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Pacific Northwest
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Opportunity Analysis for Recovering Energy from Industrial Waste Heat and Emissions

VV Viswanathan
RW Davies
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April 2006

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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EXECUTIVE SUMMARY

United States industry consumed 32.5 Quads (34,300 PJ[1]) of energy during 2003, which was 33.1% of total U.S. energy consumption [5]. The U.S. industrial complex yields valuable goods and products. Through its manufacturing processes as well as its abundant energy consumption, it supports a multi-trillion dollar contribution to the gross domestic product and provides millions of jobs in the United States each year. Industry also yields waste products directly through its manufacturing processes and indirectly through its energy consumption. These waste products come in two forms, chemical and thermal. Both forms of waste have residual energy values that are not routinely recovered. Recovering and reusing these waste products may represent a significant opportunity to improve the energy efficiency of the U.S. industrial complex.

This report was prepared by Pacific Northwest National Laboratory (PNNL) for the U.S. Department of Energy Industrial Technologies Program (DOE-ITP). It analyzes the opportunity to recover chemical emissions and thermal emissions from U.S. industry. It also analyzes the barriers and pathways to more effectively capitalize on these opportunities.

A primary part of this analysis was to characterize the quantity and energy value of the emissions. For example, in 2001, the industrial sector emitted 19% of the U.S. greenhouse gases (GHG) through its industrial processes and emitted 11% of GHG through electricity purchased from off-site utilities. Therefore, industry (not including agriculture) was directly and indirectly responsible for emitting 30% of the U.S. GHG. These emissions were mainly comprised of carbon dioxide (CO_2), but also contained a wide-variety of CH_4 (methane), CO (carbon monoxide), H_2 (hydrogen), NMVOC (non-methane volatile organic compound), and other chemicals.

As part of this study, we conducted a survey of publicly available literature to determine the amount of energy embedded in the emissions and to identify technology opportunities to capture and reuse this energy. As shown in Table E-1, non-CO_2 GHG emissions from U.S. industry were identified as having 2180 PJ, or 2 Quads (quadrillion Btu) of residual chemical fuel value. Since landfills are not traditionally considered industrial organizations, the industry component of these emissions had a value of 1480 PJ, or 1.4 Quads. This represents approximately 4.3% of the total energy used by U.S. industry.

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[1] Peta joules.

Table E-1. Energy Content of U.S. Industry's Chemical Emissions

Industry	Gas	Emissions (Tg)	Energy	
			PJ	Trillion Btu
Mining	CH_4	2.89	161	153
Agriculture	CH_4	7.72	430	408
Landfill	CH_4	12.53[2]	698	662
Petroleum systems	CH_4	1.01	56	53
Petroleum refinery	H_2	0.02	10	9
Natural gas systems	CH_4	5.59	311	295
Chemicals (Cl_2 production)	H_2	0.29	42	40
Oil & gas, mining, waste combustion, industrial fossil combustion, miscellaneous industrial processes	CO	10.3	104	99
Total NMVOC	NMVOC	7.27	368	349
Total energy content			**2180**	**2066**

Energetics Incorporated [34] investigated opportunities to reduce energy use and loss in U.S. manufacturing and mining industries. This analysis summarizes these findings to quantify thermal emissions. Table E-2 describes the origins of U.S. industry emissions and shows that these emissions have 10,500 PJ, or 10 Quads of potential energy. This represents approximately 30.8% of the total energy used in United States industry.

Table E-2. Energy Content of U.S. Industry's Thermal Emissions

Item #	Description of Opportunity Area	Estimated Energy Available (TBtu)	Estimated Recovery Efficiency	Estimated Recovery Opportunity (TBtu)	Economic Benefit if Realized, $ Billion (2005)
1	**Waste heat recovery** from gases and liquids in chemicals, petroleum, and forest products, including hot gas cleanup and dehydration of liquid waste streams	~7,000 (7400 PJ)	~12%	851 (898 PJ)	$2.15B
4	**Heat recovery from drying processes** (chemicals, forest products, food processing)	~3700 (3900 PJ)	~10%	377 (400 PJ)	$1.24B
10	**Waste heat recovery** from gases in metals and non-metallic minerals manufacture (excluding calcining), including hot gas cleanup	~1600 (1700 PJ)	~15%	235 (250 PJ)	$1.23B
18	**Waste heat recovery from calcining** (not flue gases)			74 (78 PJ)	$0.16B
19	**Heat recovery from metal quenching/cooling processes**			57 (60 PJ)	$0.28B
	Total	>10,000 (10,500 PJ)		1594 (1680 PJ)	$5.06B

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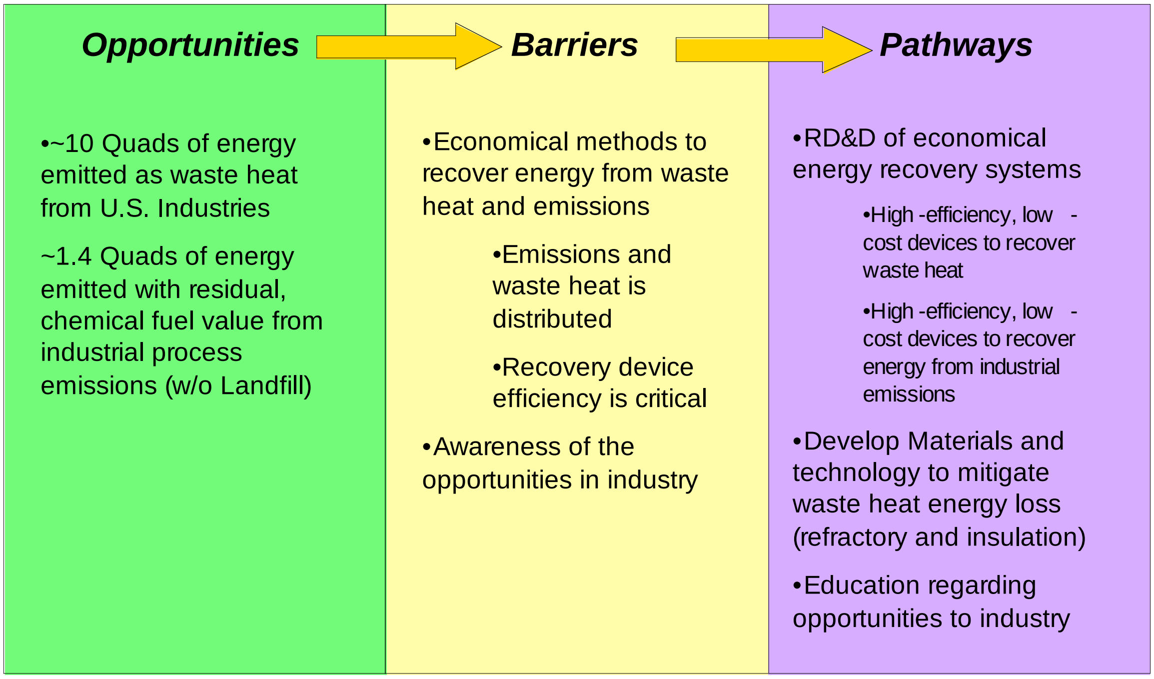
[2] Includes energy captured from CH_4 that is currently flared.

Source: Energetics [34].

Recovering chemical and thermal emissions will include research, development, and demonstration (RD&D) of low-cost, high-efficiency energy recovery systems. Recovery will also include developing technologies to mitigate waste heat and emissions through better materials and process technologies. Figure E-1 presents a consolidated view of the opportunities, barriers, and pathways associated with recovering the fuel value from chemical and thermal emissions.



Opportunities

- ~10 Quads of energy emitted as waste heat from U.S. Industries

~1.4 Quads of energy emitted with residual, chemical fuel value from industrial process emissions (w/o Landfill)

Barriers

- Economical methods to recover energy from waste heat and emissions
  - Emissions and waste heat is distributed
  - Recovery device efficiency is critical
- Awareness of the opportunities in industry

Pathways

- RD&D of economical energy recovery systems
  - High -efficiency, low - cost devices to recover waste heat
  - High -efficiency, low - cost devices to recover energy from industrial emissions
- Develop Materials and technology to mitigate waste heat energy loss (refractory and insulation)
- Education regarding opportunities to industry

Figure E-1. Opportunities, Barriers, and Pathways Associated with Recovering Fuel from Chemical and Thermal Emissions.

This report discusses the advanced materials (e.g., thermoelectric, thermionic, and piezoelectric) and other technologies (e.g., solid oxide fuel cells) that appear to be the most promising technologies for re-utilizing chemical and thermal emissions. Additional research and development as well as industry education may be required in order to make these technologies sufficiently cost-effective and widely commercialized.

