken over all prime movers of that type used in an industry according to EIA 860B. For example, there are 89 gas turbines reported in this database for the Chemical Industry. The electricity efficiency was found by summing the gross generation of all of the 89 gas turbines and dividing it by the summation of energy inputs to all of these 89 gas turbines. The results for the prime mover electric conversion efficiencies for the Chemical Industry are given in Table 16.

Table 16. Prime mover electric conversion efficiencies in the Chemical Industry

Prime mover	Efficiency	Value
Internal combustion engine	η_1	35%
Gas turbine	$\eta_3 = \eta_8$	27%
Steam turbine	$\eta_5 = \eta_9$	13%
Combined cycle	*Overall*	33%

Since "the overall efficiency of a power plant can be increased by using a combined cycle" and "combined cycles have a higher thermal efficiency than the steam -or gas-turbine cycles operating alone", it was expected that the combined cycle efficiency to be higher than the steam and gas turbines in Table 16 (Cengel and Boles, 4th Edition, pg.549). However, the combined cycle efficiency in Table 16 is slightly lower than the internal combustion engine. The reason for that might be the internal combustion engines' having higher cycle efficiency in smaller scale applications (Shepard et al., 1977; DEF, 2005). For example, since "one important disadvantage is that a gas turbine does not perform well in part-load operation", this industry may have installed internal combustion engines for their smaller scale applications (Poullikkas, 2005). If we consider that "at 50% load, the gas turbine achieves around 75% of the full-load efficiency, and at 30% load, this drops to 50% of the nominal efficiency", then it is more reasonable to run internal combustion engines with a partial load if a facility does not need to run its gas turbines or combined cycles full or 75% load for its smaller applications (Poullikkas, 2005). Therefore, since "at low load, electrical efficiency drops significantly except for fuel cells and Stirling engine based cogeneration systems that have better performance handling partial loads" it may suggest that the plants with no internal combustion engine may have run their gas turbines in partial load and that may be the explanation for lower combined cycle efficiency (Onovwiona and Ugursal, 2005).

2.4.2. Waste heat recovery efficiencies

Once prime mover electric efficiencies are determined from equation (41), waste heat recovery efficiencies can be calculated using equation (42)

$$\eta_{\text{waste heat recovery}} = \frac{\sum \text{net useful thermal energy}}{\sum \text{total waste heat}} \tag{42}$$

where

$\sum$ total waste heat = $\sum$ waste heat from boiler + $\sum$ waste heat from prime mover

and again, the summation is taken over all prime movers of a given type.

Since these energy conversion models require that waste heat from the boiler and prime mover go to the waste heat tank, the waste heat recovery efficiency values include the sum of the waste heat from the boiler and prime mover. In some plants though, waste heat from the boiler is not recovered. For those situations, my model overestimates the waste heat recovery efficiency. The results for the waste heat recovery efficiencies for the Chemical Industry are given in Table 17.

Table 17. Waste heat recovery efficiencies in the Chemical Industry

Prime mover	Efficiency	Value
Internal combustion engine	η_2	16%
Gas turbine	η_4	37%
Steam turbine	η_7	57%
Combined cycle	η_{11}	36%

2.4.3. The overall prime mover conversion efficiencies

I calculated the overall conversion efficiency for each prime mover type from (Onovwiona and Ugursal, 2005)

$$\eta_{\text{overall prime mover}} = \frac{\sum \text{net useful thermal energy} + \sum \text{gross generation}}{\sum \text{energy input to prime mover}} \tag{43}$$

The results for the overall prime mover efficiencies for the Chemical Industry are given in Table 18.

Table 18. The overall prime mover conversion efficiencies in the Chemical Industry

Efficiency	Value
$\eta_{overall\ ICE}$	45%
$\eta_{overall\ GT}$	54%
$\eta_{overall\ ST}$	65%
$\eta_{overall\ CC}$	46%
$\eta_{overall\ total}$	57%

2.4.4. Solution for the remaining unknowns

EIA 860B data, along with the 80% boiler efficiency assumption, gives all the unknowns in modes 1 through 4. As for the unknowns in modes 5 and 6, EIA 860B does not provide sufficient information. Therefore, I used MECS data to solve for those unknowns.

Mode 5 consists of two equations and four unknowns. I have already eliminated one of the unknowns by assuming $\eta_{12} = 80\%$. To get an additional equation, data for the total amount of commercial fuel supplied to boilers given in the MECS Table N6.2 can be used. That table also provides data on "Other" energy inputs without specifying how that energy is used. Following the technique described in Giraldo and Hyman (1995), I converted "Other" to an estimate of byproduct fuels. Then I assumed that all byproducts are consumed as boiler fuel. This allowed me to write

$$x_{16} + x_{27} + x_{28} = m \tag{44}$$

where m represents the value obtained from the MECS. Since the values of x_{16} and x_{27} are known from 860B and the boiler efficiency was assumed to be 80%, equation (32) can be solved for x_{28}. Then the other unknowns in this mode can be solved by using the 80% boiler efficiency assumption.

Mode 6 gives two equations and four unknowns. One of the unknowns hasalready been eliminated by assuming $\eta_{13} = 100\%$ (electric boiler). An additional equation can be obtained from MECS Table N6.2 for electricity consumed by electric boilers which gives the value of x_{31}. Then equations (27) and (28) can be solved for x_{32} and x_{33}.

The solutions for x_1 through x_{33} are given in Table 19, whereas description of each unknown is given in Table 20.

Table 19. Numerical results for inputs and outputs, PJ

Unknown	Value	Unknown	Value	Unknown	Value
x_1	0.45	x_{12}	280	x_{23}	250
x_2	1.3	x_{13}	242	x_{24}	72
x_3	0.8	x_{14}	175	x_{25}	99
x_4	0.1	x_{15}	131	x_{26}	224
x_5	0.7	x_{16}	350	x_{27}	208
x_6	39	x_{17}	70	x_{28}	922
x_7	145	x_{18}	56	x_{29}	738
x_8	106	x_{19}	207	x_{30}	185
x_9	39	x_{20}	151	x_{31}	5
x_{10}	67	x_{21}	37	x_{32}	5
x_{11}	38	x_{22}	287	x_{33}	0

Table 20. Description of the inputs and outputs

Input	Description	Output	Description
x_2	Internal combustion engine energy input	x_1	Internal combustion engine electricity output
		x_3	Internal combustion engine waste heat output
		x_4	Internal combustion engine recovered waste heat output
		x_5	Internal combustion engine unrecovered waste heat output
x_7	Gas turbine energy input	x_6	Gas turbine electricity output
		x_8	Gas turbine waste heat output
		x_9	Gas turbine recovered waste heat output
		x_{10}	Gas turbine unrecovered waste heat output
x_{12}	Steam turbine energy input	x_{11}	Steam turbine electricity output
		x_{13}	Steam turbine waste heat output
x_{16}	Steam turbine boiler energy input	x_{14}	Steam turbine recovered waste heat output
		x_{15}	Steam turbine unrecovered waste heat output
		x_{17}	Steam turbine boiler waste heat output
x_{19}	Combined cycle – gas turbine energy input	x_{18}	Combined cycle – gas turbine electricity output
		x_{20}	Combined cycle – gas turbine waste heat output
x_{27}	Combined cycle – boiler energy input	x_{21}	Combined cycle – steam turbine electricity output
x_{22}	Combined cycle – steam turbine energy input	x_{23}	Combined cycle – steam turbine waste heat output
		x_{24}	Combined cycle – boiler waste heat output
		x_{25}	Combined cycle – recovered waste heat

Table 20. (Continued)

		x_{26}	Combined cycle – unrecovered waste heat
x_{28}	Fuel fired boiler energy input	x_{29}	Fuel fired boiler steam output
		x_{30}	Fuel fired boiler recovered/unrecovered waste heat
x_{31}	Electric boiler energy input	x_{32}	Electric boiler steam output
		x_{33}	Electric boiler recovered/unrecovered waste heat

2.4.5. Onsite power and steam generation model for the U.S. Chemical Industry

Figures 9–14 and the corresponding numerical results from Tables 14 - 16 and Table 19 can now be superimposed to yield a composite model of onsite power and steam generation for the Chemical Industry, presented in Figure 15.

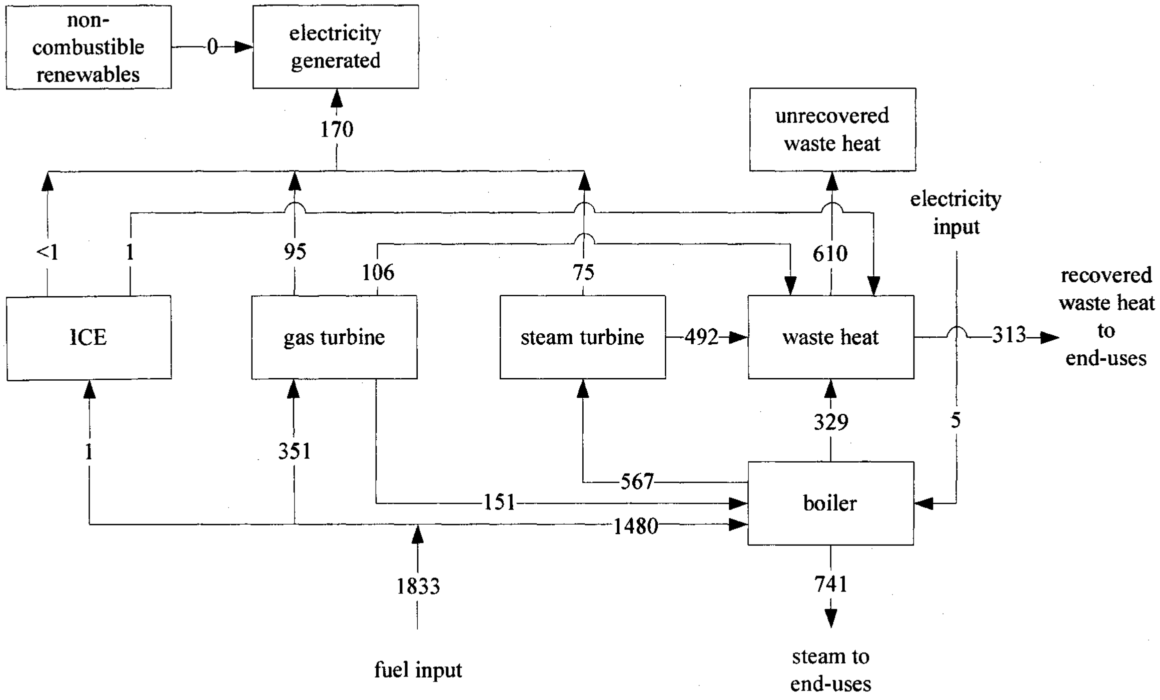

Figure 15. Onsite power and steam generation in the Chemical Industry in 1998, PJ

It should be noted that the input and output values into the boiler and the waste heat tank in Figure 15 come from internal combustion engine, gas turbine, steam turbine, combined cycle and steam production with no associated electricity generation. Therefore the boiler in Figure 15 represents inputs and outputs of several different energy conversion processes and is not a Rankine cycle boiler.

The outcomes of Figure 15 can be listed as follows:

- 35% of the energy output from the boiler goes to power generation,
- 45% of the energy output from the boiler goes directly to end-uses,
- 20% of the energy output from the boiler goes to the waste heat tank for recovery,
- 66% of the waste heat is unrecovered,
- 34% of the waste heat is recovered and goes to end-uses.

Figure 16 shows these boiler outputs distribution in a chart.

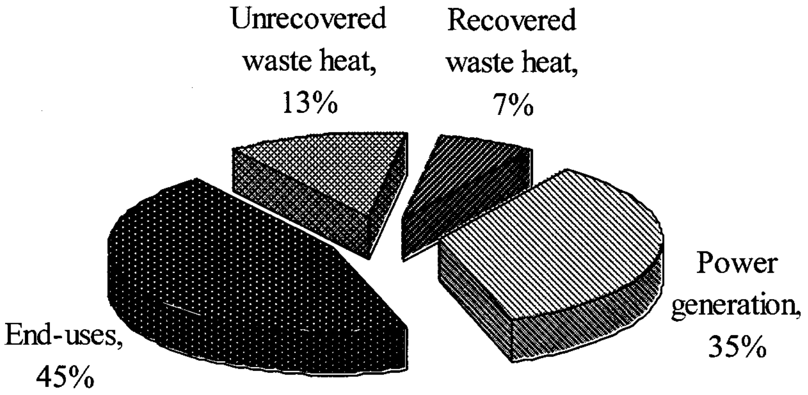

Figure 16. Distribution of boiler outputs

The onsite steam and power generation model in Figure 15 can now be combined with the adjusted MECS data in Tables 14 and 15 to produce a complete end-use model.

2.4.5.1. Integrating the onsite steam and power model with energy end-use model

Onsite steam and power model gives actual electricity conversion and waste heat recovery efficiencies in the Chemical Industry in 1998 based on operating data. These efficiencies provide onsite steam and unrecovered waste heat production amounts that are missing in the MECS database. Therefore, once they are applied to the onsite power and steam generation part of the energy end-use model, demonstration of onsite utilization of fuel is completed.

In the Chemical Industry energy end-use model, onsite steam and power generation in Figure 15 is directly pasted in the middle left side of the model. As for the Industrial Gas Manufacturing sector, the energy conversion efficiencies in Figure 15 are applied to the end-use model.

2.4.5.2. Allocation of steam and waste heat to end-uses

Tables 14 and 15 do not provide any information about the steam and recovered waste heat allocation among the end-uses. Therefore, an assumption must be made on the allocation of steam and recovered waste heat among the end-uses in the Chemical Industry or Industrial Gas Manufacturing sector. I assumed that the allocation of the fuels to end-uses is the same as the allocation of steam and recovered waste heat among the end-uses. These ratios are given in section 2.3.3.1. for the Chemical Industry, and given in section 2.3.3.2. for the Industrial Gas Manufacturing sector. I also referred to EIA

860B data for net useful thermal energy distribution among the end-uses. However, EAI 860B does not provide that data except for few facilities. If we still refer to those few facilities to have an idea about the actual distribution of recovered waste heat, we see that the process heating is the dominant application. This supports the assumption made in Giraldo and Hyman (1995).

Figure 17 gives the steam and waste heat allocation among end-uses in the Chemical Industry in 1998 along with the fuel and electricity allocation among end-uses, whereas Figure 18 gives the steam and waste heat allocation among end-uses in the Industrial Gas Manufacturing sector in 1998 along with the fuel and electricity allocation among end-uses. These figures are the key to construct energy process-step models as they show fuel, steam, waste heat and electricity inputs to each process.

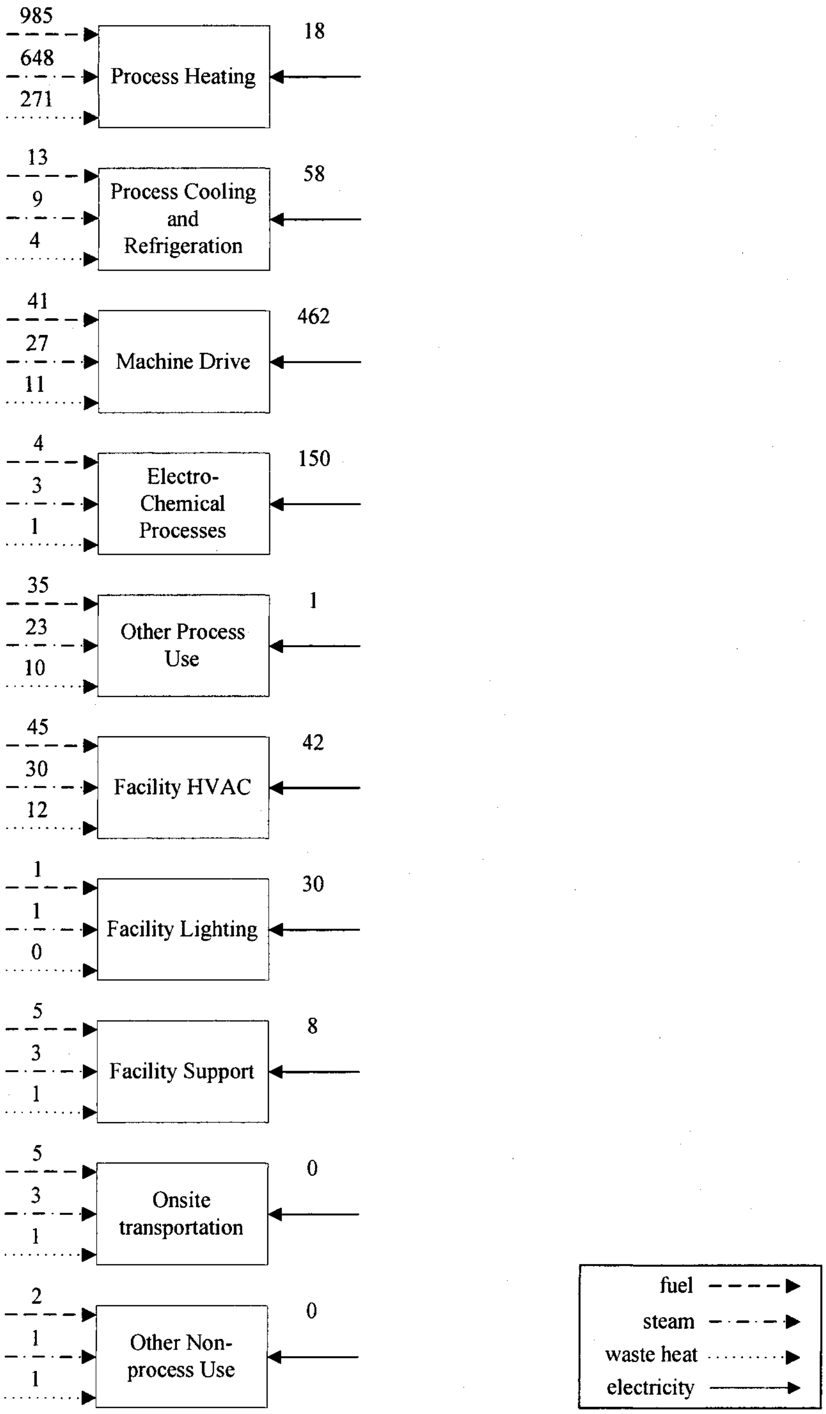

Figure 17. Fuel, steam, waste heat and electricity allocation among end-uses in NAICS 325, PJ

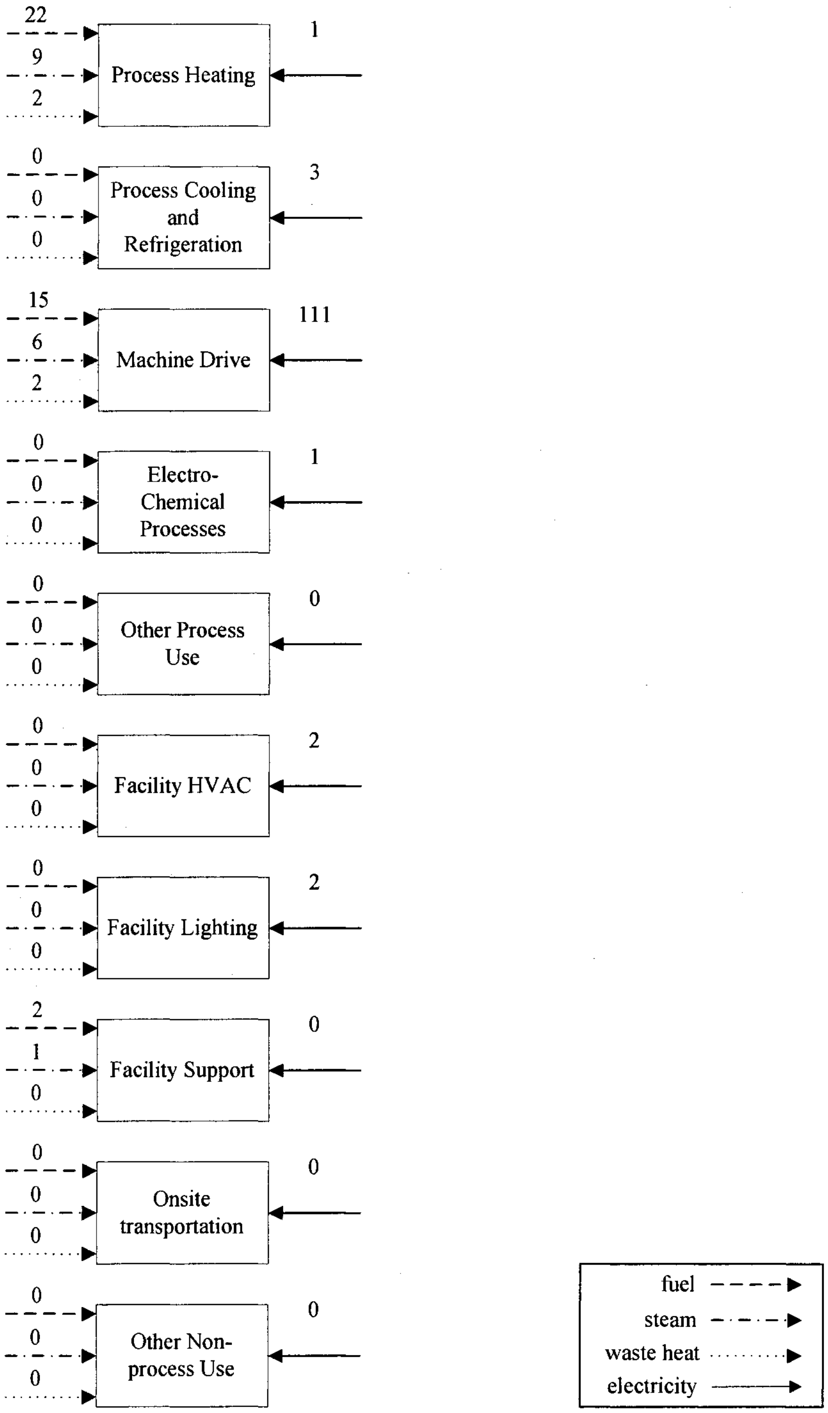

Figure 18. Fuel, steam, waste heat and electricity allocation among end-uses in NAICS 325120, PJ

2.4.6. Energy end-use model of the NAICS 325 Chemical Industry

Unrecovered waste heat and steam production data from the onsite steam and power generation model combined with the MECS data yields the energy end-use model of the U.S. Chemical Industry, given in Figure 19. It should be noted that due to the small variation between MECS and EIA 860B data as discussed in section 2.2.3., there is a 5 PJ unbalance around the onsite steam and power generation box. This 5 PJ unbalance stems from the 5 PJ difference between the MECS and EIA 860B values as it was shown in Table 7 of section 2.2.3, e.g. 165 PJ is reported by EIA 860B whereas 170 PJ is reported by MECS. Since the fuel input to onsite steam and power generation is 1833 PJ, this 5 PJ unbalance is negligible. As for the fuel distribution to end-uses, there is 1 PJ unbalance for the residual fuel oil, 1 PJ unbalance for the distillate fuel oil, 1 PJ unbalance for the natural gas, and 1 PJ unbalance for the coal. These unbalances occurred due to the rounding adjustments made on the MECS data as discussed in section 2.3.3.2.

As it is mentioned as an additional explanation to equation (4) in Section 2.3.2., the "transfer ins" are also included in purchases. Therefore, the total purchased electricity is the summation of 614 PJ purchased electricity and 21 PJ transfers in from Table 9, which gives 635 PJ.

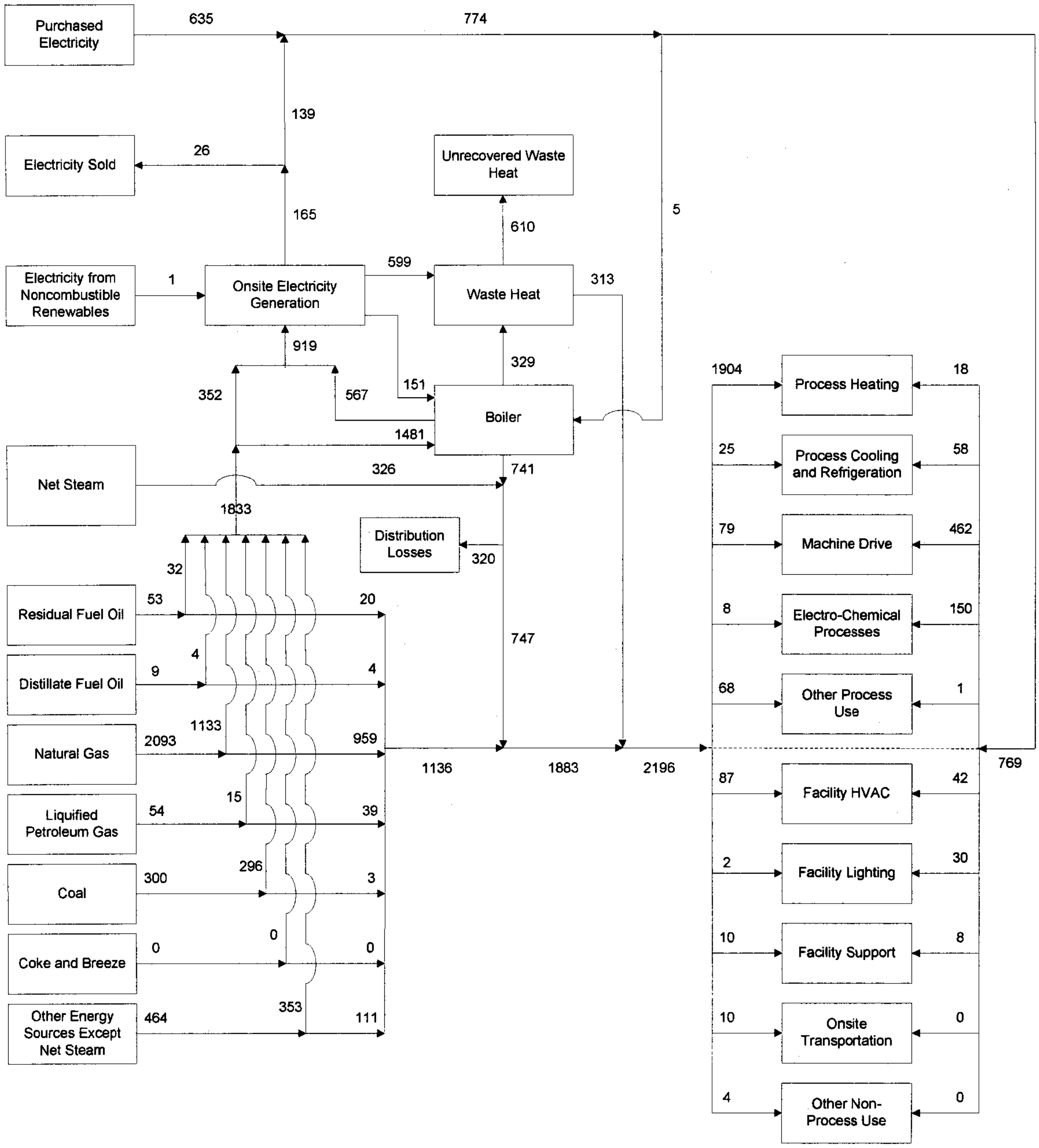

Figure 19. Energy end-use model of the U.S. Chemical Industry, 1998, PJ

As can be seen from the energy end-use model in Figure 19, the fuel inputs are distributed among:

- Onsite power and steam generation,

- End-uses.

About 66% of the total fuel input goes directly to onsite steam and power generation, which is 1833 PJ. About 95% of this amount goes to the boiler, whereas the 5% directly goes to onsite electricity generation.

The biggest contribution to the end-uses is made by the 1833 PJ of total fuel inputs for onsite power and steam generation result. The distribution of this fuel input among the end-uses after the intermediate onsite conversions is as follows:

→ 139 PJ electricity to end-uses,

→ 747 PJ steam to end-uses,

→ 313 PJ recovered waste heat to end-uses,

which adds up to a total of 1199 PJ energy to end-uses. The rest of the energy remains unrecovered. Figure 20 shows the distribution of 1833 PJ of fuel input among the end-uses after the intermediate onsite energy conversions.

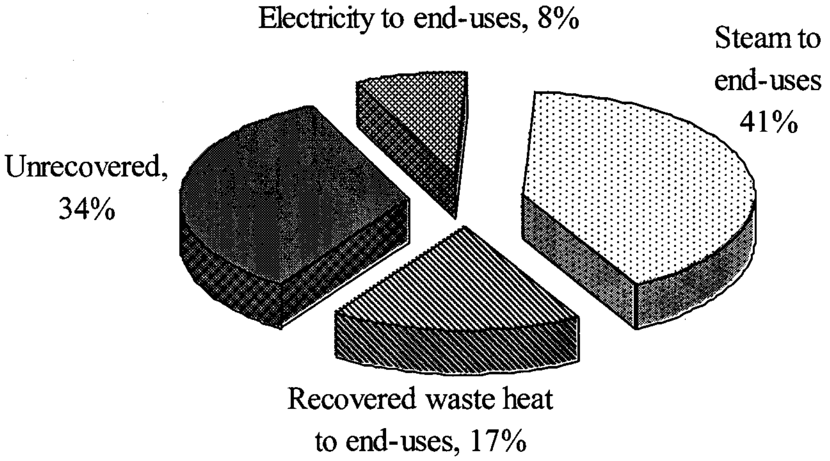

Figure 20. Distribution of total fuel input among the end-uses

Although the boiler provides 741 PJ steam energy for end-uses, the Chemical Industry uses an additional 326 PJ from net steam. On the other hand, although the Chemical Industry generates 165 PJ electricity onsite, it sells 26 PJ to the grid, which accounts for about 16% of the total electricity generated onsite.

The total electricity consumption of the end-uses is 769 PJ. The onsite power generation provides 139 PJ of this need, whereas purchased electricity provides the rest. The Figure 21 shows this distribution.

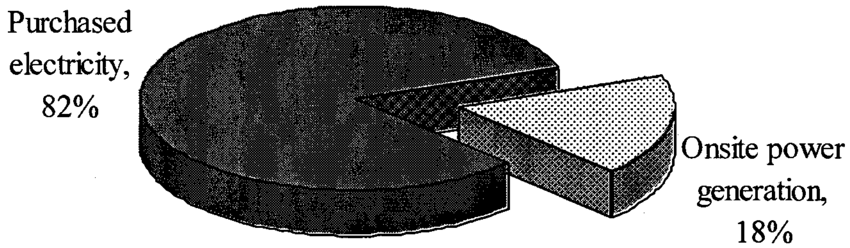

Figure 21. Source of electricity input to end-uses in the Chemical Industry

As it is seen in Figure 21, purchased electricity is the key electricity contributor to the end-uses.

Among the end-uses, process heating is the biggest energy consumer, followed by the machine drive and electro-chemical processes. Energy input to the other end-uses is considerably smaller than these. The dominant energy input to process heating is fuel, steam and recovered waste heat, while electricity is the dominant energy input to machine drive.

2.4.7. Energy end-use model of the NAICS 325120 Industrial Gas Manufacturing

Since there is insufficient information to build onsite steam and power generation for the Industrial Gas Manufacturing sector, the intermediate energy conversion efficiencies that are found for the U.S. Chemical Industry were assumed to be the same for the Industrial Gas Manufacturing sector. Therefore, those efficiencies were applied to calculate the recovered waste heat and steam production in this sector. The calculations with the revision to Figure 15 and data extracted from MECS yields Figure 22. It should be noted that there is 1 PJ unbalance for the electricity input due to the round off adjustment made on the machine drive electricity input as discussed in section 2.3.3.2.

As it is mentioned as an additional explanation to equation (4) in Section 2.3.2., the “transfer ins” are also included in purchases. Therefore, the total purchased electricity is the summation of 113 PJ purchased electricity and 4 PJ transfers in from Table 11, which gives 117 PJ.

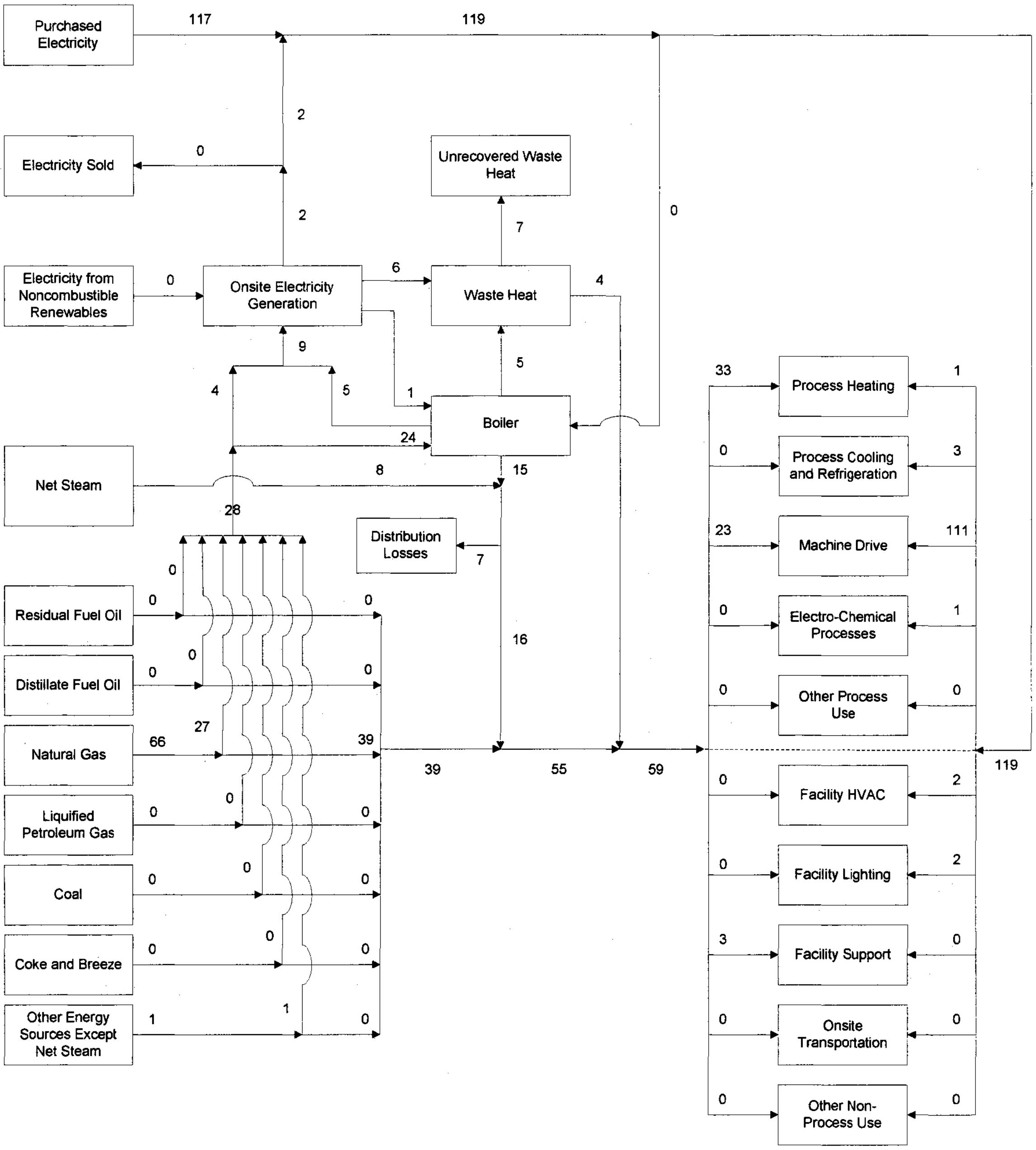

Figure 22. Energy end-use model of NAICS 325120 Industrial Gas Manufacturing in 1998, PJ

As can be seen from the energy end-use model in Figure 22, fuel input is distributed among onsite power and steam generation and end-uses. About 42% of the fuel input goes to onsite steam and power generation whereas, 58% directly goes to end-uses. All of the fuel to onsite steam and power goes to the boiler. Therefore, this subsector does not use fuel directly for power generation. Instead, power is generated onsite by the steam input from the boiler. The onsite power and steam generation model of the whole Chemical Industry, we see that Chemical Industry shows that the Chemical Industry self-generates 18% of its power requirements. The Industrial Gas Manufacturing sector contributes less than 2% of its electricity needs via onsite power generation.

Contribution of onsite electricity to end-uses is 2 PJ, which accounts for about 2% of the total electricity to end-uses. Accounting for 98% of the total electricity to end-uses, purchased electricity is the key contributor.

If we continue analyzing the energy end-use model, we see that 45% of the boiler input directly goes to end-uses, whereas 20% goes to waste heat and the rest to onsite electricity generation. We can also see that contribution of the boiler to the end-uses is bigger than that of net steam.

Although 23 PJ of energy goes to end-uses from boiler and net steam combined, 30% of this amount is lost due to distribution. Overall, 72% of the fuel and net steam input goes to end-uses.

We can see that 59 PJ is supplied to end-uses by total fuel, steam and waste heat input. On the other hand, there is 119 PJ supplied to end-uses by onsite electricity and purchased electricity combined. This shows that fuel input for onsite power and steam generation combined with net steam does not make a big contribution to the end-uses through steam production and waste heat recovery.

Among the end-uses, machine drive is the biggest energy consumer, followed by process heat. Energy input to the other end-uses is considerably smaller compared to these two. The dominant energy input to machine drive is electricity from onsite generation and purchases. For example, 111 PJ power to machine drive comes from onsite electricity generation and purchased electricity, whereas only 23 PJ comes from onsite steam, waste heat and direct fuel.

Since the Industrial Gas Manufacturing sector is dependent on electricity purchase for its electricity need, it does not sell any electricity to the grid.

We can also see that renewable energy sources does not have any contribution to total onsite electricity generation in this manufacturing sector.

2.5. Comparison of the results with previous studies

In this section, a comparison of the results provided in section 2.4 with other studies in literature will be given. The first comparison is the prime mover efficiencies found in this study vs. prime mover efficiencies presented in literature. The next comparison is the methodology used in this study and the methodologies used in earlier energy end-use models. Finally a comparison between the energy end-use model results of this study and the earlier studies will be given.

2.5.1. Prime mover efficiencies

2.5.1.1. Electric conversion efficiencies

The comparison of the electric conversion efficiency results of this dissertation with other studies appearing in the literature is summarized in Table 21.

Table 21. Comparison of the electric conversion efficiencies with other studies

Prime mover	This study	EPA	Martens	Poullikkas	Hepbasli and Ozalp	Borbely and Kreider
ICE	35%	31% - 39%	NA	NA	NA	34% - 41%
Gas turbine	27%	22% -37%	<30% - 40%	22% - 44%	29% - 31%	NA
Steam turbine	13%	<10% - 37%	NA	NA	NA	NA
Combined cycle	33%	NA	NA	<58%	NA	NA

For internal combustion engines, an EPA report gives electric efficiency values in the range of 30.6 to 39% for five different plants in the size between 100kW to 5MW (ENG, 2002). The internal combustion engines electricity conversion efficiency given in this dissertation, which relies on actual operation values from about 500 plants, lies within the range of the EPA report. This shows that, although EPA report focuses on only five plants, the selection of these plants do provide a very close estimation of actual efficiency values in the Chemical Industry. Borbely and Kreider report that ICE electric conversion efficiencies "range from 34% in small units to 41% in larger installations." (Borbely and Kreider, 2001). Another study that reports ICE electric conversion efficiency is that of Barelli and Bidini (2005). Although the 36.1% efficiency that they give is very close to the efficiency determined in this dissertation, the 35% average CHP internal combustion engine electric efficiency given in Bidini et al. (1998) is closer to the value provided in this dissertation. Finally, another EPA report gives an electric efficiency range for CHP internal combustion engines between 27% and 45% (EPA-CHP, 2005) which is close to the 28% to 39% range given in Onovwiona and Ugursal (2005).