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INTRODUCTION

This report was prepared for the United States Department of Energy Industrial Technologies Program (DOE-ITP), part of the Office of Energy Efficiency and Renewable energy (DOE-EERE), by Pacific Northwest National Laboratory (PNNL). The purpose of this work was to quantify the amount of energy available from U.S. industrial emissions and to analyze the opportunities for recovering this energy. This study is in keeping with DOE-ITP's mission, which is to improve the energy intensity of the U.S. industrial sector through research, development, validation, and dissemination of energy-efficient technologies and operating practices [33].

The U.S. industrial complex and related energy consumption supports a multi-trillion dollar contribution to the gross domestic product and provides millions of jobs each year. Part of this contribution can be attributed to the massive amount of energy industry consumes. For example, in 2003, U.S. industry used 32.5 Quads of energy (34,300 PJ)—representing 33.1% of the United States' total energy consumed that year [5]. Industry's manufacturing processes, as well as its related energy consumption, yield waste products in two forms of emissions: chemical and thermal. These emissions have residual energy value that is not normally recovered. Due to the sheer volume of these waste products, reusing them would provide a significant opportunity to improve the energy efficiency of the industrial complex and significantly affect the total amount of energy consumed in the United States.

This study surveyed available literature and quantified the amount of residual energy available from 124 prominent industrial sectors: Aluminum, Chemicals, Glass, Petroleum, Steel, Landfill, Mining, Forest Products, Metal Casting, Agriculture, and Semi-conductors. It separates each industry's waste products into two distinct types of emissions: 1) chemical emissions with residual energy fuel-value content from industrial processes and from on-site fuel combustion (used to generate energy for these processes) and 2) thermal emissions in the form of waste heat from industrial processes and from on-site fuel combustion (used to generate energy for these processes).

This report is organized into three topic areas. Chapter 1 provides a survey of the chemical emissions from industrial processes, focusing on characterizing the residual chemical fuel value in industrial emissions at standard temperature and pressure (STP). This analysis includes a survey of process-related emissions from an overall perspective followed by a series of analyses focused on the specific industries. Chapter 2 discusses the origin and quantity of thermal emissions waste heat energy available from industrial processes. Chapter 2 is largely a summary of the findings recently reported by Energetics Incorporated [34]. Chapter 3 outlines the opportunities, barriers, and pathways for new technologies that might be developed or deployed to successfully reclaim and convert the residual chemical fuel value and waste heat contained in industrial emissions back into usable energy.

CHAPTER 1: SURVEY OF CHEMICAL EMISSIONS

Approach

A primary focus of this study is to characterize the energy content, or “fuel value,” of industry’s chemical emissions. For purposes of this study, only CO, CH_4, N_2O, non-methane volatile organic compounds and NO and SO_2 are considered as sources of energy. Carbon dioxide, while not a source of energy, can be used for other useful purposes, which are outlined in Appendix A. Emission levels of other greenhouse gases (GHGs), such as NO_x, HFCs, PF_6, have been identified, but their fuel value was not calculated.

This study began with an investigation of the chemical fuel-value and an analysis of the report, “The Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2001” (1) which outlines the emissions from various industries for 1990-2001. Emission values extracted from this reference were separated into energy-related and process-related emissions. For this study, energy-related emissions, which were mainly from fossil fuel combustion for electricity generation, were ignored since these emissions were incurred as a result of purchasing power from off-site utilities.

A source for emissions data was the report “Emissions of greenhouse gases in the United States 2002,” issued by the Energy Information Administration [2]. Both reports provided an overview of the emissions for the U.S. industrial complex from a broad perspective. In order to achieve a greater granularity of this information on an industry-by-industry perspective, this analysis presents emissions from specific industries with a breakdown of emissions within each industry. In order to calculate the chemical energy content of the emissions, only the chemical energy content at standard temperature and pressure (STP) was determined, using the heat of combustion for various gases [3].

The basic information reported for industrial emissions details the overall weight of the emissions by chemical species and relates this chemical compound back to carbon. We surveyed and aggregated the available chemical species data that have appreciable fuel-value by weight and calculated the energy content of this quantity of chemical compound using the conversions shown in Table 1. The emissions data by weight and this energy content by weight provided the basis for this analysis.

Table 1. Calculated Energy Content by Unit Weight for Specific Industrial Emissions [35]

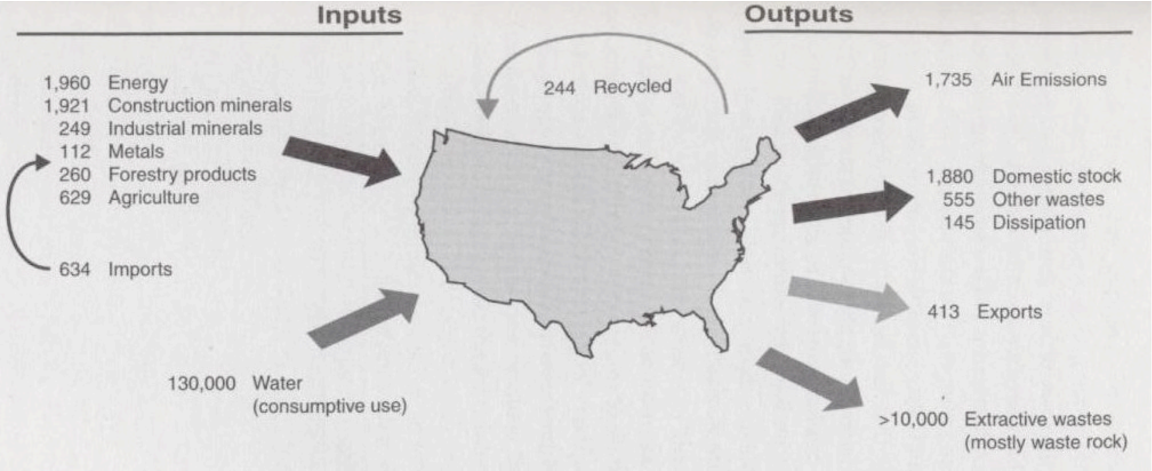
Compound	kJ/g
Methane	55.7
Carbon Monoxide	10.1
NMVOC	47.4
VOC	49.0
Hydrogen	143.0

General Emissions Survey

This report examines industrial emissions in two distinctly different categories: energy-related emission and process-related emissions. Energy-related emissions emanate from the industrial complex as a result of supplying energy to the site's facilities (e.g., from fossil fuel combustion or natural gas supply). Process-related emissions are a byproduct of non-energy-related activities (such as conversion of process chemicals and pulp and paper drying).

The U.S. economy can be seen as a materials processing subsystem. The sources of inputs include both the raw materials extracted from our country's land and flora and the raw materials imported from other countries. Within this subsystem, raw materials are processed into materials that are either consumed directly or used to manufacture other products. Once the useful life of a product is finished, it is discarded. Some products and their materials may then be reclaimed, remanufactured, and reused in what is often called a "secondary" market. But, ultimately, nearly all materials and products reach final disposal, where they are discarded as dissipated wastes.

Figure 1 illustrates the input/output flow of materials in the United States. A simple materials balance approach can be used to track the flow of these materials from their source as extracted resources, to their processing into products, to the use of those products and, finally, to their disposal as waste. Figure 1 shows that one of the primary outputs of U.S. material flows is air emissions. The potential fuel value of these air emissions, which are both thermal and chemical, is the focus of this report.

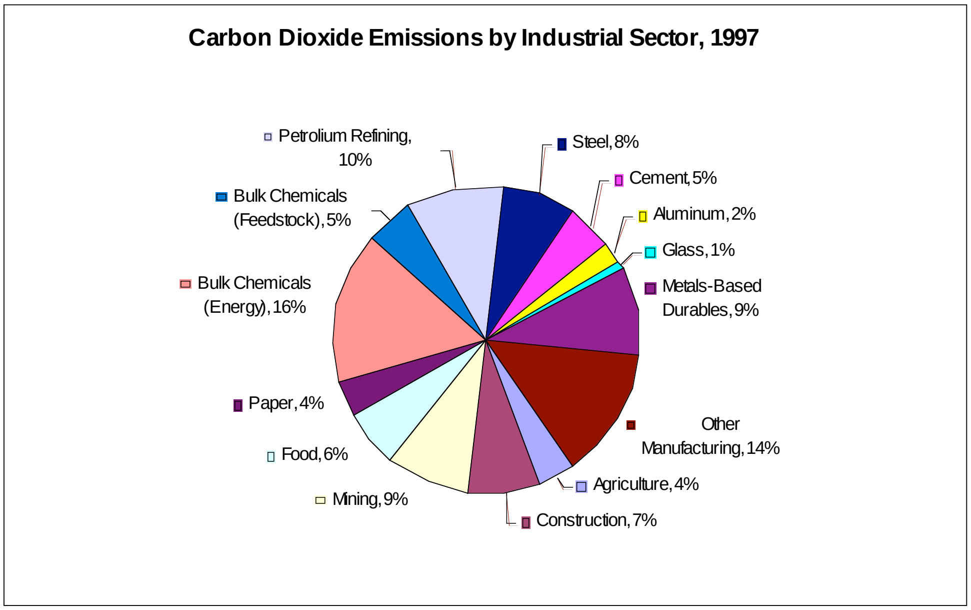


Source: Iddo, K., Wernick and Jesse H. Ausubel. "National Material Flows and the Environment." *Annual Review of Energy and the Environment* 20 (1995): pp. 463-492.

Figure 1. U.S. Materials Flow

This section focuses on air emissions with residual chemical fuel value. The emissions are diverse, depending on the specific industry and process being used. Many of the emissions have very low to zero residual chemical fuel value – such as CO_2. Nevertheless, all emissions have been presented as part of this comprehensive analysis.

CO_2 is emitted from most industries that consume energy. Figure 2 illustrates the share of CO_2 emission from each industrial sector. Carbon dioxide emissions from industrial energy use as well as process emissions from cement manufacture were 494 MtC, accounting for 33% of total U.S. CO_2 emissions. The largest CO_2-producing sector was bulk chemicals (energy).



Source: Worrell, E., and L. Price. "Policy scenarios for energy efficiency improvement in industry." *Energy Policy* 29 (2001): 1223-1241.

Figure 2. Carbon Dioxide Emissions in U.S. by Industrial Sector

Table 2 lists the GHG emissions allocated to various economic sectors [1]. More than 30% of GHG emissions are electricity related, while about 20% of these emissions are industry-related. For the scope of this study, we are only interested in emissions with recoverable energy content. Because, in most cases, electricity used by the process plant is supplied by a remotely located utility, industry cannot capture these emissions for energy use. Therefore, for the purposes of this study, electricity-related emissions have been ignored.

Table 3 presents the GHG emissions and electricity-related emissions for each economic sector. The percentage of GHG emissions from industry in Table 2 is 19%. This amount increases to 30% for the same year in Table 3 because this total includes electricity-related emissions. In 2001, electricity-related emissions from the chemical industry were 37% of total emissions, while electricity-related emissions across all sectors were only 33% of total emissions. Because 50% of all process-related industrial emissions are electricity related, generating electricity from process-related emissions will significantly lower total emissions.

Table 2. U.S. GHG Allocated to Various Economic Sectors

End-Use Sector	GHG Emissions (Tg CO_2 equivalent)		Percentage	
	1990	2001	1990	2001
Electricity	1862	2298	30	33
Transportation	1526	1867	25	27
Industry	1423	1316	23	19
Agriculture	488	526	8	8
Residential	335	379	5	6
Commercial	472	497	8	7
Total	**6106**	**6883**		

Source: Table ES-3 of [1].

Table 3. CO_2 and Electricity-Related Emissions Distributed Across Sectors

End-Use Sector	GHG Emissions (Tg CO_2 equivalent)		Electricity-Related Emissions		Percentage of Total Emissions	
	1990	2001	1990	2001	1990	2001
Transportation	1529	1870	3	3	25	27
Industry	2097	2074	674	758	34	30
Agriculture	512	546	24	20	8	8
Residential	943	1139	608	760	15	17
Commercial	1025	1253	553	756	17	18
Total	**6106**	**6882**	**1862**	**2297**		

Fossil fuel combustion, which is directly related to energy generation in the form of heat or electricity, is a major source of greenhouse gas, especially CO_2. Table 4 gives CO_2 emissions from fossil fuel combustion for the industrial, transportation, residential, and commercial sectors [1]. Note that these numbers do not include process-related emissions, which will be listed separately. These numbers cannot be compared directly with Table 2 and Table 3, since these tables include total GHG emissions in terms of Tg CO_2 equivalent, while Table 4 includes only CO_2 emissions from fossil fuel combustion.

Table 4. CO_2 Emissions from Fossil Fuel Combustion (Tg) by End-Use Sector

End-Use Sector	CO_2 (Tg)		Percentage	
	1990	2001	1990	2001
Industrial - combustion	955.3	937.7	20	17
Industrial - electricity	676.8	746.8	14	13
Transportation - combustion	1470.5	1780.9	31	32
Transportation - electricity	3.0	3.6	0	0
Residential - combustion	328.9	363.3	7	7
Residential - electricity	589.9	747.8	12	13
Commercial - combustion	221.4	235.9	5	4
Commercial - electricity	535.2	744.6	11	13
Total	4781	5560.6		

Source: Table 2-6 of [1].

In 2001, non-electricity-related industrial emissions were 1316 Tg CO_2 equivalent. Since combustion-related industrial emissions were 937.7 Tg CO_2 (Table 4), process-related industrial emissions were estimated to be 1316–937.7 = 364.2 Tg CO_2 equivalent.[3] Similarly for year 1990, process-related CO_2 emissions is 1423-955.3 = 467.7 Tg CO_2 equivalent. As seen in Table 5, non-electricity-related emissions due to fossil fuel combustion form a significant portion (70%) of emissions from the industrial sector. In addition to fossil fuel combustion, which is the main source of energy-related emissions. Table 6 shows GHG emissions from other energy-related processes [1].

Table 5. GHG Emissions from Non-Electricity-Related Fossil Fuel Combustion from the Industrial Sector

Year	Fossil Fuel Combustion ($Tg\ CO_2$)	Total ($Tg\ CO_2$ equivalent)	Percentage of Total Emissions
1990	937.7	1316	71.2
2001	955.3	1423	67.1

---

[3] As seen from Tables 18-21, the industrial emissions by weight of other gases due to fuel combustion are much lower compared to CO_2 emission. As an approximation, they can be ignored to get an estimate of process-related industrial emissions.

Table 6. Emissions of GHGs from Various Energy-Related Processes

Energy-Related Process	GHG	Emissions (Gg)		Energy (PJ)	
		1990	2001	1990	2001
Fossil fuel combustion – all sectors	CO_2	4814758	5614853		
Fossil fuel combustion – industrial	CO_2	955200	937600		
Fossil fuel combustion – electricity generation	CO_2	1804600	2242400		
Waste combustion	CO_2	14100	26900		
Natural gas flaring	CO_2	5500	5200		
Fossil fuel combustion – industrial	CH_4	107	116	6.0	6.4
Natural gas systems	CH_4	5810	5588	323.5	311.2
Coal mining	CH_4	4149	2893	231.0	161.1
Petroleum systems	CH_4	1309	1011	72.9	56.3
Fossil fuel combustion – industrial	CO	991.8	696.2	10.03	7.04
Fossil fuel combustion – industrial	NMVOCs	150.3	152	9.1	9.2
Fossil fuel combustion – industrial	N_2O	11	12	0	0

Source: Table 2-2, 2-16, 2-17 of [1].

Table 7 shows the contribution of various sectors to fuel-related GHG emissions in Tg CO_2 equivalent. The cells with high contribution to GHG have been highlighted in bold, showing which industries and fuel types can be targeted for maximum reduction in GHG emissions. While some reduction can be achieved through energy capture, an alternative approach may be to use these gases (i.e., CO_2) as feedstock to make useful products. Clearly, the emissions from Iron & Steel, Chemicals, Petroleum Refineries, and Paper sectors are significant. The total emissions excluding electricity is 1467 Tg CO_2 equivalent. This table also shows which fuels within each sector contribute to different amounts of emissions. For example, liquefied petroleum gases (LPG), natural gas liquids (NGL) contribute to 62% of emissions from the Plastic Materials and Resins sector, while coal contributes to 59% of emissions from the Cements sector. This table gives a good idea of the impact of various sectors on GHG; however, it does not provide information on the energy available from these emissions. In order to get this value, data on emission of individual gases from each sector is necessary.

Table 8 shows process-related emissions in Tg CO_2 for year 2000 from various industries. Comparing the process-related emissions in this table with the total GHG emissions in Table 7 indicates that process-related emissions are only 18% of total GHG emissions from industry. This is highlighted in Table 9, which shows fuel-related and process-related emissions from various industrial sectors. In Table 9, the fuel-related GHG is 1419 Tg CO_2 equivalent, while in Table 7 it is 1629 Tg CO_2 equivalent. This is because some emissions from the chemical sector and some from the Nonmetallic Minerals Products sector were counted twice. The total fuel-related emissions excluding electricity in Table 9 was estimated by subtracting 150 Tg CO_2 equivalent for electricity (using a number slightly less than 162 Tg CO_2 equivalent from Table 9 due to the double counting mentioned above). It also shows that energy-related emissions due to on-site electricity generation are 82% of the total GHG emissions. Emissions due to electric power generation from a remote utility have not been included in the total because these emissions cannot be captured by the industrial plant.