As for the gas turbine CHP efficiencies, Martens states that the electric efficiency ranges from less than 30% up to 40% for systems that have capacities between 10 and 40MW (Martens, 1998), which are similar to the values given by Pilavachi (2000). On the other hand, an EPA report provides electric efficiencies for 1- 40 MW CHP gas turbines to be between 21.9 to 37% (ENG, 2002). Poullikas (2005a) reports gas turbine electric efficiencies in the range of 22% and 44%. Finally, Hepbasli and Ozalp (2002) give gas turbine electric conversion efficiencies for a manufacturing plant, which has two gas turbines, as 30.5% and 28.7%. Although the efficiencies reported in these studies lie within the actual gas turbine electricity conversion efficiency for the Chemical Industry, it should be noted that none of these studies represent the whole Chemical Industry. This argument also applies to the EPA report mentioned above. Therefore, the results provided by these studies are very close estimates but not an actual representation of the U.S. Chemical Industry.

For steam turbines, an EPA report states that electrical efficiency of steam turbines varies from a high of 37% for large electric utility plants designed for the highest practical annual capacity factor, to under 10% for small and simple plants, which make electricity as a byproduct of delivering steam to processes or district heating systems (ENG, 2002). This EPA result also lies within the actual steam turbine electricity conversion efficiency of the Chemical Industry. However, once again, the results given in this EPA report were made based upon a few plants that are not part of the Chemical Industry.

Finally, Poullikkas (2004) states that the combined cycle efficiencies have "increased from 40% in 1970 to the state-of-the-art machines of today with efficiencies between 55 and 58%." Since the vast majority of the combined cycles installed in the Chemical Industry are from 1970s, Poullikkas's statement may suggest that the combined cycle efficiencies in this industry are around 40%. The efficiency values given in Poullikas (2004) agree with the other values which appear in literature (Kakaras et al., 2004; Chuang and Sue, 2005; Franco et al., 2004; Marbe et al., 2005), whereas a 33% "average efficiency for power production systems that in U.S." is given in Cardona and Piacentino (2005).

In conclusion, the electric conversion efficiency estimates found in the literature for internal combustion engines vary between 31% to 41%, whereas it varies from 22% to 44% for gas turbines, 10% to 37% for steam turbines and less than 58% for combined cycles. The electric conversion efficiencies provided in this dissertation were calculated using EIA 860B data and they are within the range of estimates found in the literature.

2.5.1.2. Waste heat recovery efficiencies

Comparison of the results of this dissertation with other studies are given in Table 22.

Table 22. Comparison of the waste heat recovery efficiencies with other studies

Prime mover	This study	Jonsson et al.	Poullikkas
ICE	16%	NA	NA
Gas turbine	37%	33%	NA
Steam turbine	57%	NA	NA
Combined cycle	36%	NA	49% - 58%

Jonsson, et. al. (2005) report a 33% waste heat recovery efficiency for a gas turbine (Jonsson and Yan, 2005). This is relatively close to the efficiency reported in this dissertation. However, since the efficiency value given in Jonsson et al. is taken from operation performance of one gas turbine, it is quite understandable that only one value cannot represent the range of gas turbines in an industry.

Poullikkas (2005) gives a range for waste heat efficiency of combined cycles to be 49% - 58%, which is higher than the value reported in this dissertation. The efficiency range for gas turbines given by Poullikkas is based upon review of earlier studies, which rely on tests results from a few plants. Therefore, the results given in that article does not represent the actual performance of an industry.

In conclusion, the waste heat recovery estimates found in the literature for combined cycles vary between 49% to 58%. There is a 33% waste heat recovery efficiency for gas turbine found in literature, whereas no information on the waste heat recovery efficiency of steam turbine and internal combustion engines came to my attention during my literature search. The waste heat recovery efficiencies provided in this dissertation were calculated using EIA 860B data and the number found for gas turbine is very close to the estimate found in literature, whereas the number for combined cycle is out of the range of the estimate found in literature.

2.5.1.3. Overall prime mover conversion efficiencies

The comparison of the results of dissertation with other studies is given in Table 23 on the next page.

Table 23. Comparison of the overall efficiencies with other studies

Prime mover	This study	EPA	Martens	Harvey et al.	Pilavachi	Najjar
ICE	45%	50%-60%	NA	NA	NA	NA
Gas turbine	54%	33%	25%-50%	55%	50%-60%	NA
Steam turbine	65%	NA	NA	NA	NA	NA
Combined cycle	46%	NA	NA	NA	NA	46%

For internal combustion engine overall efficiency, an EPA report gives CHP efficiencies as between 50% and 60% for five different plants, which has a size between 100kW to 5MW (ENG, 2002). The efficiency reported in this dissertation is lower than the efficiency range given in this EPA report. Since the results of this dissertation are for the industry as a whole, they are quite close to the EPA numbers.

For gas turbine CHP efficiencies, Martens (1998) states that waste heat recovery efficiency varies between 25 to 50% for systems with capacities between 10 and 40MW whereas Pilavachi (2000) gives values from 50 to 60%. On the other hand, Harvey et al. (1997) give a thermal efficiency value for a reheat gas turbine cycle with chemical recuperation as 54.8% (Harvey and Kane, 1997), whereas an EPA report provides a 33% efficiency. The values reported in these studies, except for the EPA study, are very close to the efficiency that reported in this dissertation. This shows that the overall efficiency for gas turbines is well predicted by those studies except for the EPA report. The reason for the EPA report not being close to the actual performance values is because of their selection of plants. If the variation in plant parameters, such as size, operation hours etc., was wide enough, then the EPA report result perhaps would be more representative.

Najjar (1996) reports an overall combined cycle efficiency that is very similar to this study. However, we see in Table 23 that the overall combined cycle efficiency is smaller than the gas turbine and steam turbine overall efficiencies. Normally, the overall efficiency for combined cycles is always greater than the individual steam and gas turbine efficiencies "because of the thermodynamic advantages of supplying heat at high temperatures and rejecting waste heat at low temperatures" (Buskies, 1996). Since gas-turbine cycles operate higher temperature than steam turbine cycles, the high temperature exhaust gases from gas turbine are used "as the energy source for the bottoming cycle such as a steam power cycle" which results in a combined gas-steam cycle with an increase in "the efficiency without increasing the cost greatly" (Cengel and Boles, 4th Edition, pg. 544). Therefore, the combined cycle efficiency given in Table 23 is not consistent with this logic. The reason for this number is more likely a mistake in the numbers given in EIA 860B database. However, although the numbers in EIA 860B may not be totally accurate, I am going to use them since it is the only place that I can find that kind of information.

In conclusion, the overall conversion efficiency estimates found in literature for internal combustion engines vary between 50% to 60% and whereas it varies between 25% to 60% for gas turbines. There is a 46% overall combined cycle efficiency found in literature, whereas no information on overall steam turbine efficiency came to my attention during my literature search. The overall conversion efficiencies provided in this dissertation were calculated using EIA 860B data and they are either within the range or very close to the estimates found in literature.

2.5.2. Energy end-use models

2.5.2.1. Comparison of the methodologies

The comparison of the methodology used in earlier energy end-use models starts with that of Giraldo and Hyman (1995) and Andersen and Hyman (2001), since these two studies are most closely related to this dissertation. Giraldo and Hyman (1995) and Andersen and Hyman (2001) used 1991 and 1994 data to construct an end-use model for the paper and steel industries, respectively. Compared to these studies, the energy end-use models presented in this dissertation not only uses more recent data, but also includes addition of several major methodological refinements. For example, these studies assumed that all cogeneration was via steam topping cycle. In this dissertation, cogeneration includes internal combustion engines, gas turbines, steam turbines and combined cycle, which reveals the details of onsite energy conversions comprehensively. Another difference between the end-use models in this dissertation and Giraldo and Hyman (1995) and Andersen and Hyman (2001) is that the end-use models in this dissertation were created by using additional federal data, which resulted in obtaining the actual energy conversion efficiencies for onsite steam and power generation. This was either assumed or taken from typical values in literature in Giraldo and Hyman's (1995) and Andersen and Hyman's (2001) end-use models. The other difference between my energy end-use model and theirs is that there is a recirculation of recovered waste heat from the process heating end-use in Giraldo and Hyman's model, which is eliminated in my model and in Andersen and Hyman's (2001) model to avoid double counting. Furthermore, while these two studies used separate boiler efficiencies for each fuel, in this study, a generic boiler efficiency was used based on literature, which is followed by a sensitivity analysis. Moreover, Giraldo and Hyman (1995) and Andersen and Hyman (2001) do not present the uncertainty involved in MECS database, whereas it is included in this dissertation. Finally, steam distribution losses were not taken into account in Giraldo and Hyman (1995) and Andersen and Hyman (2001), whereas they are included in this study by deducting 30% of the boiler steam output due to distribution loss. Although this assumption brings some uncertainty, it is still an improvement compared to 0% distribution loss assumption.

The other studies that are close to this dissertation are that of ADL (ADL, 2000) and DOE's energy footprints (EERE, 2004). The ADL energy end-use model categorizes energy sources into three components: fuel, steam and electricity without showing the type and quantity of the fuels individually. In my energy end-use models, in contrast, type and quantity of each fuel inputs are separately demonstrated. Furthermore, the allocation of each fuel to generic end-uses are also quantitatively demonstrated in the end-use models of this dissertation. In ADL end-use model, steam and electricity generation is given, but, without separately accounting for waste heat created and recovered. In my end-use models, they are individually accounted. Nevertheless, the components of steam and electricity in the ADL model has the same components of my models, e.g. purchases, transfers and on-site production. On the contrary, their allocations to specific end-uses are not shown in their diagram, but shown in a separate table. Additionally, steam distribution losses are not included in ADL's energy end-use model, whereas they are incorporated in my energy end-use model. Finally, I used 1998 data whereas ADL used 1994 data.

Energy footprints (EERE, 2004) are given for each industry as three graphical components, starting from an overview model to more specific models, whereas my end-use models give compact representation of whole industry in one diagram. The energy footprint demonstrates total energy input to generate heat and power. The model categorizes energy input into three components: fossil and biomass fuels, energy supply and utility/power plant. In my model, I divide fossil and biomass fuels inputs into: residual fuel oil, distillate fuel oil, natural gas, LPG and NGL, coal, coal and breeze, and other. My energy end-use model clearly demonstrates amount of each fuel input by type for steam and power generation and end-uses individually. A further discrepancy between my and their model is that energy supply given in energy footprint does not show the amount of purchased steam separately. As for the waste heat created and recovered, my model quantifies and demonstrates these whereas energy footprint does not. Energy footprint allocates energy input among several machine drive components, such as: pumps, fans, etc., while my energy end-use model do not. Energy footprint models also provide motor losses and system losses associated with machine drive as well as electricity generation and transmission losses based on assumptions. They also provide distribution and equipment losses as well. My end-use model does not include these losses except for steam distribution loss.

In summary, the main methodological differences in this study are:

- Cogeneration includes: internal combustion engines, gas turbines, steam turbines and combined cycle, which reveals the details of onsite energy conversions comprehensively,
- Utilization of an additional federal database, which resulted in obtaining the actual energy conversion efficiencies for onsite steam and power generation,
- Demonstration of individual fuel allocation among generic end-uses,
- Estimation of steam and waste heat allocation among generic end-uses.

2.5.2.1. Energy end-use model of the U.S. Chemical Industry

The quantitative comparison of the results with Giraldo and Hyman (1995) and Andersen and Hyman (2001) are not available because they did not perform an analysis on the Chemical Industry. However, a comparison of the results from ADL and DOE's energy footprints is given in Table 24.

Table 24. Comparison of fuels, steam, electricity and losses, PJ

		This study, 1998	**Energy Footprints, 1998**	**ADL, 1994**
Fuels	Residual Fuel Oil	53	-	63
	Distillate Fuel oil	9	-	14
	Natural Gas	2093	-	2002
	Liquefied Petroleum Gas	54	-	4
	Coal	300	-	271
	Coke and Breeze	0	-	2
	Other energy sources	464	-	432
	Total fuel purchase/consumption	2973	3299	2788
Steam	Steam generated on-site	1308	1384	1384
	Steam purchased	204	-	118
	Steam transferred	122	-	-
	Total steam used	1634	1384	1502
Recovered waste heat	Total recovered waste heat	313	-	-
Electricity	Onsite electricity generation	165	-	168
	Electricity from renewables	1	-	0
	Electricity sold	26	-	27
	Electricity purchase	635	635	563
End-uses	Process heating	1922	2272	2011
	Process cooling	83	74	59
	Machine Drive	541	490	651
	Electro-chemical processes	158	143	131
	Other process use	69	51	88
	HVAC	129	129	61
	Lighting	32		21
	Facility support	18		13
	Onsite transportation	10	5	4
	Other non-process use	4	8	4
Losses	Unrecovered heat	610	-	-
	Distribution losses	320	340	413
	Motor losses	-	27	-
	Purchased fuel losses	-	99	-

This comparison shows that the fuel consumption value presented in this study is higher than in the values given in DOE's energy footprint and ADL. The fuel consumption values in this dissertation and ADL are taken directly from the MECS Table N3.2. The reason for the difference between the values given in this dissertation and ADL is because this study models 1998, whereas ADL models 1994. As for the difference between the DOE's energy footprint fuel consumption values and the values in this dissertation: DOE's energy footprint takes the summation of all fuel inputs in the MECS Table N3.2, except for the "Net Electricity." The fuels listed in this MECS table, except for the "Net Electricity" are: residual fuel oil, distillate fuel oil, natural gas, LPG, coal, coke, and other. In this analysis, the "other" fuels are broken into:

Other = Byproducts + Net Steam + Fuels not listed separately

as it is given in equation (5) along with explanation on how to derive this equation based on definitions given in MECS. The "Other" value in the MECS Table N6.2 is 790 PJ as it can be seen in Table 12 of this dissertation. This value includes 464 PJ "Byproducts" and 326 PJ "Net Steam." Therefore, in my model, the "Other" fuels are included as "Other energy sources except net steam," which removes 326 PJ of 790 PJ to the net steam box in the model. DOE's energy footprint does not remove this 326 PJ "Net steam" value from their fuels consumption analysis: which shows 3299 PJ fuel consumption in their model whereas it is 2973 PJ in my model (3299 PJ – 2973 PJ = 326 PJ). Their not removing the "Net steam" from the fuel consumption analysis creates an unbalance in their steam analysis later on. Besides, since they show steam and fuel analysis separately, this gives an impression to the reader that "fuel analysis" includes fuels only. However, it is not. It includes "net steam", which is an energy source, but not a fuel. Moreover, when they do the steam analysis, they do not recognize that including some part of the steam consumption into their fuel analysis, creates an unbalance.

Onsite electricity generation, electricity from renewables and electricity sale values provided in this study are very close to the values given by ADL. As for the electricity purchase values, this study and energy footprints give the same value, whereas ADL shows a smaller electricity purchase in the Chemical Industry. The reason for seeing same values in DOE's energy footprint and in this dissertation is that both study take this value from the MECS Table N13.1. without making any modifications or additional assumptions. The ADL value is also directly taken from the MECS Table N13.1. but for the year 1994. It is interesting that, although MECS Table N13.1. provides both "Electricity purchased/transferred" and "Electricity sold", DOE's energy footprint only includes purchased electricity amount in their model.

The purchased steam value in this dissertation and the ADL directly come from the MECS Table N11.3. In addition to the purchased steam value, this dissertation provides the amount for "transferred steam" as it was calculated in section 2.3.3.1. ADL does not provide any information regarding transferred steam. As for the DOE's energy footprint, although purchased electricity amount is given, neither purchased steam nor transferred steam amounts are provided.

For onsite steam generation: DOE's energy footprint and ADL report the same value. DOE's energy footprint value is summation of 1228 PJ steam generation by central boiler and 156 PJ steam generation by CHP. On the other hand, ADL value comes from the following equation that they developed for onsite steam generation:

Steam generated on-site = (total fuel in – (cogenerated electricity * 4500/3412) – (conventional electricity) * 6200/3412)) * 80%.

Therefore, they found the 1312 TBtu shown in Figure 7 from:

Steam generated on-site = (1855 TBtu – (151 TBtu * 4500/3412) – (9 * 6200/3412)) * 80% = 1312 TBtu.

As opposed to ADL's "one equation" approach to solve for on-site steam generation, in my energy end-use model, I analyze on-site steam generation with a comprehensive analysis, as explained in sections 2.3.4.6.1. through 2.3.4.6.7. resulting in Figure 15. Considering the very extensive search that they do on industrial boiler efficiency, it was surprising not to see same magnitude analysis on the key part of their model.

If we further analyze ADL's on-site steam generation, we see another interesting assumption. The 1855 TBtu energy input to the boiler in Figure 7 of the ADL energy end-use model comes from this calculation:

1855 TBtu = 2644 TBtu – 34 TBtu – 755 TBtu

Therefore, they first assign the value for BLD (buildings) in Figure 7, and then they assign the value for P/A (process/assembly). Finally they assign the rest of the fuel for the on-site steam generation. The BLD value in their model is defined as summation of HVAC, Facility lighting, Facility support, Onsite transportation and Other non-process use, which are MECS non-process uses in my model. Although they define the BDL like this and although they give the fuel consumption for these components separately in their Table 7-1, they do not include these components in their model. Because, "the steam use estimated for the BLD component was assumed to be used for the heating, ventilation, and air conditioning" (HVAC), as opposed to including all of the BLD components they define (ADL, 2000). Therefore, they assume that steam is only used for HVAC in BLD and the steam amount is equal to the fuel consumption by HVAC. So, the 34 TBtu in Figure 7 comes from the MECS Table N6.2. for HVAC. As for the 755 TBtu in Figure 7, it is the summation of fuel inputs to all process/assembly components in their Table 7-1. Therefore, they include all of the process/assembly components in their analysis, which correspond to MECS non-process end-uses.

In terms of allocation of steam, ADL allocates majority of the steam to process heating and some to machine drive and other process applications, whereas I allocate steam among the end-uses by using the same fuel allocation ratio among the end-uses. ADL makes the allocation estimates "by discussion with industry experts since published data was not readily available" (ADL, 2000).

If we compare energy allocations among the end-uses, we see that my energy allocation to process heat is 64%, whereas ADL's and DOE's energy footprint's are 66% and 60%, respectively. If look at the allocation of energy to machine drive, we see that it is 18% in my model, whereas it is 21% and 25% in ADL's and DOE's energy footprint's, respectively. This shows that the energy allocation estimates made in these three models are within the similar range.

If we check the energy balances in these three models, in my model: all inputs and outputs are balanced expect for 5 PJ difference due to the small variation between MECS and EIA 860B data as discussed in section 2.2.3. The other unbalances are in the magnitude of 1 PJ due to rounding and they are negligible within the 1833 PJ total. If we look at the ADL's model energy balance, there is 1 PJ unbalance in net electricity. I believe that it is due to rounding. There is no unbalance in net demand for electricity. However, if we look at Boiler/Steam/Cogeneration (BSC) box in their model in Figure 7, 1855 TBtu is coming from fuels and 9 TBtu as electricity, which adds up to 1864 TBtu:

1855 TBtu + 9 TBtu = 1864 TBtu

If we check the outputs from the BSC box: there is 9 TBtu going to conventional electricity, 151 TBtu for cogenerated electricity and 1312 TBtu for steam generated on-site:

9 TBtu + 151 TBtu + 1312 TBtu = 1472 TBtu

As it is seen, 392 TBtu energy is missing:

1864 TBtu – 1472 TBu = 392 TBtu

This amount is actually the loss, but it is not shown in the model, which creates an unbalance around the BSC box. In the summary part of their report, they state that "the difference between the total energy into the BSC component (electricity and steam) represents losses due to boiler inefficiency" (ADL, 2000). As for the buildings and the process/assembly components, they do not show any outputs, e.g. the distribution of energy input among the process heating, machine drive etc. However, they provide that information separately in a table (Table 7-1) and the numbers in that table are balanced, except for few values which has 1 TBtu off probably due to rounding.

If we check the energy balance in the DOE's energy footprint model in Figure 8 the steam generated by central boilers and combined heat/power is shown as 1312 TBtu. However, if we look at the steam allocation among the process uses we see that it is 1055 TBtu. Therefore, 257 TBtu energy is missing:

1312 TBtu – 1055 TBtu = 257 TBtu

Since there is already 328 TBtu boiler losses shown in the model, this 257 TBtu difference cannot be boiler loss. Therefore, this amount remains as unbalanced energy. If we refer to the 309 TBtu (326 PJ) "Net steam" that they include among the fuels, there is still an unbalance in their steam distribution due to 52 TBtu missing energy:

309 TBtu – 257 TBtu = 52 TBtu

However, if we look at their model in Figure 8, there is a "Distribution losses" box. This may explain where this missing energy goes. Because there is always loss in steam distribution. Therefore, this missing 52 TBtu is more likely hidden in the distribution loss box.

As for the electricity distribution in DOE's energy footprint model, electricity allocation to processes in Figure 8 is balanced:

17 TBtu + 1 TBtu + 5 TBtu + 55 TBtu + 418 TBtu + 26 TBtu + 136 TBtu = 658 TBu

2.5.2.2. Energy end-use model of the Industrial Gas Manufacturing sector

Since there is no other energy end-use model for the Industrial Gas Manufacturing sector in literature, a comparison is not available at this point.

2.6. Summary of the results

This section summarizes the onsite steam and power generation model, and the energy end-use model results along with discussions.

2.6.1. Onsite steam and power generation model

The onsite power and steam generation model of the U.S. Chemical Industry shows how energy input is allocated among boilers and prime movers in that industry based on the actual conversion efficiencies.

The result shows that the use of ICEs for onsite power generation is negligible compared to the other prime movers. The reason for that would be: the internal combustion engines are “widely used for electric power production at locations where the total amount of power is not large” (Shepard et al., 1977, pg.85). Therefore, if the majority of the plants need more electricity than internal combustion engines can meet, it would be one of the reasons for their not installing many ICEs. Another reason could be gas turbines’ having relatively more advantageous characteristics. For example, gas turbines “do not need cooling water for operation, and are relatively transportable in smaller size. For these reasons they make excellent units for emergency or for meeting short terms peak loads." (Shepard et al., 1977, pg. 85). As for the steam turbines, they are probably preferred over internal combustion engines due to their possibility to be combined with gas turbines, which results in higher efficiency.

The results showed that waste heat recovery efficiencies are higher for steam turbines than that of ICEs, gas turbines and combined cycles. My interpretation of these results is that, because of the high ratio of steam to electricity demand in many industrial processes, many installed steam turbines may run at partial load while the boilers to which they are connected are generating steam primarily for process heat. Under those circumstances, the activity is closer to mode 5 than to mode 3. However, because there is insufficient data in 860B on this matter, I have to model all activities in which a steam turbine is present as mode 3. As a result, all the steam from the boiler must be routed through the steam turbine and recovered as waste heat before being sent to the end-uses. This modeling requirement results in lower electric conversion efficiencies and higher waste heat recovery efficiencies than if I could have modeled some of these activities as mode 5. Besides, overall it is more efficient to generate higher pressure/temperature steam, generate small amount of electricity, and then send the steam out for heating purposes. Therefore it is just to make steam for heating purposes like the University of Washington steam plant does.

Finally, since it is very crucial for energy efficiency and management perspective to identify energy losses in specific parts of the plants, the unrecovered waste heat amounts given in this model identifies the lost waste heat at the prime mover level.

2.6.2. Prime mover efficiencies

Although some of the other studies provide a very close estimate on the prime mover efficiencies, the reliability of the results provided in this dissertation is much higher than the results of other studies. Because, the results of this dissertation rely on actual operation performance of all plants in the Chemical Industry with a size bigger than 1 MW, whereas other studies rely on operation performance of few plants from various manufacturing sectors.

2.6.3. Energy end-use models

It is seen from the energy end-use models that the majority of the fuel input is used directly for the end-uses in both Chemical Industry and the Industrial Gas Manufacturing sector. Although the rest of the fuel is used to generate steam and power, most of this energy contributes to the end-uses as steam. Therefore, the purpose of fuel consumption at non-utility plants is to run their end-uses.

Power generation from the prime movers is small compared to the electricity need of these sectors and the utilization of non-combustible renewable energy sources to reduce the dependence on purchased electricity is negligible.

The majority of the fuel input for electricity production goes to the waste heat recovery tank. The waste heat recovery efficiency value in the model might suggest different processes for the recovery of waste heat or better maintenance of equipment as its contribution to end-uses could be improved. Distribution losses is another target for potential improvement.

Process heat consumes the majority of the onsite steam and the fuel to end-uses. Mass and energy balance of each process step can identify all energy losses during a process, which can lead to less energy consumption.

Another point that deserves attention in the energy end-use models is the non-electric energy consumption by machine drive. It is seen that the U.S. Chemical Industry consumes 79 PJ for machine drive, whereas the Industrial Gas Manufacturing sector consumes 23 PJ. It is seen in Figure 17 that the machine drive in this industry consumes 41 PJ of fuel. Since compressed air is required in many processes in these industries, the machines that consume fuel may be reciprocating air compressors. This kind of compressor is driven by natural gas and/or diesel. Different models of this type of compressor can be found in one of the manufacturer's website (Gardner Denver Compressors, 2005). The argument of air compressors' being reported as machine drive is supported by the ADL's statement "it is believed that machines driven by compressed air would be reported in MECS primarily as electric energy use for driving a blower or compressor." (ADL, 2000). Therefore, the machine drive fuel consumption that is reported by MECS would account for these type of compressors. Other examples of machine drives that consume fuel to produce mechanical work include diesel pumps mostly used in agriculture to pump water.

A comparison of the energy consumption for end-uses in 34 subsectors of the Chemical Industry shows that the Industrial Gas Manufacturing sector accounts for 29% of the total machine drive energy consumption in the Chemical Industry. Since the Industrial Gas Manufacturing sector is the 6th largest energy consumer subsector of the

Chemical Industry as it is stated in Chapter 1, this high fuel consumption by this industry is reasonable.

3. PROCESS FLOW DIAGRAMS OF THE INDUSTRIAL GASES

There are various manufacturing techniques used to produce a given chemical. Selecting a representative production technology for a particular chemical in this dissertation omits other techniques from consideration. Therefore, it should be noted that although the "representative" production technology is a widely used technology, it can not give a full accurate analysis because of not accounting for the other techniques. However, in order to help government, industry, academics and policy makers to grasp the present status of energy consumption in this industry, only representative production technologies will be analyzed in this study.

The representative manufacturing process flow diagrams of the Industrial Gas Manufacturing sector products are presented in this chapter. These process flow diagrams will be the basis for constructing mass and energy flow diagrams for the Industrial Gas Manufacturing sector products in Chapters 4 and 5.

The Industrial Gas Manufacturing sector has seven products: acetylene, carbon dioxide, nitrogen, oxygen, argon, hydrogen, and fluorocarbons and other chemicals not specified by kind. The representative manufacturing processes for these products are given below.

3.1. Acetylene

Acetylene (C_2H_2), which is the simplest hydrocarbon, used to be the main feedstock of the Chemical Industry before the development of petrochemistry in 1940s in the U.S. The production of acetylene in the U.S. peaked in 1960s and then decreased gradually since then. Although many technologies were used in the past, "today, only three processes remain for the commercial production of acetylene:

- The *calcium carbide route*, in which the carbide is produced electrically,
- The *arc process*,
- The *partial oxidation of natural gas*.

Other once popular processes have become uneconomical as the price of naphtha has increased." (Pässler et al., 2000). Although there is no quantitative information about the share of these technologies in commercial acetylene production, partial combustion of natural gas is mentioned as the most common technology (Kirk-Othmer, 1997; Pässler et al., 2000; Shreve et al., 1984; Brown et al., 1996; Speight, 2002; Chemical Market Reporter, 1998).

A simplified representation of this process is given in Figure 23 from Speight (2002).

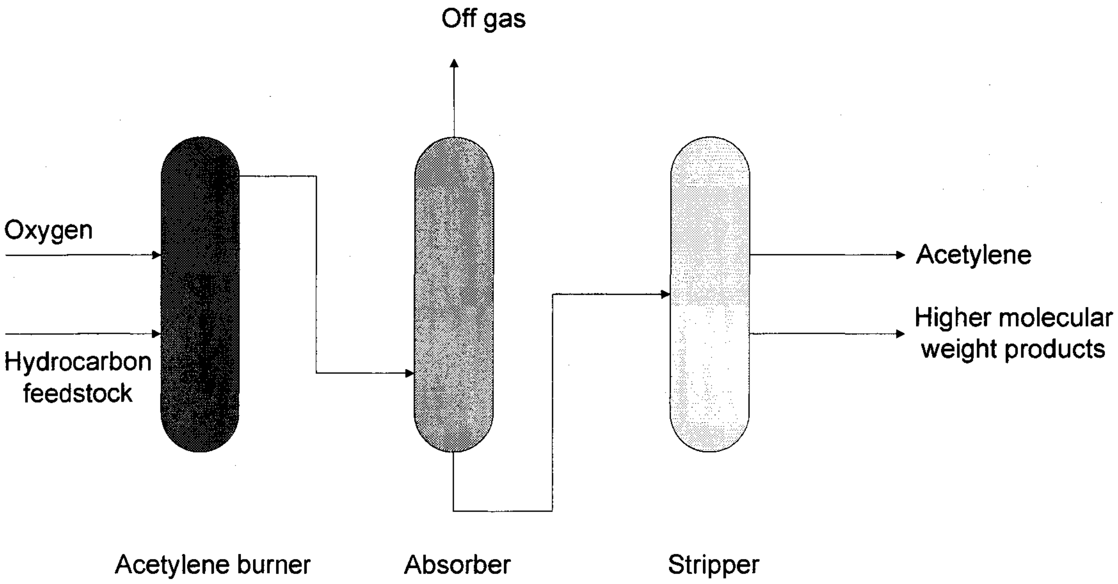

Figure 23. Acetylene production

Acetylene production described in Figure 23 starts with mixing oxygen and hydrocarbon feedstock. Hydrocarbon feedstocks used in acetylene production for partial combustion are listed in Pässler et al. (2000) as "...methane, ethane, natural gas liquids (NGL), liquefied petroleum gas (LPG), naphtha, vacuum gas oil, residues, and even coal or coke. Natural gas is especially suitable because it is available in many parts of the world and because its only other uses are for heating and for the production of synthesis gas", which is then used to produce ammonia, methanol etc. Since it is also stated in other sources that the major feedstock for acetylene production is natural gas, which is mainly methane, the oxygen in this process is mixed with methane (or natural gas) before combustion. In Figure 23, after oxygen and methane reacts in the burner, product gases which includes acetylene, are cooled by quench oil or water sprays to 38 °C. At the end of the cooling process, the product gas composition by volume are acetylene, 8 to 10; hydrogen, 50 to 60; methane, 5; carbon monoxide, 20 to 25; and carbon dioxide, <5. Soot particulars in the products are separated by filtering. Then clean gas composition is compressed to 1.14 MPa. Acetylene is separated by a selective solvent. Carbon dioxide is flashed and stripped from the solvent. Finally acetylene is fractioned out with a >99% purity by volume (Shreve et al., 1984).

Therefore, I am selecting "partial combustion of natural gas" process as the representative acetylene production technique. A more detailed discussion of acetylene production via partial combustion of natural gas, the BASF process, can be found in Pässler et al. (2000). The BASF process "is the most widely used process for the partial combustion of natural gas." Pässler et al. (2000).

3.2. Carbon dioxide

Carbon dioxide is an odorless gas which was discovered in the 16th century as a byproduct of coal combustion and fermentation. Carbon dioxide is mainly used for cooling purposes. It naturally exists in atmosphere. Commercially it is manufactured either as a recovery or as a byproduct from production of other chemicals (Pierantozzi, 2003; Kirk-Othmer, 1991; Shreve, 1984; JVP, 2004; Topham, 2000).

The major commercial carbon dioxide production processes today are (Kirk-Othmer, 1991; Shreve, 1984; JVP, 2004; Johnson Matthey, 2005):

- Recovery from ammonia production.
- Recovery from combustion products of carbonaceous fuels.
- Neutralization of acids by using limestone (calcium carbonate).
- Byproduct of fermentation process of organic substances, such as corn.
- Recovery from natural volcanic activity, geothermal sources, high concentrate carbon dioxide containing natural gas wells and oil wells.

There is no quantitative information on the share of these technologies in industry for commercial carbon dioxide production. However, qualitative information that refers to some of these technologies as “major”, “dominant”, or “most common” suggests that the most common commercial carbon dioxide production technology is carbon dioxide production by recovery from ammonia production (JVP, 2004; Kirk-Othmer, 1991; Johnson Matthey, 2005; Topham, 2000).

For example, it is stated by Topham (2000) that “much of the carbon dioxide generated in the world is a byproduct of ammonia and hydrogen production, which make much more carbon dioxide than is ever recovered". Another comparison between the commercial carbon dioxide production technologies given by Kirk-Othmer (1991) states that "more carbon dioxide is generated from ammonia and hydrogen plants than from any other source."

There are also statements in the literature that the other commercial carbon dioxide production techniques are not used widely. For example, "although the combustion of carbonaceous materials generates a large amount of carbon dioxide, this material is usually only present in the gaseous products of such reactions at concentrations of about 10%, which is considered to be too low to allow the economic recovery of carbon dioxide from such streams, and these types of emissions are not commonly used as sources of carbon dioxide" (Johnson Matthey, 2005). In another example, Topham (2000) states that "the production of carbon dioxide by the calcinations of calcium carbonate is no longer economically important".

Conversely, there is a contradictory information about carbon dioxide production via fermentation. For example, Kirk-Othmer (1991) states that "a very small percentage of commercial CO_2 is produced by fermentation". On the other hand, Topham (2000) states that "large quantities of carbon dioxide are generated by fermentation process". However, these two references agree that the most common carbon dioxide production technique is carbon dioxide as a byproduct from ammonia production.

One carbon dioxide producer, Universal Industrial Gases Inc., states that "commercial carbon dioxide typically is manufactured by separation and purification from relatively carbon dioxide rich gases produced by combustion or biological processes, whereas economically viable sources of carbon dioxide include ammonia plants and fermentation operation." (Universal Industrial Gases Inc., 2005). In addition, carbon dioxide as a byproduct from ammonia process has a very high purity before purification and liquefaction processes, whereas carbon dioxide from flue gas has a concentration of 10-18% (Topham, 2000).

According to the discussions above, although carbon dioxide from flue gas is a highly utilized carbon dioxide production technique, carbon dioxide as a byproduct from ammonia production is also a commercially significantly utilized technique. On the other hand, there is no quantitative information about which of these two techniques is used more than another. However, whichever technique is used to produce carbon dioxide in the first place, purification and liquefaction processes are applied eventually. Therefore, both ammonia production and flue gas recovery processes are followed by purification, liquefaction and solidification. Furthermore, carbon dioxide in the flue gas can be purified to the same level concentration that occurs for ammonia production. After that, purification and liquefaction of carbon dioxide is the same for both processes. impurity in ammonia production stream and the recovered flue gas stream are about the same. For these reasons, it does not matter which technique was used to produce carbon dioxide at the first place. Therefore, the representative carbon dioxide production technique is purification and liquefaction.

Table 25 provides the CIR data for carbon dioxide production in 1998 as a gas, liquid and solid. It shows that only about 2% of the total carbon dioxide production in 1998 was solid carbon dioxide.

Table 25. Carbon dioxide production in 1998, kg, (CIR, 1998)

Product	**Value**
Carbon dioxide, gas	$5.1\text{x}10^9$
Carbon dioxide, liquid	$7.4\text{x}10^9$
Carbon dioxide, solid	$2.6\text{x}10^8$

Carbon dioxide gas amount in Table 25 includes all carbon dioxide that is not vented "regardless of whether or not it will be used as a gas or to make liquid in this plant or in any other plant" (Census, 2004). It also "excludes amounts produced and consumed in the manufacture of urea and soda ash" (Census, 2004).

Liquid carbon dioxide production amount given in Table 25 covers "all liquid carbon dioxide produced including liquid that will be used to make dry ice" (Census, 2004). On occasion, carbon dioxide gas is purchased from another plant to make liquid carbon dioxide. In this case, only the liquid carbon dioxide produced is reported by the plants since the carbon dioxide gas is reported by the carbon dioxide gas producer (Census, 2004). Therefore, the liquid carbon dioxide is not necessarily made from purchased gas only. Sometimes they produce liquid carbon dioxide directly, e.g. converting the carbon dioxide gas into liquid immediately. So there are two ways of producing liquid carbon dioxide:

- Purchase gas from other plants and liquefy it,
- Produce gas at the plant but immediately convert it into liquid.

The second way of making liquid carbon dioxide is not same as the carbon dioxide gas statement above, which says that "regardless of whether or not it will be used as a gas or to make liquid in this plant or in any other plant". "Gas" producers measure the amount of "gas" that they produce. However, in the second way of carbon dioxide making, producers do not record the gas that they produce. These producers make liquid from gas. This explains why the liquid carbon dioxide production amount in Table 25 is bigger than the carbon dioxide gas amount. If all of the liquid carbon dioxide was made from the carbon dioxide gas, then carbon dioxide liquid and carbon dioxide gas numbers in Table 25 had to be the same. But, some carbon dioxide gas is used as a gas and some used to make liquid carbon dioxide. So not all of the carbon dioxide gas is consumed for liquefaction. And liquid producers make their own gas to be used to make liquid straight away.

As for the dry ice amount in Table 25, it includes "all dry ice and pellets produced" (Census, 2004). If liquid is purchased from another plant to make dry ice, the dry ice maker plant reports only the dry ice produced, because the liquid carbon dioxide is reported by the liquid carbon dioxide producer.

3.2.1. Carbon dioxide purification and liquefaction

Carbon dioxide purification and liquefaction process steps for carbon dioxide recovered from flue gas can be summarized from EG&E (2002):

- Cooling to remove water,
- Scrubbing out the impurities in condensed water, e.g. amine, ammonia etc.,
- Removal of residual sulfur compounds,
- Removal of moisture and oxides of nitrogen,
- Capture of mercury via adsorber,
- Compression for liquefaction.

These process steps will be used to construct national scale carbon dioxide purification and liquefaction material flow model in Chapter 4.

3.2.2. Carbon dioxide solidification

Solid carbon dioxide is produced by lowering the temperature below the triple point. It can be done by allowing the liquid carbon dioxide to expand to atmospheric pressure (Kirk-Othmer, 1991; Topham, 2000). Solid carbon dioxide formed in this manner is called "snow". The "snow" is then compressed into 10-25 kilograms blocks. Since "it continually sublimes even in well-insulated containers, solid carbon dioxide is rarely stored at the point of manufacture, but it is made and distributed on demand." (Topham, 2000).

The process steps of solid carbon dioxide can be listed as follows, based on the process definition given in Topham (2000) and Kirk-Othmer (1991):

- Liquid carbon dioxide is piped from the liquid storage facility,
- Liquid carbon dioxide is allowed to expand,
- Solid carbon dioxide "snow" forms along with some carbon dioxide gas during expansion,
- Solid carbon dioxide is compressed as a large block by a hydraulic press,
- Large block of solid carbon dioxide is conveyed on a belt to an automated system of band saws,
- The block is cut into smaller pieces.

Regarding the solidification process of carbon dioxide, there is no quantitative information about how much of the carbon dioxide vaporizes or is lost during the compression and storage process. Therefore, the material flow model will not include the solidification process for carbon dioxide.

According to the solid carbon dioxide production amount given in Table 25, excluding the carbon dioxide solidification process results in 2% lost in the overall carbon dioxide production material flow model. Therefore, carbon dioxide solidification will not be included into the material flow models part of this dissertation. However, since the energy consumption is not necessarily related to the production amount, the solidification process will be included in the carbon dioxide energy process-step model in Chapter 5.

3.2.3. Summary

We can summarize the discussions above as follows:

- There are two major carbon dioxide production technologies: byproduct from ammonia production and recovery from flue gas. No matter which of these techniques is used to produce carbon dioxide, the purification and liquefaction of carbon dioxide is the same for both processes. Therefore, "purification and liquefaction" was selected as the representative carbon dioxide production process regardless of whether the source of the CO_2 is ammonia or flue gas,
- Solidification will not be included in the material flow model analysis since its production amount is negligible relative to carbon dioxide gas and liquid carbon dioxide production,

- Solidification will be included in the energy process-step model analysis since it may require significant energy consumption although the production amount is small.

3.3. Nitrogen and Oxygen

Nitrogen and oxygen are both extracted from air either cryogenically or non-cryogenically. Cryogenic technique means that processes occur at low temperature, e.g. <120 K. On the other hand, non-cryogenic air separation processes "use physical property differences other than boiling point to produce commercially valuable gaseous products" (Industrial Gases Inc., 2005).

Häussinger et al. (2000) states that "Nitrogen is obtained from air. The processes used to separate nitrogen from air can be classified as:

- Cryogenic processes,
- Adsorption processes,
- Membrane separation.

Older methods, such as the chemical removal of oxygen from air, are of second importance." For oxygen production, Kirschner and Hill (2000) gives the current technologies as:

- Oxygen from cryogenic air separation,
- Oxygen from adsorptive air separation,
- Oxygen from membrane air separation.

An example nitrogen and oxygen production process via liquefaction of air is given in Figure 25 from Speight (2002).

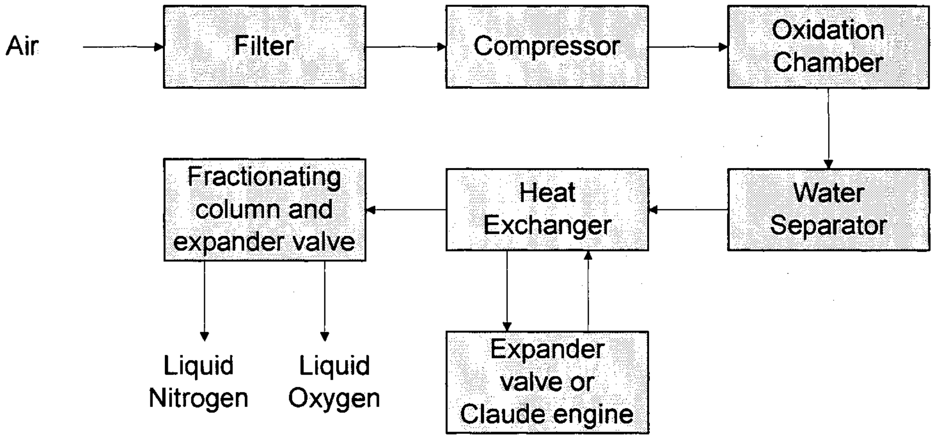

Figure 24. Nitrogen and Oxygen production by liquefaction of air

In Figure 24, the first step requires filtration of air to remove particulates. In the second step, filtered air is compressed to 77 psi. Compressed air then goes to oxidation chamber for conversion of traces of hydrocarbons into carbon dioxide and water. After this process step, air goes into a water separator for the removal of some of the water. In the next step, air is cooled down to -196 °C through the heat exchanger. This process converts the rest of the water into ice. Carbon dioxide solidifies as well. Solid water and carbon dioxide are then separated from the main components. Now the nitrogen-oxygen mixture at -168 °C and 72 psi enters the fractioning column. In this process, an expansion valve causes the temperate to drop further. Now the column temperature is -190 °C. Since the boiling point of nitrogen (-196 °C) is lower than the boiling temperature of oxygen (-183 °C, nitrogen rises in the column which finalizes the separation of these two gases (Shreve et al., 1984).

More detailed explanations on nitrogen production from cryogenic separation of air can be found in Häussinger et al.(2000a), Hardenburger and Ennis (2005), and Barron

(2000). A very thorough explanation of nitrogen production using membrane separation of air can be found in Häussinger et al. (2000a) and Hardenburger and Ennis (2005). The summary of the processes given by Häussinger et al. (2000a) and Hardenburger and Ennis (2005) is given in Chapter 5 of this dissertation for the purpose of analyzing their energy requirements.

As for oxygen production, a very comprehensive description of oxygen production via cryogenic air separation can be found in Kirschner and Hill (2000), Hansel (2005), Agrawal et al. (2003) and Barron (2000). Alternatively, a comprehensive explanation of non-cryogenic air separation process can be found in Hansel (2005). A summary of these processes are given in Chapter 5 of this dissertation for the purpose of analyzing their energy requirements.

There is a lack of consensus in the literature regarding which of these technologies dominate commercial nitrogen and oxygen production. For example, Kirk-Othmer (1991) states that "oxygen and nitrogen are produced principally by the liquefaction of air." This statement is supported by Dillion (1992) and Shreve et al. (1984) as well. The oxygen and nitrogen production technique presented in the Drexel oxygen and nitrogen production model is also liquefaction of air, which further supports the argument of major commercial nitrogen and oxygen production technology. Moreover, the Chemical Market Reporter states that "the U.S. market for industrial gases has been traditionally been dominated by cryogenic production technology. This technology has been used to produce large volumes of liquid gases and to achieve high purities" (CMR, 1997). It is also stated in the same article that "there has always existed a market for gases produced by non-cryogenic methods, which was, however, very small as a percentage of the overall industrial gas market." The article furthermore reports that non-cryogenic technologies are usually practiced for specialized cases, where small quantities are needed and high purity is not demanded.

On the other hand, Current Industrial Reports states that non-cryogenic nitrogen production by Industrial Gas Manufacturing sector in 1998 was 65% of the total nitrogen production (CIR, 1998b). Similarly, it is reported that non-cryogenic oxygen production by Industrial Gas Manufacturing sector in 1998 accounted for 76% of the total oxygen production (CIR, 1998b).

Another source that provides information about non-cryogenic nitrogen and oxygen production is Speight (2000). However, this reference provides both cryogenic and non-cryogenic production techniques as characteristic nitrogen and oxygen production without stating which technology is dominant.

Koros and Mahajan (2000) state that "the majority of nitrogen and oxygen are produced by cryogenic distillation of air." This article also states that oxygen separation membranes would be commercially attractive if a separation factor is increased via technological developments. As for nitrogen production, this article reports that "it is estimated that membranes currently produce 30% of all gaseous nitrogen." However, they do not provide any information about the basis for this estimation.

Hardenburger and Ennis (2005) claim that "industry estimates indicate that non-cryogenic separation will eventually account for greater than 30% of all commercial nitrogen production." This statement was based upon a reference and it agrees with Koros and Mahajan's (2000) statement.

The information on commercial membrane technology utilization given by Rautenbach et al. (1998) states that "the market share of membrane technology is tremendously growing and is projected to increase to over 10% of the total nitrogen market by the year 2000." They make this assessment based on information given in another published article. However, the estimate made in this article conflicts with the estimate made by Koros and Mahajan (2000) and Hardenburger and Ennis (2005).

Häussinger et al. (2000a) also states that the most important nitrogen production techniques are cryogenic and non-cryogenic (membrane). However, it does not provide any information about which technology is commercially more dominant.

Similarly, Strathmann (2005) states in his reviews article on membranes and membrane separation processes that "today, membranes are used on a large scale to produce potable water from seawater, to clean industrial effluents and recover valuable constituents, to concentrate, purify, or fractionate macromolecular mixtures in the food and drug industries, and to separate gases and vapors", which indicates the large scale utilization of membranes to separate gases. However, it does not provide quantitative information on commercial application of membranes for nitrogen and oxygen production.

Another review article on the membrane usage in gas separation states that "the most important large application of carbon membrane is in the production of low cost and high purity nitrogen from air." (Ismail and David, 2001). This statement still does not give precise information on percentage of the industry generating nitrogen via membrane technology.

Kirschner and Hill (2000) provide detailed information about oxygen production via cryogenic and non-cryogenic technologies. Although this article does not provide information about the commercially dominant technique, it uses Current Industrial Reports as a reference to show oxygen production trends in the United States.

Consequently, there is conflict and lack of precise quantitative information on dominant commercial nitrogen and oxygen production technology in the literature. Since the information provided in CIR are collected from the manufacturers themselves, it is reasonable to assume that the information provided in this source would be close to the actual situation.

According to the CIR, non-cryogenic processes utilized by Industrial Gas Manufacturing plants are: membranes, psa (pressure swing adsorption), vpsa (vacuum pressure swing adsorption) etc. However, the information about the share of these technologies is not provided in this source. Therefore, we do not know which of these techniques is utilized dominantly.

In conclusion, based on the discussions above, I am selecting "cryogenic separation of air" as representative cryogenic nitrogen production technique. As for the non-cryogenic nitrogen production, I am choosing "membrane" as representative non-cryogenic nitrogen production technique.

In addition, based on the discussions above, I am selecting "cryogenic separation of air" as representative cryogenic oxygen production technique. As for the non-cryogenic oxygen production, I am choosing "membrane" as representative non-cryogenic oxygen production technique.

More discussions on cryogenic nitrogen and oxygen production can be found in Section 4.4.3.1.

3.4. Argon

Argon and other rare gases (neon, krypton, and xenon) are produced commercially as byproducts from large cryogenic air separation plants (Speight, 2002). Since argon is of particular interest of this dissertation the following discussion focuses on argon, although the process includes production of all other rare gases.

The argon production statement made by Speight (2002) is supported by Agrawal et al. (2003), Hwang et al. (2005), Speight (2002), Brown et al. (1996), Kirk-Othmer (1991), and Praxair (2005).

Argon is produced as a byproduct in cryogenic air separation plants by distillation of liquid air performed in a double-column arrangement. It is produced in side columns operated in conjunction with the standard double-column plant (Speight 2002, Shreve et al., 1984. A simplified process flow diagram for argon production via double-column distillation is given in Figure 25.

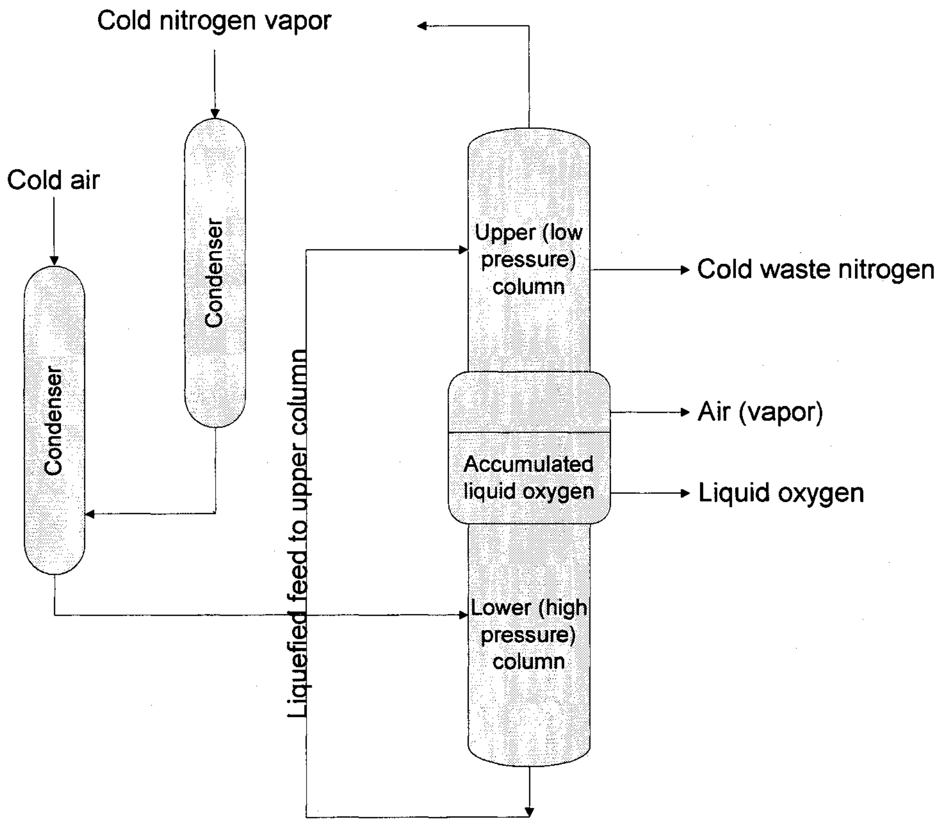

Figure 25. Argon production

The boiling temperature of argon is lower than oxygen. Therefore, argon concentration increases in the upper column which is above the oxygen product level. The next step is to withdraw the crude argon product from the top of the column. At this stage, the crude argon includes oxygen and nitrogen. In order to remove oxygen from the argon, hydrogen is added followed by catalytic combustion; the resulting water is removed by drying the gas. In order to remove nitrogen from the argon, another distillation step is required. After completing removal of oxygen and nitrogen, argon having a purity of 99.99% is obtained (Shreve et al., 1984).

In conclusion, I am selecting "cryogenic air separation" as representative commercial argon production technology. More discussions on argon production can be found in Section 4.4.3.1.

3.5. Hydrogen

Existing commercial hydrogen production techniques are:

- Steam reforming of natural gas,
- Partial oxidation of coal, coke, or residue.

(Baade et al., 2001; Padró and Keller, 2005; Häussinger et al., 2000b; Kirk-Othmer, 1997; Shreve et al., 1984; Brown et al. 1996; Speight, 2002).

Padró and Keller (2005) state that "Steam methane reforming is widely used, especially in the United States, to provide high purity hydrogen to the chemical, petrochemical, and refining industries." In addition, Häussinger et al. (2000b) states that "most of the hydrogen for industrial uses is produced from natural gas and oil, either as a main product or as a byproduct, a process involving a chemical conversion." Moreover, Muradov and Veziroglu (2005) report that "currently, most of the industrial hydrogen production is based on steam methane reforming." Koroneos et al. (2004) also state that "most of the hydrogen (97%) is made by steam reforming of natural gas, which is mainly methane and other fossil fuels. Another justification of steam reforming of natural gas as a dominant commercial hydrogen production was the statement that "the most common method for hydrogen production is steam reforming of natural gas" by Spath and Mann (2001). Therefore, based on these statements, it can be assumed that the dominant hydrogen production is steam reforming of natural gas.

A simplified flow diagram of steam reforming process of hydrocarbon feed stock is given in Figure 26 (Speight, 2002).

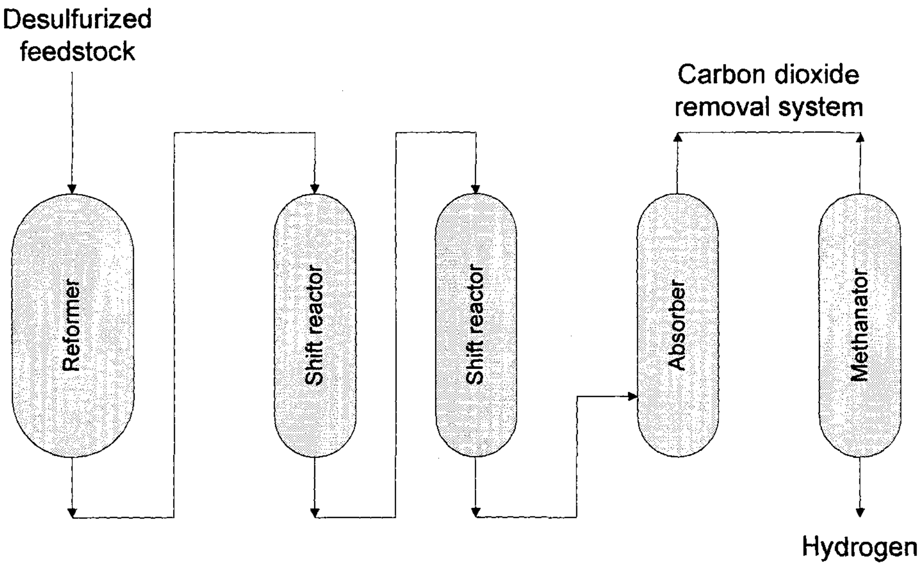

Figure 26. Hydrogen production via steam reforming of natural gas

The first step is desulfurization of the hydrocarbon feedstock by heating to 370 °C. In this step the presence of a metallic oxide catalyst is required in order to convert the organosulfur compounds to hydrogen sulfide.

The next step is steam addition and heating the mixture to 760 – 980 °C and 600 psi over a nickel catalyst. Air is added into the reformer (in the case of having both primary and secondary reformers, air can be added into second reformer). Temperature is maintained high by reaction between oxygen of the air and some of the hydrocarbon. Before the mixture enters into the shift reactor, more steam is added. In the shift reactor, more hydrogen and carbon dioxide is produced via chromic oxide catalysts at 425 °C.

The next step is to cool the mixture to 38 °C. The cooled mixture then enters the absorber where carbon dioxide is absorbed. After this step, carbon dioxide left over from the previous step enters the methanator where carbon dioxide is converted to methane (Shreve et al., 1984).

In conclusion, based on the discussion above, I am selecting “steam reforming of natural gas” as representative commercial hydrogen production technique.

3.6. Fluorocarbon gases

Fluorocarbon gases are composed of carbon, fluorine, and chlorine with either a small amount of hydrogen or no hydrogen. The most common fluorocarbon manufacturing technology is by reacting chlorinated hydrocarbons with anhydrous hydrogen fluoride (Shreve et al., 1984; Speight, 2002; Dillon, 1992).

A simplified fluorocarbon gas production process is given in Figure 27 (Speight, 2002).

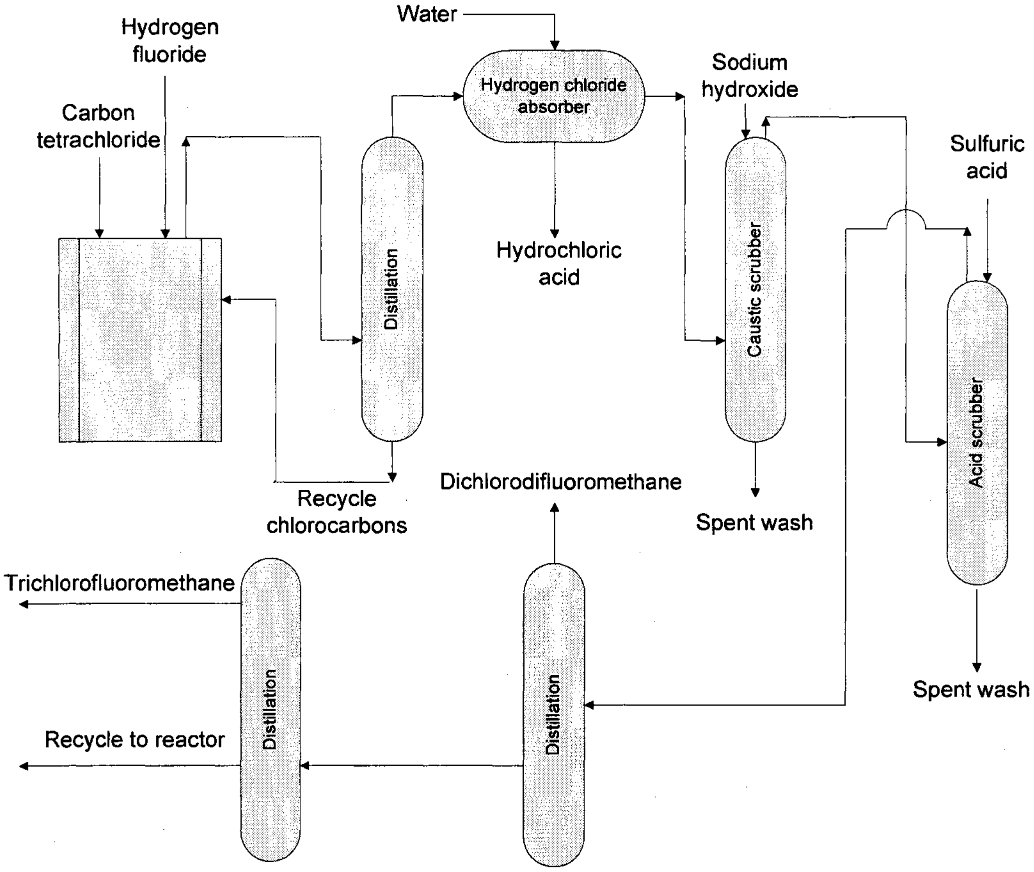

Figure 27. Fluorocarbon production

The manufacturing process starts with bubbling anhydrous hydrogen fluoride and carbon tetrachloride through molten antimony pentachloride catalysts in a reactor. The temperature in this atmospheric pressure reactor is between 65 °C and 95 °C. The next step is distillation of the gaseous mixture which contains fluorocarbon and unreacted chlorocarbon. The distillation process separates and recycles the chlorocarbon. Via absorption of water, the waste hydrogen chloride is recycled. In the next step, the mixture enters a caustic scrubber where the last traces of hydrogen chloride and chlorine are removed. After this step, the purity is increased by scrubbing with sulfuric acid. Finally, dichlorodifluoromethane and trichlorodifluoromethane is produced after distillation (Speight, 2002). Discussions on fluorocarbon production can be found in Section 4.4.5. in more detail.

3.7. Summary of the results

We can summarize the findings in this chapter based on the information and the discussions given. First of all, since there are more than one process designs to manufacture a chemical, selection of a representative process or technology disregards the other process designs from consideration. Therefore, it should be noted that although the "representative" production technology is a widely used technology, it cannot give a full accurate analysis of the whole industry or sector because of not accounting for all of the utilized techniques. Based on this argument, we can give a concise list of the findings in this chapter as follows:

- "Partial combustion of natural gas" process was selected as the representative acetylene production technique,
- "Carbon dioxide production as recovery from flue gas" was selected as the representative carbon dioxide production technique,
- "Cryogenic separation of air" was selected as the representative cryogenic nitrogen and oxygen production technique,
- "Membrane" technology was selected as the representative non-cryogenic nitrogen and oxygen production technique,
- "Cryogenic separation of air" was selected as the representative argon production technique,

- "Steam reforming of methane" was selected as the representative hydrogen production technique.

Since the literature search in Section 3.2. showed that there are two main carbon dioxide production techniques, selection of a representative carbon dioxide production technique leaves out the other main carbon dioxide production technique from the analysis. Although there is no satisfying data on the non-selected carbon dioxide production technique that fits for the purpose of this dissertation, not including it into the analysis reduces the accuracy of the analysis. However, once there is data on that technology, it can be added into the analysis. This would be a good research topic for someone else in the future to provide a more complete analysis on carbon dioxide production on a national scale.

4. MATERIAL FLOW MODELS

A material flow model represents mass inputs and outputs for an industrial process. It is created based on a mass balance for each step of an industrial process. Once a material flow for each process step is created for an industrial process based on unit mass, that material flow model can be scaled against national data by using national data on product output. This provides an overall national picture of material inputs and outputs for an industrial process.

"The need to collect material flows information to support national security decisions may be self-evident, but other uses of material flows information are also important perhaps less obvious. Analysis of material flows data have prevented technologies that would severely strain material availability (e.g., the contemplated switch from tin-lead solder to a formula using bismuth and indium) from moving forward. Analyses of material flows data have also led to surprising and counterintuitive insights into environmental pollutants." (National Research Council, 2004).

Material flow models represented in this chapter were developed based on the representative commercial production processes selected in Chapter 3. Majority of the representative commercial manufacturing techniques were taken from the Drexel models (Brown et al., 1996). The Drexel models "incorporate appropriate level of detail which was prepared as part of a comprehensive energy analysis and is available without violating confidentiality of information for a given plant" (Wang et al., 2004).

Relevant efforts to create material flow models for manufacturing industries were done by Giraldo and Hyman (1996) for the paper and paperboard industry and Andersen and Hyman (2001) for the steel industry. Although the data used in these studies was updated, the industrial processes were based on the Drexel models.

Another study that develops a material flow model for manufacturing a product first discusses "the major process used to produce ethylene and its co-products, followed by a discussion of the U.S. Petrochemical Industry" (Worrell et al., 2000). Their process flow diagram is taken from Phylipsen et al. (1998) and it is not scaled against national production data.

A further study similar to my dissertation in terms of developing a material flow model is based on Drexel model of the U.S. Petroleum Refineries sector (Wang et al., 2004). In their results, they give mass-based process allocation by final product per unit mass. Their results include mass, energy intensity for each product manufactured in Petroleum Refineries sector. In addition, their study includes market value-based process energy allocation for unit mass product manufactured, which provides an economic perspective into the analysis.

Finally, the scope of a task given to the National Research Council by DOE, EPA, NSF and U.S. Geological Survey is similar that of this dissertation. The main objective of the task given to National Research Council was to establish a committee to address the material flows accounting issues for improved public policy making. The objectives of this committee, listed below by quoting from their publication, reveal the similarity of their scope to this dissertation (National Research Council, 2004):

- "Examine the usefulness of creating and maintaining material flows accounts for developing sound policy on environment, materials and energy",

- "Evaluate the technical basis for materials flow analysis",
- "Assess the current state of material flows information, including what data are collected, where they reside, quality, scale, completeness of data; formats; accessibility, and the tools and methods available for analyzing the data",
- "Describe how the public and private sectors are currently using this information and how material flows accounts can be improved through partnerships or access to additional data"
- "Determine who should have institutional responsibility for collecting, maintaining, and providing access to additional data for material flows accounts."

Although the National Research Council committee's objectives are broader than the scope of this dissertation, there are several common objectives such as: assessment of material flow analysis, addressing the data related issues and serving for improved policies.

One of the outcomes of the National Research Council research states that "The committee concludes that there are some good sources of data relevant to material flows, but the data are not yet adequate to populate formal material flows accounts. The committee further concludes that these inadequacies impede the develop of sound public policy and business decisions. The committee recommends that a national-level effort be initiated to identify and fill significant data gaps that presently impede the development of effective material flow accounts." (National Research Council, 2004). The report by this committee repeatedly addresses the inadequacy of data on material and stresses the importance of fulfilling this gap. This shows that the data availability problem exists for materials as well. Their report also discuss the challenges of doing research on material flow analysis.

It should be noted that since energy process-step models are based on energy inputs to each process step, most of the discussion above is also valid for the energy process-step models that are covered in Chapter 5.

4.1. Materials data

In order to obtain a national scale representative material flow model, data on material inputs and outputs for each of the representative production processes given in Chapter 3 must be obtained. Once the data is collected for each representative processes for unit mass production of each industrial gases, these models then can be scaled against the national data on material production. For example, the representative acetylene production technique selected in Chapter 3 is partial combustion of natural gas. After the selection of this technology as "representative", material inputs and outputs data for each process-step of this representative technology must be found in the literature. For instance, the Drexel model given for unit acetylene production shows all material inputs and outputs of each steps of acetylene production process. Since this model is given for unit mass acetylene production, it can be scaled against the national data using the federal industrial gas production data for acetylene in Table 4 of Chapter 1.

The sources of useful data on national material production and data associated problems are discussed in the following sections.

4.1.1. Economic Census

The most comprehensive data on material production for manufacturing processes is federal data called Economic Census, published every five years, ending in 2 and 7, by the U.S. Census Bureau. "The Economic Census is the major source of facts about the structure and functioning of the Nation's economy. It provides essential information for government, business, industry, and the general public." (Economic Census, 1999). This database is organized using NAICS. In the relevant Economic Census reports, data on value of product shipments and/or production is given in Table 6a (Census-3251A, 1997), whereas data on material consumed is given in Table 7 (Census-3241, 1997). Some of the data is given in dollars and others are given in terms of physical output.

The specific uses of the Economic Census can be listed as follows (Economic Census, 1999):

- "Policy making agencies of the Federal Government use the data to monitor economic activity and assess the effectiveness of the policies",
- "State and local governments use the data to assess business activities and tax bases within their jurisdictions and to develop programs to attract business",
- "Trade associations study trends in their own and competing industries, which allows them to keep their members informed of market changes"
- "Individual businesses use the data to locate potential markets and analyze their own production and sales performance relative to industry or area averages".

The standard errors of the data are given as "A", which means a standard error of 100 percent or more, and "s" means that sampling error exceeds 40 percent. The data which does not meet quality standards are withheld and denoted by "S". Therefore, standard errors in the Economic Census database are defined differently than in MECS.

For further information about the Economic Census "scope, coverage, classification system, data items, and publications for each of the economic censuses and related surveys is published in the *Guide to the 1997 Economic Census and Related Statistics* at www.census.gov/econguide." (Economic Census, 1999). As for the further information on the methodology, procedures, and history of the censuses, one can refer to "*History of the 1997 Census* at www.census.gov/econ/www/history.html." (Economic Census, 1999).

4.1.2. Annual Survey of Manufacturers

The Annual Survey of Manufactures (ASM) is also conducted by the Census Bureau and it gives statistical data similar to the Economic Census. However, it is not as detailed and not as accurate since it uses a smaller sample. Therefore, "there are selected statistics not included in the ASM. Among these are the number of companies and establishments, detailed product and material data, and substate geographic data" (ASM, 1998). ASM database is published every year between the Economic Census.

"The ASM sample is selected at 5-year intervals beginning the second survey year subsequent to the census" (ASM, 1998). For example, the 1998 "sample was selected from the 1992 census and has been used since 1994. A new sample will be introduced for the 1999-2003 surveys" (ASM, 1998).

4.1.3. Current Industrial Reports

Current Industrial Reports (CIR), another publication of the Census Bureau, provides another good source of data. It gives production and shipments data for the selected manufacturing industries in textiles and apparel, chemicals, primary metals, computer and electronic components, industrial equipment, aerospace equipment, and consumer goods. The Economic Census "provides a complete list of all producers of the products covered by the CIR program and serves as the primary source for CIR sampling" (Economic Census, 1999). CIR is published every year at the U.S. level, whereas in some cases it is published quarterly or monthly. In this database, although some industries are covered each year, some of the industries are not covered every year. "When detailed product data are collected in the CIR, they are not also collected in census" (Economic Census, 1999).

4.1.3.1. Reliability of the Current Industrial Reports database

The possible errors in the CIR database are listed in CIR (1998b) as follows:

- "Inability to obtain information about all cases in the survey",
- "Response errors",
- "Definitional difficulties",
- "Differences in the interpretation of questions",
- "Mistakes in recording or coding the reported data",
- "Other errors of collection, response, coverage, and estimation".

CIR states that "although no direct measurement of the biases due to these nonsampling errors has been obtained, precautionary steps were taken in all phases of the collection, processing, and tabulation of the data in an effort to minimize their influence" (CIR, 1998b). Therefore, although an effort is made to minimize the nonsampling errors, the CIR database involves some errors.

4.1.4. Private Sector database

Trade associations and publications provide lots of information and data. Such data may not be compatible with the U.S. Census Bureau data. One reason for incompatibility can stem from trade associations collecting data on the activities of members who may be classified in different NAICS. Even in the case of a classification system that agrees with NAICS, the membership may not be a statistically valid random sample of the industry.

On the other hand, there are cases where a good correlation exists between private data sources and the data from government sources. For example, Chemical and Engineering (C&E) News uses an industry classification similar to NAICS. However, C&E News does not break the industry into subsectors; however, NAICS does. For instance, inorganic chemicals are classified as "Inorganic Chemicals" according to C&E News, whereas they are broken into two subsectors according to NAICS, namely; "Inorganic Chemicals Manufacturing" and "Industrial Gas Manufacturing".

Other private sector databases that include the chemical industry are Chem-Intell: Chemical Manufacturing Plants, North American Chemical Processing database, and Major Industrial Plant database, which were discussed in Chapter 2. These databases are proprietary and require a fee for access. Therefore a study using these private databases would not allow the reader to duplicate the analysis done in that study.

4.2. Issues with data

The problems associated with the available data are described in the following sections. An approach to solve these problems before integrating the data into a material flow model is given in Section 4.3.

4.2.1. Input and outputs

The Economic Census provides good data on raw materials consumed and product shipments. For the purposes of my modeling, I am interested in material production data.

Not all of the raw materials acquired in a given year are converted into a finished product during the same year. Also, not all of the finished products are shipped in the same year in which they are produced. Some insight into the relationship between raw materials consumption, production and product shipments in a given year can be gained from inventory data. Economic Census data is available for the following three categories of inventory: Materials and Supplies, Work in Progress, and Finished Goods. A generic demonstration of relationship between raw material input and output is given in Figure 28, where highlighted path represents that there are no additions and/or withdrawals from inventory.

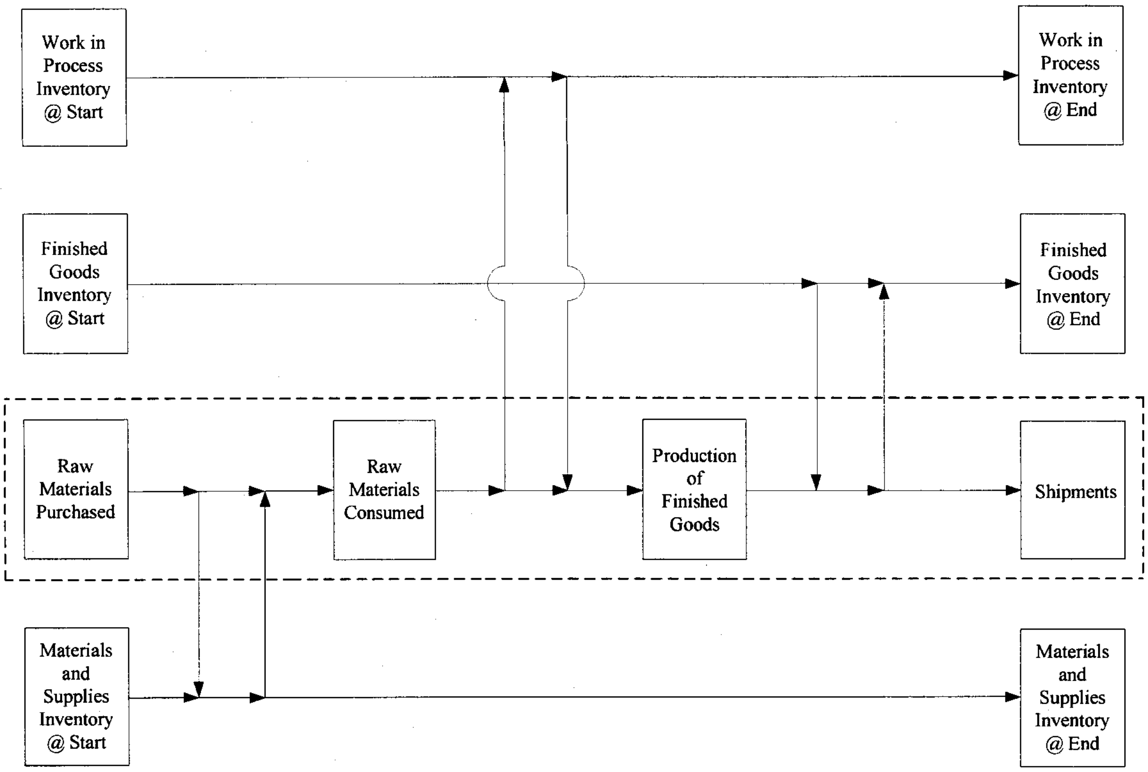

Figure 28. Generic relationship between inputs and outputs

Figure 28 shows that although raw material is purchased, there could be materials and supplies from previous year that may be added to the raw material consumption of that particular year. Or, some of the raw material purchased may be added to materials and supplies to be used in the following year. Therefore, the raw material consumption given in Economic Census database may not necessarily represent the actual raw material amount purchased in that particular year. As for the production data, some of the raw materials purchased in that particular year may be used for work in process inventory at start, whereas some of the work in process products may be added into production of finished goods. Therefore, the shipments from the plant may not necessarily represent the actual production amount for that particular year.

4.2.2. Monetary vs. Physical Units

Using the relationships depicted in Figure 28 to convert shipment data to production data is further complicated by the fact that inventory data generally is given only in economic terms (e.g. dollar value), rather than physical units (e.g., tons). Sometimes raw material and product shipment data is also given only in monetary terms, which are subject to change when prices changes. Therefore, monetary terms are not as useful as physical terms to measure production. The monetary term for a product can be converted to physical terms by finding the price of that product in terms of per unit mass in a particular year. Information on the price of many products at the market can be found in Chemical Market Reporter at least once a year.

Value of shipments reported in the Current Industrial Reports (CIR) and the Annual Survey of Manufacturers (ASM) databases can be interpreted in terms of kilograms once the prices for the products are known. However, the price range for a product may fluctuate in a year. In this case, an average price value can be taken. This, though, brings some level of uncertainty into the production value calculated based on the average price. But, it still provides knowledge about production value for a particular product.

Another argument that should be considered interpreting value of shipments is: in some cases, plants do not ship all of the products that they produce in the same year, or they use some of the product at the plant. Sometimes they stock and ship the following year, or sometimes they ship all of the products they produce. In some cases, plants ship not only all the products that they produce but also the products that they stocked from previous years. Table 26 provides production and shipment values for some chemicals as an example to reveal the variation in production amount and value of shipments.

Table 26. Production vs. value shipments of some industrial gases, kg, (CIR, 1998a)

Chemical	1998		1997	
	Production	**Shipment**	**Production**	**Shipment**
Acetylene	1.4×10^8	8.8×10^7	1.4×10^8	8.2×10^7
Nitrogen	2.9×10^{10}	2.8×10^{10}	2.5×10^{10}	2.5×10^{10}
Oxygen	2.5×10^{10}	2.4×10^{10}	2.3×10^{10}	2.1×10^{10}

Table 26 shows that acetylene shipment was 30% and 45% less than its production in 1997 and 1998, respectively. On the other hand, nitrogen and hydrogen shipments are within the range of 0% - 9% less than their production in 1997 and 1998. This shows that in some cases, the data on value of shipment would indicate actual production amount very closely, whereas in some cases, such as in acetylene, it may not be a good indicator of production amount. However, in the case of lack of data on actual production, data on value of shipments would still be useful as long as considering the possible uncertainty it brings into analysis.

4.3. Methodology

Construction of material flow model of a substance in a national scale is generated following the methodology described below,

- Search and selection of the representative manufacturing process,
- Description of the representative manufacturing process,
- Mass balance of the representative manufacturing process for unit mass production of each industrial gas,

- Mass balance of the representative manufacturing process in a national scale.

Search, selection and description of the representative manufacturing processes for industrial gases are provided in Chapter 3. Mass balance of the representative manufacturing process for unit mass production of each industrial gas and mass balance of the representative manufacturing processes on a national scale are given in this chapter.

4.4. Material flow models

4.4.1. Acetylene material flow model

The representative acetylene production method was chosen as partial combustion of natural gas as discussed in Chapter 3. A simplified representative acetylene production material flow model was constructed based primarily upon the Drexel acetylene material flow model (Brown et al., 1996) and secondarily Speight (2002). It is given in Figure 29, where process steps are numbered as (1), (2), etc. according to the order in which they occur.