Table 10, compiled by combining Tables ES-8 and Table 2-2 of [1], provides industrial emissions by weight of various gases from energy-related (E) and process-related (P) sources. Industrial fossil fuel combustion contributes to 70% by weight of GHG emissions. The other energy-related emissions contribute a lot less; however, the other emissions consist of natural gas, which has an energy content of 892 kJ/mole, while that of CO_2 is 0. The main purpose of this table is to once again highlight the importance of fossil fuel combustion in emissions. Since industrial fossil fuel combustion is mainly used for providing process heat, better thermal management should significantly reduce emissions.

Table 11 shows emissions from processes within various industries. This table has been compiled from Tables ES-1, ES-8, ES-10, 3-2 of [1]. All energy-related emission sources, such as fossil fuel combustion, natural gas flaring, and natural gas systems, have been included, providing a greater level of detail than Table 10.

Table 7. Contribution to GHG in Tg CO_2 Eq. from Various Sectors

EIA/NAICS Sector	Total	Net Electricity Used	Res Fuel Oil	Dist Fuel Oil	Nat Gas	LPG, NGL	Coal	Coke, Breeze	Other
Nitrogeneous fertilizers	31.8	1		0	0	0			0.5
Phosphatic fertilizers	6.7	0.4	0.1	0	1.6	0	2.9		1.7
Alumina and aluminum	32.7	**18.5**	0	0.1	10	0.1	0.2	0.2	3.7
Transportation equipment	32.8	**14.6**	0.4	1.1	11.2	0.2	2.7	0.1	2.3
Cements	30.5	2.9	0	0.2	1.4	0	**21.1**	0.6	4.1
Chemicals	395.2	43.3	7.7	0.7	**143.7**	**111.9**	28.2	0.7	**50.8**
Computers and electronics	14	10.3	0.1	0.1	3.4	0	0		0.1
Iron and steel mills	157.1	11.9	2.3	0.4	**26.2**	0	**63.9**	**36.4**	1.7
Petroleum refineries	513.8	8.9	5.5	0.3	**50.3**	2.1	0		**446.8**
Plastics materials and resins	68.1	5	0.2	0.1	13.7	42.1	1.6	0	4.5
Paper	198.8	18	11.9	0.7	**31.1**	0.3	26		**110.9**
Synthetic rubber	19.9	0.6	0	0	1.1	**14.8**	1.3		0.9
Semi-conductors and related devices	4.7	3.5	0	0	1.1	0			0
Nonmetallic mineral products	69.2	10.1	0.3	1.2	**23.6**	0.2	**26.7**	1	6.2
Textile mills	17.4	7.7	0.9	0.3	5.5	0.1	1.9		1.1
Wood products	36.5	5.4	0.1	1	3.9	0.2	0.2	0	**25.7**
Total	1629.2	162.1	29.5	6.2	327.8	172	176.7	39	661
% of Total		9.9	1.8	0.4	20.1	10.6	10.8	2.4	40.6

Source: http://ecm.ncms.org/ERI/new/GHG.htm, Table 2.

Table 8. Process-Related Emissions for the Year 2000 in Tg CO_2 Eq.

Industrial Sector	Process	CO_2	CH_4	N_2O	Other (HFC, PFC, SF_6)	Total Emission within Sector
Chemicals	Substitution of ozone-depleting substances				57.8	94.6
Chemicals	HCFC-22 production				29.8	
Chemicals	Titanium dioxide production	2.0				
Chemicals	Soda ash manufacture and consumption	1.1				
Chemicals	Petrochemical production		1.7			
Chemicals	Nitric acid production			2.2		
Iron and steel	Iron & steel production	65.7				67.7
Iron and steel	Ferroalloy production	2.0				
Cement	Cement manufacture	41.1				41.1
Agricultural chemicals	Ammonia manufacture	16.0				31.8
Agricultural chemicals	Nitric acid production			15.8		
Stone, clay & glass	Lime manufacture	13.3				21.5
Stone, clay & glass	Limestone & dolomite use	9.2				
Electric utilities	Electrical transmission and distribution				14.4	14.4
Aluminum	Aluminum production	5.4			7.9	13.3
Plastics	Nitric acid production			1.8		9.9
Plastics	Adipic acid production			8.1		
Semiconductors	Semiconductor manufacture				7.4	7.4
Total		155.8	1.7	27.9	117.3	**302.7**

Sources: [2]; Table 3-1 of [1], http://ecm.ncms.org/ERI/new/GHG.htm.

Table 9. Comparison of Fuel-Related and Process-Related Emissions in Year 2000 in Tg CO_2 Eq.

EIA Sector	Fuel-Related GHG	Process-Related GHG	Total GHG
Electric power sector	1926.8	14.4	1941.2
Petroleum refineries	513.8		
Chemicals	232.7	94.6	327.3
Iron and Steel Mills	157.1	67.7	224.8
Paper	198.8		198.8
Plastics Materials and Resins	68.1	9.9	78
Cements	30.5	41.1	71.6
Nitrogeneous Fertilizers	31.8	31.8	63.6
Nonmetallic mineral products	38.7	21.5	60.2
Alumina & aluminum	32.7	13.3	46
Wood products	36.5		36.5
Transportation	32.8		32.8
Synthetic rubber	19.9		19.9
Computer and electronic products	14		14
Semiconductors and related devices	4.7	7.4	12.1
Phosphatic fertilizers	6.7		6.7
Total	1419	287	1706
Total w/o electricity	1269	287	1556
% of Total	81.6	18.4	100

Source: http://ecm.ncms.org/ERI/new/GHG.htm.

Table 10. Energy- and Process-Related Industrial Emissions in Tg Gas

Source	Energy (E) Process (P)				Energy (PJ)	
		1990	**2001**	**Gas**	**1990**	**2001**
Fossil fuel combustion – industrial	E	955.3	937.7	CO_2		
Fossil fuel combustion – industrial	E	0.11	0.12	CH_4	6.27	6.82
Fossil fuel combustion – industrial	E	1.0	0.7	CO	10.0	7.0
Fossil fuel combustion – industrial	E	0.2	0.2	NMVOC	9.1	9.2
Waste combustion	E	14.1	26.9	CO_2		
Natural gas flaring	E	5.5	5	CO_2		
Natural gas systems	E	5.81	5.588	CH_4	323.5	311.2
Coal mining	E	4.149	2.893	CH_4	231.0	161.1
Petroleum systems	E	1.309	1.011	CH_4	72.9	56.3
Iron and steel	E	85.4	59.1	CO_2		
Cement manufacture	E	33.3	41.4	CO_2		
Ammonia manufacture & Urea	P	19.3	16.6	CO_2		
Lime manufacture	P	11.2	12.9	CO_2		
Limestone and dolomite use	P	5.5	5.3	CO_2		
Aluminum production	P	6.3	4.1	CO_2		
Soda ash manufacture and consumption	P	4.1	4.1	CO_2		
Titanium dioxide production	P	1.3	1.9	CO_2		
Carbon dioxide production	P	0.9	1.3	CO_2		
Ferroalloys	P	2	1.3	CO_2		
Petrochemical production	P	0.06	0.07	CH_4	3.3	3.9
Landfills	P	10.1	9.66	CH_4	562.4	537.9
Total					**1218.6**	**1093.4**

Source: Tables ES-8 and 2-2 of [1].