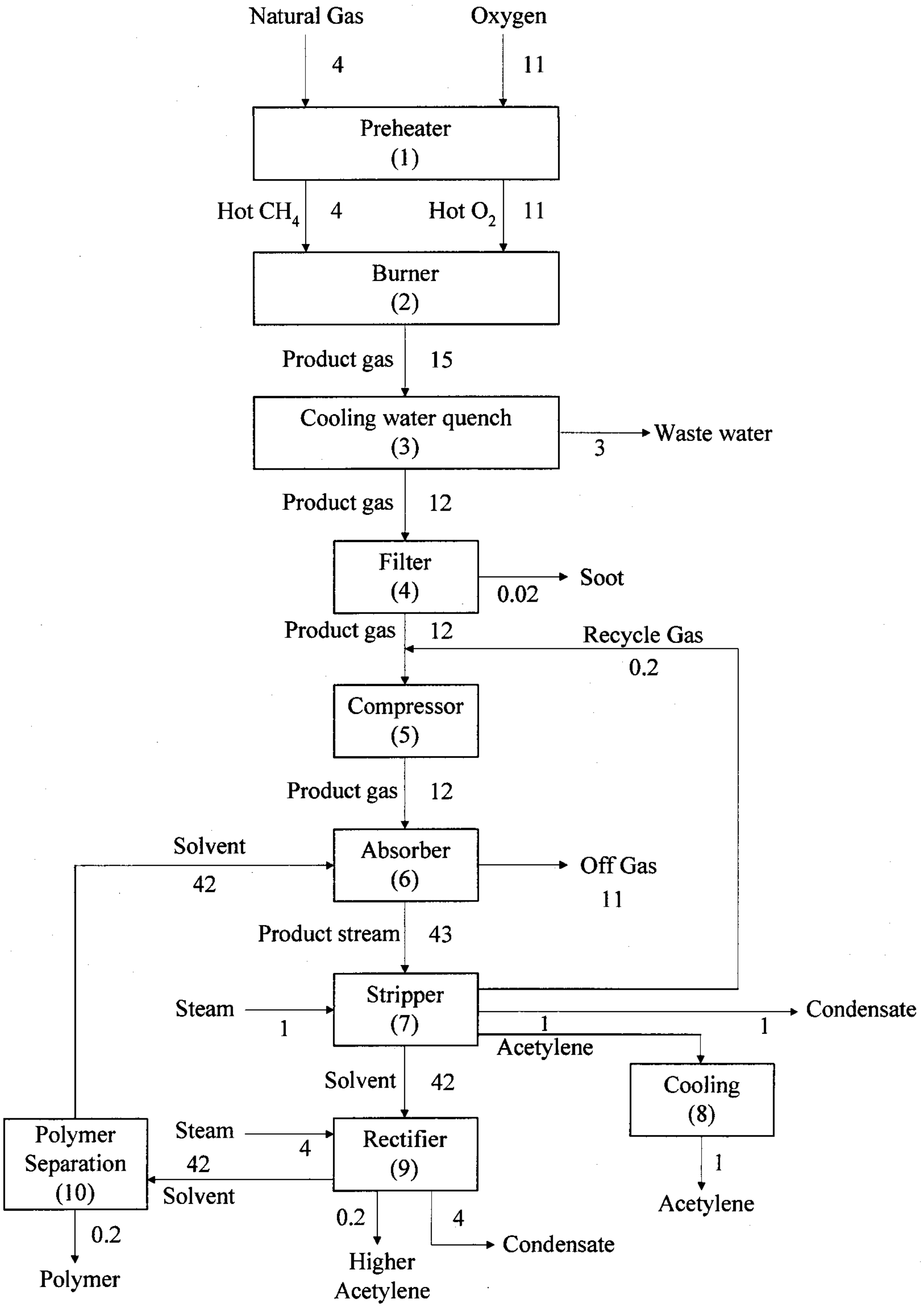

Figure 29. Representative unit acetylene production material flow model, kg

The material input and output values in Figure 29 were obtained from the Drexel Acetylene material flow model (Brown et al., 1996). Comparison of the inputs and outputs of this model with other material flow models is given in Table 27 for unit mass acetylene production.

Table 27. Comparison of the inputs, products and emissions per kg acetylene produced, kg

	Drexel	**Pässler et al.**
Process	Partial combustion of natural gas	Partial combustion of natural gas
Purity	-	99.7%
Inputs		
Natural Gas/CH_4	4	6
Air/Oxygen	11	5
Products		
Acetylene	1	1
Emissions		
Carbide	-	-
Carbon monoxide	-	-
Dust	-	-
Coke	-	0.5
Naphthalenes	-	0.4
BTX	-	0.1
Soot	0.02	-

As it is seen in Table 27, there are differences between the fuel and oxidizer input values for unit acetylene production in Brown et al. (1996) and Pässler et al. (2000). In addition, each process yields different emissions. Since there is no description of the processes in Drexel, an explanation to these differences is unavailable. However, Pässler et al. (2000) discuss soot removal and explain why there is no soot emission from the BASF process (named after BASF company): "All the soot formed is consumed when crude oil feedstock is used, eliminating all the problems associated with the storage, disposal, or utilization of acetylene soot." (Pässler et al., 2000). Other than this statement, there is no information that explains the differences in fuel and oxidizer input or emissions. Several other acetylene production techniques via partial combustion of natural gas are described in detail in Pässler et al. (2000). They describe acetylene production by partial combustion of natural gas using a technique, called BASF, as the most common technique. The other acetylene production techniques by partial combustion of natural gas discussed by Pässler et al. (2000) are *Montecatini* and the *SBA processes*, which "have also attained some importance". One of the differences between the BASF and Montecatini process is the burners that are used. Another difference is the pressure for acetylene synthesis, which "saves compression energy, improves heat recovery from the quench water, which is obtained at 125 °C, and is claimed to make soot removal easier because the cracked gas is scrubbed with water above 100 °C" Pässler et al. (2000). As for the difference between the BASF and the SBA process, the SBA burner has the same components as the BASF burner. "However, it has a telescope-like reaction chamber and a device for shifting the quench up and down. Thus it is possible to adjust the length of the reaction zone for optimum residence time at any throughput. The walls of the reaction chamber are sprayed with demineralized water to prevent coke deposits" Pässler et al. (2000).

Having chosen the representative material flow model for unit acetylene production, the next step is to calibrate the model in a national scale. In order to do that, national acetylene production in 1998 must be used. Current Industrial Reports (CIR) provides production totals for certain industries, including Industrial Gas Manufacturing sector, based on their NAICS codes. Therefore, CIR can be used to scale the numbers in Figure 29 to reflect national consumption of all substances used in acetylene production in 1998.

CIR data reports that acetylene production in 1998 was $1.4\text{x}10^8$ kg (CIR, 1998). This production amount reported in CIR database includes "products sold; products transferred or added to inventory after adjustments for breakage, shrinkage, and obsolescence, plus any other inventory adjustment: and products that undergo further manufacture at the same establishment." (CIR, 1998b). According to the Chemical Market Reporter (CMR, 1998), acetylene production capacity in 1998 was $1.9\text{x}10^8$ kg (CMR, 1998). If we compare the Chemical Market Reporter acetylene production amount with the CIR value, in order to produce $1.4\text{x}10^8$ kg acetylene, the plants would have operated at about 75% of their capacity. However, if we look at the average production estimation for plants based on the information given in several Chemical Market Reporter articles, we see that plants usually operate at 90% of their capacity (CMRa, 2001; CMRb, 2001). Several possible reasons for this could be: the reduced need for acetylene in the market in 1998, an error in CIR acetylene production estimate, or an error in the Chemical Market Reporter acetylene estimate.

Scaling $1.4\text{x}10^8$ kg acetylene production with the inputs and outputs provided in Figure 29 results in the representative national acetylene production material flow model in 1998 given in Figure 30.

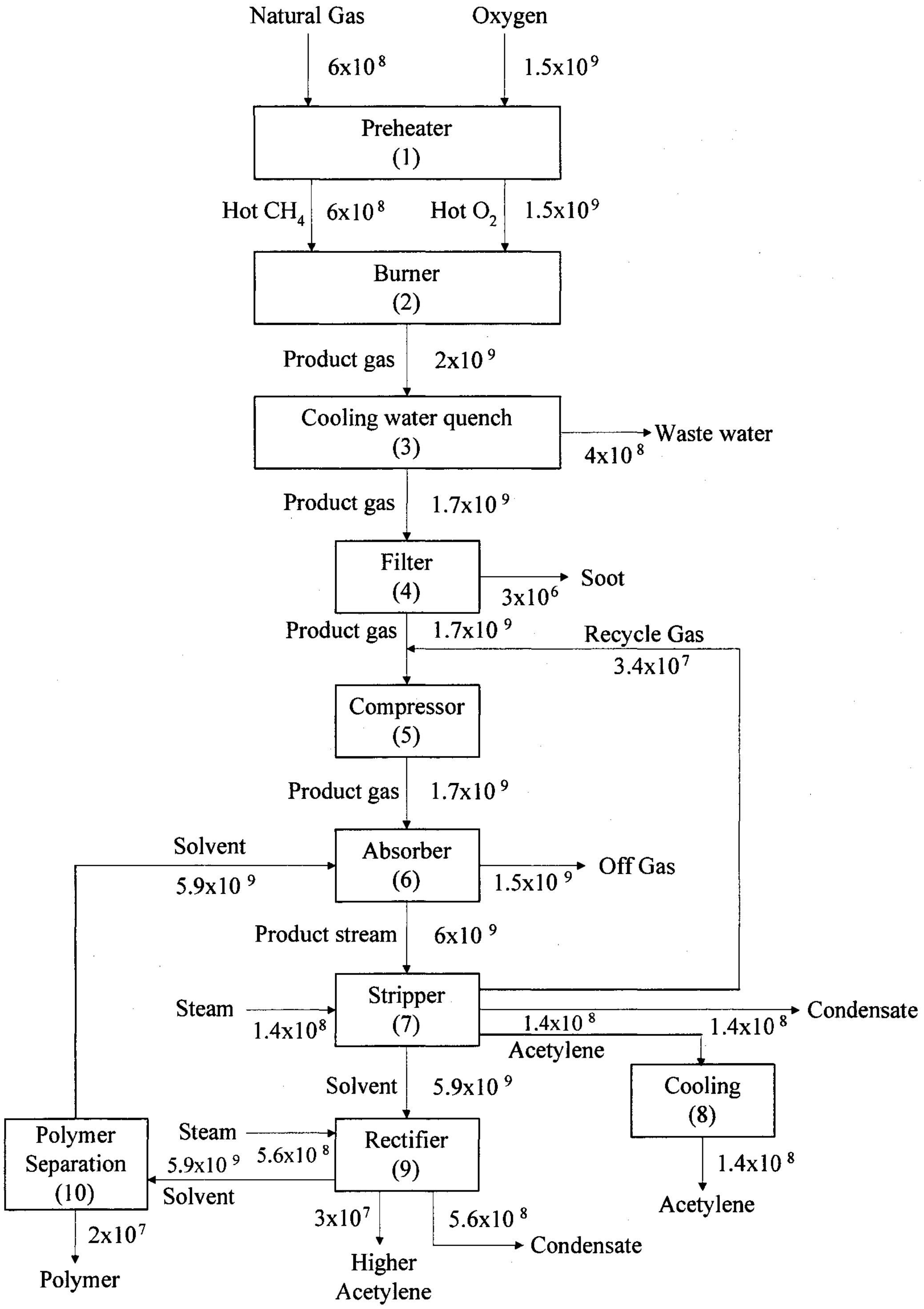

Figure 30. Material flow model of acetylene production in 1998, kg

Figure 30 shows the material inputs and outputs during acetylene production in the nation in 1998. However, we know from Chapter 1 that 92% of the industrial gases are produced by the Industrial Gas Manufacturing sector. Therefore, it suggests that the vast majority of the material consumption and emissions shown in Figure 30 occurred at Industrial Gas Manufacturing sector plants.

4.4.2.Carbon dioxide material flow model

As discussed in Chapter 3, there are two major commercial carbon dioxide production techniques: carbon dioxide as a byproduct of ammonia production and carbon dioxide as a recovery from flue gas. However, whichever technique is used to produce carbon dioxide, purification and liquefaction processes are applied eventually. Besides, carbon dioxide impurity in the ammonia production stream and recovered flue gas stream are about the same. Therefore, which of these two techniques is used as the source of carbon dioxide, it is followed by purification, liquefaction and solidification anyway.

Since the commercial carbon dioxide is available as liquid, gas and solid forms, the material flow models should be given separately for each phase including the purification. However, carbon dioxide solidification is not included into the material flow model analysis in this study since its production amount accounts for less than 2% of the total carbon dioxide production.

The liquefaction and purification of carbon dioxide is given in Figure 31 below scaled by using CIR's pure liquid carbon dioxide production data.

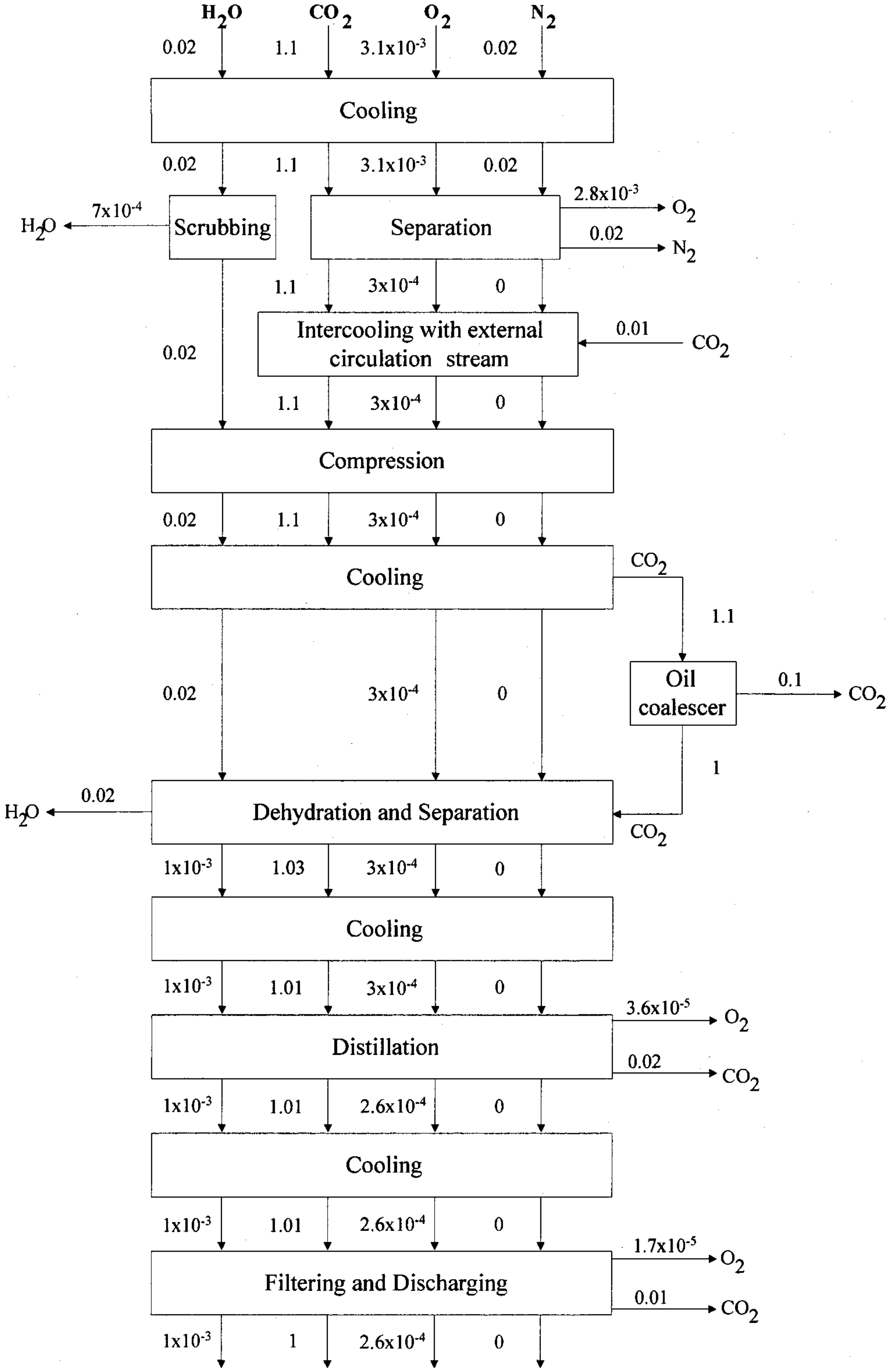

Figure 31. Representative unit carbon dioxide purification and liquefaction material flow model, kg

Having chosen the representative material flow model for unit carbon dioxide purification and liquefaction, the next step is to calibrate the model on a national scale. In order to do that, the national carbon dioxide production amount in 1998 must be used. CIR database values provided in Table 25 gives us the gas, liquid and solid carbon dioxide production in 1998. Since Figure 31 is given for liquid carbon dioxide, scaling the values in this figure by 7.4×10^9 kg results in national scale 99.9% pure liquid carbon dioxide production material flow model.

The "gas" carbon dioxide production cannot be scaled using Figure 31, because the purification and liquefaction processes in Figure 31 occur simultaneously, starting with reducing the gas temperature as an initial step towards liquefaction. Therefore, gas carbon dioxide production material model is not given due to lack of data and this creates a major gap in the overall carbon dioxide production analysis.

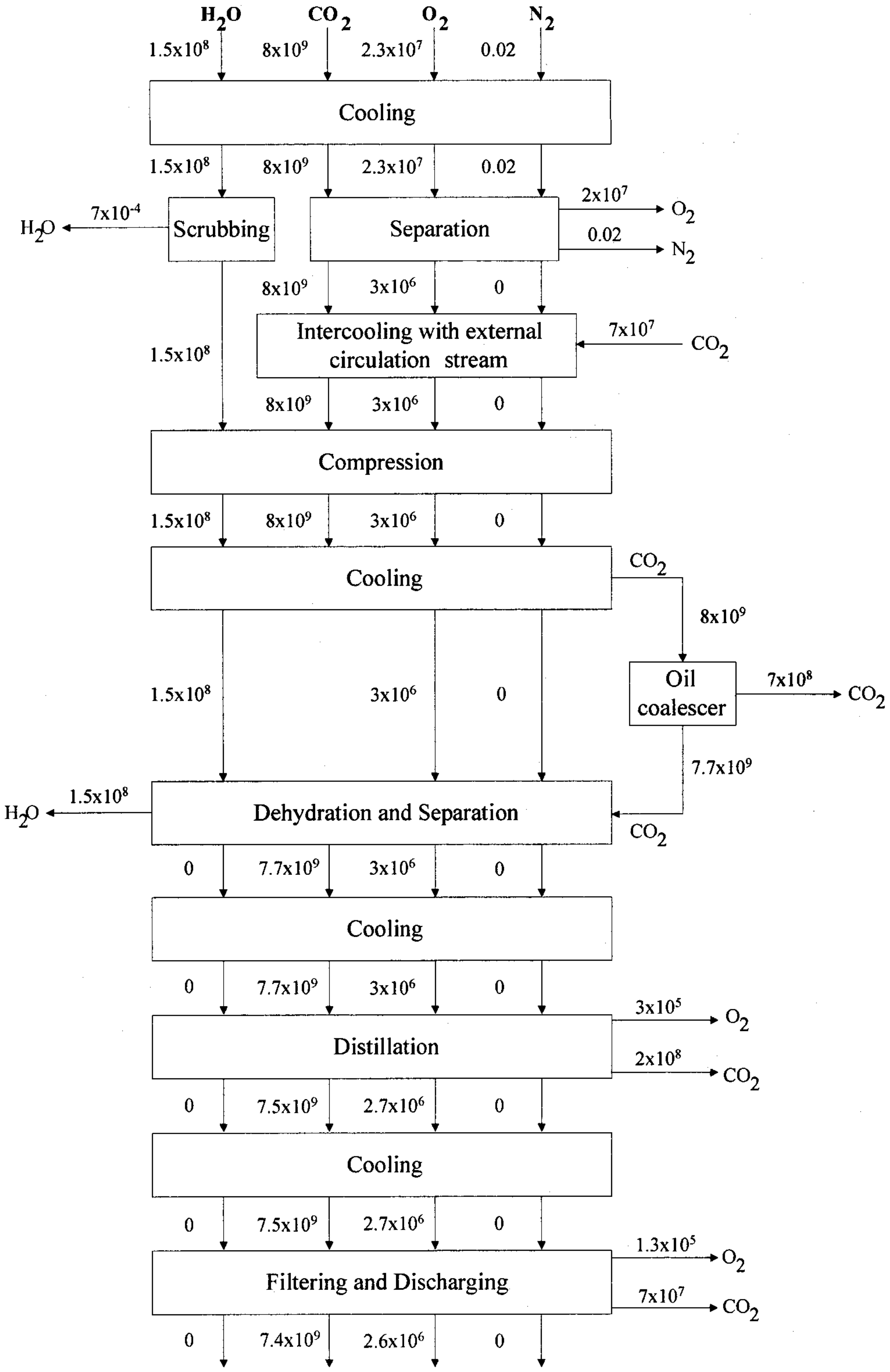

Figure 32. Material flow model of carbon dioxide purification and liquefaction in 1998, kg

Figure 32 shows the national scale material flow model for carbon dioxide purification and liquefaction in 1998. It is seen at the initial step of this figure shows that $8\text{x}10^9$ kg carbon dioxide gas is consumed to produce $7.4\text{x}10^9$ kg liquid carbon dioxide in a national scale.

While the EG&G report includes simulation for carbon dioxide recovery from flue gas, it does not include purification of the recovered carbon dioxide gas separately. Since the purification process provided in that report is treated as a simultaneous process with liquefaction, it cannot be separated to account for the purification of carbon dioxide gas only. Therefore, the EG&G simulation does not provide complete information to construct material flow model for carbon dioxide gas purification.

The other sources that I searched also do not include the material inputs and outputs for each step of flue gas recovery carbon dioxide gas purification. However, to gain some insight into carbon dioxide gas production, we can inspect carbon dioxide gas purification from another commercially important technique, e.g. carbon dioxide gas purification as a byproduct from ammonia production.

As it was mentioned in Chapter 3, the purity of carbon dioxide gas as a byproduct from ammonia process is already very high compared to the purity of carbon dioxide gas from flue gas (Topham, 2000). Therefore, purification of flue gas recovery carbon dioxide might require more process steps compared to purification of carbon dioxide as a byproduct of ammonia production. In the Drexel ammonia model, the only process step to purify carbon dioxide gas is a CO_2 absorber (Brown et al., 1996). On the other hand, in the ammonia production simulation in Jiménez-González (2000), carbon dioxide gas is separated in absorption tower before going to the ammonia synthesis process, then it is absorbed in a carbon dioxide stripper. Drexel does not provide any information on the purity level of carbon dioxide gas, whereas Jiménez-González (2000) reports a 100% purity. Neither Drexel nor Jiménez-González (2000) provide any specific information on the emissions during carbon dioxide purification process. However, Jiménez-González (2000) provides a comparison chart showing material inputs and outputs for 1000 kg ammonia production. Table 28 shows the data from the comparison chart in that article. Although the "data concern only for the process for the production of ammonia" (Jiménez-González, 2000), it still gives a useful information about the material inputs and outputs during carbon dioxide production, which is a part of ammonia production.

Table 28. Comparison of inputs, products and emissions per 1000 kg ammonia produced, kg.

Parameter	**Case study**	**BUWAL 250**	**Boustead**	**PEMS**	**EFMA**
Process type	Steam reforming	Steam reforming	n.r.	n.r.	Steam reforming
Inputs					
Natural gas	446.75	467	760 [a]	760 [a]	458
Air	1,796.85	n.r.	5.02	6.6	1,100
Water	1,200 (12,000 [e])	920	11,166	11,000	1,500
Products					
Ammonia	1,000	1,000	1,000	1,000	1,000
Carbon dioxide	1,179	1,159	[b]	[b]	1,150 – 1,300
Emissions					
Ar	13	n.r.	n.r.	n.r.	n.r.
Methane	2	7.14	n.r.	16 [c]	n.r.
CO	3	0.025	0.002	0.04 [c]	<0.03
CO_2	53	436	1,975 [d]	2,055 [d]	500
Non-CH_4 VOC	n.r.	0.928	n.r.	n.r.	n.r.
Hydrogen	3	n.r.	n.r.	n.r.	n.r.
Ammonia	6	n.r.	0.001	0.001	n.r.
NO_x (as NO_2)	9	0.304	1.17	2.6 [d]	0.6 – 1.3
SO_x (as SO_2)	n.r.	0.01	0.036	0.78	<0.01

n.r. Not reported
[a] Sum of fuel and feedstock
[b] Reported as emissions
[c] Includes transport emissions. No transport distance indicated
[d] Emissions are sum of process-related emissions and energy-related emissions
[e] If cooling water is added to reaction water

Table 28 shows that although these five different studies are to produce same amount of ammonia, there is a big variation in some of the inputs and outputs. Discussions on these variations can be found in Jiménez-González (2000). In Table 28, there are also many data not reported. It should be noted that the data in this table were taken from commercial, trade association and federal databases which are generally not accessible by public.

Another point that deserves attention in Table 28 is that the variation in inputs and outputs values and the absence of data is similar to acetylene data in Table 27. This suggests that although the process may be the same, there may still be big variation in inputs and outputs due to the differences in process conditions. This also shows that even if the process is the same, selecting one particular study or model as representative to scale against the national data could yield results that are significantly different than the results obtained by choosing another model as representative. For example, if the ammonia production was within the scope of this dissertation and if Jiménez-González (2000) study was chosen as representative, the values in the national scale ammonia production material flow model are different than the values in the national scale ammonia production material flow model constructed based on BUWAL 250, or any other studies given in Table 28. This case not only applies to ammonia production, but also to all other chemicals. Therefore, this should be considered when examining the results of the representative material flow models in this dissertation. Otherwise it would mislead the efforts for better policy making.

In summary, I have not found quantitative information on each process step of carbon dioxide gas production only or carbon dioxide gas production and purification. Therefore, a material flow model for carbon dioxide gas production is not available at present. This missing piece will create a major gap in the emissions from industrial processes, because the emission flow model in Chapter 6 is created partially by using the emission values given in the material flow models. This missing piece will also create a gap in the material flow model analysis part of the dissertation as well because "gas" carbon dioxide production is not negligible as it is seen in Table 25.

4.4.3. Nitrogen, oxygen and argon material flow models

Nitrogen, oxygen and argon are produced simultaneously in a combined cryogenic process. Therefore, a single material flow model will be given for cryogenic oxygen, nitrogen and argon production. On the other hand, there are non-cryogenic techniques where nitrogen and oxygen are produced separately in different processes. The Current Industrial Reports database states that non-cryogenic nitrogen production in 1998 was 65% of total nitrogen production as shown in Table 29.

Table 29. Nitrogen production in 1998, kg, (CIR,1998a)

Process	**Production**
Nitrogen via cryogenic processes	$1.0\text{x}10^{10}$
Nitrogen via non-cryogenic processes	$1.86\text{x}10^{10}$
Total	$\mathbf{2.86x10^{10}}$

For the oxygen production, the Current Industrial Reports provides 1998 data as shown in Table 30.

Table 30. Oxygen production in 1998, kg, (CIR,1998a)

Process	**Production**
Oxygen via cryogenic processes	$6.1\text{x}10^{9}$
Oxygen via non-cryogenic processes	$1.9\text{x}10^{10}$
Total	$\mathbf{2.5x10^{10}}$

There are several different non-cryogenic techniques to produce nitrogen and oxygen. For example, according to CIR, the non-cryogenic processes to produce oxygen and nitrogen are: membranes, psa, vpsa etc. However, the information about the usage of membranes vs. psa/vpsa is not provided in this source. Therefore, based on the CIR information, we do not know which of these non-cryogenic techniques, if any, dominates. On the other hand, as it was discussed in Chapter 3, "air separation by membranes" was selected as the representative technology for non-cryogenic nitrogen and oxygen production based on the articles reviewed. But this selection will introduce an uncertainty into the analysis due to not including the other non-cryogenic techniques.

4.4.3.1. Cryogenic nitrogen, oxygen and argon production material flow model

The process steps of the cryogenic nitrogen production technique which is called the "typical cryogenic air separation process" by Häussinger et al.(2000a), Hardenburger and Ennis (2005), and Barron (2000) are listed below:

- Air is compressed,
- Cooled to remove excess water vapor,
- Passed through a heat exchanger to further cool it,

- Purified to remove residual carbon dioxide, water vapor, and other contaminants which could freeze in the process by reversing heat exchangers,
- In the reversing heat-exchanger process, the incoming compressed air is cooled by countercurrent heat exchange with cold oxygen-rich waste gas and nitrogen product exiting the process.

For cryogenic oxygen production, the process steps are briefly listed based on the information in Kirschner and Hill (2000), Hansel (2005), Agrawal et al. (2003) and Barron (2000):

- Purification of the incoming compressed air to remove particles, carbon dioxide, and water,
- Refrigeration and economization of refrigeration contained in the product and waste streams,
- Separation by distillation.

Since the process steps described in these sources are very similar to the process steps in the Drexel cryogenic oxygen, nitrogen and argon production model, the representative cryogenic oxygen, nitrogen and argon material flow model will be constructed based on Drexel. The first step is to build a material flow model for normalized argon production because cryogenic air separation is the typical argon production technique as discussed in Chapter 3. However, since the references listed for nitrogen and oxygen production do not have quantitative material inputs and outputs for each process step, a comparison with the Drexel model inputs and outputs is not available.

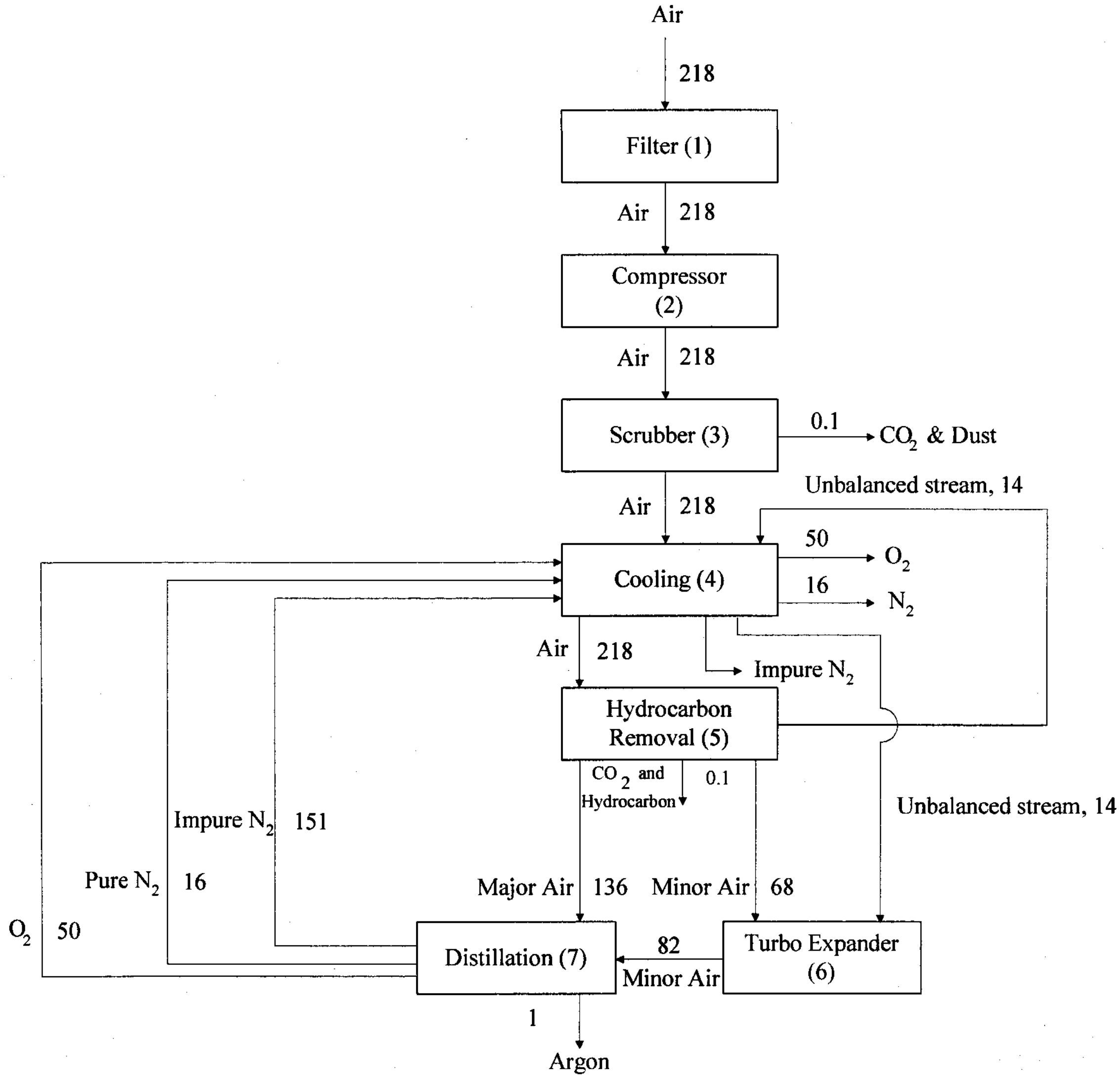

Figure 33. Material flow model of cryogenic nitrogen, oxygen and unit argon production, kg

In Figure 33, air composition by weight is as follows: 77% nitrogen (pure and impure) and 23% oxygen. So the nitrogen amount is slightly (about 2%) less than the actual nitrogen amount in the air composition, whereas the opposite applies to oxygen. Oxygen, nitrogen and argon in this process diagram are delivered as gases. If output in the form of liquids are desired, then additional cost and energy consumption will be involved.

Having chosen the representative material flow model for cryogenic nitrogen, oxygen and argon production, the next step is to scale the model to the national data. CIR reports that $9.1x10^8$ kg argon was produced cryogenically in 1998 (CIR, 1998). Scaling the Figure 33 on the basis of CIR argon production data, assuming that the Drexel model is the only process used to produce argon, results in Figure 34.

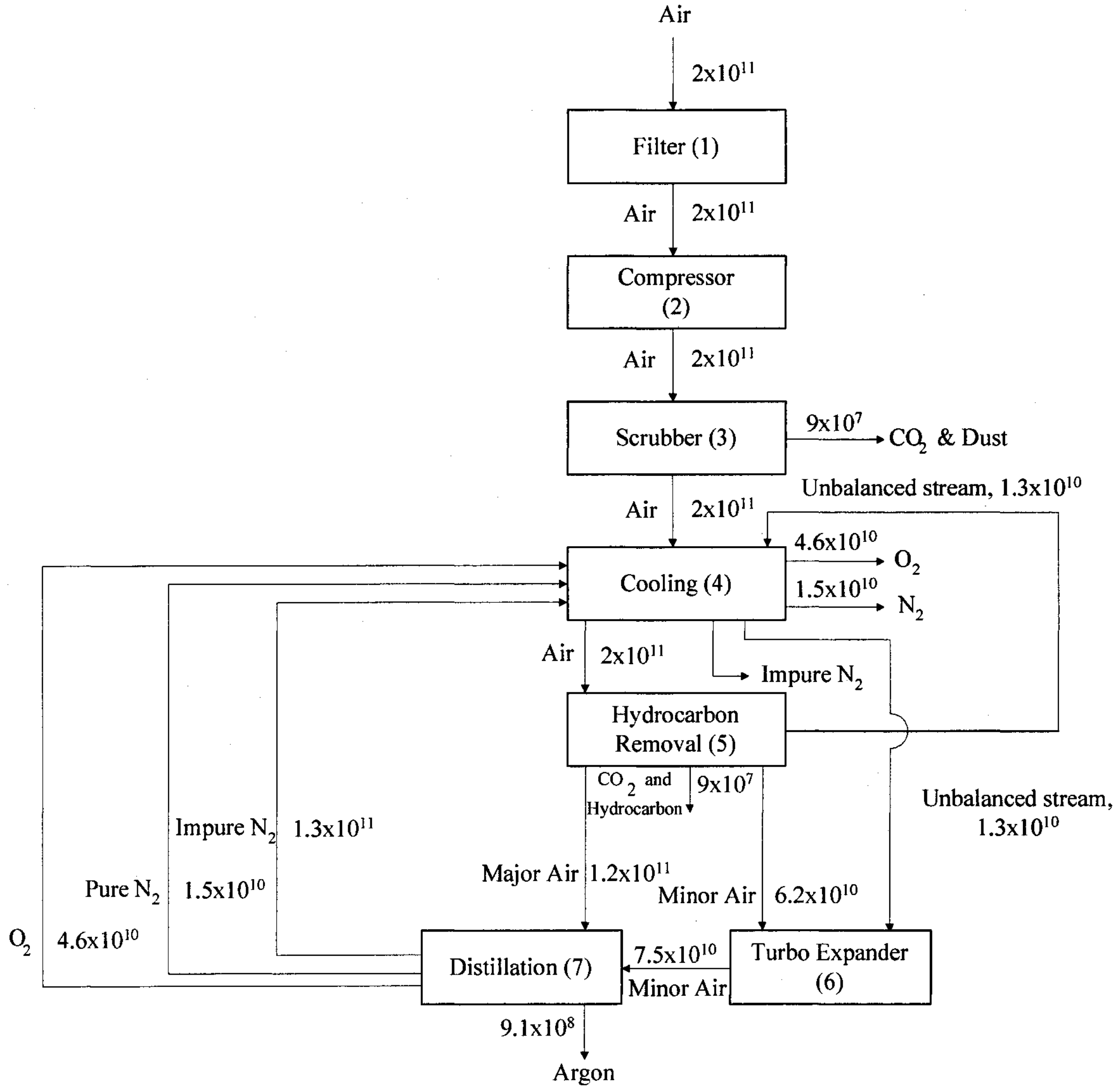

Figure 34. Material flow model of argon production in 1998, kg

Figure 34 shows that for $9.1\text{x}10^{8}$ kg argon production, there are $4.6\text{x}10^{10}$ kg oxygen, $1.5\text{x}10^{10}$ kg pure nitrogen and $1.3\text{x}10^{11}$ kg impure nitrogen produced. The CIR data in Table 29, we see that $1\text{x}10^{10}$ kg nitrogen was produced cryogenically in 1998. This shows that the Drexel model overestimates the cryogenic production of pure nitrogen by approximately 40%. If we look at Table 30, we see that $6.1\text{x}10^{9}$ kg oxygen was produced cryogenically in 1998. This shows that model in Figure 34 overestimates the oxygen production by approximately 7.5 times. A possible reason for obtaining nitrogen and oxygen production numbers greater than the CIR values would be due to the some of the argon producers vent the plant' nitrogen and oxygen. The CIR database introduction states that ventilated gases are not included in the production numbers. Therefore, this may explain the reason for CIR numbers' being smaller than the numbers in Figure 34.

Another possible reason for higher values in Figure 34 could be explained by CIR database' including high purity products only. Although CIR does not give any information about the purity levels of industrial gases, in Table 8 of CIR (1998a), it states that the argon production includes "high purity" only. Therefore, if the Drexel model includes both lower and higher purity levels, then this would result in greater production values compared to CIR for the case which CIR includes "high purity" only. However, since there is no information on purity levels of gases in Drexel, we do not know for sure if this explains the difference between the Drexel and CIR numbers.

Another point that deserves attention in Figure 34 is the impure nitrogen amount that is discharged. It shows that the impure nitrogen amount is about 9.5 times more than the purified nitrogen. Although I found information about the maximum achievable purity level of nitrogen after purification process, I have not found any information about how much impure nitrogen is discharged during the cryogenic nitrogen production. If there was information about this, then it could have explained the difference in CIR and Drexel numbers for nitrogen production. For example, if the ventilated impure nitrogen value in Drexel is smaller than the amount in actual performance at plants, then this would have explained why the pure nitrogen number given in Drexel is bigger than CIR value.

One more approach to explain the difference between Drexel and CIR database could be this: The temperature of discharged argon at process step (7) is –171 °C, which is about 15 °C higher than the boiling point of argon at 101 kPa. We can verify that argon at this temperature and pressure is an ideal gas by checking its reduced pressure (P_R) to see if it obeys that "at low pressures (P_R<<1), the gases behave as an ideal gas regardless of temperature" (Cengel and Boles, 4th Edition, pg. 92).

$$P_R = \frac{P}{P_{critical}} = \frac{101}{4.86x10^3} = 0.02$$

Since 0.02 is fifty times smaller than 1, it shows that argon at this temperature and pressure behaves as an ideal gas.

If we look at the CIR database page 4-25, we see that all numbers included in this database are given for "70 degrees Fahrenheit at 1 atm pressure", which corresponds to 21 °C and 101 kPa (CIR, 1998b). As it is obvious, argon is an ideal gas at this temperature and pressure. This is actually how the numbers given in terms of volume in CIR database were used to calculate the mass by using the ideal gas law. For example for argon, the CIR database gives the production amount in terms of volume to be 550x10^6 m^3 (CIR, 1998a). The argon production in 1998 was then calculated as follows:

$$m = \frac{P\,x\,V}{\frac{R_{universal}}{Molar\ mass}xT} = \frac{101\ kPa\ x\ 550x10^6 m^3}{\frac{8.314\ kPa\ .\ m^3/kmol.K}{40\ kg/kmol}x294\ K} = 9.1x10^8 kg$$

Since the temperature and the pressure of argon in Drexel model are different than the temperature and pressure of argon in CIR, we can check to see how different the mass of argon would be by using the Drexel temperature and pressure for the argon volume given in CIR:

$$m = \frac{P\,x\,V}{\frac{R_{universal}}{Molar\ mass}xT} = \frac{101\ kPa\ x\ 550x10^6 m^3}{\frac{8.314\ kPa\ .\ m^3/kmol.K}{40\ kg/kmol}x102\ K} = 2.6x10^9 kg$$

This gave a higher mass number for argon compared to the number found using CIR temperature and pressure. However, this still cannot explain the difference between the Drexel numbers and CIR numbers for nitrogen and oxygen in Figure 34. Because, the volume, temperature and pressure in CIR were specified so that they give the argon production in 1998. So, for different temperature and pressure, mass of argon would be different than the argon production in 1998.