Table 11. Process-Related Emissions from Various Industries

Industry	GHG	Emissions (Gg)		Energy Recoverable?
		1990	2001	
Fossil Fuel combustion – industrial	CO_2	955300	937700	No
Industrial processes	CO	4124	2327	Yes
Industrial processes	NO_x	769	755	No
Industrial processes	NMVOCs	2426	1829	Yes
Industrial processes	SO_2	1306	1008	No
Aluminum	CO_2	6315	4114	No
Aluminum	CF_4	2.37	0.54	No
Aluminum	C_2F_6	0.253	0.1	No
Natural gas flaring	CO_2	5500	5200	No
Natural gas systems	CH_4	6324	6068	Yes
Natural gas systems	CH_4	5809	5585	Yes
Oil operations	CH_4	1310	1009	Yes
Oil and gas	CO	302	153	
Oil and gas	NMVOCs	555	357	
Oil and gas	SO_2	390	281	
Iron and steel	CO_2	85400	85400	No
Chemicals				
Ammonia	CO_2	19306	16588	No
Lime	CO_2	11238	12859	No
TiO_2	CO_2	1308	1857	No
Nitric acid	N_2O	58	57	No[4]
Adipic acid	N_2O	49	16	No
N_2O product use	N_2O	14	15	No
Mg	HFCs, PFCs, SF_6			
Soda ash	CO_2	4100	4100	No
Petrochemical production	CH_4	56	71	Yes
Solvent use	NMVOCs	3493	2863	
Cement	CO_2	33300	41400	No
Limestone and dolomite use	CO_2	5500	5300	No
Municipal solid waste landfill	CH_4	11600	14952	Yes
Industrial landfills	CH_4	814	1048	Yes
Recovered CH_4	CH_4			
Gas to energy (7-4)	CH_4	-733	-2395	
flared 7-4	CH_4	-457	-2866	
oxidized 7-4	CH_4	-1123	-1076	
Total CH_4 from landfills	CH_4	10100	9662	

Source: Tables 3-2, ES-8, ES-1, ES-10, 7-4 of [1].

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[4] Energy content of N_2O is quite small.

Tables 10 and 11 can be synthesized into one table that shows chemical compounds in industrial emission by source. Tables 12 and 13 show CH_4 and CO emissions from various sources, respectively. The data has been converted from Tg CO_2 equivalent to Gg CH_4 and CO using energy conversion units shown in Table 1. Table 14 provides data for non-methane volatile organic compounds (NMVOCs). The values in Table 1 were used to estimate the chemical energy content in the various emissions.

Table 12. Methane (CH_4) Emissions from Various Sources

Source	CH_4 (Gg)		Energy (PJ)	
	1990	2001	1990	2001
Fossil fuel combustion – industrial[5]	107	117	6.0	6.5
Landfills	10100	9662	562.4	538.0
Agriculture	7480	7720	416.6	430.1
Natural gas systems	5810	5586	323.4	311.0
Coal mining	4148	2890	231.0	161.0
Petroleum systems	1310	1010	72.9	56.2
Petrochemical production	57	71	3.2	4.0
Total	29012	27056	1615	1507

Source: Table ES-10 of [1].

Table 13. CO Emissions from Various Sources

Source	CO (Gg)		Energy (PJ)	
	1990	2001	1990	2001
Stationary fossil fuel combustion	4999	4169		
Stationary fossil fuel combustion – industrial	1071[6]	1071	10.83	10.83
Oil and gas	302	153	3.05	1.55
Waste combustion	978	2916	9.89	29.49
Industrial processes[7]	4124	2327	41.71	23.54
Solvent use	4	44	0.04[8]	0.45
Total energy			65.52	65.86

Source: Table ES-14 of [1].

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[5] Table 2-15 of [1].

[6] Only data for 2001 available

[7] Need breakdown.

[8] This may be difficult to capture. Not a lot of energy content.

Table 14. Emission of Non-Methane Volatile Organic Compounds

Source	NMVOCs (Gg)		Energy (PJ)	
	1990	2001	1999	2001
Stationary fossil fuel combustion	912	1087		
Stationary fossil fuel combustion – industrial		152	7.7[9]	7.7
Oil and gas	555	357	28.0	18.0
Waste combustion	222	333	11.2	16.8
Industrial processes	2426	1829	122.4	92.3
Solvent use (extends across all industries)	5217	4584	263.2	231.3
Total energy from NMVOCs			441.6	367.5

Source: [1].

Tables 15 and 16 provide emission estimates for gases whose chemical energy content is not easily recoverable due to kinetic limitations for combustion (Table 15) or that do not have any chemical energy content (Table 16).

Table 15. SO_2 and NO_x Emissions (Gg)

Source	SO_2 (Gg)		Energy (PJ)		NO_x (Gg)		Energy (PJ)	
	1990	2001	1990	2001	1990	2001	1990	2001
Stationary fossil fuel combustion	18407	12367			9884	7826		
Stationary fossil fuel combustion – industrial					2393[10]	2393	2.25[11]	2.25
Oil and gas	390	281	0.55	0.39	139	117	0.13	0.11
Waste combustion	39	30	0.05	0.04	82	149	0.08	0.14
Industrial processes	1306	1008	1.83	1.41	769	755	0.72	0.71
Total energy			2.43	1.84			3.18	3.21

Source: Table ES-1 of [1].

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[9] Only data for 2001 available.
[10] Only data for 2001 available.
[11] Assume 50% is NO, which has energy content of 13.5 kcal/mol.

Table 16. HFCs, PFCs, SF_6, Gg

Source	1990	2001
Substitution of ozone-depleting substances	0.18	12.74
HFC-22 production	7.00	3.96
Semi-conductor manufacture	0.58	1.10
Aluminum production	3.62	0.82
Mg production and processing	1.08	0.50

Source: Table ES-12 of [1].

Table 17, compiled from Tables 1-9 of [1], gives the emission of various gases in Gg from various industrial processes. Table 18 compares emissions in 1990 and 2001 using the IPCC Tier I approach, as described in [1]. A total energy content of 1870 PJ was available from all gases (as shown in Table 17). The energy content of methane emissions are 1437 and 1346 PJ for Tables 17 an 18, respectively. These numbers are quite close to the value of 1507 PJ shown in Table 12.

Table 17. Emissions of Various Gases, Tg, from Various Industrial Processes

GHG	Source	Gg		Energy PJ	
		1990	2001	1990	2001
CO_2					
	Fossil fuel combustion – industrial	955300	937700		
	Iron and steel	85400	59100		
	Cement manufacture	33300	41400		
	Chemicals: ammonia manufacture & area	19300	16600		
	Chemicals: lime manufacture	11200	12900		
	Natural gas flaring	5500	5200		
	Chemical: limestone and dolomite use	5500	5300		
	Aluminum production	6300	4100		
	Soda ash manufacture and consumption	4100	4100		
	Titanium dioxide production	1300	1900		
	Carbon dioxide production	900	1300		
	Ferroalloys	2000	1300		
	Biomass combustion	183700	183700		
	Total CO_2 Emissions	1314000	1275000		
CH_4					
	Fossil fuel combustion	107	116	6.0	6.4
	Natural gas systems	5810	5588	323.5	311.2
	Petroleum systems	1309	1011	72.9	56.3
	Petrochemical production	56	71	3.1	4.0
	Landfills	10099	9663	562.4[12]	538.1
	Enteric fermentation	5612	5468	312.5	304.5
	Coal mining	4149	2893	231.0	161.1
	Rice cultivation	1309	1011	72.9	56.3
	Total CH_4 emissions and energy content	28451	25821	**1584.3**	**1437.5**
N_2O					
	Agricultural soil management	863	949	0.27	0.29
	Nitric acid	58	57	0.02	0.02
	Adipic acid	49	16	0.02	0.00
	Total N_2O emissions and energy content	970	1022	**0.31**	**0.31**
NO_x CO					
	Total CO emissions [13]	130575	10063		
CO					
	Stationary fossil fuel combustion	4999	4169		
	Stationary fossil fuel combustion industrial	1071[14]	1071	10.8	10.8
	Oil and gas	302	153	3.1	1.6
	Waste combustion	978	2916	9.9	29.5
	Industrial processes[15]	4124	2327	41.7	23.5
	Solvent use (extends across all industries)	4	44	0.04	0.5
	Total CO emissions and energy content	6479	6511	**65.54**	**65.9**
NMVOCs					
	Total NMVOC emission[16]	20937	15148		
	Stationary fossil fuel combustion	912	1087		
	Stationary fossil fuel combustion - industrial	181	152	9.1	7.7
	Oil and gas	555	357	28.0	18.0
	Waste combustion	222	333	11.2	16.8
	Industrial processes	2426	1829	122.4	92.3
	Solvent use (extends across all industries)	5217	4584	263.2	231.3
	Total energy from NMVOCs			**433.9**	**366.1**
	Total energy from all emissions (PJ)				**1870**

Source: Tables 1-9, 2-15, 2-16, 2-17 of [1].

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[12] Clearly, the non-industrial processes such as landfill, mining, and enteric fermentation have high potential for energy capture.

[13] Includes stat and mobile fossil fuel combustion, oil & gas, waste combustion, industrial processes, solvent use. (Source: Table ES-14 of EPA report [1] on USGHG 2003.)

[14] Only data for 2001 available.

[15] Need breakdown.

[16] Includes stat and mobile fossil fuel combustion, oil & gas, waste combustion, industrial processes, solvent use. (Table ES-14 of EPA report [1] has breakdown.)