We can summarize the comparison of the production ratios in Drexel model and in CIR as shown in Table 31, which shows that Drexel numbers are inaccurate.

Table 31. Drexel vs. CIR cryogenic production of O_2 and N_2 per unit argon production

	Oxygen	**Nitrogen**	**Argon**
Drexel	50	16 (pure), 143 (impure), 159 (pure and impure)	1
CIR	7	11	1

Considering that CIR is based on a rigorous statistical analysis reflecting the situation closest to actual manufacturing circumstances, then the most plausible explanation of the differences between Drexel and CIR would more likely be that the Drexel values do not reflect the national scale production pattern for these chemicals. Alternatively, we may also consider that there would be more than one cryogenic technologies to produce these chemicals.

In conclusion, we can summarize that:

- Numbers in Tables 29 and 30 cannot be balanced,
- Drexel numbers do not work in terms of explaining the ratio of oxygen to nitrogen.

Therefore, this problem cannot be solved at present, but can be another research topic for someone else in the future to study.

4.4.3.2. Non-cryogenic nitrogen production material flow model

Nitrogen production technique using membrane separation of air can be summarized as follows (Häussinger et al., 2000a; Hardenburger and Ennis, 2005):

- Compression of air,
- Filtration of air to remove any residual oil, which can be detrimental to membrane longevity, from the compressor and excess water vapor for optimal membrane performance,
- Heating to the optimum process temperature,

- Feeding axially into the center of thousands of the hollow fibers packed in a tube-and-shell configuration,
- Nitrogen is concentrated during its passage down the fibers and is collected as the nitrogen product.

Although the process for membrane separation of air process is explained in detailed in these sources, material inputs and outputs for process steps are not given. Therefore, a material flow model for non-cryogenic nitrogen production is not available. Since the non-cryogenic production technique accounts for 65% of the total nitrogen production in 1998, this missing material flow model leaves a major gap in the analysis.

4.4.3.3. Non-cryogenic oxygen production material flow model

Hansel (2005) reports that "a non-cryogenic air separation process, which is increasingly employed for small- to moderate-scale oxygen production units, is based on the adsorption of nitrogen (but not oxygen) onto zeolites." Brief summary of the process steps of this batch process is:

- Removal of water and carbon dioxide by the first stratum,
- Adsorption of nitrogen from the flowing air by the second stratum,
- In the two-bed system, the unit one adsorbs water and carbon dioxide and then nitrogen from the air,
- The unit two is being evacuated to remove the previously adsorbed nitrogen,
- After a certain period, the second bed is brought into sequential use, while the first is evacuated,

- Depending on the operating cycle chosen, the product may be up to about 93% oxygen, whereas the balance is nitrogen and argon.

Although the manufacturing process for adsorption of nitrogen onto zeolites process is explained in detailed in these articles, material inputs and outputs for process steps are not given. Therefore, a material flow model for non-cryogenic oxygen production is not available. Since the non-cryogenic production technique accounts for 76% of the total oxygen production in 1998, this missing material flow model will leave a large gap in the analysis.

4.4.3.4. Summary

Drexel model for cryogenic oxygen, nitrogen and argon production is not satisfactory. So, using Drexel model to find the effects of the production processes of these industrial gases on the energy and emission on a national scale give us an inaccurate result. Another model or data on cryogenic production of these industrial gases would give accurate results. However, my search on finding another model or public data giving all inputs and outputs for each step of cryogenic process to produce these industrial gases resulted with no satisfying information. Therefore, national scale material flow model for the production of cryogenic oxygen, nitrogen and argon remains as a gap in this dissertation. However, it could be a good research for someone else in the future.

As for the non-cryogenic production of oxygen and nitrogen, national scale material flow models for the industrial gases are not available at present due to the lack of data on inputs and outs for each process step. Therefore, this will be a gap in the dissertation. However, a research on national scale non-cryogenic oxygen and nitrogen production in the future would be a good research topic for someone else to reveal the energy and emissions effects of these processes on a national scale.

4.4.4. Hydrogen material flow model

As discussed in Chapter 3, the dominant hydrogen production technique is steam reforming of natural gas. The representative hydrogen production material flow model is given for unit hydrogen production in Figure 35 based on the Drexel hydrogen model.

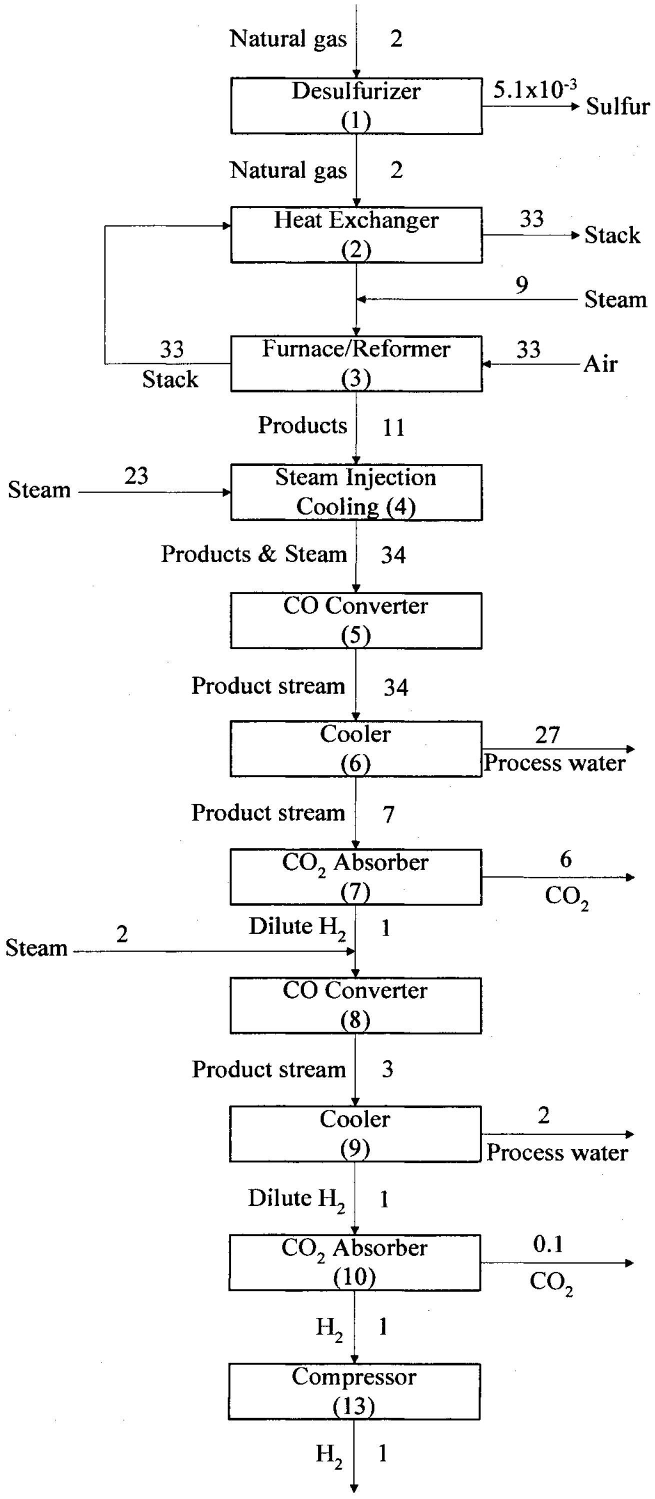

Figure 35. Representative unit hydrogen production material flow model, kg

Comparison of the inputs and outputs of this model with other hydrogen production material flow models is given in Table 32 for unit mass hydrogen production.

Table 32. Comparison of the inputs, products and emissions per kg hydrogen produced, kg

	Drexel	**Koroneos et al.**
Process	Steam reforming of natural gas	Steam reforming of natural gas
Purity	-	99.95%
Inputs		
Natural gas	2	2.09
Air	33	NA
Steam	9	6.91
Product		
Hydrogen	1	1
Emissions		
H_2O	29	-
CO_2	6	10.66
Benzene	-	0.0014
CO	-	0.0059
CH_4	-	0.146
NO_x	-	0.0126
N_2O	-	$4x10^{-5}$
Non-methane Hydrocarbons	-	0.0263
Particulates	-	0.002
SO_x	-	0.0097

NA: Not available in the report

Water consumption in Koroneos et al. study is given as:

- 24% for reforming and shift reactions,
- 71.22% for steam production,
- 4.8% for other processes.

As for the water emissions it is stated that a quantitative value is not reported since the amount was very small.

Having chosen the representative material flow model for unit hydrogen production, the next step is to scale the model to the national data. CIR reports that 1.3×10^8 kg hydrogen was produced in 1998 (CIR, 1998). Scaling 1.3×10^8 kg hydrogen production with the material inputs and outputs provided in Figure 35 results in the representative national scale argon material flow model in 1998 shown in Figure 36.

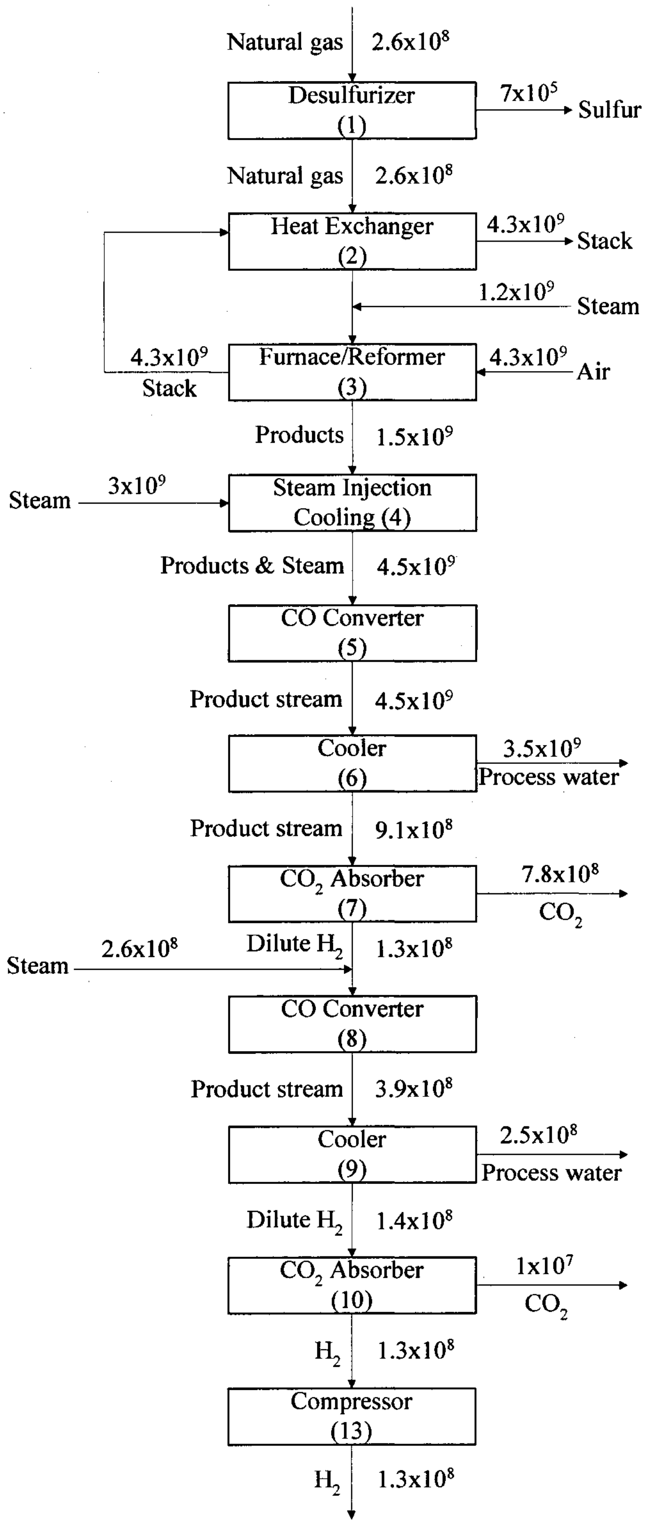

Figure 36. Material flow model of hydrogen production in 1998, kg

4.4.5. Fluorocarbon material flow model

According to the U.S. Census Bureau database, fluorocarbons and all other industrial gases that are not specified by kind account for about 6% of the total shipment value of all industrial gases in 1998 (CIR, 1998).

Table 33. Industrial gas Manufacturing sector product shipments in 1998, $, (CIR, 1998)

Chemical	**Value shipment ($)**	**% in the total**
Acetylene	151,052,000	4%
Carbon dioxide	460,410,000	12%
Nitrogen	1,255,401,000	32%
Oxygen	1,026,928,000	26%
Argon	327,361,000	8%
Hydrogen	512,688,000	13%
Fluorocarbons and all other not specified by kind	227,078,000	6%
Total	**3,960,918,000**	**100%**

As it is shown in Table 33, since fluorocarbon and other not specified products of industrial gases constitutes small portion, their contribution to the material flow in a national scale would be assumed negligible. Therefore, fluorocarbons are not included in the material flow model because they are less than 1% of the total industrial gas production as mentioned in Section 1.5 and discussed in detail later in this section.

The products listed as "fluorocarbons and all other industrial gases that are not specified by kind" are an example of lack of federal data on actual production. In this case, data on value of shipment can be used but with caution. Based on the examples provided in Table 27, it should be noted that value of shipments for "fluorocarbons and all other industrial gases that are not specified by kind" may or may not represent actual production. Considering the arguments on the reliability of data on value of shipments, we can refer to Economic Census database for the value of shipments of "fluorocarbons and all other industrial gases that are not specified by kind".

In Table 33, Economic Census database provides value of shipments for "fluorocarbons and all other industrial gases that are not specified by kind" in terms of US dollars. The production amount of these chemicals may be estimated if their price in 1998 can be found. However, fluorocarbons consist of a great variety of products and some of the fluorocarbon prices, e.g. CFC-12, were changing dramatically as a result of the Montreal protocol. Therefore, estimation of fluorocarbon production by converting the shipment information to production amount using fluorocarbon prices may not result in accurate estimate.

The Economic Census does not list fluorocarbons data separately in 1998. However, the CIR for 2002 does provide fluorocarbon product shipment value separated from all other chemicals not specified by kind (CIR, 2002).

Table 34. Fluorocarbon shipments in 2002, $1000

Product	**Value**	**% of total**
Fluorocarbon	591,962	37%
All other industrial gases that are not specified by kind	1,024,469	63%
TOTAL	**1,616,431**	**100%**

Table 34 shows us that, in 2002, the fluorocarbon shipments accounted for 37% of the "fluorocarbon and all other industrial gases that are not specified by kind". If we apply this ratio to 1998 values, then we can estimate that fluorocarbon shipments in 1998 were 227,078,000 x 37% = $84,018,860.

According to NAICS, “all other industrial gases that are not specified by kind” are listed as:

- Chlorodifluoromethane
- Dichlorodifluoromethane
- Fluorinated hydrocarbon gases
- Helium
- Monochlorodifluoromethane
- Neon
- Nitrous oxide

In the Economic Census database, value of shipments of these gases are given as summation. However, there is data for “shipment quantity” for helium in 1998, in terms of million cubic feet (CIR, 1998a; CIR, 1998b). If we use the assumption of “all materials inputs and outputs leave or enter the overall manufacturing system at 25 °C and 1atm” from Jiménez-González (2000), then the density of helium is 0.163 kg/m^3. If we multiply this by 114 m^3 shipment quantity given in U.S. Census Bureau database, then we obtain that helium shipment in 1998 was about $1.9\text{x}10^7$ kg. Since there is no data on production and shipment of helium in earlier or later years, we do not have any information about the ratio between helium production and shipment which we can apply to 1998 data. However, if we assume that all helium produced at the plants in 1998 was shipped, then the helium production accounts for about less than 1% of the total industrial gas production in 1998.

The U.S. Geological Survey states that private sector helium price in 1998 was about \$1.5 per m^3, with some producers posting surcharges to this price (GS, 1998). If the helium production in 1998 was $1.9x10^7$ kg, then the value shipment for helium in 1998 was about \$$175x10^6$. If the assumptions made for fluorocarbon value of shipments were correct, then the assumptions made for helium value of shipment calculations are over estimating the helium shipment value in 1998 by about \$$32x10^6$. However, these results still suggest that fluorocarbon and helium production may constitute the majority of "fluorocarbons and all other industrial gases that are not specified by kind" by mass. This argument is supported by not seeing any of the "all other industrial gases that are not specified by kind" in the federal database because of their negligible contribution to the total.

In conclusion, a national scale material flow model for fluorocarbon production is not included in this dissertation due to its negligible production amount compared to other industrial gases. However, negligible production amount does not necessarily mean that energy consumption to produce fluorocarbon is also negligible. Therefore, energy consumption during fluorocarbon production is included in the energy process-step analysis in Chapter 5.

4.4.6. Summary of the results

A brief summary of the findings and the conclusions in this chapter can be given as follows:

- National scale material flows for acetylene and hydrogen were given in Sections 4.4.1. and 4.4.4.

- Material flow model for carbon dioxide gas production was not given due to the lack of data (Section 4.4.2.). It creates a major gap in the analysis since carbon dioxide gas production amount is very big as it is seen in Table 25,
- Material flow model for solid carbon dioxide production was not given due its negligible production quantity relative to liquid and gas carbon dioxide production amounts (Section 4.4.2.),
- Drexel model for nitrogen, oxygen and argon is inaccurate as discussed in Section 4.4.3.4.,
- Material flow model for cryogenic production of oxygen and nitrogen were not given due to the lack of consistent and satisfying data as explained in Section 4.4.3.4. This creates a big gap in the material flow analysis part of the dissertation since cryogenic nitrogen and oxygen production amount is very big as it is seen in Tables 29 and 30. However, once there is data, it can be included into the analysis. This could be a good research topic for someone else in the future to complete the material flow analysis of this sector for improved policy making.
- Material flow model for non-cryogenic production of oxygen and nitrogen were not given due to the lack of satisfying data. This creates a big gap in the material flow analysis part of the dissertation since non-cryogenic nitrogen and oxygen production amount is very big as it is seen in Tables 29 and 30. However, once there is data, it can be included into the analysis. This could be a good research topic for someone else in the future to complete the material flow analysis of this sector for improved policy making.

- Fluorocarbon production is relatively small compared to all other industrial gas production. Therefore, they are not included in the material flow analysis as discussed in detail in Section 4.4.5. However, since negligible production amount does not necessarily require negligible energy consumption during the manufacturing, Fluorocarbons are included into the energy process-step models analysis in Chapter 5.

5. ENERGY PROCESS STEP MODELS

This chapter presents energy process-step models for the Industrial Gas Manufacturing sector products on a national scale.

Energy process-step model is a representation of energy flow for an industrial process. To construct it, first, the key energy consuming process steps need to be identified. Then, energy usage in each step should be found. In order to scale each process-step against national data, energy end-use model given in Figure 18 can be used since it gives allocation of energy to each end-uses in Industrial Gas Manufacturing sector in a national scale.

There have been prior efforts to create energy process-step models (Worrell et al., 2000; ADL, 2000; Wang et al., 2004; Brown et al., 1996; Giraldo and Hyman, 1996; Andersen and Hyman, 2001). The biggest challenge in modeling national scale energy process-step models for manufacturing industries is lack of data as "no consistent data sources were found across all industrial NAICS that covered energy use by process step." (ADL, 2000).

If we take a closer look at the earlier studies, we see that Worrell et al. use some recent technologies for process step flows. However, in one of their energy process-step models, they utilize a Drexel model in order to give breakdown of energy consumption for an industrial process. Worrell et al. use an assumed power generation efficiency for energy balance of a chemical manufacturing. This brings an uncertainty to the analysis, which they point out but are not able determine its magnitude. Also, the electricity from cogeneration is not included into the industry total energy use in Worrell et al. (2000), which is a major missing part in an energy analysis as some of the processes consume large amount of electricity from cogeneration. Finally, Worrell et al. does not provide industrial process flows, mass and energy balances, and products information for the Industrial Gas Manufacturing sector products.

A further example study that provides energy flow model similar to this dissertation is done by Wang et al. of Energy Systems Division of Argonne National Laboratory (Wang et al., 2004). Their study is created based on Drexel model but for Petroleum Refineries sector. In their analysis, they develop a refinery process flow chart based on data and process model taken from a Drexel model. In their results, they give "energy-based process energy allocation by final product" per unit mass. Their results include mass, allocated energy use and energy intensity for each product manufactured in Petroleum Refineries sector. In their study, energy use is allocated in terms of electricity, fuel and steam, which is the same way I do in Chapter 2 and Chapter 5 for Industrial Gas Manufacturing sector. In addition, their study includes market value-based process energy allocation by fuel for unit mass product manufactured, which provides an economic perspective. They also provide emissions from petroleum recovery, transportation etc., whereas I include emissions from industrial processes and from prime movers during power and steam generation.

5.1. Methodology

An energy process-step model of a product on a national scale is generated following this methodology:

1. Search and selection of a representative manufacturing process,

2. Description of the representative manufacturing process,
3. Identification of energy inputs in the representative manufacturing process per unit mass of output,
4. Scaling of the energy inputs in the unit mass representative manufacturing process based on national level production,
5. Reconciliation of national scale manufacturing process with the end-use model based on federal data.

The first two steps for industrial gases were provided in Chapter 3 of this dissertation. Therefore, in this chapter concentrates on steps 3 though 5.

5.2. Energy process-step models

5.2.1. Acetylene energy process-step model

Partial combustion of natural gas was selected as the representative acetylene production technique in Chapter 3. Therefore, the representative acetylene energy process-step model in this section is given for that technique.

Figure 37 shows energy process-step model for unit mass acetylene production. The model in this figure is constructed primarily based upon the Drexel acetylene energy process-step model (Brown et al., 1996) and secondarily Speight (2002).

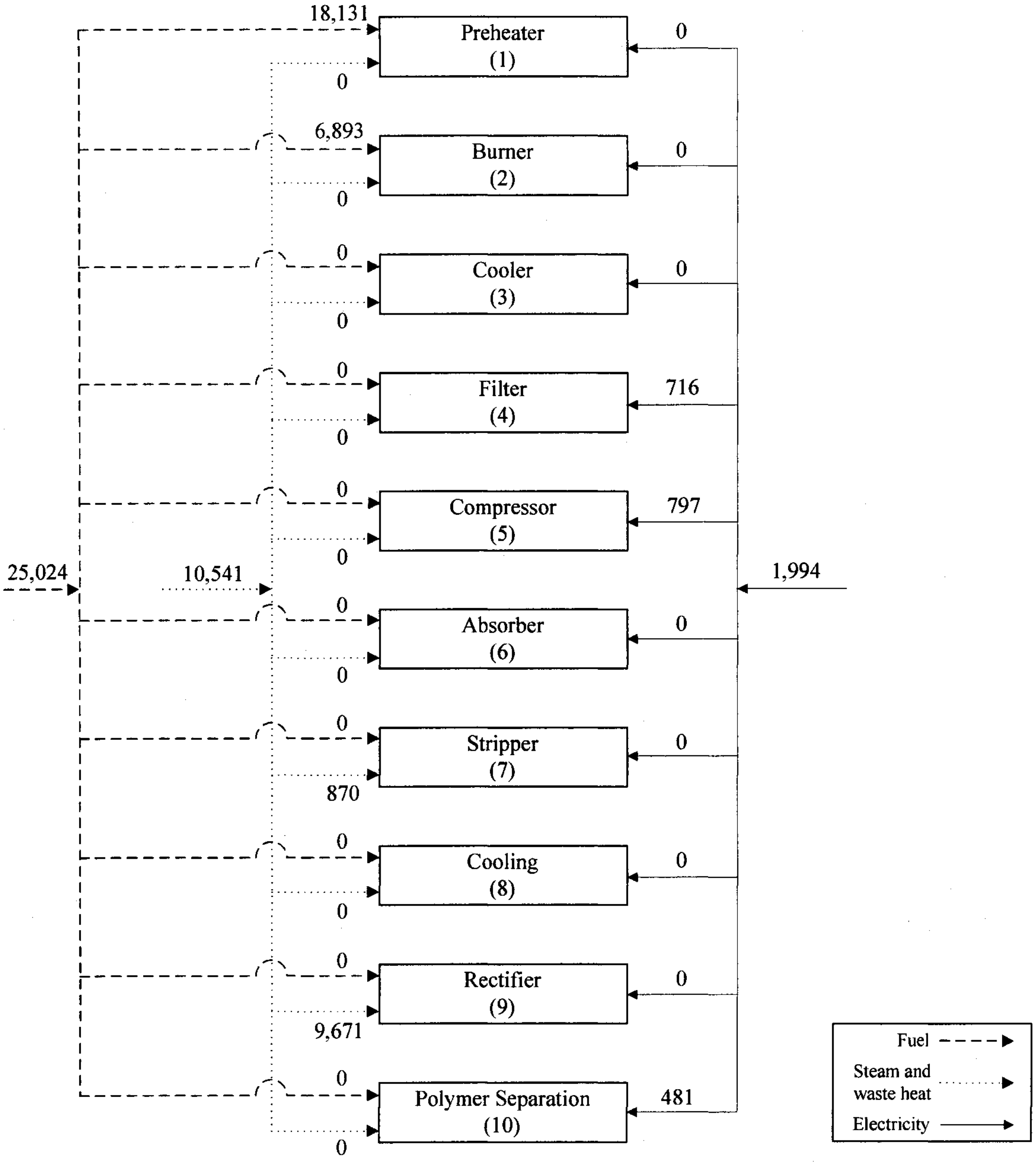

Figure 37. Representative unit mass acetylene production energy process-step model, kJ/kg

Figure 37 shows the energy consumption in each step of the process per unit acetylene production. This figure provides energy inputs in terms of electricity, fuel, and steam and waste heat. Energy inputs per unit acetylene production are given in Table 35 along with comparison with another study.

Table 35. Comparison of energy inputs per unit acetylene produced, kJ/kg

	Drexel	**Pässler et al.**
Process	Steam reforming of natural gas	Partial combustion of natural gas
Energy input		
Electricity	1,994	34,900
Fuel	25,024	12,000
Steam	10,541	11,700
Total	**37,559**	**58,600**

As it is seen in Table 35, although there is about 10% difference in steam consumption between Brown et al. (1996) and Pässler et al. (2000), the differences in electricity and fuel consumptions are significant. In order to explain the difference in fuel consumption we need to look at the process steps that consumes fuel. In both Drexel and Pässler et al., natural gas and oxygen are preheated separately by burning some fuel. "The separate preheating of the reactants to the highest temperature possible before introduction into the burner reduces the consumption of oxygen and the hydrocarbon within the burner. It also causes a higher flame propagation speed and therefore a higher mass flow within the acetylene burner." Pässler et al.(2000). Therefore, in acetylene production, separate preheating of the feedstock is an unavoidable process step. Although Drexel shows the fuel intake for preheating, Pässler et al. does not show how much fuel is consumed during preheating. Therefore, a comparison of the fuel consumptions at preheating step of the Drexel and Pässler et al. cannot be made. However, we can track the fuel consumption in Drexel since all of the energy inputs are stated separately and clearly. This approach may explain the differences with Pässler et al. in general. So, the next fuel consuming step in the acetylene production is at the burner. After preheating, natural gas and oxygen at high temperature enter the burner for combustion. Therefore, the natural gas entering to the burner is the fuel. However, since natural gas is also the feedstock for acetylene production at the same time, the energy content of natural gas entering the burner can be considered both as a fuel and as a feedstock. If we consider it as a fuel, then we obtain 25,024 kJ as shown in Table 35. On the other hand, if we consider it as a feedstock and remove it from fuel consumption account, then the fuel consumption value in Table 35 becomes 18,131 kJ. In this case, the total fuel consumption in Drexel is about 34% higher than the Pässler et al. Since there is no detailed information about preheating process in Pässler et al. to see what kind of application they used to have smaller fuel consumption, an explanation to this 34% difference is unavailable.

As for the electricity consumption, we see a big difference between Drexel and Pässler et al. In order to explain this difference, we need to refer to the process steps requiring electricity consumption. In Drexel, the only electricity consuming process step is "compression". However, in Pässler et al., there is a very detailed process diagram for purification, which includes more electricity consuming components than in the Drexel process. Therefore, the acetylene production process in Pässler et al. might be more electricity consuming than Drexel acetylene production process for the expense of obtaining higher purity. Since Drexel does not provide any information about the purity level of acetylene, we do not know if this argument is correct. However, it is more likely that the explanation to more electricity consumption in Pässler et al. is to purify acetylene to a higher level.

In order to scale the values given in Figure 37 against the national data, we can use the acetylene production amount given in Table 4 of Chapter 1. The scaled values are given in Figure 38.

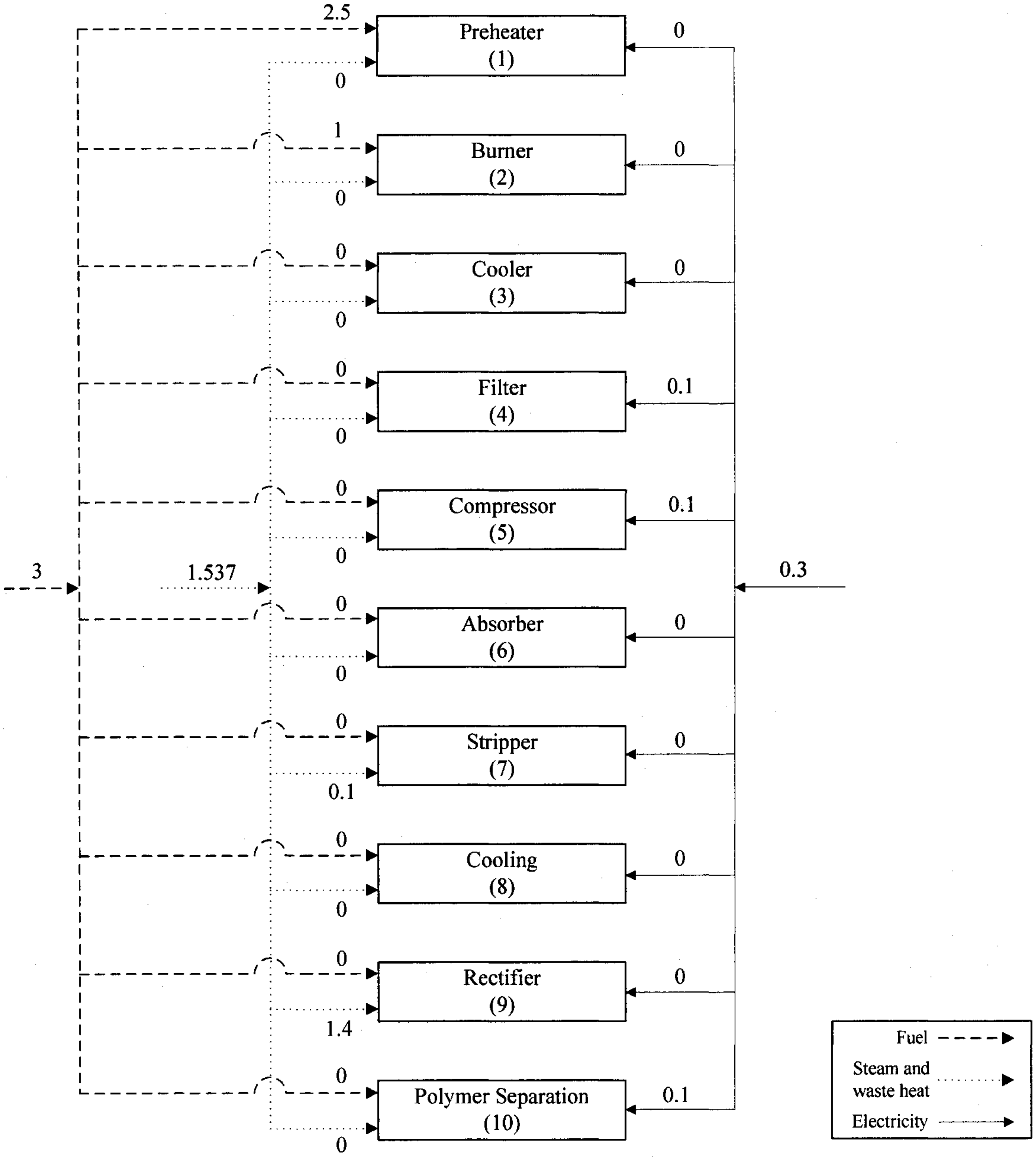

Figure 38. Energy process-step model of acetylene production in 1998, PJ

The next step is to calibrate these values against the national energy end-use model given in Figure 18 of Chapter 2, so that this energy process-step model better represents energy flows during acetylene manufacturing in 1998. The approach to doing this is presented in section 5.3.

5.2.2. Carbon dioxide energy process-step model

In Chapter 3, carbon dioxide production as a recovery from flue gas was selected as the representative carbon dioxide purification and liquefaction process. So the national scale material flow model will be given for this technique. However, some detailed discussions on energy consumption during carbon dioxide production will be given in this chapter for carbon dioxide production as a byproduct of ammonia process as well for the purpose of comparison with our representative technique.

As it was discussed in Chapter 3, both carbon dioxide recovery from flue gas and carbon dioxide as a byproduct from ammonia production are commercially most utilized techniques. However, since there is no quantitative information about which of these two techniques is used more than another, the representative technique selection was made based on the availability of data on these two techniques. In this chapter, we can take a closer look at these two techniques in terms of the quantitative energy data on them.

The energy consumption during carbon dioxide production as a byproduct from ammonia production can be attributed to ammonia production as the main purpose of the process is to produce ammonia. This argument is supported by Kim and Overcash (2000), who state that the “energy requirement is more heavily allocated to ammonia than carbon dioxide”. In addition, if we look at the energy consumption analysis provided in Jiménez-González et al. (2000), the energy requirement listed specifically for carbon dioxide production is 2,800 MJ per 1000 kg ammonia production, whereas it is 16,756 MJ per

1000 kg ammonia production for ammonia production. Furthermore, Jiménez-González et al. (2000) point out that this 2,800 MJ is not for the carbon dioxide production process itself, but for purification of carbon dioxide. This also supports that the energy consumption during ammonia production, which results in carbon dioxide as a byproduct, belongs entirely to ammonia production. Finally, Kim and Overcash (2003) generalizes the energy consumption during purification process with this statement "about 50% of the energy consumed in chemical processes is used for purifying the product, byproduct or recycled stream". This discussion suggests that the energy consumption during ammonia production should not be accounted as part of carbon dioxide production, only the energy consumption during carbon dioxide purification, liquefaction and solidification.

The Drexel energy process-step model for carbon dioxide as a byproduct of ammonia production does not include carbon dioxide purification, liquefaction or solidification. On the other hand, Jiménez-González et al. (2000) ammonia production process defines the carbon dioxide separation and purification process as "the synthesis gas passes through an absorption tower to separate carbon dioxide before going to the ammonia synthesis process." The absorption tower does not require any energy to separate the carbon dioxide, therefore the energy required for carbon dioxide purification occurs following separation. Jiménez-González et al. (2000) states that "removed carbon dioxide is desorbed in a carbon dioxide stripper." So, the stripping and pumping are the only energy consuming steps according to the carbon dioxide separation and purification process steps described in Jiménez-González et al. (2000). The possible energy requiring components and process steps may briefly be listed as follows:

- Pumps to move liquids,
- Compressors to move gases,
- Heating and cooling to get to proper operation temperature,
- Stripping to absorb fluid.

If we look at energy requirement in carbon dioxide purification from flue gas in EG&G (2002), it shows that about 0.77 MJ energy is required, 0.47 MJ of which is heat, while 0.30 MJ is electricity, in order to produce 1 kg pure carbon dioxide. Alternatively, the carbon dioxide purification energy requirement in Jiménez-González et al. (2000) corresponds to 2.37 MJ energy per unit carbon dioxide. This comparison suggests that energy requirement to purify carbon dioxide obtained as a byproduct of ammonia production is more than to purify carbon dioxide obtained from flue gas. However, it contradicts with the statement made by Topham (2000), which states that "carbon dioxide from ammonia plants is usually high degree of purity before being subjected to purification and liquefaction". Therefore, use of carbon dioxide as a byproduct from ammonia production results in the production of very pure carbon dioxide (Topham, 2000). Topham's (2000) statement conflicts with the results from both Jiménez-González et al. (2000) and EG&G (2002).

Although Jiménez-González et al. (2000) provide information about carbon dioxide purification, it does not contain information about carbon dioxide liquefaction. On the other hand, EG&G (2002) does describe a carbon dioxide purification & liquefaction process along with its energy requirement. Since the EG&G (2002) includes both liquefaction and purification in detail, the carbon dioxide purification and liquefaction process from EG&G (2002) will be given as representative carbon dioxide purification and liquefaction process.

5.2.2.1. Energy process step model for carbon dioxide purification and liquefaction

In EG&E (2002)'s carbon dioxide purification and liquefaction process, compressed flue gas condenses the water by lowering the temperature to -23 °C. The condensed water scrubs out impurities, such as amine, ammonia etc. This process liquefies approximately 95% of the carbon dioxide. Topham (2000) states that "critical parameters of carbon dioxide, $T_{critical} = 31$ °C and $P_{critical} = 7.4$ MPa, show that it may be liquefied at any temperature between 31 °C and its triple point -56.6 °C by compression to the required liquefaction pressure at that particular temperature and removal of the heat of condensation" This agrees with the EG&G's (2002) carbon dioxide liquefaction approach.

By taking the EG&G's carbon dioxide purification & liquefaction process as a representative carbon dioxide purification and liquefaction process we obtain Figure 39 for unit pure and liquefied carbon dioxide production.

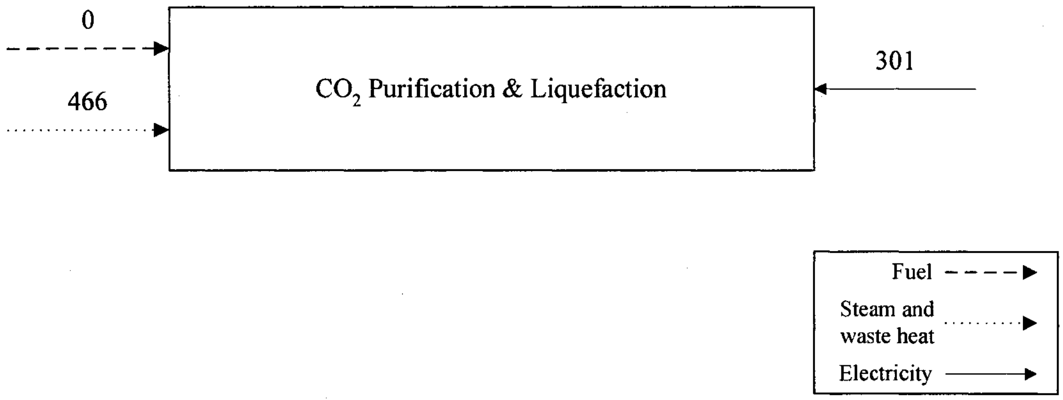

Figure 39. Representative CO_2 purification and liquefaction energy process-step model, kJ/kg

The representative carbon dioxide purification and liquefaction energy process-step model in Figure 39for unit liquid carbon dioxide production can be scaled using the liquid carbon dioxide production data in Table 27.

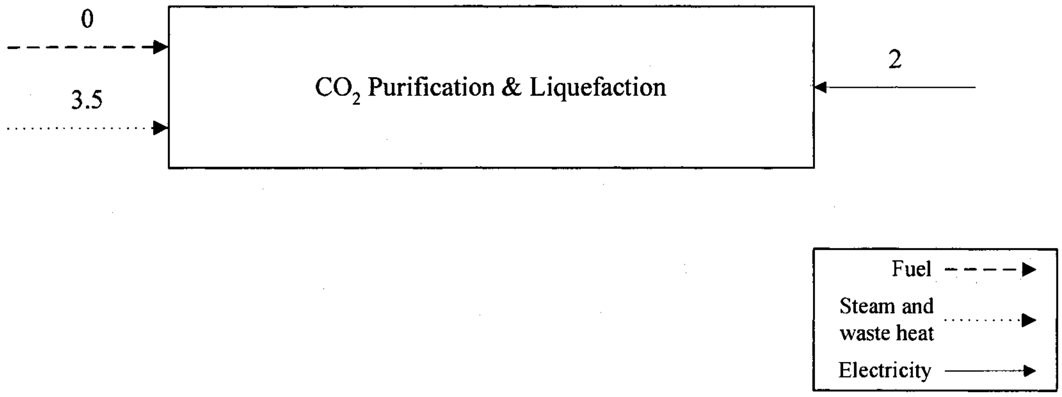

Figure 40. Energy process-step model of carbon dioxide purification and liquefaction in 1998, PJ

Figure 40 shows energy-process step model of carbon dioxide purification and liquefaction in 1998 based on the scaling performed on EG&G (2002) process model. The next step is to compare the energy consumption values given in this figure with the national energy end use consumption data. This is discussed in section 5.3.

5.2.2.2. Energy process-step model for carbon dioxide solidification

Although process steps of solid carbon dioxide formation are given in Topham (2000), quantitative information about energy requirement of this process is not provided. Very similar descriptions of the carbon dioxide solidification is also given in Kirk-Othmer (1991). However, there is no quantitative information about energy inputs during the solidification process in this reference either.

Nonetheless, it is clear that the energy consuming process steps for carbon dioxide solidification as described in Chapter 3 are:

- Compression of "snow" carbon dioxide to a solid block,
- Automated system of band saws,
- Cutting the solid block into smaller pieces.

Further, we can see that these steps are all electricity dependent. Even though it is relatively difficult to estimate the amount of electricity to run an automated system of band saws and to run the cutting blade, the energy required to compress "snow" carbon dioxide to a solid block can be approximated as described below.

Topham (2000) states that the density of "snow", formation of carbon dioxide after allowing the liquid carbon dioxide to expand to atmospheric pressure, is about 500 kg/m^3. After compression, the density of the solid carbon dioxide block is about 1550 kg/m^3

(Topham, 2000). Therefore, if we find the energy required to compress dry ice from 500 kg/m^3 to 1550 kg/m^3, then that value provides the required electricity input to the compressor after accounting for compressor efficiency.

The energy required to produce a volume change ΔV under constant uniform pressure P can be found from

$$E = P\,\Delta V \tag{1}$$

The volume change in the solid carbon dioxide can be found from

$$\Delta V = m\,(d_2 - d_1) / d_1\,d_2 \tag{2}$$

where $\Delta V = V_2 - V_1$ and d_1 and d_2 are the initial and final mass densities.

The total solid carbon dioxide production from Table 27 is $2.6\text{x}10^8$ kg. This information together with the density values presented above can be substituted into equation (2) to yield the volume change as $\Delta V = 3.5\text{x}10^5\ m^3$.

Now, in order to find the energy required to compress carbon dioxide from 500 kg/m^3 to 1550 kg/m^3, we need to find the pressure. The initial pressure of the carbon dioxide "snow" is $P_{initial} = 101$ kPa (atmospheric pressure). In order to calculate P_{final}, we can make the use of the fact that an elastic body subjected to a uniform hydrostatic pressure P will change volume ΔV according to

$$\Delta V = -\,P / k \tag{3}$$

where k is the "bulk modulus" or "modulus of compression of the material" (Beer, 1992). If we know the bulk modulus of solid carbon dioxide, we can calculate the final pressure from equation (3) as we already calculated the change in volume above. However, the bulk modulus of dry ice varies with pressure. Therefore, without knowing the pressure, bulk modulus cannot be found. As a result, the final pressure of the solid carbon dioxide can not be calculated from equation (3).

As an alternative, we can turn to dry ice manufacturers to get information about the pressure required to form dry ice. For example, one of the dry ice producers Polar Ice Inc. replied to my email by stating that "liquid CO_2 is injected into a chamber, where it turns to a "snow" at atmospheric pressure, then "dry ice snow" is compressed by a hydraulic press at 11 MPa to form a solid dry ice block" (Polar Ice Ltd., 2005). On the other hand, Yara Gas and Chemicals's reply to my question was 4 MPa (Yara Gas and Chemical, 2005).

If we take Polar Ice Ltd.'s pressure as P_{final}, then the average pressure is 11 MPa + 101 kPa) / 2 = 5.6 MPa. If we substitute this in equation (1), then we find that the estimate energy input to make dry ice is E = 5.6 MPa x $3.5x10^5$ m^3 = $1.96x10^{12}$ J. This estimation shows us that 0.00196 PJ energy was consumed in 1998 to make dry ice.

If we take Yara Gas and Chemical's pressure as P_{final}, then the average pressure is 4 MPa + 101 kPa) / 2 = 2.1 MPa. If we substitute this in equation (1), then we find that the estimated energy input to make dry ice is E = 2.1 MPa x $3.5x10^5$ m^3 = $7.35x10^{11}$ J. Then the estimate energy requirement to produce solid carbon dioxide in 1998 for this case is $7.35x10^{-4}$ PJ.

Another estimate can be made without using the pressure applied to form dry ice blocks or pellets. For example, a hydraulic press manufacturer company, which provides equipment for carbon dioxide production, gives information about the energy consumption of their dry ice pellet maker hydraulic press to be 14,400 kJ (4 kWh) to produce 0.198 kg of dry ice (Tom CO_2 equipment, 2005). If we take the characteristics of their hydraulic press as typical for this industry, then we can estimate the total energy input for hydraulic presses to produce the 1998 production level of solid carbon dioxide from (14,400 kJ x $2.6x10^8$ kg) / 0.198 kg = 18.9 PJ.

Several different approaches were demonstrated above to estimate the energy requirement for solid carbon dioxide production. The approach using equation (1) gave a considerably smaller value than the estimate made by using "energy consumption of a dry ice pellet maker hydraulic press". Since equation (1) is ideal, some difference was expected but not at this magnitude. Possible explanation to this difference is more likely the inaccuracy of the information given by the manufacturer.

If we compare these estimated energy consumption values of solidification with the energy consumption values of purification and liquefaction in Figure 40, we see that energy consumption for solidification is smaller for the ideal case and bigger for the pellet maker hydraulic press case.

5.2.3. Nitrogen and Oxygen energy process-step model

As it is discussed in Chapter 3, cryogenic and non-cryogenic productions data from the CIR was assumed to be the most reliable. Therefore, the representative energy process-step model scaling will be done based on the information given in CIR.

5.2.3.1. Nitrogen energy process-step model

Current Industrial Reports provides us that non-cryogenic nitrogen production in 1998 was 65% of the total nitrogen production as it is shown in Table 30. By using that information, we can scale the energy requirements for cryogenic and non-cryogenic nitrogen production technologies in 1998.

5.2.3.1.1. Cryogenic process

Cryogenic nitrogen production process steps were given in Chapter 4. The energy consumption of cryogenic nitrogen production from air is reported by Häussinger et al. (2000a) as "the specific energy consumptions of nitrogen generators range from 0.1 kWh/m^3 N_2 to 0.3 kWh/m^3 N_2 for the gas and depend on capacity and pressure." If we take the average of these values and multiply them by the CIR cryogenic nitrogen production, then we can estimate energy consumption for cryogenic nitrogen production in 1998 as follows:

Average energy consumption per volume = (0.1+0.3)/2 = 0.2 kWh/m^3

Mass of nitrogen @ STP and 1 m^3 volume is :

$$m = \frac{P \, x \, V}{\dfrac{R_{universal}}{Molar\ mass} xT} = \frac{101 \ kPa \ x \ 1 \ m^3}{\dfrac{8.314 \ kPa \ . \ m^3 / kmol.K}{28 \ kg / kmol} x300 \ K} = 1.13 \ kg$$

Average energy consumption per mass = 0.2 kWh/1.13 kg = 0.18 kWh/kg N_2

Average energy consumption per mass = 0.18 kWh/kg x 3,600 kJ/kWh = 648 kJ/kg

Average energy consumption on a national scale = 648 kJ/kg x 1.0x10^{10} kg = 6.48 PJ.

This shows us that based on the Häussinger et al. (2000a)'s estimate, total energy consumption for cryogenic nitrogen production in 1998 on a national scale was 6.48 PJ. Although this does not give us what portion of it was fuel, steam, waste heat or electricity, it is still a very useful information.

5.2.3.1.2. Non-cryogenic process

Nitrogen production technique using membrane separation of air process was listed in Chapter 4. It was seen that the nitrogen production from air separation by membrane is an electricity consuming technique. Although Hardenburger and Ennis (2005) do not provide quantitative information about energy consumption during this process, Häussinger et al. (2000a) states that "experimental data obtained during testing various small nitrogen generators from different vendors gave electrical consumption figures from 0.7 to 0.26 kWh per m^3 (STP) of nitrogen, depending on feed air quantity, purity and nitrogen recovery." If we take the average of these values and multiply them by the Current Industrial Reports non-cryogenic nitrogen production amount given in Table 30, we can estimate the energy consumption for non-cryogenic nitrogen production in 1998 as follows:

Average energy consumption per volume = (0.7+0.26)/2 = 0.48 kWh/m^3

Mass of nitrogen @ STP and 1 m^3 volume is :

$$m = \frac{P \, x \, V}{\dfrac{R_{universal}}{Molar\ mass} xT} = \frac{101 \ kPa \ x \ 1 \ m^3}{\dfrac{8.314 \ kPa \ . \ m^3 / kmol.K}{28 \ kg / kmol} x300 \ K} = 1.13 \ kg$$

Average energy consumption per mass = 0.48 kWh/1.13 kg = 0.42 kWh/kg N_2

Average energy consumption per mass = 0.42 kWh/kg x 3,600 kJ/kWh = 1,529 kJ/kg

Average energy consumption in a national scale = 1,529 kJ/kg x 1.86×10^{10} kg = 0.03 PJ.

Since the electrical consumption values given in this source is based on experimental data for various nitrogen generators, energy estimate would be close to actual case.

5.2.3.2. Oxygen energy process-step model

Current Industrial Reports provides us that non-cryogenic oxygen production in 1998 was 76% as it is seen in Table 30. By using this information, we can scale the energy requirements for cryogenic and non-cryogenic oxygen production technologies in 1998.

5.2.3.2.1. Cryogenic process

The process steps of oxygen production via cryogenic air separation was given in Chapter 4. Barron (2000) reports that the ideal energy amount required for cryogenic separation of air to produce oxygen is 191 kJ/kg based on: "the minimum work of separation occurs when the separation process is carried out reversibly and isothermally at temperature of the surroundings" and "the ideal work of separation for air (a mixture of 78.1 mol % nitrogen, 21.0 mol % oxygen, and 0.9 mol % argon) at a temperature of 300 K".

If we take the information given in Barron (2000) to calculate energy consumption for cryogenic separation of air to produce oxygen in a national scale, we find the energy requirement in cryogenic oxygen production in 1998 to be 191 kJ/kg x 6.1×10^{10} kg = 1.17 PJ. However, it should be noted that this for an ideal case, which means that more than 1.17 PJ energy consumption should be expected for an actual case, depending on the efficiency.

5.2.3.2.2. Non-cryogenic process

The process steps of non-cryogenic oxygen production process was described in Section 4.4.3.3. Power inputs for a non-cryogenic oxygen plant, which produces 3,996 tons of 80% purity oxygen in a day at nominal load conditions, are provided by Kessler (2000) as: 1,178 MW fuel, and 116.5 MW electricity. It means that 1,178 MW x 24 h = 28,272 MWh fuel is consumed to produce 3,996 tons of oxygen, which corresponds to 28,272 MWh x 3,600 kJ/kWh = 0.10 PJ. As for the electricity: 116.7 MW x 24 h = 2,801 MWh energy is consumed to produce 3,996 tons of oxygen production, which corresponds to 2,891 MWh x 3,600 kJ/kWh = 0.01 PJ.

If we scale these values against the Current Industrial Reports non-cryogenic oxygen production amount in 1998, we find the fuel consumption to be 0.10 PJ/3,996 ton x 1.9×10^{10} kg = 475 PJ, and the electricity consumption to be 0.01 PJ/3,996 ton x 1.9×10^{10} kg = 48 PJ as shown in Figure 41.

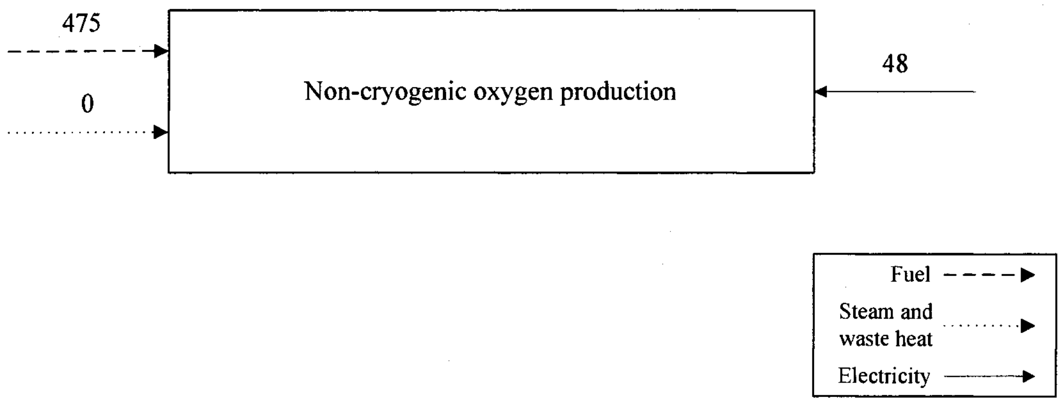

Figure 41. Oxygen energy process-step on a national scale in 1998, PJ

The fuel consumption in Figure 41 cannot be accurate. Because, if we look at Figure 18, we see that total fuel consumption in Industrial Gas Manufacturing sector for process end-uses is 37 PJ. So 475 PJ fuel consumption for non-cryogenic oxygen production is wrong. Besides, it does not match with any other fuel consumption numbers given for other industrial gases either. Therefore, the fuel consumption estimate given by Kessler (2000) turns out to be wrong when it is presented in a national scale. As a result, this model will not be included in the energy process-step analysis in this dissertation. Since my search on finding another non-cryogenic oxygen production model or data resulted with unsatisfactory information, energy process-step model for non-cryogenic oxygen production will be a gap in the dissertation. However, it could be research topic for someone else in the future to address the fuel, steam and electricity consumption during the non-cryogenic oxygen production on a national scale.

5.2.4. Argon energy process-step model

Since the dominant commercial argon production technology is the liquefaction of air as it was selected in Chapter 3, energy process-step model for argon production will be constructed for this technology based on Drexel model. However, we found out in section 4.4.3. that Drexel model does not work explaining the weight ratio between nitrogen and oxygen. Therefore, energy process-step model for argon production using Drexel may not be accurate either. But, we can still use Drexel model to see if makes a lot of difference in the total energy use in this industry. So, the national scale argon energy process-step model was developed based on the process steps given in Drexel model. And it was scaled against the national argon production amount given in Table 4. The energy process-step model for cryogenic argon production on a national scale is given in Figure 42.

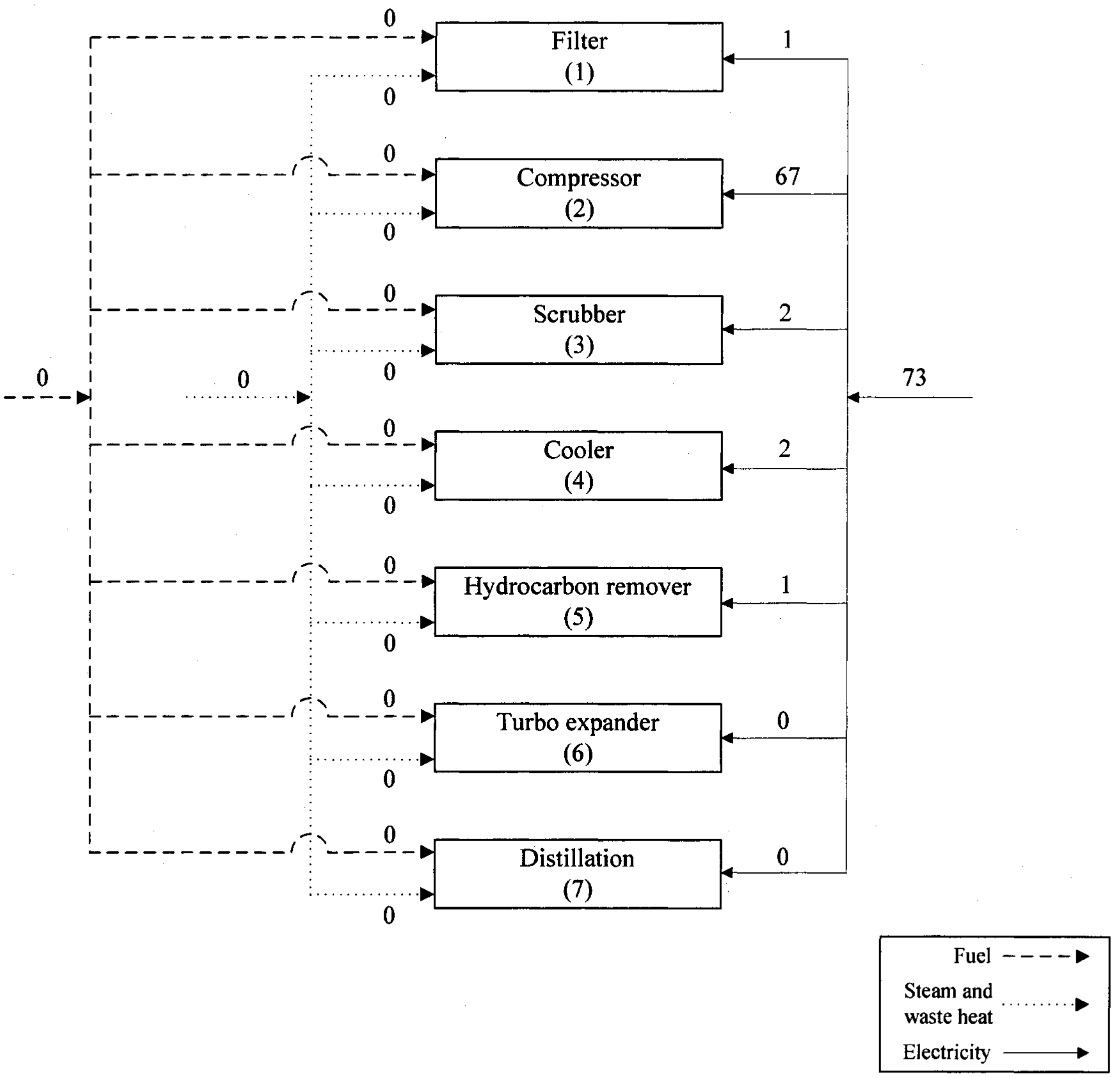

Figure 42. Energy process-step model of argon production in 1998, PJ

Figure 42 shows that there is no fuel and steam & waste heat consumption in cryogenic argon production, whereas there is 73 PJ electricity consumption. Compared to the electricity consumption values given for acetylene, oxygen, nitrogen and carbon dioxide, this value is relatively higher. This is more likely because it includes some portion of the cryogenic nitrogen and oxygen production.

If we look at Section 5.2.3.1.1., we see that total energy consumption estimate for cryogenic nitrogen production on a national scale was 6.48 PJ. On the other hand, if we look at Section 5.2.3.2.1., we see that total energy consumption estimate for cryogenic oxygen production on a national scale was 1.17 PJ. Although they represent total energy consumption without allocating it among fuel, steam, waste heat and electricity, we can still use these numbers to compare them with the Drexel argon model numbers to gain an overall sight.

So, we see that the total energy consumption estimate using Drexel argon model gives 73 PJ, whereas cryogenic nitrogen and oxygen energy consumption estimates from Sections 5.2.3.1.1. and 5.2.3.2.1. give about a total of 8 PJ. If we subtract 8 PJ energy consumption from 73 PJ to estimate the energy consumption for argon production only, it gives us 65 PJ, which is very high relative to the numbers given in Sections 5.2.3.1.1. and 5.2.3.2.1. for cryogenic nitrogen and oxygen.

This shows that there is a big difference between the energy consumption estimates for cryogenic argon using Drexel model and the cryogenic nitrogen and oxygen production given in Sections 5.2.3.1.1. and 5.2.3.2.1. This may suggest that the Drexel model for argon does not estimate the energy consumption accurately. Because, it is unlikely to expect less energy consumption for cryogenic oxygen and nitrogen production compared to cryogenic argon production unless argon process requires additional electricity requirement for highest purity that can be achieved. In this case, since purification process is the most energy consuming step, then it makes sense to expect more energy consumption in argon process for the expense of very high purity level. However, I have not found any information to verify this argument at present.

In conclusion, we can still use Drexel argon energy estimate to see if it fits into the total energy consumption in the whole Industrial Gas Manufacturing sector. This analysis is made in Section 5.4.

5.2.5. Hydrogen energy process-step model

Steam reforming of natural gas was selected as the representative hydrogen production technique in Chapter 3. Therefore, the energy process-step model will be given for this process on a national scale.

The Drexel model for hydrogen was used to construct the energy process-step model for hydrogen production as shown in Figure 43. In this figure, Drexel values were scaled by the CIR hydrogen production data from Table 4.

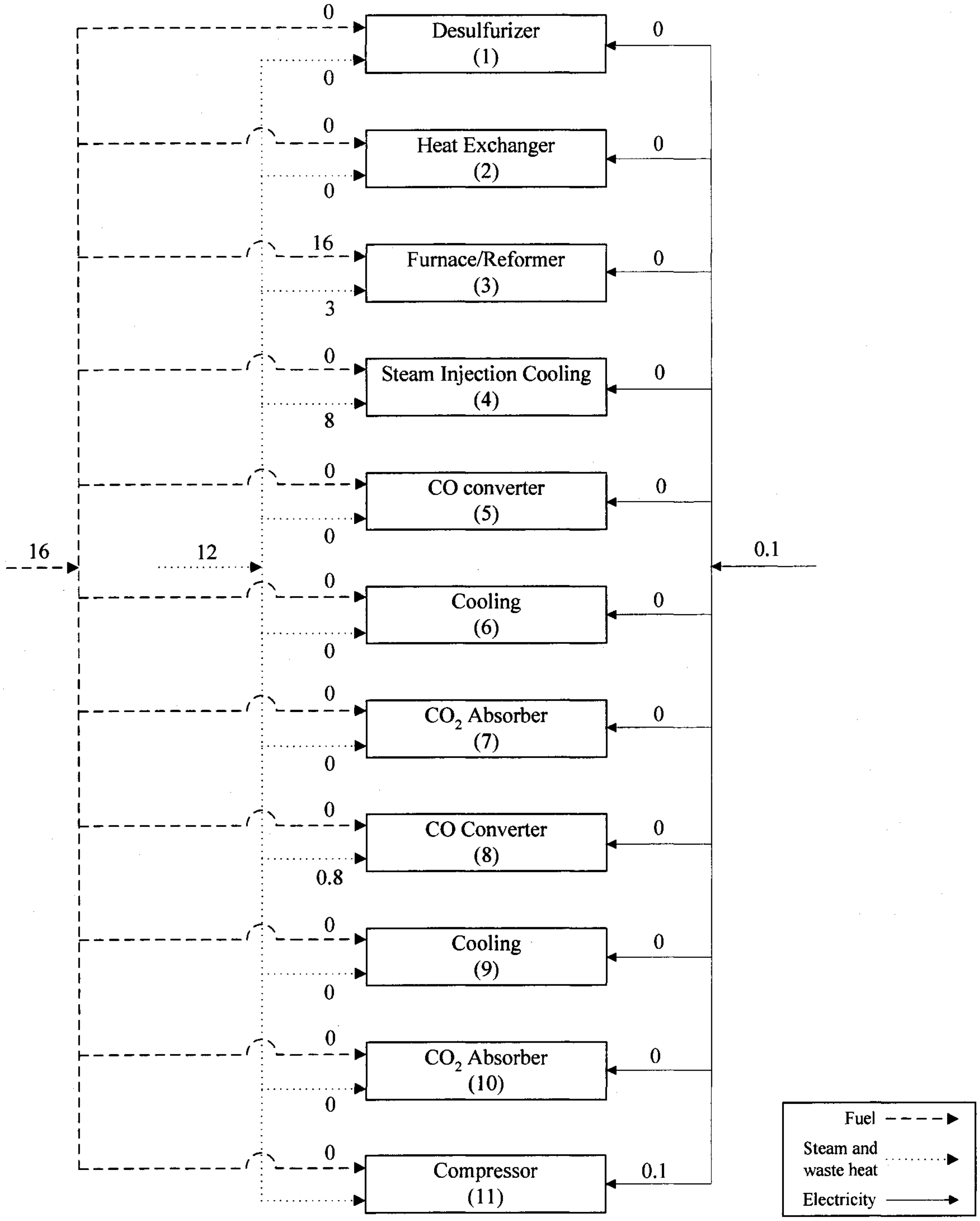

Figure 43. Energy process-step model of hydrogen production in 1998, PJ

The fuel, steam & waste heat, and electricity consumption estimates given in Figure 43 are discussed in Section 5.4. to see how do they fit into the total energy consumption given by MECS for the whole Industrial Gas Manufacturing sector.

5.2.6. Fluorocarbon energy process-step model

The NAICS definition of Industrial Gas Manufacturing sector products includes fluorocarbon gases as a product of this sector. However, it does not identify the list of fluorocarbon gases included in this category.

There are several different type of fluorocarbon production techniques in literature including patents. Information on fluorocarbon production can be found in various sources (ADL, 2002; Banks et al. 1972; Banks, 1970; OECD, 1976; Rudner, 1958; Davies et al., 1990).

In terms of energy consumption, an ADL report on fluorocarbons provides some estimates given in Table 36 (ADL, 2002).

Table 36. Energy consumption estimates for fluorocarbon manufacturing, PJ/kg

Fluorocarbon	**Energy**
134a	$1.05\text{x}10^{-7}$
R-22	$3.6\text{x}10^{-8}$
R-12	$3.0\text{x}10^{-8}$
Total	$\mathbf{1.71x10^{-7}}$

In the ADL report, it is stated that "no data was found for the embodied energy in manufacturing other HFCs" (ADL, 2002). Although there is data on energy requirement "to provide raw materials in a form that can be used at the plants and to process them through intermediates" into a fluorocarbon (McCulloch and Lindley, 2003), my search on finding some information on fuel, steam & waste heat and electricity consumption during fluorocarbon production process steps also resulted with no satisfying data. In addition, my contact to fifteen different fluorocarbon producers regarding the energy consumption during fluorocarbon production remained unanswered. Therefore, this is the energy consumption estimates available for fluorocarbon production at present. Since it does not include energy consumption estimates for all of the fluorocarbons, it will create a gap in our analysis.

The national scale energy consumption for fluorocarbon production can be estimated using the information given in Table 36 and the fluorocarbon production estimate of $2.4\text{x}10^6$ kg from Section 4.4.5. Therefore, national scale energy consumption for fluorocarbons = $1.71\text{x}10^{-7}$ PJ/kg x $2.4\text{x}10^6$ kg = 0.4 PJ.

Energy consumption during fluorocarbon production as a comparison to the total energy consumption in the Industrial Gas Manufacturing sector is discussed in Section 5.4.

5.3. Reconciliation of energy process-step models with federal data

The energy process-step models presented in section 5.2 represent estimated nationwide energy consumption for industrial gases manufacturing. However, these models contain many assumptions, as discussed in Chapter 3, regarding which processes are used etc. In order to calibrate nationwide energy flows for industrial gases, the values in Figures 42-47 need to be reconciled with the end-use model developed using national data.

The MECS-based end-use model in Figure 18 for industrial gases provides a suitable foundation to scale the values given in Figures 38-43. However, the end-use model is not given for each product, but as a summation of energy consumption for manufacturing all products in the Industrial Gas Manufacturing sector. Therefore, the values in the end-use model must be broken down for each product.

$$\sum\begin{pmatrix} \textit{End-uses}_{CO_2} + \textit{End-uses}_{N_2} + \textit{End-uses}_{O_2} + \textit{End-uses}_{C_2H_2} \\ + \textit{End-uses}_{Ar} + \textit{End-uses}_{H_2} + \textit{End-uses}_{Fluorocarbons} \end{pmatrix} = \textit{End-use values}$$

Additionally, the end-use values must be further broken down among process-steps. Briefly, in order to be able to scale the values in Figures 38-42, the end-use values must be divided two dimensionally: among products and among process-steps.

Figure 44 shows fuel, electricity and steam & waste heat inputs to process end-uses separately for each process uses only. This figure was basically extracted from process end-uses part of Figure 18.

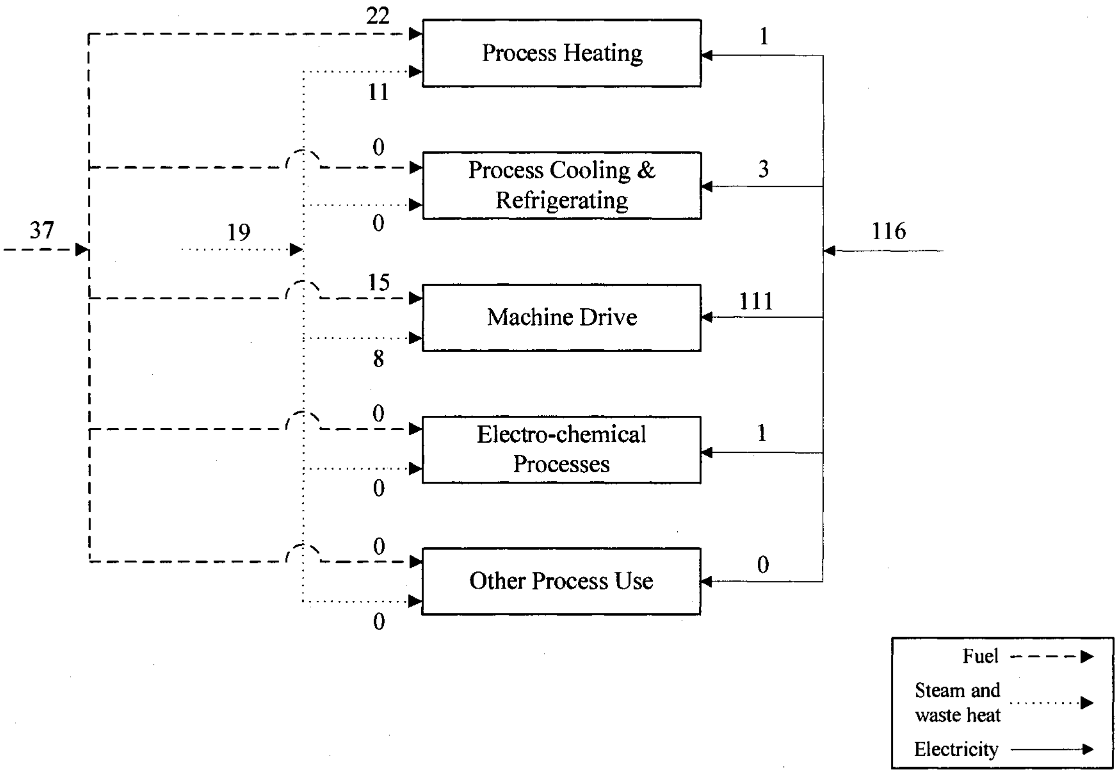

Figure 44. Allocation of fuel, electricity and steam among process end-uses in 1998, PJ

In order to use these values for scaling the values given in Figure 38-43, the break down procedure explained in section 5.3.1. can be followed.

5.3.1. Breakdown procedure of fuel, steam & waste heat and electricity values

The fuel (F) consumption values assigned to process heating (PH) can be represented as follows:

$$Fuel\ \ consumption\ \ for\ Process\ \ Heating\ _{Acetylene} = W\ _{PH-F}$$

$$Fuel\ \ consumption\ \ for\ Process\ \ Heating\ _{CO_2} = X\ _{PH-F}$$

$$Fuel\ \ consumption\ \ for\ Process\ \ Heating\ _{O_2} = Y\ _{PH-F}$$

$$Fuel\ \ consumption\ \ for\ Process\ Heating_{N_2} = Z_{PH-F}$$

$$Fuel\ \ consumption\ \ for\ Process\ Heating_{Ar} = P_{PH-F}$$

$$Fuel\ \ consumption\ \ for\ Process\ Heating_{H_2} = Q_{PH-F}$$

$$Fuel\ \ consumption\ \ for\ Process\ Heating_{Fluorocarbon\ gas} = R_{PH-F}$$

The summation of them gives the total fuel consumption for process heating, which can be written as follows:

$$\begin{gathered} W_{PH-F} + X_{PH-F} + Y_{PH-F} + Z_{PH-F} + P_{PH-F} + Q_{PH-F} + R_{PH-F} = \\ Total\ Fuel\ consumption\ \ for\ PH = F_{PH} \end{gathered} \tag{1}$$

We can demonstrate the electricity (E) consumption values assigned to process heating using a similar notation described above. Then this results with:

$$\begin{gathered} W_{PH-E} + X_{PH-E} + Y_{PH-E} + Z_{PH-E} + P_{PH-E} + Q_{PH-E} + R_{PH-E} = \\ Total\ Electricity\ consumption\ \ for\ PH = E_{PH} \end{gathered} \tag{2}$$

Similarly, the steam & waste heat (S&WH) consumption values assigned to process heating can be represented as follows:

$$\begin{gathered} W_{PH-S\&WH} + X_{PH-S\&WH} + Y_{PH-S\&WH} + Z_{PH-S\&WH} + P_{PH-S\&WH} + Q_{PH-S\&WH} + R_{PH-S\&WH} = \\ Total\ Steam\ \&\ waste\ heat\ consumption\ \ for\ PH = S\&WH_{PH} \end{gathered} \tag{3}$$

The fuel consumption values assigned to cooling and refrigerating (PC&R) can be represented in a same fashion:

$$W_{PC\&R-F} + X_{PC\&R-F} + Y_{PC\&R-F} + Z_{PC\&R-F} + P_{PC\&R-F} + Q_{PC\&R-F} + R_{PC\&R-F} = \text{Total Fuel consumption for } PC\&R = F_{PC\&R} \tag{4}$$

Similarly, the electricity consumption values assigned to process cooling and refrigerating can be represented as follows:

$$W_{PC\&R-E} + X_{PC\&R-E} + Y_{PC\&R-E} + Z_{PC\&R-E} + P_{PC\&R-E} + Q_{PC\&R-E} + R_{PC\&R-E} = \text{Total Electricity consumption for Process } C\&R = E_{PC\&R} \tag{5}$$

The steam & waste heat consumption values assigned to process cooling and refrigerating can be represented as follows:

$$W_{PC\&R-S\&WH} + X_{PC\&R-S\&WH} + Y_{PC\&R-S\&WH} + Z_{PC\&R-S\&WH} + P_{PC\&R-S\&WH} + Q_{PC\&R-S\&WH} + R_{PC\&R-S\&WH} = \tag{6}$$

$$\text{Total Steam \& waste heat consumption for } PC\&R = S\&WH_{PC\&R}$$

We can demonstrate the fuel consumption values assigned to machine drive (MD) as follows:

$$W_{MD-F} + X_{MD-F} + Y_{MD-F} + Z_{MD-F} + P_{MD-F} + Q_{MD-F} + R_{MD-F} = \text{Total Fuel consumption for Machine Drive} = F_{MD} \tag{7}$$

Similarly, the electricity consumption values assigned to machine drive can be represented as follows:

$$W_{MD-E} + X_{MD-E} + Y_{MD-E} + Z_{MD-E} + P_{MD-E} + Q_{MD-E} + R_{MD-E} = \text{Total Electricity consumption for Machine Drive} = E_{MD} \tag{8}$$

The steam & waste heat consumption values assigned to machine drive can be represented as follows:

$$W_{MD-S\&WH} + X_{MD-S\&WH} + Y_{MD-S\&WH} + Z_{MD-S\&WH} + P_{MD-S\&WH} + Q_{MD-S\&WH}$$

$$+ R_{MD-S\&WH} = \tag{9}$$

$$\mathit{Total\ Steam\ \&\ waste\ heat\ consumption\ for\ Machine\ Drive} \ = \ S\,\&\,WH_{MD}$$

The fuel consumption values assigned to electro-chemical processes (ECP) can be represented as follows:

$$W_{ECP-F} + X_{ECP-F} + Y_{ECP-F} + Z_{ECP-F} + P_{ECP-F} + Q_{ECP-F} + R_{ECP-F} =$$

$$\mathit{Total\ Fuel\ consumption\ for\ Electro-Chemical}\ \mathrm{Pr}\mathit{ocesses} = \ F_{ECP} \tag{10}$$

The electricity consumption values assigned to electro-chemical processes can be represented as follows:

$$W_{ECP-E} + X_{ECP-E} + Y_{ECP-E} + Z_{ECP-E} + P_{ECP-E} + Q_{ECP-E} + R_{ECP-E} =$$

$$\mathit{Total\ Electricity\ consumption\ for\ Electro-Chemical}\ \mathrm{Pr}\mathit{ocesses} = \ E_{ECP} \tag{11}$$

The steam & waste heat consumption values assigned to electro-chemical processes can be represented as follows:

$$W_{ECP-S\&WH} + X_{ECP-S\&WH} + Y_{ECP-S\&WH} + Z_{ECP-S\&WH} + P_{ECP-S\&WH} + Q_{ECP-S\&WH}$$

$$+ R_{ECP-S\&WH} = \mathit{Total\ Steam\ \&\ waste\ heat\ consumption\ for} \tag{12}$$

$$\mathit{Electro-Chemical\ Processes} = \ S\,\&\,WH_{ECP}$$

The fuel consumption values assigned to other process uses can be represented as follows:

$$W_{OPU-F} + X_{OPU-F} + Y_{OPU-F} + Z_{OPU-F} + P_{OPU-F} + Q_{OPU-F} + R_{OPU-F} =$$

$$\textit{Total Fuel consumption for Other Process Uses} \;=\; F_{OPU} \tag{13}$$

The electricity consumption values assigned to other process uses (OPU) can be represented as follows:

$$W_{OPU-E} + X_{OPU-E} + Y_{OPU-E} + Z_{OPU-E} + P_{OPU-E} + Q_{OPU-E} + R_{OPU-E} =$$

$$\textit{Total Electricity consumption for Other Process Uses} \;=\; E_{OPU} \tag{14}$$

The steam & waste heat consumption values assigned to other process uses can be represented as follows:

$$W_{OPU-S\&WH} + X_{OPU-S\&WH} + Y_{OPU-S\&WH} + Z_{OPU-S\&WH} + P_{OPU-S\&WH} +$$

$$Q_{OPU-S\&WH} + R_{OPU-S\&WH} = \tag{15}$$

$$\textit{Total Steam \& waste heat consumption for Other Process Uses} \;=\; S\,\&\,WH_{OPU}$$

Now, we can write corresponding F_{PH} (total fuel for Process Heat), E_{PH} (total electricity for Process Heat), $S\&WH_{PH}$ (total steam & waste heat for Process Heat), $F_{PC\&R}$ (total fuel for Process Cooling & Refrigeration), $E_{PC\&R}$ (total electricity for Process Cooling & Refrigeration), $S\&WH_{PC\&R}$ (total steam and waste heat for Process Cooling & Refrigeration), F_{MD} (total fuel for Machine Drive), E_{MD} (total electricity for Machine Drive), $S\&WH_{MD}$ (total steam & waste heat for Machine Drive), F_{ECP} (total fuel for Electro-chemical Process), E_{ECP} (total electricity for Electro-chemical Process),

$S\&WH_{ECP}$ (total steam & waste heat for Electro-chemical Process), F_{OPU} (total fuel for Other Process Uses), E_{OPU} (total electricity for Other Process Uses), and $S\&WH_{OPU}$ (total steam & waste heat for Other Process Uses) values from the end-use model in Figure 44 as follows:

$$F_{PH_{end-use}} = 22\ PJ$$
$$F_{PC\&R_{end-use}} = 0\ PJ$$
$$F_{MD_{end-use}} = 15\ PJ$$
$$F_{ECP_{end-use}} = 0\ PJ$$
$$F_{OPU_{end-use}} = 0\ PJ$$

$$S\&WH_{PH_{end-use}} = 11\ PJ$$
$$S\&WH_{PC\&R_{end-use}} = 0\ PJ$$
$$S\&WH_{MD_{end-use}} = 8\ PJ$$
$$S\&WH_{ECP_{end-use}} = 0\ PJ$$
$$S\&WH_{OPU_{end-use}} = 0\ PJ$$

$$E_{PH_{end-use}} = 1\ PJ$$
$$E_{PC\&R_{end-use}} = 3\ PJ$$
$$E_{MD_{end-use}} = 111\ PJ$$
$$E_{ECP_{end-use}} = 1\ PJ$$
$$E_{OPU_{end-use}} = 1\ PJ$$

Following section gives a brief summary of the findings and demonstration of the above values in a table along with discussions.