Table 18. Tier 1 Analysis: GHG Emissions in 1990 and 2001

IPCC Source	GHG	1990			2001		
		(T CO_2 Eq.)	(Tg Gas)	Energy Content (PJ)	T CO_2 Eq.	(Tg Gas)	Energy Content (PJ)
Iron & Steel Production	CO_2	85.41			59.07		
Cement Production	CO_2	33.28			41.36		
Aluminum Production	CO_2	6.31			4.11		
Stationary combustion-Oil	CO_2	669.99			671.62		
Stationary combustion-Coal	CO_2	1697.29			1993.78		
Stationary combustion-Gas	CO_2	976.63			1168.23		
Natural gas flaring	CO_2	5.5			5.2		
Waste incineration	CO_2	14.1			26.9		
Ammonia production & urea	CO_2	19.3			16.6		
Ferroalloys	CO_2	1.98			1.33		
Limestone and dolomite use	CO_2	5.47			5.28		
Soda ash manufacture and consumption	CO_2	4.14			4.15		
TiO_2 production	CO_2	1.31			1.86		
Lime production	CO_2	11.24			12.86		
Total CO_2	CO_2	3493.05			3963.65		
Adipic acid production	N_2O	15.2	0.049	0.015	4.92	0.016	0.005
Nitric acid production	N_2O	17.85	0.0576	0.018	17.6	0.057	0.018
Stationary combustion	N_2O	12.52	0.040	0.012	14.18	0.046	0.014
Agriculture	N_2O	15.2	0.049	.015	4.9	0.016	0.005
Agricultural soils	N_2O	193.7	0.62	0.19	216.6	0.700	0.22
Manure management	N_2O	16.2	0.052	0.016	18.0	0.058	0.02
Total N_2O and energy content	N_2O	270.6	0.873	**0.27**	276.22	0.890	**0.276**
Fugitive emissions from natural gas operations	CH_4	122.01	5.81	323.53	117.35	5.59	311.17
Solid waste disposal	CH_4	212.07	10.10	562.33	202.93	9.66	538.10
Fugitive emissions from oil operations[17]	CH_4	27.49	1.31	72.89	21.23	1.01	56.29
Manure management	CH_4	31.28	1.49	82.94	38.85	1.85	103.02
Stationary combustion industrial	CH_4	2.25	0.107	6.0	2.44	.116	6.4
Rice production	CH_4	7.12	0.34	18.88	7.64	0.36	20.26
Petrochemical production	CH_4	1.17	0.06	3.10	1.49	0.07	3.95
Silicon carbide production	CH_4	0.07	0.00	0.19	0.06	0.00	0.16
Agriculture residue burning	CH_4	0.68	0.03	1.80	0.76	0.04	2.02
Enteric fermentation	CH_4	117.9	5.6	312.5	114.8	5.47	305.1
Total CH_4 and energy content	CH_4	520.9	24.9	**1390**	507.55	24.17	**1346.3**

Source: Table R-15 of [1].

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[17] Fugitive emissions from natural gas operations has very high energy content. Not covered in petroleum refining.

Combustion-Related Emissions Survey

Fossil-fuel combustion appears to be the origin of a significant portion of the air emissions from industrial facilities. Typically, these emissions emanate from a known exhaust location rather than from vastly distributed sources. Because combustion-related emissions are so significant, this section of the report focuses particular attention on the residual chemical fuel value of emissions from industrial combustion-related processes. This analysis does not include emissions that are a result of electricity generated at a remote site (i.e., electricity purchased from a utility) because these emissions cannot be captured by industry for residual fuel use.

The majority of combustion-related emissions are CO_2. Other emissions include CH_4, CO, and NMVOCs, in addition to NO_x, SO_x and other non-energetic gases. Data on CH_4, CO, NMVOC, and NO_x emissions were provided in the EPA report [1]. This information is illustrated in Tables 19-22.

Table 19. CH_4 Industrial Emissions from Stationary Combustion

Fuel Source	CH_4 Emissions (Gg) from Stationary Combustion				Energy (PJ)			
	1990	1995	1998	2001	1990	1995	1998	2001
Coal	16	16	15	20	0.89	0.89	0.84	1.11
Fuel oil	8	7	7	7	0.45	0.39	0.39	0.39
Natural gas	39	45	45	42	2.17	2.51	2.51	2.34
Wood	43	50	48	48	2.39	2.78	2.67	2.67
Total	106	118	115	117	5.90	6.57	6.40	6.52

Source: Table 2-15 of [1].

Table 20. CO Industrial Emissions from Stationary Combustion

Fuel Source	CO Emissions (Gg) from Stationary Combustion				Energy (PJ)			
	1990	1995	1998	2001	1990	1995	1998	2001
Coal	95	88	96	118	0.96	0.89	0.97	1.19
Fuel oil	67	64	46	43	0.68	0.65	0.47	0.43
Natural gas	205	313	305	345	2.07	3.16	3.08	3.49
Other fuels	253	270	303	303	2.56	2.73	3.06	3.06
Internal combustion	177	222	294	263	1.79	2.24	2.97	2.66
Total	**797**	**957**	**1044**	**1072**	**8.06**	**9.68**	**10.55**	**10.84**

Source: Table D-4 of [1].

Table 21. NMVOC Industrial Emissions from Stationary Combustion

Fuel Source	NMVOC Emissions from Stationary Combustion (Gg)				Energy (PJ)			
	1990	1995	1998	2001	1990	1995	1998	2001
Coal	7	5	6	10	0.3535	0.2525	0.303	0.505
Fuel oil	11	11	7	8	0.5555	0.5555	0.3535	0.404
Natural gas	52	66	54	52	2.626	3.333	2.727	2.626
Other fuels	46	45	31	28	2.323	2.2725	1.5655	1.414
Internal combustion	49	59	61	54	2.4745	2.9795	3.0805	2.727
Total	165	186	159	152	8.3325	9.393	8.0295	7.676

Source: Table D-5 of [1].

Table 22. NO_x Industrial Emissions Gg from Stationary Combustion

Fuel Source	NO_x Emissions from Stationary Combustion (Gg)				Energy (PJ)			
	1990	1995	1998	2001	1990	1995	1998	2001
Coal	36	541	475	496	0.03	0.51	0.45	0.47
Fuel oil	88	224	190	147	0.08	0.21	0.18	0.14
Natural gas	181	1202	1066	875	0.17	1.13	1.00	0.82
Other fuels	119	111	104	111	0.11	0.10	0.10	0.10
Internal combustion	792	774	933	764	0.75	0.73	0.88	0.72
Total	1216	2852	2768	2393	1.15	2.69	2.61	2.25

Source: Table D-3 of [1].

As stated in the EPA report [1], there was significant uncertainty in estimating the emission values for CH_4, CO, NMVOC, and other gases from stationary combustion. The level of confidence in this data can be improved by studying alternative approaches to establishing the residual fuel content in industrial combustion emissions. To make alternative estimates to verify this data, we calculated the emission values for CH_4 using the emission factors for each fuel (weight of emission/unit energy usage) given in Table D-2 of [1] and using the fuel consumption data from Table D-1 of [1]. Table 23 gives the value of methane emissions using this technique for years 1990, 1995, 1998, and 2001. The methane emission values in this table are close to the values presented in Table 19.

Table 23. Calculation of CH_4 Industrial Emissions by Stationary Combustion from Fuel Consumption Data

1990					1998				
Fuel	**(TBtu)**	**(PJ)**	**CH_4 EMF[18] (g/GJ)**	**CH_4 (Gg)**	**Fuel**	**(TBtu)**	**(PJ)**	**CH_4 EMF (g/GJ)**	**CH_4 (Gg)**
Coal	1612	1701	10	17.0	Coal	1459	1539	10	15.4
Petroleum	4024	4245	2	8.5	Petroleum	3588	3785	2	7.6
Natural gas	7821	8251	5	41.3	Natural gas	8984	9478	5	47.4
Wood	1447	1526	30	45.8	Wood	1603	1691	30	50.7
Total	14904	15723		**112.6**	Total	15634			**121.1**

1995					2001				
Fuel	**(TBtu)**	**(PJ)**	**CH_4 EMF (g/GJ)**	**CH_4 (Gg)**	**Fuel**	**(TBtu)**	**(PJ)**	**CH_4 EMF (g/GJ)**	**CH_4 (Gg)**
Coal	1577	1663	10	16.6	Coal	2017	2128	10	21.4
Petroleum	3676	3878	2	7.8	Petroleum	3549	3744	2	7.5
Natural gas	8924	9415	5	47.1	Natural gas	8287	8743	5	43.7
Wood	1652	1743	30	52.3	Wood	1580	1667	30	50.0
Total	15829			**123.8**	Total	15433			**122.5**

Source: Table D-1 of [1] or Annex 3 of [4] – correction of 0.95 and 0.9 already present – please refer to Table D-1 in [1] for details.

Table 23 has different values of energy consumption for various fuels than the *EIA 2003 Annual Energy Review* [5] and the calculated value from [2]. This is because the data in Table 23 corresponds to fuel consumption for electricity use only, while the *EIA 2003 Annual Energy Review* corresponds to fuel consumed for electricity use as well as for process use. The EIA 2003 data can be used as an alternative method to calculate energy content in combustion-related industrial emissions.

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[18] EMF: emission factor.

Table 24. Calculation of CH_4 Emissions Using Fuel Consumption Data from Tables 2.1 and 2.2 of EIA *Annual Energy Review* [5]

1990					**1998**				
Fuel	**TBtu**	**Corrected TBtu**	**PJ**	**CH_4 Emission (Gg)**	**Fuel**	**TBtu**	**Corrected TBtu**	**PJ**	**CH_4 Emission (Gg)**
Coal	2756	2618	2762	27.6	Coal	2335	2218	2340	23.4
Natural gas	8502	7652	8073	40.4	Natural gas	9806	8825	9311	46.6
Petroleum	8278	7864	8297	16.6	Petroleum	9116	8660	9137	18.3
Wood	1442	1442	1521	45.6	Wood	1603	1603	1691	50.7
Total	20978	19576	20653	**130.2**	Total	22860	21307	22479	**139.0**
1995					**2001**				
Fuel	**TBtu**	**Corrected TBtu**	**PJ**	**CH_4 Emission (Gg)**	**Fuel**	**TBtu**	**Corrected TBtu**	**PJ**	**CH_4 Emission (Gg)**
Coal	2488	2363	2494	24.9	Coal	2230	2119	2235	22.4
Natural gas	9637	8673	9150	45.8	Natural gas	8725	7853	8284	41.4
Petroleum	8614	8183	8633	17ÏC.3	Petroleum	9220	8759	9241	18.5
Wood	1652	1652	1743	52.3	Wood	1443	1443	1522	45.7
Total	22391	20872	22020	**140.2**	Total	21618	20173	21283	**127.9**

Table 24 gives the methane emission values using fuel consumption from the *EIA 2003 Annual Energy Review*. As expected, the CH_4 emissions energy consumption is less than from total energy consumption (for electricity and for industrial processes). To determine the contribution of each fuel to CH_4 emissions within each industrial sector, we used the data for total CO_2 emissions for year 1998 within each sector [2]. We calculated the energy consumption using an appropriate CO_2 emission coefficient for each sector. To calculate the amount of CH_4 emitted from each industrial sector and each fuel type, we used the CH_4 emission coefficient values given in the IPCC revised 1996 report. The total energy data used for this report was from the manufacturing sub-sector of the industrial sector, excluding agriculture, mining, and construction.

Table 25. Methane Emissions from Fuel Usage for the Year 1998 from Each Sub-Sector

Industry	SIC Code	Methane Emissions (Gg) By Fuel Used				
		Petroleum	**Natural Gas**	**Coal**	**Other**	**Total**
Petroleum	29	7.7	5.6	0	43.7	57.1
Chemicals	28	2.5	13.2	5.9	3.0	24.6
Metals	33	0.1	3.3	13.9	1.4	18.7
Paper	26	0.8	4.4	7.8	0.7	13.7
Food	20	0.1	2.5	2.3	0.4	5.3
Glass	32	0.2	1.6	4.1	0.3	6.2
Other manufacturing	No Code	0.4	5.1	1.8	0.8	8.1
Total		11.8	35.9	35.7	50.3	**133.7**

Table 25 shows the CH_4 emissions for the year 1998 from each sub-sector. The detail surrounding these calculations can be found in Appendix B. Since agriculture, mining, and construction were excluded, the CH_4 emissions in Table 23 are less than that obtained in Table 24 using the EIA 2003 Annual Energy Review [5]. As mentioned earlier, due to the uncertainty involved in the industrial emission values from stationary combustion, this analysis was undertaken in order to show the viability of data presented in Tables 19-23. We calculated the CH_4 emissions value using fuel consumption data available from various sources and compared the computed values with the data presented in Table 19.

Table 26 summarizes the computed results for years 1990, 1995, 1998, and 2001 using two computational approaches. The relative agreement between this data with that of Table 19 for all three data sources lends confidence to these numbers. Furthermore, they prove that according to these approaches, little residual chemical fuel value resides in combustion-related industrial emissions. It should be noted that the data corresponding to fuel consumption for both electricity and industrial processes serves only to provide an upper bound estimate on methane emissions. The same emission factor for methane cannot be used when the fuel is used just for industrial processes.

Table 26. Summary Table of Methane Emissions from Industrial Fossil Fuel Combustion 1990-2001

Source	**Fuel Consumption**								
	Year 1990		**Year 1995**		**Year 1998**			**Year 2001**	
	IPCC Annex 3 Electricity Use Only	**EIA 2003 [5] Electricity & Industrial Processes**	**IPCC Annex 3 Electricity Use Only**	**EIA 2003 Electricity & Industrial Processes**	**EIA 2002 [2] Electricity & Industrial Processes**	**IPCC Annex 3 [1] Electricity Use Only**	**EIA 2003 [5] Electricity & Industrial Processes**	**IPCC Annex 3 [1] Electricity Use Only**	**EIA 2003 [5] Electricity & Industrial Processes**
Petroleum	4024	8278	3676	8183.3	5615	3588	8660	3549	8759
Natural gas	7821	8502	8924	8673.3	6226	8984	8825	8287	7852.5
Coal	1612	2756	1577	2363.6	2278	1459	2218	2017	2118.5
Other	1447	1442	1652	1652	1359	1603	1603	1580	1443
Total fuel consumption	14904	20978	15829	20872.2	15479	15634	22860	15433	20173
CH$_4$ emissions (Gg)	112.6	130.2	123.8	140.2	133.7	121.1	139.0	122.5	127.9
Energy (PJ)	**6.27**	7.25	**6.8**9	7.81	7.45	**6.74**	7.74	**6.82**	7.12

Industry-Specific Emissions Survey

This section of the report identifies and evaluates the residual chemical fuel-value that might be present within the emissions of specific, select industries. The intent is to perform a more detailed analysis of emissions from these industries in order to identify emissions that were not captured in the overall analysis.

Aluminum Industry

Alcoa [6] estimated emissions from bauxite refining, anode production, and aluminum smelting to be equal to 110 million metric tons of CO_2 equivalent/year. This does not include indirect emissions from electricity. The main emissions were CF_4 and C_2F_6. Tables 27-29 provide data on energy use in the aluminum industry (www.eia.doe.gov/emeu/iab/aluminum/index.html). Electricity and electricity-related losses represents 85% of energy use (Table 26). 63% of the total energy input to the aluminum industry is consumed during electrolytic reduction of aluminum oxide or alumina to aluminum (Table 29).

Table 27. Total Energy Use in the Aluminum Industry

Year	Total Energy Use Including Electricity Losses (TBtu)	Total Energy Use Without Losses (TBtu)
1985	685	248
1988	727	258
1991	774	297
1994	621	241

Source: www.eia.doe.gov/emeu/iab/aluminum/index.html.

Table 28. Total Energy Use in the Aluminum Industry by Fuel for 1994

Fuel	Energy (TBtu)
Natural gas	70
Other fuels	45
Net electricity	199
Electricity losses	413
Total	727[19]

Source: www.eia.doe.gov/emeu/iab/aluminum/index.html.

Note that total energy consumption from fuel is 115 TBtu energy (70 + 45).

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[19] This data probably corresponds to year 1988, rather than 1994.

Table 29. Heat and Power Consumption by End Use

End Use	% of Heat and Power Consumed
Electrochemical processes	63%
Process heating	23%
Machine Drive	7%
Non-process use	4%
Other	3%

Source: www.eia.doe.gov/emeu/iab/aluminum/index.html.

The electricity intensity is 6.8 kWh per pound of aluminum produced. As shown in Table 29, about two thirds of total energy in the aluminum industry is consumed during the electrolytic reduction of alumina to aluminum. Alumina refining using natural gas (extraction from bauxite ore), corresponds to 10% of industry use, while scrap melting and anode production, which use equal amounts of both electricity and natural gas, each represent 5% of total energy use. Electricity is also used in power casting and rolling mills, as well as for heat, light and cooling [www.eia.doe.gov/emeu/iab/aluminum/index.html].