5.4. Summary of the results

There are a total of 105 unknowns on the left hand side of equations (1) through (15). If we had complete energy process-step models for each product, we would know the value of each term. However, we can still gain a sight about the energy consumption in industrial processes by comparing the findings in Chapter 5 with the MECS end-use numbers in Figure 44.

Energy process-step models in Chapter 5 provided us energy consumption estimates during the production of industrial gases on a national scale. Due to the lack of data or consistent information, some of the energy process-step models are incomplete. Before analyzing the findings, we can summarize what we have got so far:

- Complete acetylene energy process-step model which shows allocation of fuel, steam and electricity to each process step (Figure 38),
- Partially complete carbon dioxide energy process-step model, e.g., energy process-step model was given for carbon dioxide purification and liquefaction only (Figure 40). Missing piece: carbon dioxide gas production energy process-step model. The solidification of carbon dioxide is purposely not included into the analysis due to its negligible energy consumption as discussed in Section 5.2.2.2.,
- Information on energy consumption for cryogenic nitrogen production (Section 5.2.3.1.1.). However, lack of information on allocation of that energy among the process steps. Also, lack of information on what portion of that energy is fuel, steam, waste heat or electricity. Therefore, although we have complete estimate on how much energy is required to produce cryogenic nitrogen on a national

scale, we do not have information on how it is allocated among the process steps and therefore among the end-uses,

- Information on energy consumption for non-cryogenic nitrogen production (Section 5.2.3.1.2.). However, lack of information on allocation of that energy among the process steps. Also, lack of information on what portion of that energy is fuel, steam, waste heat or electricity. Therefore, although we have complete estimate on how much energy is required to produce non-cryogenic nitrogen on a national scale, we do not have information on how it is allocated among the process steps and therefore among the end-uses,
- Information on energy consumption for cryogenic oxygen production (Section 5.2.3.2.1.). However, lack of information on allocation of that energy among the process steps. Also, lack of information on what portion of that energy is fuel, steam, waste heat or electricity. Therefore, although we have complete estimate on how much energy is required to produce cryogenic oxygen on a national scale, we do not have information on how it is allocated among the process steps and therefore among the end-uses,
- Information on energy consumption for non-cryogenic oxygen production (Section 5.2.3.2.2.). The problem with this information is that the fuel consumption estimate is inaccurate, whereas electricity consumption estimate is reasonable. Therefore, the fuel consumption estimate is not included, whereas electricity consumption estimate is included into the analysis,

- Complete argon energy process-step model which shows allocation of fuel, steam and electricity to each process step (Figure 42). However, energy consumption estimate in this model is more likely inaccurate as discussed in Sections 4.4.3.1. and 5.2.4. In addition, it should also be noted that this energy process-step model includes energy consumption for nitrogen and oxygen as well. But it will be included in the analysis anyway to see how much it fits or differs when we consider the total energy consumption in the Industrial Gas Manufacturing,
- Complete hydrogen energy process-step model which shows allocation of fuel, steam and electricity to each process step (Figure 43),
- Information on energy consumption for some of the fluorocarbons (Section 5.2.6.), which creates a gap in the analysis due to not having energy consumption estimates for the production of all fluorocarbons. We do not have information on what portion of that energy is fuel, steam, waste heat or electricity either. Therefore, we have an incomplete estimate on how much energy is required to produce fluorocarbons on a national scale.

If we put all of the results that we found together we obtain Table 37 below, which summarizes fuel, steam & waste heat, and electricity consumption estimates in Chapter 5.

Table 37. Comparison of End-use model data and the energy process-step models values, PJ

	End-use model	This study	C_2H_2	CO_2	N_2-C	N_2-NC	O_2-C	O_2-NC	Ar	H_2	F.
Fuel total	**37**	**20**	**4**	**0**	**NA**	**NA**	**NA**	**NA**	**0**	**16**	**NA**
Process Heating	22	20	4	0	-	-	-	-	0	16	-
Process C&R	0	0	0	0	-	-	-	-	0	0	-
Machine Drive	15	0	0	0	-	-	-	-	0	0	-
Electroch. Proc.	0	0	0	0	-	-	-	-	0	0	-
Other proc. uses	0	0	0	0	-	-	-	-	0	0	-
Steam & w.h. total	**19**	**16.5**	**2**	**3.5**	**NA**	**NA**	**NA**	**NA**	**0**	**11**	**NA**
Process Heating	11	3	0	0	-	-	-	-	0	3	-
Process C&R	0	8	0	0	-	-	-	-	0	8	-
Machine Drive	8	0	0	0	-	-	-	-	0	0	-
Electroch. Proc.	0	0	0	0	-	-	-	-	0	0	-
Other proc. uses	0	5.5	2	3.5	-	-	-	-	0	<1	-
Electricity total	**116**	**124**	**<1**	**2**	**NA**	**NA**	**NA**	**48**	**74**	**<1**	**NA**
Process Heating	1	0	0	0	-	-	-	0	0	0	-
Process C&R	3	2	0	0	-	-	-	0	2	0	-
Machine Drive	111	71	<1	2	-	-	-	0	69	<1	-
Electroch. Proc.	1	<1	<1	0	-	-	-	0	0	0	-
Other proc. uses	0	51	<1	0	-	-	-	48	3	0	-
Grand total	**172**	**169.5**	**5.8**	**5.5**	**6.5**	**<0.1**	**1.2**	**48**	**74**	**28**	**0.4**

F: fluorocarbon, NA: not available, C: cryogenic, NC: non-cryogenic

Table 37 enables us to compare the energy consumption estimates in Figure 44 with the energy consumption estimates given in this chapter.

To refresh our memory: Figure 44 is basically "process end-uses" part of the energy end-use model in Chapter 2. It was created mainly based on MECS database. The steam and waste heat estimates on that figure was made using extensive analysis as explained in Sections 2.3.4.6.1. through 2.3.4.6.2. The allocation of fuel, steam & waste heat, and electricity among the process end-uses were made based upon the MECS database and some assumptions as explained in Sections 2.3.2.2., 2.3.4.2., 2.3.4.3. and 2.4.5.2.

Although the numbers in energy end-use model were estimated based on a comprehensive analysis, they may still have some certain level of inaccuracy due to the possible errors in MECS database and the assumptions made. Therefore, it should be considered when making the comparison.

As for the energy consumption estimates given in the energy process-step models in Chapter 5: they were constructed by scaling the various public database and models in literature on the selected representative technology. The selection of the representative production technology for each industrial gas was the major assumption in those models. As discussed earlier, even for a particular production technology, there might be many process designs. So, the selection of a representative technology leaves out many of the possibly used process designs from the analysis. Therefore, the numbers in these models involve some level of inaccuracy. However, in order to gain a sight about this sector and to make an initiative step towards better analyzing this highly complicated sector, the risk of obtaining inaccurate numbers was taken. Therefore, this should be considered when making the comparison.

As it is seen, there are many missing pieces in Table 37. However, it still gives us a sight about the energy consumption during industrial processes and how close the estimates in energy process-step models in Chapter 5 compared to the estimates in energy end-use model in Chapter 2. This comparison will not only give us an information on approximate energy consumption during manufacturing, but also will tell us how good our "representative production technology" selections were.

We can start our comparison from the first row in Table 37, e.g. fuel total. It shows that the fuel consumption estimate from the energy end-use model is 37 PJ, whereas it is 20 PJ from the energy process-step models. The possible explanation to the difference is our not having information on fuel consumption in the production of cryogenic nitrogen, non-cryogenic nitrogen, cryogenic oxygen, non-cryogenic oxygen and fluorocarbon. If we look at the grand total at the very last row of Table 37, we see that we do have information on total energy consumption for these industrial gases, but we do not know "what form of energy is that total made out of". If we allocate the corresponding total energy at the very last of row of Table 37 among fuel, steam & waste heat, and electricity accordingly, we may obtain an estimate close to 37 PJ.

If we look at the total steam and waste heat consumption row in Table 37, we see that the energy end-use model estimates 19 PJ energy consumption, whereas energy process-step models estimate 16.5 PJ. The explanation to this difference would be same as the explanation we made for total fuel consumption above.

The electricity consumption estimate made in energy end-use model is 116 PJ, whereas it is 124 PJ in energy process-step models as both seen in Table 37. The possible reason for seeing a higher estimate in energy process-step models is more likely because of the inaccuracy of the argon process-step model as discussed earlier. As it is seen in Table 37, cryogenic argon production process requires electricity consumption only. If we assume that cryogenic nitrogen and cryogenic oxygen processes also require electricity only, then we can extract the grand total energy consumption for these processes from the last of Table 37 to add them into the "electricity total" row of Table

37. This assumption results that 6.5 PJ + 1.2 PJ = 7.7 PJ total electricity is required to produce nitrogen and oxygen cryogenically. If we compare this with the electricity consumption in cryogenic argon production, we see that Drexel model based argon process-step model's estimate is very much higher than the total electricity requirement estimate of cryogenic nitrogen and oxygen. This verifies one more time that the Drexel nitrogen, oxygen and argon model is inaccurate. However, if we remove the argon process-step model estimate from the "electricity total" row in Table 37 -since it is inaccurate- then we have 124 PJ – 74 PJ = 50 PJ, which very much smaller than the energy end-use model estimate of 116 PJ. Even if we include the 7.7 PJ cryogenic nitrogen and oxygen electricity consumption into the total, we still have 50 PJ + 7.7 PJ = 57.7 PJ. Therefore, it may suggest that argon production may require more electricity consumption relative to other industrial gases. It would be, for example, because it may require very high purity, which requires large amount of energy consumption. Or it could be due to another process related reason which would be a good research topic for someone else. In conclusion, the difference between the energy end-use model estimate for electricity and the energy process-step models estimates for electricity is very large unless we account argon process-step model. This may suggest that argon process-step model have been useful in terms of bringing the question of "larger electricity consumption possibility" during argon production.

Finally, if we look at the grand total at the last row of Table 37, we see that energy end-use estimate is 172 PJ, whereas energy process-step models estimate is 169.5 PJ. This shows that the energy consumption estimates for process end-uses by energy end-use model and by energy process-step models have very close agreement. This may suggest that the selection of "representative" processes in Chapter 3 were able to provide us an overall sight about this sector. This may also suggest that the argon process-step model may have some level of accuracy.

We can summarize this comparison as follows:

- Energy end-use model estimates are very close to the energy process-step models estimates,
- Energy consumption distribution among nitrogen, oxygen and argon production is unknown. This would be a good research topic for someone else in the future,
- Due to the complication of this sector, it was still possible to gain an overall sight about the estimate energy consumption for processes as shown in Chapters 2 and 5,
- Energy flow models in this dissertation can be improved to obtain closer estimates on this sector by refining the assumptions, accounting more than one representative process and searching for more data in the future by someone else.

Now, we have completed the comparison of the findings in Chapter 5 with the findings in Chapter 2. Since there are many data "not available" in Table 37, we could not make comparisons for each process end-use, e.g. comparison of fuel consumption for process heating etc. The lack of information on this very important data unable us to make a reconciliation. However, we can still describe the approach to reconciliation of the energy end-use model values and the energy process-step values, so that once the missing values in Table 37 are obtained, this approach may be applied.

The first step of the reconciliation approach is to find the fuel consumption ratios among each product. Then these ratios can be applied to end-use model total fuel value. This would redistribute the fuel consumption values among each product. Then, the fuel consumption for each product needs to be distributed among the process steps. This can be done by following the same logic as fuel distribution to each product, e.g. the fuel consumption ratios to each process-step is found for each product. Then, once the end-use fuel value is assigned to one particular product, that value can be further divided among each process-step based on the ratios found earlier. This approach can be applied for steam and electricity consumption as well.

For example, if we look at acetylene energy process-step model in Figure 40, the total electricity input to processes is 0.28 PJ, 36% of which goes to filter, 39% to compressor, and 25% to polymer separation. So the electricity consumption by acetylene according to the end-use model suggestion should be distributed among filter, compressor and polymer separation by using these ratios. However, this reconciliation approach may result in violation of conservation of energy. For example, if the electricity input found after distributing the end-use model value results in more than a 100% compressor efficiency, then it means that the distribution of the electricity based on the ratios found is a wrong approach. Or, it means that may be the process model do not reflect the real situation, e.g. there is more than one compressor or instead of a filter, there is an alternative component. Or furthermore, the electricity input values given in that process step model would be wrong.

If this reconciliation does not work, then more sophisticated approach can be taken. For example, the assumptions in the energy end-use model could be changed, which is beyond the scope of this dissertation but could be a recommended future work. In the end-use model, for instance, assumption for steam allocation would be adjusted so that it reflects the steam distribution in each process-step in a more enhanced way. For example, the steam distribution in the end-use model in this dissertation was made using the same ratios of fuel allocation to end-uses. However, in some cases, steam allocation is not same as the fuel allocation. If we look at Drexel hydrogen model as an example, it shows that steam allocation among the end-uses are: 68% to process cooling (steam injection to product combustion gases), 25% to process heating, and 7% to other process use (CO_2 converter). If we look at the fuel distribution in the same model, we see that fuel is consumed only for process heating. Therefore, the steam allocation to end-uses is not same as fuel allocation to end-uses. As a second example, if we look at the carbon dioxide production, which is the second biggest steam consuming process among other industrial gases, the Drexel model for carbon dioxide production shows that the fuel and steam allocation among the end-uses are exactly the same. Since the steam allocation to end-uses were assumed to be the same as fuel allocation to end-uses in both of the end-use models in this dissertation, this reconciliation would have been a good check to see if this assumption creates conflict between national data and the process step models. For example, in Table 37, the high steam values compared to end-use values would be because of the steam assumption made in the end-use model. Therefore, this reconciliation would give an opportunity to refine the end-use model.

In conclusion, this methodology can, in principle, be applied to calibrate the process-step models on a national scale. However, the calibration cannot be performed without having credible quantitative material flow and energy process-step models. At this point, since such models were not found in the literature for several industrial gases, e.g. CO_2 and argon, the calibration procedure could not be performed. This lack of suitable models is a major obstacle that needs to be overcome before the calibration approach described above can be applied in the future by someone else.

6. EMISSION FLOW MODEL

The emission flow model completes the portrayal of this manufacturing sector. The emissions included in this model are CO_2, SO_2 and NO_x, because these gases constitute the majority of the discussions on environmentally hazardous emissions (Jacobson, 2001; EIA, 2002; Wolf and Lützke, 2000; Elsner et al., 2000; Senkan and Castaldi, 2003; Shadle et al., 2002; Eissen et al., 2004; Lawrence et al., 2002; Worrell et al., 2001).

Sources of emissions are:

- Boilers,
- Prime movers,
- Fuel combustion in industrial processes,
- Non-combustion industrial processes.

Boilers burn a wide range of fuels and the emissions include CO_2, SO_2 and NO_x in the flue gas (Kuprianov, 2005; Kaylen, 2005; Staiger et al., 2005; Barisic et al., 2005). Gas turbines and internal combustion engines also emit these chemicals. For example, Raugei et al. (2005) reports CO_2 emissions in the range of 360 to 678 kg/MWh, CO emissions in the range of 0.13 to 0.25 kg/MWh, and NO_x emission in the range of 0.32 to 1.14 kg/MWh for three industrial gas turbines. As for the industrial processes, some chemicals are produced via combustion of fossil fuels. For example, hydrogen production involves the combustion of fossil fuel and air at the furnace/reformer. This process produces CO_2 which is discharged to atmosphere since it is a surplus chemical. CO_2 is emitted from non-combustion processes as well. For example, argon is produced from air and the small amount of CO_2 in air is discharged during purification process.

My emission flow model is based on emissions from boilers, gas turbines and industrial processes. Internal combustion engines are not included because there no data on internal combustion engine emissions in the Industrial Gas Manufacturing sector, which is probably because they do not use internal combustion engine but steam turbines and gas turbines instead. The industrial process emissions values in my emissions flow model are taken from the results of Chapter 4. On the other hand, emissions from the prime movers in the Industrial Gas Manufacturing sector were taken from an EPA database.

A generic representation of a process flow diagram common to all chemical processes created by Turton et al. is given in Figure 45 (Turton et al., 1998).

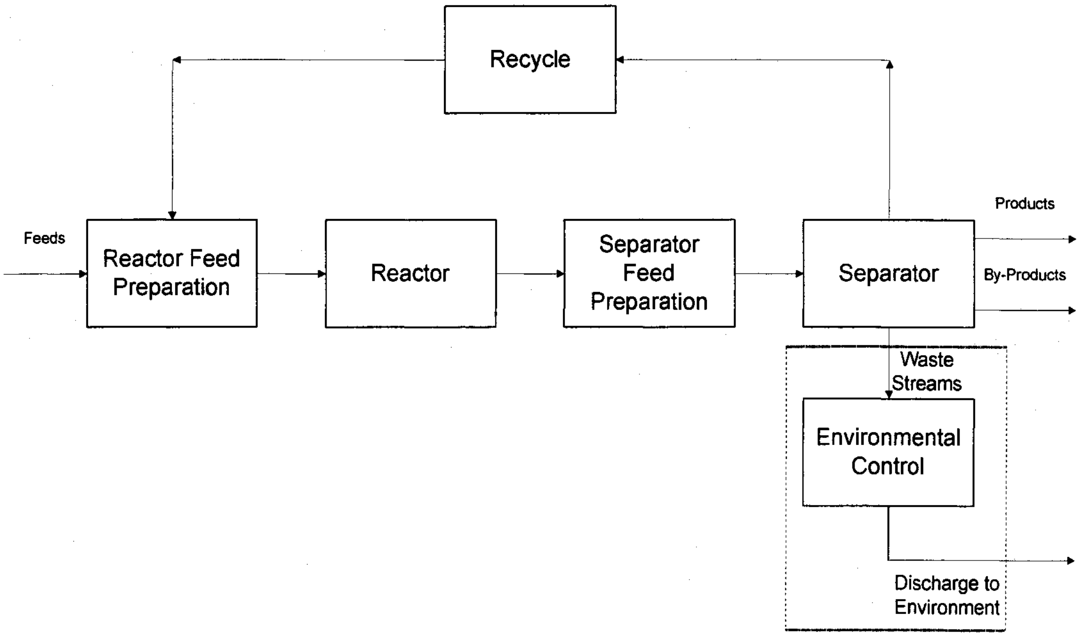

Figure 45. Generic input-output structure of chemical processes

In their process flow diagram, chemical processes are divided into six consecutive procedures ending with environmental control and finally discharge of gases, liquids and solids to the environment. It should be noted that this structure is a generalized illustration and in some cases the structure would be more/less complicated. Although this generic representation includes the emissions from industrial processes, it does not show the emissions from the boilers which supply steam for chemical processes. So my emission flow model completes this generic depiction by integrating emissions from the boilers. However, the boilers are used for both electricity generation and to supply steam for industrial processes. Therefore, the emissions from the boilers are associated both with electricity generation and supplying steam for industrial processes. Since there is no estimation provided regarding what portion of the boiler emissions would be contributed to industrial processes, my emission model gives the boiler emissions as one entry.

There have been prior efforts to create emission patterns for industrial process emissions and manufacturing industries (Worrell et al., 2001; Ruth et al., 2000; Olcese and Toselli, 2004; Carnevale et al., 2004; Mannschreck et al., 2001; Costa and Baldasano, 1995).

Worrell et al. (2001) provides CO_2 emissions from cement making process and power generation in global cement industry. They define the cement making process without giving mass inputs and outputs. Then they discuss energy usage during cement making by giving estimated electricity and fuel consumption at each step of cement manufacturing process for 1,000 kg cement production. They estimate the CO_2 emissions during cement manufacturing "based on production trends and energy use" (Worrell et al., 2001). However, they state that "because of the difficulty of data collection, we have only estimated the emissions for the year 1994". As for the estimation of CO_2 emissions from fuel consumption, they "review the 1994 data on the average specific fuel consumption per tonne of clinker for key countries, or for the closest year to 1994 for which there was available data." (Worrell et al., 2001).

Ruth et al. (2000) provide a benchmark for evaluating energy usage in the cement industry. The benchmark values that they estimate are given for the process steps of raw material preparation, clinker production and cement grinding. They take the energy consumption values given in the literature for cement-making process as actual performance and then they make estimates for "best practice" to compare with the actual performance. They also investigate the carbon reduction opportunities for the hypothetical plants they examine. Although they provide evaluation of carbon dioxide emissions from a "hypothetical plant", they do not provide any estimate about total carbon dioxide emission in the whole cement industry, nor about other emissions either from prime movers or industrial processes.

Olcese and Toselli (2005) developed a model estimating reactive gaseous emissions from industrial stacks. They do not provide validation to their model "due to the lack of experimental data", however, they suggest that the model could be used to predict the emissions. Therefore, this model does not provide an actual emissions from an industry but provides a model that may predict the emissions.

Carnevale et al.'s (2004) model provides estimates for both gas pollutants and particles. They use an emissions database and the activity information for 1998 in their model to estimate NO_x, CO, CO_2, SO_2 and VOC emissions in industry, transport, agriculture etc. Their emission model "has been validated performing episodic and seasonal simulations over Northern Italy" and the methodology that they propose "is not linked to any emission database and thus can be applied to other sites and/or emission inventories." However, the model does predict emissions from industrial processes.

6.1. CO_2 emissions

CO_2 emissions were about 80% of the total U.S. greenhouse emissions between 1990 and 2001 (EIA, 2002). CO_2 is the main cause of global warming and one of the stratospheric ozone layer depletion contributors, which is also called as "major greenhouse gas" (Jacobson, 2001; Rehan and Nehdi, 2005; Dyominov and Zadorozhny, 2005). The most important source of CO_2 emissions is primarily from fossil fuel combustion at the industrial boilers and gas turbines, and secondarily from industrial processes (EIA, 1999; Holloway, 2001). However, although this statement may be true for the manufacturing sector, CO_2 emission from transportation sector is higher than the CO_2 emissions from the manufacturing sector as it is seen in Figure 2.

The largest source of CO_2 emissions within the U.S. industrial sector is the manufacturing sector, which "accounts for 85% of the industrial energy-related carbon dioxide emissions and also accounts for approximately 84% of industrial energy consumption" (EIA, 2002). In 1998, the carbon intensity of energy supply in the chemical industry was 45.84 million metric tons per 10^{15} Btu of energy consumed. Energy related carbon dioxide emissions in this industry in 1998 are given in Figure 46 (EIA, 2002).

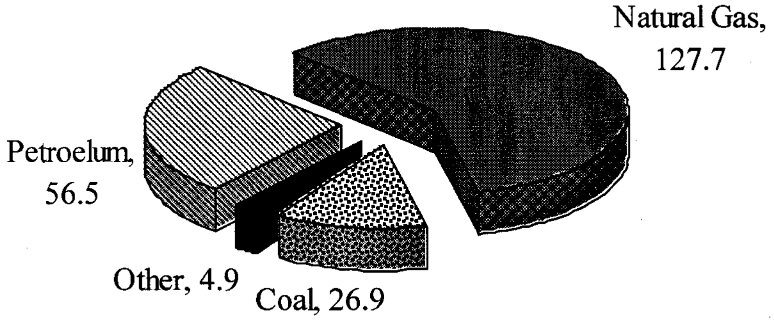

Figure 46. CO_2 emissions from the Chemical Industry by fuel in 1998, mmt CO_2

Figure 47 shows CO_2 emissions trend in the Chemical Industry due to the consumption of natural gas, petroleum, coal and other fuels in 1991, 1994 and 1998.

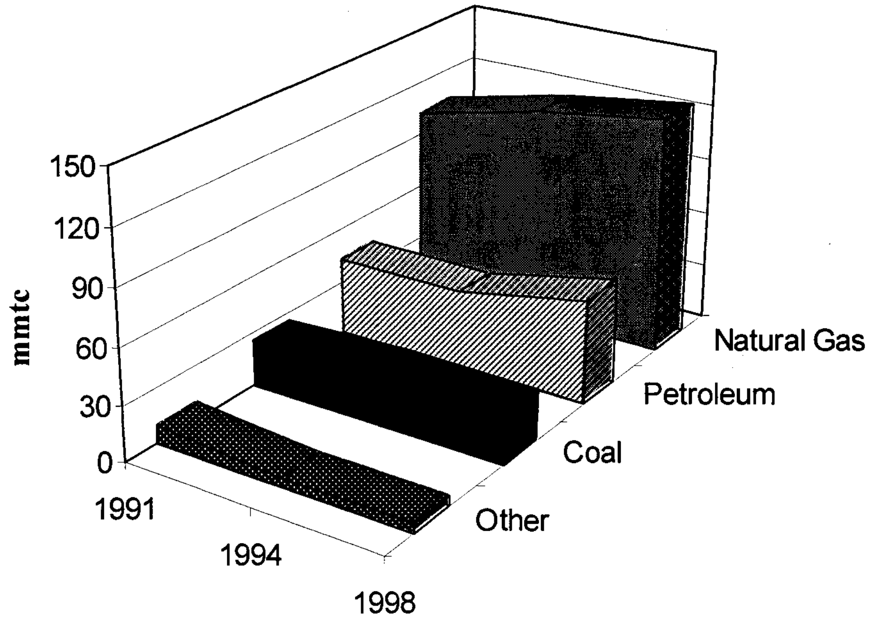

Figure 47. CO_2 emissions trend in Chemical Industry by fuel from 1991 to 1998, mmtc

It is seen from Figure 47 that, carbon dioxide emission from natural gas and petroleum consumption increase, whereas it remains about the same for the coal consumption. On the other hand, carbon dioxide emission from the consumption of other kind of fuels decreased.

An EIA report on emissions of greenhouse gases in the U.S. gives that 69.3 million metric tons CO_2 was emitted during industrial processes in 1998, which accounted for 1.24% of the total U.S. CO_2 emissions in 1998 (EIA, 2002). Since the Chemical Industry produces many products, there are numerous industrial processes in this industry emitting carbon dioxide. If we examine the carbon dioxide emission from the industrial processes, an EIA report provides data based on two research reports (EIA, 2002). Figure 47 shows carbon dioxide emissions from carbon dioxide production processes between 1990 and 2001 based on this EIA report (EIA, 2002, pg.36).

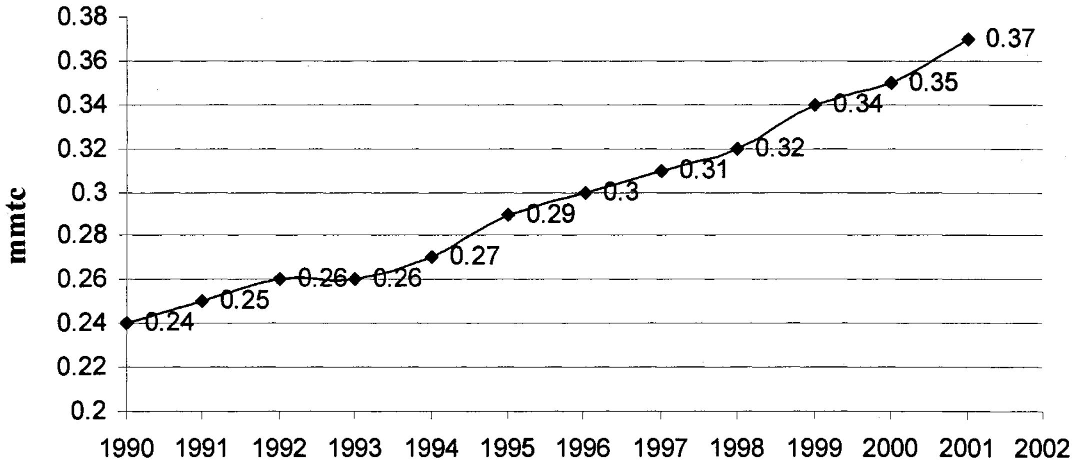

Figure 48. CO_2 emissions from carbon dioxide production processes, mmtc

Figure 48 shows that carbon dioxide emissions from carbon dioxide production increased by 35% from 1990 to 2001. The values given in Figure 48 includes carbon dioxide emissions from carbon dioxide produced by all industries. However, we know from Chapter 1 that 92% of the industrial gases, which includes carbon dioxide, is produced by the Industrial Gas Manufacturing sector. If we assume that the carbon dioxide emissions during carbon dioxide production given in this figure originated from Industrial Gas Manufacturing sector, then it suggests that the CO_2 emissions from the commercial carbon dioxide production in 1998 by the Industrial Gas Manufacturing sector was 0.32 mmtc, which corresponds to 1.2×10^9 kg CO_2. The total carbon dioxide production in 1998 by Industrial Gas Manufacturing sector was 1.3×10^{10} kg as it is seen in Table 4. Therefore, according to the EIA's (2002) database, carbon dioxide emission from carbon dioxide production process was 10% of the total carbon dioxide production.

Although the data says that carbon dioxide emissions during carbon dioxide production is charged to carbon dioxide production, it does not specify what carbon dioxide production technique is the emission source. If the carbon dioxide is recovered from ammonia production, then it could be argued that the CO_2 emissions should be charged to ammonia production rather than to the CO_2 purification and liquefaction processes. On the other hand if the carbon dioxide is recovered from flue gas, the CO_2 emissions are a result of burners or boilers which produce the flue gas in the first place. During CO_2 recovery from flue gas, CO_2 is absorbed that would otherwise be emitted into the atmosphere. Therefore, regardless of which of these two techniques is used to produce commercial CO_2, it is an accounting issue whether to charge the CO_2 emissions to CO_2 production or to the process that yields the CO_2 in the first place. Since EIA has chosen to charge these emissions to CO_2 production, the same accounting convention is followed in this dissertation.

6.2. SO_2 emissions

Sulfur oxide gases are formed when sulfur containing fuel is burned, e.g. coal and oil. "When fuels containing sulfur and wastes are burnt, sulfur dioxide is formed. Important emission sources are industrial furnaces, chemical plants, the cement industry, metal smelting, ceramics, the cotton industry, domestic heating, and traffic." (Wolf and Lützke, 2000). Industrial processes which uses coal or crude oil for process heating also emit sulfur oxide (EIA, 2005).

An EPA report on 1998 emissions provides the national sulfur dioxide emissions by percentage based on the principal sources as follows (EPA-SO_2, 1998):

- 67% fuel combustion (electric utility),
- 15% fuel combustion (industrial),
- 3% Fuel combustion (other),
- 2% Metals processing,
- 7% On-road and non-road engines and vehicles,
- 6% All other.

As it is seen from the above list, over 65% of the sulfur dioxide released to the atmosphere comes from electric utilities. It is stated in the report that the "all other" sources include solvent utilization, storage and transport, waste disposal and recycling and all industrial processes. This suggests that sulfur dioxide emissions from industrial processes are small relative to the sulfur emissions from other sources.

6.3. NO_x emissions

"The principle nitrogen oxides present in the atmosphere are nitric oxide (NO) and nitrogen dioxide (NO_2), collectively referred to as NO_x." (Bowman, 1992). The primary NO_x sources are due to fossil fuel combustion of motor vehicles, electric utilities, industry, commercial and residential sources (EIA, 2005).

According to the EIA (2002) the principle anthropogenic nitrous oxide emission between 1990 and 2001 shows that industrial NO_x emissions are a lot smaller than NO_x emissions from energy consumption and agricultural activities. Furthermore, the industrial NO_x emission shows a 53% decrease between 1990 and 2001. In 2001, estimated NO_x emissions from industrial processes was 58 thousand metric tons (EIA, 2002).

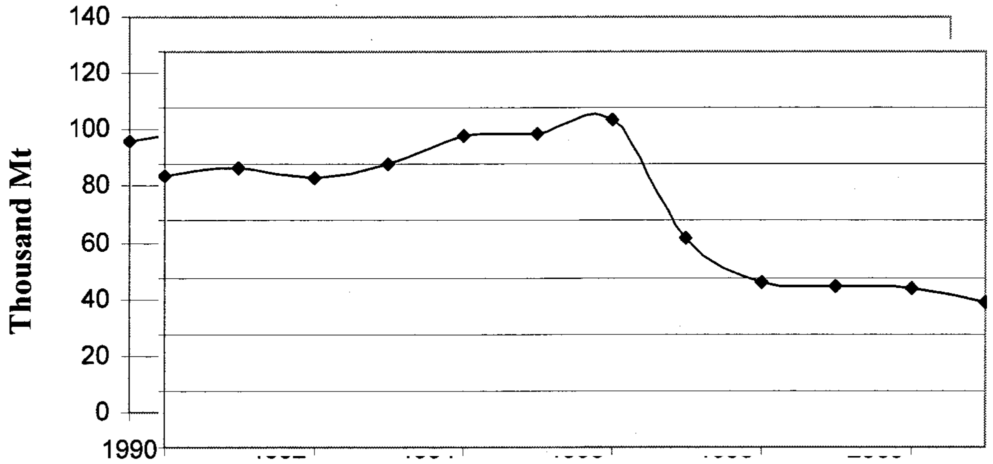

Figure 49. Estimated NO_x emissions from industrial processes between 1990-2001, thousand Mt

Figure 49 shows estimated NO_x emissions from industrial processes in the U.S. (EIA, 2002), whereas Figure 50 shows sources of industrial NO_x emissions (EIA, 2002).

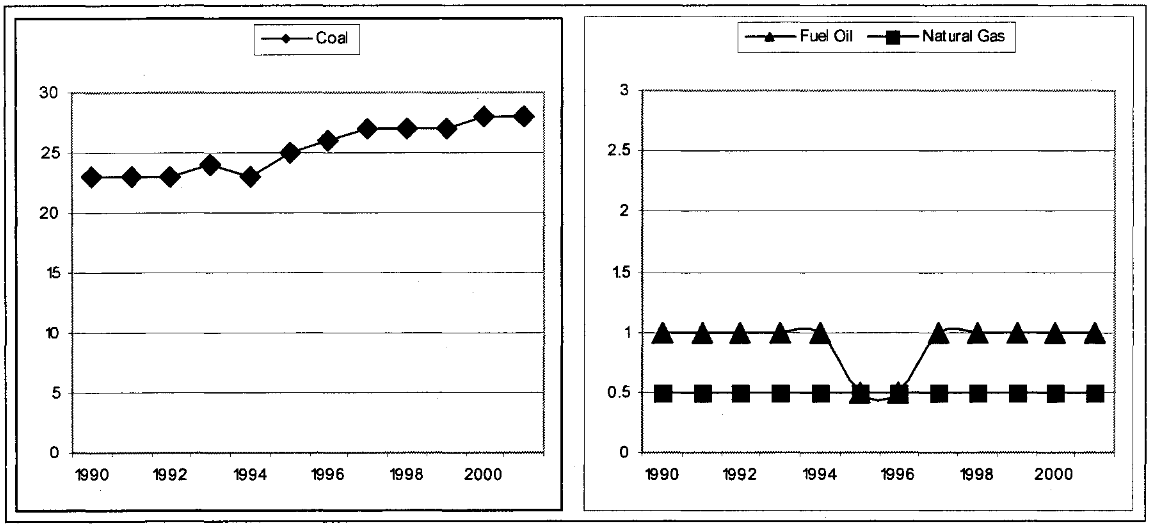

Figure 50. Sources of industrial NO_x emissions, Thousand Mt

It is seen in Figure 50 that the biggest NO_x emissions source from industrial processes is utilization of coal. On the other hand, fuel oil and natural gas utilization released about same amount of NO_x from industrial processes.

6.4. Methodology

In this section, the methodology to construct emission flow model of the Industrial Gas Manufacturing is given. Information about sources of data and some issues related to the database are provided as well.

6.4.1 Data

Unfortunately “emissions data from chemical processes are sparse” (EPA, 2005). However, EPA provides some data for emissions from fuel consumption by utilities, non-utilities, transportation etc.

6.4.1.1. Data sources

Environmental Protection Agency (EPA) provides data on emissions that are responsible for environmental hazards such as global warming and acid rain. The data provided by EPA can be used to create emission flow patterns of industrial processes for the years from 1996 to 2000, as the data is given only for this time period. Within these years, 1998 is the first year that plant level data for non-utilities was published. There are many data sources provided by EPA on emissions, such as: AP42, LCAccess, AirData, National Emission Inventory Data, AQS, and eGRID. However, my search among these database revealed that the “The Emissions & Generation Resource Integrated Database (eGRID)” is the most useful database for the scope of this dissertation (EPA-eGRID, 2005). Table 38 lists the description of the other data sources and their applicability to this dissertation.

Table 38. Other data sources and their applicability to this dissertation

Data source	Applicability
EPA-AP42	**Description:** "EPA42: Compilation of Air Pollutant Emission Factors" has two reports: "Volume 1: Stationary point and area sources" and "Volume 2 : Mobile sources" (EPA-AP42, 2005). Since the Volume 2 is for the mobile sources, it is out of the scope of this dissertation. ▪ Chapter 8 of the Volume 1 includes emissions from the manufacture and use of inorganic chemicals and chemical products. However, although it includes 14 chemicals, it does not include any of the Industrial Gas Manufacturing sector products. ▪ The ammonia production process description is very clear and useful. CO_2 recovery methods that are given in this source are in agreement with the other references given in Chapter 3. However, although the ammonia production process given in this source is from 1995, it gives the same steps that given in Drexel models (see Brown et al., pg.212). ▪ There is data for a "typical ammonia plant" which emits CO_2 during ammonia production process (there is no information or percentage about what they mean by "typical"). This data includes: - No data for CO_2 emission from desulphurization unit regeneration - There is data for CO_2 emission from steam stripper - Emission factor rating for CO_2 emission in this process is rated as "E", which corresponds to "poor" (see emission factor quality system in page 17 of EPA AP-42, Section 5.2, Synthetic Ammonia). **Conclusion:** CO_2 production from ammonia production is explained very clearly. However, as it is seen in Chapter 3, there are many sources explaining CO_2 production from ammonia in Ullman's, Kirk-Othmer's etc. Therefore, EPA-AP42 does not provide anything different. Besides, the quality of the CO_2 emission data is rated as "poor" by EPA. Finally, it does not include any of the Industrial Gas Manufacturing sector products. Therefore, this aspect of the EPA-AP42 is not useful for the purpose of this dissertation. However, in EPA-eGRID "Emissions estimated by applying EPA-AP42 emissions factors to fuel data from EIA-767, EIA EIA-759, FERC-423, EIA-860B…" (eGRID, 2003, pg. 33). Therefore, since my emission model is based upon EPA-eGRID, I indirectly utilize from EPA-AP 42.
National Emission Inventory (NEI) database	**Description:** EPA National Emission Inventory (NEI) database "contains information about sources that emit criteria air pollutants and their precursors, and hazardous air pollutants. The database includes estimates of annual air pollutant emissions from point, non-point, and mobile sources in the 50 States." (EPA-NIE, 2005) for CO_2, SO_2, NO_x, ozone, VOC, NH_3 and particular matter emissions. Since point sources includes "Stationary sources that are identified individually by name and location, such as electric generating plants and factories.", this falls into the scope of this dissertation. However, it does not classify facilities based on NAICS. In addition, it does not provide emissions from industrial processes. Finally, it does not give emissions from prime movers separately. **Conclusion:** This database is not useful for the scope of this dissertation because it neither provides emissions from industrial processes nor from prime movers, and it does not classify facilities based on NAICS.

Table 38. (Continued)

EPA-Air Quality System (AQS) database	**Description:** EPA Air Quality System (AQS) "provides air monitoring data - ambient concentrations of criteria and hazardous air pollutants at monitoring sites, primarily in cities and towns." (EPA-AQS, 2005). It includes CO2, SO2, NOx, lead, particular matter, and ozone emissions. **Conclusion:** This database is not useful for the scope of this dissertation, because it does not provide emissions from plants (industrial process and prime mover emissions at the plants).
EPA-AirData	**Description:** "AirData presents annual summaries of air pollution data from two EPA databases: - AQS (Air Quality System) database, - NEI (National Emission Inventory) database provides estimates of annual emissions of criteria and hazardous air". **Conclusions:** This database is out of the scope of this dissertation because it is basically made out of two databases which are not useful for this dissertation.
LCAccess	**Description:** The National Risk Management Research Laboratory's Life-Cycle Assessment (LCA) web site's "purpose is to promote the use of LCA to make more informed decisions through a better understanding of the human health and environmental impacts of products, processes, and activities. The site is divided into six primary areas to help educate people new to the concept of LCA while serving as a focal point for LCA practitioners and decision-makers to stay current with the field of LCA. LCAccess provides information on why one would want to perform an LCA, an overview of LCA, how to find LCI data sources, available LCA resources, on-going efforts in the field of LCA and upcoming LCA events." (EPA-LCAccess, 2005). **Conclusion:** For the Industrial Gas Manufacturing sector products, this website suggests "EPA's eGRID" as source of information. Since I already investigated and used eGRID, this website does not suggest anything new.
Trade Associations	**Description:** Trade associations collect, analyze and disseminate data on industry activities. **Conclusion:** The data and the survey and the analytical techniques used in trade association databases may not be compatible with those used by the U.S. Census Bureau. In particular, trade associations collect data on the activities of its members, who may not necessarily classified under the same NAICS code. Even they are, they may not be statistically valid random sample of the industry. To be more precise: The plants that are considered under the "Industrial Gas Manufacturing sector" according to the MECS may not be considered "Industrial Gas Manufacturing sector" plants according to these databases. For instance, since industrial gases are inorganic gases, some of the plants that are put under "Industrial Gas Manufacturing sector" in the MECS database might be put under the category of "Inorganic Chemicals sector" in these databases just because industrial gases are inorganic gases. Finally, since trade association databases include inputs only from the members and they are accessible only by members, whereas government database is collected from nationally representative sample plants and then statistically analyzed before published which is open to public. Therefore, governmental industrial database provides not only the most comprehensive, but also the most reliable database. However, the National Emission Inventory (NEI) database uses trade association emission databases as one of the sources they use.

The list of other sources can be extended further as not all of the investigated data sources were included in here for the purpose of being brief. However, my search on examining and comparing the quality and coverage of the EPA's eGRID database with other databases concluded that this is the database that best fits for the scope of this dissertation.

6.4.1.2. EPA's eGRID database

EPA's eGRID includes data on emissions, heat input and power generation at the prime mover level for both utilities and non-utilities. It provides annual emissions data on CO_2, SO_2, and NO_x, and emission rates for these gases in terms of lbs/MMBtu and lbs/MWhr. In addition, eGRID gives emission rates of these gases specifically for the ozone season. Although this would be a very useful data as well, my particular purpose to create emission flow model of the Industrial Gas Manufacturing sector focuses on annual emissions of CO_2, SO_2 and NO_x. Future studies that give flow patterns of these gases during ozone season can explore contribution of these gases to ozone layer depletion. The eGRID also has emission data on mercury, which is not within the scope of this dissertation.

Although eGRID provides a very comprehensive and consistent data for the years 1996 through 2000, there are differences between the data given for each year because of changes in the electric power industry. For example, some of the facilities may change owner and name, and some of facilities may change their status from utility to non-utility or vice versa. These changes occur occasionally, and can effect the data. This should be noted when creating charts to show chronological trends.

6.4.1.3. Manufacturing Energy Consumption Survey

MECS provides data on fuel consumption both as fuel and non-fuel, e.g. feedstock. For example, natural gas used as a raw material for the production of chemicals in industrial processes falls into the "fuels consumed as feedstock" category. The MECS table that contains data on fuel consumption as a feedstock is:

MECS Table N2.2. Non-fuel (Feedstock) Use of Combustible Energy

An example data for natural gas consumption as a feedstock is obtained from this MECS table and given in Table 39 as a comparison with the natural gas consumption as a feedstock in the material flow models in Chapter 4.

Table 39. Natural gas consumption as a feedstock, PJ

	Chemical Industry	Industrial Gas Manufacturing
MECS	766	44*
Chapter 4	NA	1.28*

NA: not available, because material flow models in Chapter 4 were scaled against Industrial Gas Manufacturing sector products only.
* : does not include natural gas used in ammonia process to produce carbon dioxide, because the representative carbon dioxide production technique was selected as the carbon dioxide recovery from flue gas in Section 3.2.

Table 39 shows that the natural gas consumption as a feedstock given in the material flow models in a national scale is much smaller than the MECS number. The main reason for this difference would be more likely due to the missing material flow models in Chapter 4 due to the lack of data. Once the data becomes available to create material flow models for all of the Industrial Gas Manufacturing sector products, then the comparison with MECS data can be made.

6.4.2 CO_2, SO_2 and NO_x emissions data for each prime mover

Extraction of the emissions data for CO_2, SO_2 and NO_x from the prime movers of the Industrial Gas Manufacturing sector are given for 1998 in Table 40.

Table 40. CO_2, SO_2 and NO_x emissions from the Industrial Gas Manufacturing in 1998

Prime Mover	Fuel to p.m. / boiler	Fuel input (PJ)	NO_x emission (tons)	SO_2 emission (tons)	CO_2 emission (M tons)
Gas turbine	Natural gas	37	831	5.95	1.35
Steam turbine	Waste heat	3	36	0.22	0.04
Boiler	Oil and natural gas	1	151	1.3	0.13
	Coal	2	294	714	0.06

Although there is utilization of internal combustion engines for power generation in the Chemical Industry, as it is seen from the Table 40 that the Industrial Gas Manufacturing sector does not utilize internal combustion engines. Therefore, there is no emissions from this prime mover. Another point that deserves attention is the utilization of waste heat. So the waste heat indicated in this table must be input to a combined cycle system in order to produce emission.

6.5. Summary of the results

By extracting gas turbine and steam turbine emissions and energy inputs to these prime movers from Table 40, and the emissions from Chapter 4, the emissions in the Industrial Gas Manufacturing sector can be modeled as shown in Figure 51.

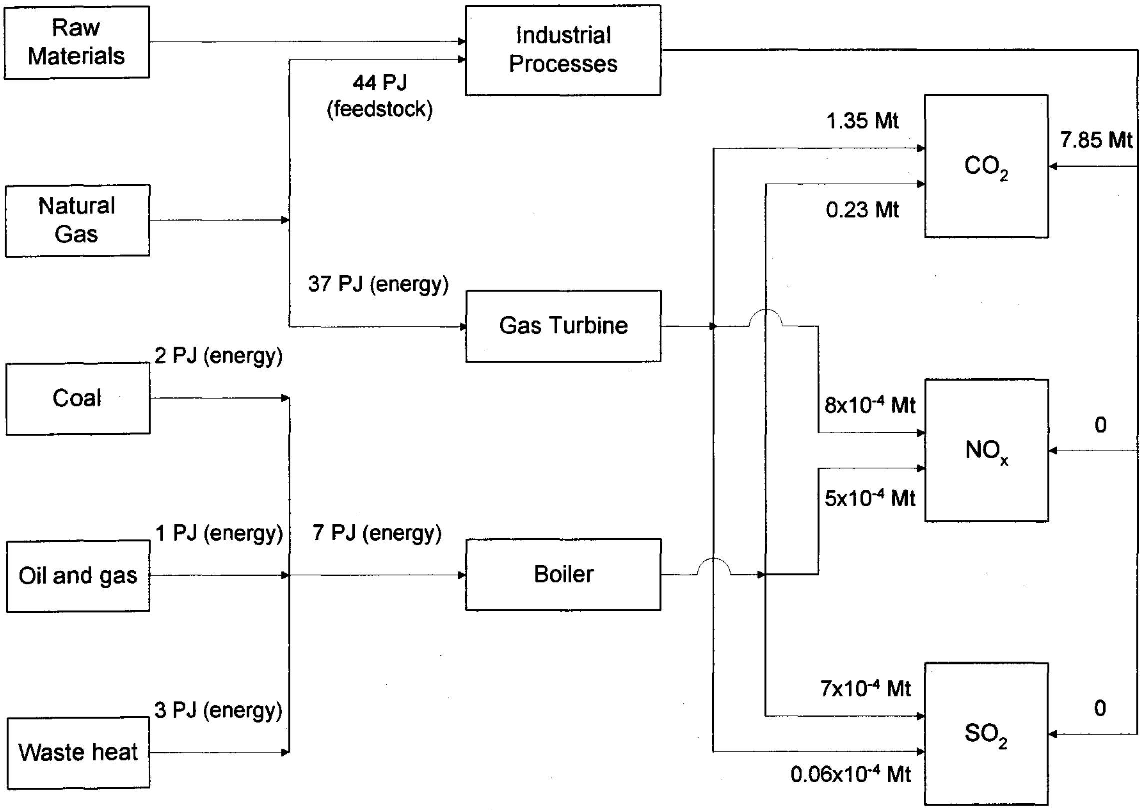

Figure 51. Emission flow model of the Industrial Gas Manufacturing in 1998

If we look at the national scale material flow models given in Chapter 4, we see that there is no NO_x or SO_2 emissions from the industrial processes. This depends on the pollution control system in the reformers and the sulfur level in the fuels. Since there is no EPA data on SO_2 emissions from industrial processes in Industrial Gas Manufacturing sector -or any other sector-, a comparison is not available. However, as it is mentioned in section 6.2., 6% of the national sulfur dioxide comes from combination of industrial processes, solvent utilization, storage & transport, and waste disposal & recycling. This suggests that industrial process originated sulfur dioxide emission is very small. On the other hand, there is EPA data for NO_x emissions from industrial processes in Figure 50.

However, the values given in Figure 50 are for the entire manufacturing sector. In order to make a comparison, we need to break the values given in Figure 50 into specific industries (chemical) and subsectors (industrial gas manufacturing). There is information to help this breakdown, which states that "industrial production of adipic and nitric acid, which releases nitrous oxide as a byproducts, accounted for emissions of 4.2 percent of total U.S. nitrous oxide emissions" in 2001 (EIA, 2002, pg.52). However, we know from Chapters 1 and 3 that neither adipic acid nor nitric acid are Industrial Gas Manufacturing sector products. Therefore, this information cannot provide any insight about NO_x emissions by Industrial Gas Manufacturing sector in Figure 50.

As for the CO_2 emissions, there is enough information to make comparison. Figure 50 gives us the estimate CO_2 emissions from commercial carbon dioxide production by Industrial Gas Manufacturing sector in 1998 as 0.32 Million metric ton carbon, which corresponds to $0.3x10^9$ kg carbon x (44 kg/kmol CO_2 / 12 kg/kmol C) = $1.2x10^9$ kg CO_2. The national scale representative commercial carbon dioxide purification and liquefaction material flow model in Figure 32 gives that the CO_2 emission was $6.66x10^8$ kg. The difference between the EIA's estimate and the estimate made in Chapter 4 is probably due to the lack of data for carbon dioxide gas purification and solidification. Once the data available for these, then a comparison would be made. On the other hand it should be noted that since the EIA estimate was made based on two data sources only, it is difficult to conclude that EIA's estimate would be very reliable to make comparison.

If we compare the CO_2 emissions from carbon dioxide production with the CO_2 emissions from the prime movers, we see that there is $1.6x10^9$ kg CO_2 emitted by the steam and the gas turbines in the Industrial Gas Manufacturing sector, whereas there is 7.9×10^9 kg CO_2 emission from carbon dioxide production. This shows that prime mover emissions were about 5 times less than the industrial process emission. This results contradicts with the arguments given in section 6.1., which claims that the major source of CO_2 is fossil fuel combustion at the industrial boilers and prime movers. A possible explanation to this contradiction would be the values given in the representative material flow models selected.

The national scale representative material flow models in Chapter 4 provides CO_2 emissions for the nitrogen, oxygen, argon and hydrogen production. However, if we look at Figure 34, we see that CO_2 emission from the scrubber is given as the sum of CO_2 and dust. Since there is no information provided in the source of the model, we do not know what percent of this sum accounts for the carbon dioxide. Therefore, we cannot reach a conclusion about the CO_2 emission from commercial argon production from Figure 34. Also, in Figure 36 again, the CO_2 emission from the hydrocarbon removal is given as a summation of CO_2 and hydrocarbon. Since we do not know the ratio in this summation either, we cannot estimate CO_2 emissions from that process step.

Furthermore, since there was no information about the material inputs and outputs of non-cryogenic nitrogen and oxygen production, the national scale material flow models for non-cryogenic oxygen and nitrogen production are missing in Chapter 4. This and the CO_2 emissions that are not given separately prevent us from having a complete emission flow model from the industrial processes in the Industrial Gas Manufacturing sector.

7. CONCLUSIONS

The objective of this study was to determine the energy consumption patterns and allocation of energy among the end-used in the U.S. Chemical Industry and the Industrial Gas Manufacturing sector in 1998. An additional objective of this dissertation was to model the national scale material inputs and outputs, and energy consumption at each step of the industrial process for six products, and emissions by power generation and by industrial processes in the Industrial Gas Manufacturing sector in 1998. Some of these objectives were met.

In comparison to earlier studies of energy use and emissions in the U.S. Chemical Industry (Brown et al. 1996; Worrell et al. 2000; EERE, 2004; ADL, 2000), this dissertation provides the most detailed analysis of on-site steam and power generation, and waste heat recovery. This dissertation also attempted to provide the first detailed assessment of energy and emission patterns in the Industrial Gas manufacturing sector.

This chapter summarizes the results, assumptions made, uncertainty in the results, conclusions that were drawn from these results, original contributions to the field, and finally recommendations for future researchers.

7.1. Summary of the results

This section summarizes the results given in Chapters 2 through 6.

7.1.1. Energy end-use model

The results of the energy end-use models of the U.S. Chemical Industry and the Industrial Gas Manufacturing sector are:

- The major fuel consumed in both U.S. Chemical Industry and Industrial Gas Manufacturing sector is natural gas, 2093 PJ and 66 PJ, respectively,
- 38% of the total fuel consumption in the U.S. Chemical Industry goes directly to end-uses, whereas 58% goes directly to end-uses in the Industrial Gas Manufacturing sector,
- About 9% of the total fuel consumption in the U.S. Chemical Industry is converted to power, whereas it is 7% in Industrial Gas Manufacturing sector,
- 34% of the waste heat is recovered in the U.S. Chemical Industry, whereas it is 36% in Industrial Gas Manufacturing sector,
- About 320 PJ steam is lost during distribution in the U.S. Chemical Industry, whereas 7 PJ is lost in Industrial Gas Manufacturing sector,
- About 16% of the power generated onsite is sold to the grid by the U.S. Chemical Industry, whereas there is no electricity sold by Industrial Gas Manufacturing sector,
- More fuel than electricity is consumed for end-uses in the U.S. Chemical Industry, whereas the opposite is true in the Industrial Gas Manufacturing sector,
- The biggest electricity consuming end-use is machine drive in both the Chemical Industry and the Industrial Gas Manufacturing sector: consuming 60% and 93% of the total electricity input to end-uses, respectively,
- Process heating is the largest fuel, steam and waste heat consuming end-use in both the Chemical Industry and Industrial Gas Manufacturing sector,

- Compared to machine drive and process heating, energy use for all other end-uses is small in both of these industries,
- Total fuel consumption for manufacturing processes in the Industrial Gas Manufacturing sector was estimated as about 37 PJ,
- Total steam consumption for manufacturing processes in the Industrial Gas Manufacturing sector was estimated as about 19 PJ,
- Total electricity consumption for manufacturing processes in the Industrial Gas Manufacturing sector was estimated as about 116 PJ,
- Total energy consumption estimate for processes found to be 37 PJ + 19 PJ + 116 PJ = 172 PJ,
- There are no utilization of renewable energy sources in these industries.

7.1.2. Material flow model

The results of the material flow models can be summarized as:

- The major commercial acetylene production technology is partial oxidation of natural gas,
- There are two major commercial carbon dioxide production technologies: byproduct from ammonia production, and recovery from flue gas. The carbon dioxide in flue gas needs to be purified to be at the same level of concentration that occurs for ammonia production, but there is little information in the literature about this step. Once through this step, the technique to purify and liquefy carbon dioxide is the same for both processes,

- There is a conflict in the literature on whether the major commercial nitrogen and oxygen production is via cryogenic or non-cryogenic processes,
- There is very little useful qualitative or quantitative information in the literature on the major commercial non-cryogenic nitrogen and oxygen production technology,
- The major commercial argon production technology is liquefaction of air,
- The Drexel model for nitrogen, oxygen and argon does not represent an accurate picture of materials flows on a national scale. It is not a representative model for commercial nitrogen, oxygen and argon production,
- The major commercial hydrogen production technology is steam reforming of natural gas,
- The major raw materials consumed for the production of industrial gases are air and natural gas,
- There is little available in the literature on other (mainly chlorofluorocarbon) gas products.

7.1.3. Energy process-step model

The results of the energy process-step models for industrial gas production in 1998 in the U.S. are given below. However, it should be noted that these results were obtained based on the representative process models selected. As explained in Section 1.6.1., the industry constantly transits from one technology to another, which means that any industry is often a mix of old and new technologies. For this reason, although selection of a representative technology provides a very general view of the sector, it ignores some of the process designs that are being used. Therefore, the results given below should be interpreted with caution in policy making decisions because: they are rough estimates based on a selected representative technology for each industrial gas.

- The major energy consuming step in acetylene production is preheating with an estimate fuel consumption of 3 PJ roughly. The second largest energy consuming step is rectifier, which consumes about 1.4 PJ steam & waste heat,
- Estimated energy consumption for the purification and liquefaction of carbon dioxide is: 3.5 PJ steam & waste heat, and 2 PJ electricity approximately,
- Energy consumption estimate for cryogenic nitrogen production was found to be about 6.5 PJ, whereas it is about 1.2 PJ for cryogenic oxygen production,
- Estimated energy consumption for non-cryogenic nitrogen production was found to be about 0.03 PJ, whereas 48 PJ electricity consumption was estimated for non-cryogenic oxygen production,
- The major energy consuming step in argon production is compression of air with an estimated energy consumption of 67 PJ. However, as discussed under Sections 4.4.3.4., 5.2.4., and 5.4. this model does not estimate the energy consumption for argon production accurately,
- The major energy consuming step in hydrogen production is the reformer, which consumes approximately 16 PJ fuel,
- The largest fuel consuming process in the Industrial Gas Manufacturing sector was estimated as the oxygen production, whereas the largest electricity

consuming process was estimated as argon production, and the largest steam & waste heat consuming process as hydrogen production,

- Total energy consumption estimate for process-steps found to be about 170 PJ, which is within 11% of the reported MECS total,
- Total fuel consumption for manufacturing processes in the Chemical Industry is 1,078 PJ,
- Total steam consumption for manufacturing processes in the Chemical Industry was estimated as about 1,000 PJ,
- Total electricity consumption for manufacturing processes in the Chemical Industry is 689 PJ.

7.1.4. Emissions flow model

- According to the EPA reports, carbon dioxide production is the biggest CO_2 emitting manufacturing process in the Industrial Gas Manufacturing sector, but this likely reflects an accounting problem. See earlier discussion under Section 6.1.,
- There is no SO_2 or NO_x emission during the manufacturing processes of industrial gases,
- There is no national scale data on SO_2 or NO_x emissions from industrial processes for the Chemical Industry or Industrial Gas Manufacturing with which to compare the results from this dissertation with,
- Gas turbines are the biggest CO_2, SO_2 and NO_x emitting prime mover in the Industrial Gas Manufacturing sector,

7.2. Summary of the assumptions

This section summarizes the assumptions made in Chapters 2 through 6.

7.2.1. Energy end-use model

The major assumptions made in the energy end-use models are:

- Allocation of steam among the end-uses was assumed to be the same as the allocation of fuel among the end-uses,
- Allocation of recovered waste heat to end-uses was assumed to be the same as the allocation of fuel among the end-uses,
- The efficiency of fuel-fired boilers in the Industrial Gas Manufacturing sector was assumed to be 80%,
- The boiler efficiency was assumed to be independent of whether or not prime mover is part of a combined cycle,
- The boiler efficiency was assumed to be independent of whether or not waste heat was recovered,
- Differences between the fuel-fired boiler efficiencies due to the type of fuel burned, boiler vintage, maintenance, boiler configuration, operating schedules and the age of the boiler were neglected,
- 30% steam distribution loss was assumed due to heat transfer, ineffective steam traps etc.,
- MECS and EIA 860B data sources were treated as interchangeable due to the very small difference between them as discussed in Section 2.2.3.

7.2.2. Material flow and energy process-step model

The major assumptions made in the material flow and energy process-step models are:

- Drexel acetylene production model was assumed to be representative for scaling against federal databases to obtain national material and energy flows for acetylene production,
- The two major carbon dioxide production technologies were ammonia production and recovery of carbon dioxide from flue gas. After concentration from flue gas, both of these sources feed into a purification and liquefaction process that is treated as the same for this dissertation,
- Häussinger et al.'s (2000a) cryogenic and non-cryogenic nitrogen production energy process-step model was assumed as the representative cryogenic nitrogen production energy process-step model, and thereafter it was used for scaling the energy consumption values against the national database in order to obtain a nationally characteristic energy consumption for cryogenic and non-cryogenic nitrogen production,
- Barron's (2000) cryogenic oxygen production energy process-step model was assumed as the representative cryogenic oxygen production energy process-step model, and thereafter it was used for scaling the energy consumption values against the national database in order to obtain a nationally characteristic energy consumption for cryogenic oxygen production,

- Kessler's (2000) non-cryogenic oxygen production energy process-step model was assumed as the representative non-cryogenic oxygen production energy process-step model, and thereafter the energy consumption values provided in this source were scaled against the national database in order to obtain a nationally characteristic energy consumption for non-cryogenic oxygen production,
- Drexel hydrogen production material flow model was assumed as the representative hydrogen production material flow and energy process-step model, and thereafter it was used for scaling the material input and output values and energy inputs against the national database in order to obtain a nationally characteristic material and energy flow for hydrogen production.

7.2.3. Emissions flow model

The major assumption made in emissions flow model is: emissions values reported in representative industrial gas material flow models were assumed to be the characteristic emissions for manufacturing industrial gases.

7.3. Summary of the uncertainties in the results

This section summarizes the uncertainties in the results in Chapters 2 through 6.

7.3.1. Energy end-use model

Since there is no information in the literature about the actual allocation of steam among end-uses in the Chemical Industry and the Industrial Gas Manufacturing sector, the uncertainty associated with the assumption of "allocating steam among the end-uses is the same as allocation ratio of fuel among the end-uses" could not be estimated.

However, since the biggest steam consuming process in the Industrial Gas Manufacturing sector is hydrogen production as shown in Table 38, the steam and fuel allocation in the production of hydrogen can provide some insight. The Drexel hydrogen model shows that steam allocation among the end-uses are: 68% process cooling (steam injection to product combustion gases), 25% process heating, and 7% other process use (CO_2 converter). However, in hydrogen production, fuel is consumed only for process heating. As a second example, if we look at carbon dioxide production, the second biggest steam consuming process, the Drexel model for carbon dioxide production shows that the fuel and steam allocation among the end-uses are exactly the same. However, since steam consumption for hydrogen production is a lot bigger than that of carbon dioxide production, the allocation ratio in the Drexel hydrogen production could have been used as an assumption. Besides, some of the steam used in hydrogen production is serving as feedstock in addition to energy input. However, this assumption also brings an uncertainty, because steam and fuel allocation ratios among the end-uses are different for each product. Finally, since there is no information on the actual steam allocation among end-uses, the uncertainty of the assumption made in this study could not be estimated. However, if we compare the steam allocations in the Drexel hydrogen production model with the assumption made in this study, then the assumption overestimates the steam use in process heating, whereas it underestimates the steam use in process cooling and other process uses.

The same arguments for the steam allocation assumption applies to the recovered waste heat allocation assumption as well. And, there is no information on actual waste heat allocation among the end-uses in the Industrial Gas Manufacturing. Furthermore, although Drexel models provide steam allocation among each process, they have no indication of recovered waste heat allocation among the processes.

The uncertainty of the assumption of "boiler efficiency's not being dependent on whether the prime mover is part of a combined cycle or not" is likely to be small, because the function or characteristics of the boiler do not change if it is part of a Rankine cycle or not. When it is part of a combined cycle, the boiler is actually a waste heat regenerator.

The uncertainty of the "boiler efficiency was assumed that it does not depend on whether the waste heat recovered or not" assumption is likely to be small, because the function or characteristics of boiler does not change even if the waste heat that it releases is recovered or not.

The uncertainty of the "differences between the fuel-fired boiler efficiencies due to the type of fuel burned, boiler vintage, maintenance, boiler configuration, operating schedules and the age of the boiler were assumed to be neglected" may not be small. However, the level of uncertainty in this assumption could not be determined, because the actual effects values or status of these boiler parameters are not known.

There is an uncertainty associated with the assumption of 80% boiler efficiency for all fuel-fired boilers in the Industrial Gas Manufacturing sector. The sensitivity of the results to this assumption was analyzed in section 2.2.2. According to that analysis, a 30% change in the boiler efficiency creates only a 4% change in the prime mover efficiency. Therefore, the uncertainty due to this assumption can be neglected.

Another issue that should be addressed is regarding the industrial gases' being produced 92% by the Industrial Gas Manufacturing sector, and 8% by the other sectors as discussed in Section 1.4. Therefore, the national scale industrial gas production numbers in the CIR database includes both Industrial Gas Manufacturing sector's production amount and the other sectors production amount which constitutes 8% of the total industrial gas production. Since the material flow models in Chapter 4 were scaled using CIR data, they represent industrial gas production by both Industrial Gas Manufacturing sector and the other sectors, which constitutes 8% of the total. This should be accounted when the material input and outputs in Chapter 4 are considered.

MECS and EIA 860 B data sources were treated as interchangeably due to the small difference between them as explained in Section 2.2.3. This also assumes that the MECS/EIA 860B data is consistent for each subsector. However, MECS would be higher for some subsectors and lower for others. Therefore, this assumption bring some level of uncertainty.

7.3.2. Material flow, energy process-step, and emissions models

Although the selection of representative production techniques for each industrial gas was made based upon qualitative statements in literature, it brings uncertainty into the material flow, energy process-step and emissions flow models, because it does not include all existing technologies or process designs. However, the magnitude of these uncertainties can not be identified because of lack of precise information on what are the process designs at each plant in the sector. This is a problem that other studies in this field encountered as well. For example, Worrell et al. (2000) states that "Our estimates are based on surveys of individual plants in the industry as well as engineering estimates on the basis of literature values and surveys. This introduces uncertainties in the results, however, we are not able to estimate the magnitude of the uncertainties. Comparison with other official energy consumption statistics is difficult due to the aggregation levels, as well as different sub-sector divisions used in the statistics and this report." (Worrell et al., 2000). Another example study that lacks sensitivity and uncertainty analyses is Jiménez-González et al. (2000). My personal contact with the corresponding author Prof. Overcash regarding the reasons for these analyses in their model was answered as follows: "As for the sensitivity analysis, we have not been so thorough. While each process has a number of assumptions, these are generally engineering rules of thumb or are thermodynamically based (either energy or mass balances). These can aggregate, but may also compensate. We have received some reviews from industrial sources and believe the results of a single LCI is about +/- 10% - 30%. This is expected for a first stage engineering design." (Overcash, 2005). Therefore the other studies probably omit uncertainty analysis for the same reasons (ADL, 2000; Wang et al., 2004; Brown et al., 1996; Giraldo and Hyman, 1996; Hyman and Andersen, 2001).

Another uncertainty comes along with the process steps associated to the representative model. In most of the cases there is sufficient qualitative information to understand which technique is commercially most utilized. However, there are usually more than one possible process designs for a particular technique. For example, in Table 29, there are three different studies' data for steam reforming process for 1,000 kg ammonia production. Although the process in these three studies is the same, the inputs and the emissions vary. It shows that, even for a particular technique, there could be many process designs which have different inputs and outputs for the same amount of particular product. Therefore, selecting one process design and scaling it against the national data brings some uncertainty because it actually represent that particular process design in a national scale rather than representing a production pattern for a particular product. It means that the material flow models in Chapter 4 should be interpreted by considering this fact. However, as a future study and once data becomes available, more than one process design can be scaled against the national data to show the variation in the inputs and outputs in a national scale. This would enable policy makers to see multiple scenarios in a national scale.

7.4. Summary of the major original contributions to the research field

This section summarizes the major contributions made by this dissertation to the original research field.

7.4.1. Energy end-use model

The major original contributions to the field are:

- This is the first study to present an energy end-use model for the Industrial Gas Manufacturing sector of the Chemical Industry as the earlier energy end-use models were done for the entire Chemical Industry,
- This is the first study to present an approach to calibrate energy process-step models for multiple products using end-use models based on federal databases,
- This is the first study that combined EIA 860B data with MECS to get estimates for the waste heat recovery,

- This is the first end-use model that includes performance of prime movers based on actual operational data of the plants in the sector, which were reported in EIA 860B,
- This is the first study that provides actual electricity conversion efficiencies for steam turbines, gas turbines, internal combustion engines and the combined cycles based on the actual operating performance database, and those results were used in the end-use models,
- This is the first study that provides actual electricity production from cogeneration of each prime mover separately. If we look at other studies, for example Worrell et al. (2000), we see that "electricity production from cogeneration is currently not included in the calculation due to lack of reliable data." Therefore, this study overcame this barrier by discovering the EIA 860B data. The future studies now can use this database to complete their analyses,
- This is the first study to perform sensitivity analysis of the boiler efficiency assumption,
- This is the first end-use model that included uncertainty analysis of the MECS database,
- This is the first study that provided the actual energy conversion efficiencies for the prime movers used in the U.S. Chemical Industry. The values reported in this dissertation can be a very good reference point for the future studies to check the accuracy of their results or to have information about the actual performance of

the prime movers in the Chemical Industry rather than relying on existing studies which are either made based upon few plants or made upon estimates.

7.4.2. Material flow and energy process-step models

This is the first study to develop an approach to calibrate existing models of chemical processes in a national scale, which showed that the existing process models are either not given for all chemicals or they are given in the form that cannot be calibrated against the national data. This revealed the inadequacies of the existing models and data. For example the Drexel model for nitrogen, oxygen and argon does not represent an accurate picture of materials and energy flows on a national scale. Since the entire approach in this dissertation and enhanced policy making depend on credible quantitative models, lack of adequate models results in a major gap.

Another contribution to the field is providing a critical evaluation of the commercial production processes to select representative production method for each industrial gas. It showed that selection of representative production technique leaves out the other techniques from analysis even though they do not constitute the portion of the market based on the qualitative arguments in literature. It also points out that even the major technique may involve different material inputs and outputs depending on the process design, as shown in Table 28.

Therefore, material flow models analysis on a national scale suggests that it is very difficult to obtain a full accurate model that includes all of the process designs in the sector in one model. This shows that the numbers obtained after scaling the representative process inputs and outputs against the national data should be interpreted with caution in policy making.

7.4.3. Emissions flow model

The major contributions to the field are:

- This study developed a new modeling framework to display emissions from prime movers/boilers together with emissions from industrial processes involving combustion and industrial processes not involving combustion,
- This is the first study that estimated national scale CO_2 ,SO_2 and NO_x emissions from the manufacturing processes of Industrial Gas Manufacturing sector, which is one of the major missing information in literature.

7.5. Conclusions

This research demonstrated the difficulties of analyzing the materials, energy, and emissions flows in the Chemical Industry and Industrial Gas Manufacturing sector. One of the main problems encountered was the lack of precise information about the commercial technologies and processes used to produce chemical products. Another problem was the lack of consistent and reliable public databases on energy and material consumption during those processes. Its multiple products, use of different production techniques, lack of access to actual plant data due to confidentiality, and lack of information on steam and recovered waste heat allocation among the end-uses raised the necessity to make many assumptions in the analysis. In a sense, this research verified one more time that "surprisingly, there is not much information on energy use and energy intensity in the Chemical Industry available in the public domain." (Worrell et al., 2000). For example, there is still "no readily accessible database on steam losses" since ADL searched (ADL, 2000). It is seen in ADL's report that the need for data is understood by DOE and "DOE is currently undertaking such effort" (ADL, 2000). Therefore, this dissertation shows that there has not been much change in the availability of energy information/data on the Chemical Industry since 2000. This problem has been the main barrier to energy, materials and emissions modeling in this industry and this is the major reason for not being able to apply the calibration procedure to the energy end-use model and energy process-step models in this dissertation, thereby causing this dissertation to fall short of one of its major objectives as given in Chapter 1 (see objective 8). Therefore once these following data is collected, what we originally set out to accomplish can be achieved:

- Steam, fuel, waste heat and electricity allocation to each process step, e.g. how much electricity is consumed for machine drive during each industrial gas production,
- Material inputs and outputs to each process step, e.g. how much hydrocarbon feedstock is used in furnaces during each industrial gas production.

The problem of lack of these kind of data can be solved by the government agencies or policy makers by sponsoring future research on developing databases or government can collect data from manufacturers as the way they do in EIA 860B (non-statistical) or MECS (statistical). As a result of these research, more accurate material flow inputs and outputs on a national scale can be obtained eventually.

Nevertheless, this study is the most comprehensive and detailed analysis of the materials, energy and emissions flows of the U.S. Chemical Industry and the Industrial Gas Manufacturing sector, as well as the first study to reveal the energy allocation and associated emissions at the prime mover level.

This study also verified that some of the production technologies such as carbon dioxide manufacturing have not changed in many years. For example, the process steps for carbon dioxide shown in Drexel models developed based on 1976 data are the same that of Jiménez-González et al. (2000). However, energy consumption during CO_2 manufacturing has reduced compared to Drexel's, probably because of recovering the waste heat. Although this study determined the steam and recovered waste heat values for the Chemical Industry and Industrial Gas Manufacturing sector, it still needed to make an assumption to allocate them among end-uses.

This study showed that majority of the MECS data has an uncertainty less than 10%. Although earlier studies such as ADL (2000), Worrell et al. (2000) and EERE (2004) did not address the issue, this dissertation showed that their results includes some uncertainty due to the uncertainty in the underlying MECS data. In addition, comparison of the results of these studies showed that a thorough understanding of the MECS data is required before using it in modeling. For example, in DOE's energy footprint (EERE, 2004), their improper addition of "Other" to fuel consumption led their study to have an unbalanced steam analysis. If the MECS database was understood clearly, then the "other" should be divided into "byproducts", "net steam" and "fuels not listed separately".

The emission flow model represented in this study is a combination of an EPA database and the material flow model results, some of which were not completed due to the lack of data. However, the efforts in estimating the emissions from the industrial processes in the Industrial Gas Manufacturing sector should be considered as a first crude effort that is subject to revision as better data comes available.

7.6. Recommendations and outlook

This section provides some recommendations for improved energy, material and emissions models for future research, and some recommendations for an improved industrial public database.

7.6.1. For future research

My analysis was made using 1998 data, however, similar analysis can be done for1991, 1994 and 2002. This can reveal the trends and can also be used to calibrate energy forecasting models. Combining these results with standardized assumptions for operating and environmental pressures and temperatures, an exergy analysis of onsite power and steam generation can be conducted. In addition, the inclusion of economic data will facilitate a thermoeconomical analysis of onsite power and steam generation. In order to make some improvements in this model, additional details about end-uses and losses can be incorporated. For example, losses in motor driven equipment could be identified. Also, cascading of waste heat from high temperature processes to low temperature processes could be integrated into the model as well. Furthermore, this energy end-use model can be used to create energy process-step models for the manufacturing processes of these sectors products. A brief list of other potential future research is:

- There is no data on steam allocation among end-uses in the Chemical Industry or any other industry. It would be a good research topic to analyze steam allocation among end-uses in the manufacturing sector,
- There is no data on recovered waste heat allocation among end-uses in the Chemical Industry or any other industries, therefore research on this area would fill a major gap in the field. The outcomes of this kind of research would improve the existing energy models and therefore would help policy makers to better understand the sector,
- Energy end-use models similar to the ones in this dissertation can be established for other subsectors of the U.S. Chemical Industry to obtain complete pattern of the U.S. Chemical Industry. Analogous models can also be developed for other industries,
- Commercial industrial gas production techniques should be identified on a percentage basis, e.g. what percent of the industry uses what process. Based on these percentages, material flow models can be constructed on a national scale by including multiple processes for each industrial gas production,
- Emissions flow model can be developed for the Chemical Industry and other industries in the same way it was developed in this dissertation for the Industrial Gas Manufacturing sector,

- There is not as many data on national scale NO_x and SO_x emissions from manufacturing sector as there are data on NO_x and SO_x emissions from other sectors. Therefore, similar efforts on researching NO_x and SO_x emissions from industrial processes should take place to fill this gap and have sufficient data on NO_x and SO_x emissions from industrial processes.

7.6.2. For improved industrial public database

- Steam production amounts should be added into the MECS survey for each industry. That would minimize the assumptions made in energy flow models,
- Recovered waste heat amounts should be added into the MECS survey, which would also minimize the assumptions made in energy flow models,
- Allocation of steam among the end-uses should be tabulated in the MECS database in the same way fuel allocation among the end-uses is tabulated,
- Allocation of recovered waste heat among the end-uses should be tabulated in the MECS database in the same way fuel allocation among the end-uses is tabulated,
- Energy consumption of "other" in the MECS database should be tabulated separately by showing each component included in this category individually,
- Fuel consumption should be identified for each or selected product manufacturing. It would be very impractical to do it in one step, so it can be achieved step by step. For example, in addition to giving natural gas consumption as feedstock and non-feedstock, it can be divided among the sources it was used, for example: chemical production as feedstock and electricity generation as non-feedstock. This might be the first step to distinguish where the natural gas is used

as a feedstock quantitatively. Then the following steps could be to further break it down until it clearly states what amount goes to what product manufacturing,

- Drexel nitrogen, oxygen and argon model should be updated or fixed, so that it would not mislead the users,
- Majority of the existing material flow models are given in the form that cannot be used to construct national scale representative material flows,
- Energy consumption values given in Drexel models should be used with caution as they do not include cogeneration, which is being utilized widely. This omission results in overestimating energy consumption,
- Drexel models do not include some of the major technologies, e.g. membrane separation of air for nitrogen and oxygen production. Therefore, it should not be assumed that they represent all of the existing major production technologies,
- EIA 860B database should continue collecting information to follow the actual energy consumption and electricity generation trends in the sector,
- Economic Census, CIR and ASM should include relative standard errors in their database in the same way as the MECS does. This would help the data user to better quantify the errors involved,
- An emission database should be developed to reveal the emissions from industrial processes in each sector.

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