Table 30 estimates the residual energy content in the aluminum industry's emissions. Emissions from the aluminum reduction process include HF, CO, CO_2, VOCs, SO_2, PFCs, CF_4, and C_2F_6 (epa.gov/ttn/chief/ap42/ch12/final/c12501.pdf). Because there was insufficient data to develop a factor for CO, it was assumed that 20% of CO_2 emissions originate from oxidation of emitted CO. The hydrocarbons and SO_2 emissions from reduction cells have not been presented due to lack of data. SO_x emissions originate from sulfur in anode coke and pitch. The concentration of SO_x in VSS cell emissions range from 200-300 ppm. The concentration of uncontrolled SO_2 emissions from anode baking furnaces ranges from 5-47 ppm. High molecular weight organics and other emissions from anode paste are released from HSS and VSS cells. A fluidized bed of alumina is used to adsorb fluorides, while a scrubber removes part of SO_2 emissions. The U.S. annual production is 22 billion lbs (or 10 million tons) of primary aluminum (from bauxite) and secondary aluminum (from recycled metal).

Table 30. Emissions from Aluminum Production

Source	Emission	(lb/ton Al produced)	(lb produced)	(kg)	(Gg)
Soderberg process	CO_2	3670	36700000000	16681818182	16681.82
Prebake process	CO_2	3080	30800000000	14000000000	14000
Al production	CO_2	3375	33750000000	15340909091	15340.91
Al production	CF4	1.2	12000000	5454545	5.454545
Al production	C_2F_6	0.12	1200000	545454	0.545455
Al production	Particulate fluoride	118.7	1187000000	539545455	539.5
	CO_2				12272.73
	CO	Assume 20% of CO_2 comes from CO			**3068.2** = 31.0 (PJ energy)
Estimated energy content of CO					**31 (PJ)**[20]

Ongoing R&D is aimed at finding alternative anode and aluminum smelting technologies that could significantly reduce the aluminum industry's emissions. These technologies include a newly developed anode that could reduce air pollution from aluminum smelting by 50% [7]. These new technologies could significantly change the emissions situation in the future.

Chemical Industry

In 1998, all of the United States' chemical plants consumed 5.07 Quads of fossil energy as primary source to supply the plants with heat and power. 2.8 Quads of fuel energy was used for boilers and process heating/cooling across various sub-sectors. 0.93 Quads was used for machine drive (such as pumps, fans, and detailed compressors), processes, and for lighting/HVAC. About 1.35 Quads was lost at off-site electric power generation facilities (which are beyond the scope of this report for energy recovery). On-site losses amounted to 1.36 Quads. Some of these losses are detailed below [8]:

- 0.382 Quads in boilers (includes electricity generation losses)
- 0.322 Quads in pipes and valves (includes electrical transmission losses)
- 0.656 Quads due to equipment inefficiency
- ~ 2 Quads - losses from waste heat, flared gases, byproducts (comprehensive studies not available).

Renewables account for only 0.1% of total power generation. Increasing the use of renewable energy provides an opportunity to reduce emissions from the chemical industry. The chemical industry could also reduce electricity use and decrease overall emissions by directly converting chemical energy into electrical energy by using fuel cells. Fuel cells provide an option for utilizing the energy content of these emissions to both generate power and ultimately, reduce emissions [8].

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[20] 31 PJ has been included in the Executive Summary table.

Worrell [9] studied the energy use and intensity of the U.S. chemical industry. This study was the first one to provide a detailed break-up of energy use for various chemical products that consume a lot of energy. According to this study, the United States chemical industry contributes 11% of the U.S. industrial production and uses 20% (5141 TBtu) of the total industrial energy (26047 Tbtu or 26 Quads). The chemical industry contributes about 20% (77 MtC) of industry's total CO_2 emissions. Table 31 and Table 32 provide some other results from the Worrell study.

Table 31. Primary Energy Use in the Chemical Industry (Electricity Plus Fuel, Excluding Feedstock)

Sector	Primary Energy (TBtu)	CO_2 Emissions (MtC)
Chemicals SIC 28	5141	77
Total manufacturing	26047	398
%	20	19

Table 32. Primary Energy Use for Some U.S. Chemical Subsectors in 1994

Chemical Subsector	SIC	Energy (PJ)	CO_2 Emissions (MtC)
Industrial organics, NEC*	2869	1653	25
Industrial inorganics, NEC	2819	830	11
Plastics Materials and Resins	2821	518	7
Nitrogeneous fertilizers	2873	344	10
Alkalies and Cl_2	2812	286	4
Others		1146	16
Total	28	5141	77

*Note: "NEC" stands for "not elsewhere classified." Industrial organics, NEC, accounts for the largest share of energy use in the chemical sector. Some of the key energy-intensive products within this subsector are ethylene, propylene, butadiene, and methanol.

Ethylene and its derivatives are feedstocks for many plastics and resins (SIC 2821). The United States produces 28% of the world's ethylene. During ethylene production, hydrocarbon feedstocks (ethane, naphtha) are heated in pyrolysis furnaces, separated into gas products, then cooled/compressed. Methanol is produced by the reaction of CO and H_2, with an energy intensity of 38 GJ/tonne, with most of this energy used for hydrogen production.

Table 33 gives the energy consumption for key chemicals. For this study, it can be assumed that the emissions will be directly related to energy use. In order to get total emissions, we added the emissions from feedstock.

Table 33. Energy Consumption for Key Chemicals

Product	Specific Energy Consumption (GJ/tonne)	1994 Production (Mtons)	Total Energy Use (PJ)	% of SIC 28 Energy Use
Ethylene & co-products	67.5	26.2	1768	29.3
Methanol	38.4	4.9	188	3.1
Polyethylene	9.3	5.7	53	0.9
Polypropylene	10.5	4.4	45	0.7
PVC	11.6	5.4	62	1.0
Nitrogen	1.8	28.6	49	0.8
Oxygen	1.8	22.7	44	0.7
Ammonia	39.8	16.2	645	10.5
Urea	2.8	7.6	21	0.3
Chlorine	19.2	11.1	213	3.5
Total			**3112**	**51.5**

Table 34 is an example of the various units used to denote energy consumption. Some of the energy is used as fuel, while some is used as electricity. The energy content is represented as LHV or HHV. The energy intensity is sometimes normalized to the fuel used for energy, while at other times, it is normalized to the sum of fuel + feedstock. Sometimes, the energy intensity is normalized to primary energy, where the amount of fuel corresponding to electricity is calculated using 33% efficiency. Table 34 gives an example of these representations for ethylene, ammonia, and chlorine production.

Table 34. Various Energy Units Used to Represent Energy Use in the Chemical Industry

Chemical	Fuel Used (PJ) LHV	Energy Intensity (GJ/tonne)	Feedstock Used (PJ)	Energy Intensity, Including Feedstock, HHV (GJ/ton)	Electricity (kWh/ton)
Ethylene	520	26			
Ammonia	268		368	39.3	
Cl_2 production	38	47.8			4380

The Worrell report gave a detailed energy breakdown for various processes used to produce ethylene, ammonia, and chlorine; however, no emissions data were given. Using the energy consumption data from Tables 23-26, we can calculate CO_2 emissions and CH_4 emissions with the appropriate emission factors.

During chlorine production, hydrogen is released at the cathode. This hydrogen could be captured and used in a fuel cell to provide some of the electricity needed for the electrolysis cell. According to Table 17 of [9], the total electricity used for chlorine production was 173 PJ, out of which 150 PJ was consumed by electrolysis. The fuel use was 38 PJ, for a total energy consumption of 211 PJ. The energy content of hydrogen generated was 3.4 PJ. Assuming a fuel cell is 50% efficient, this can provide 1.7 PJ of electricity, or ~ 1% of total electricity needs for chlorine production.

According to the *U.S. Manufacturing Energy Consumption Survey* (USMECS), in 1994, the chlor-alkali industry consumed 136 PJ of total energy and used 62 PJ of electricity. These numbers are different from those used by Worrell [9]. This difference was due to the fact that the MECS excludes some chlorine production, which underestimates energy use. Table 35 provides our calculation for electricity needed to produce 11.1Mtons Cl_2, along with the hydrogen evolved and its energy content.

Table 35. Computation of Electricity Use for Electrolysis and Energy Content of Evolved Hydrogen

Cl_2 prod	11.1	(Mtons/yr)
MW	70.7	(g/mole)
Grams	1.11E+13	(g/year)
Moles	1.57E+11	(year)
Equivalents	3.14E+11	(equivalents)
Coulombs	3.03E+16	(coulombs)
Cell operation Volts	4.1	(V)
Joules	1.24E+17	(J)
	1.24E+02	(PJ)
LHV H_2	1.07E+13	(kcal)
	4.49E+13	(kJ)
	44.91	(PJ)*

*1.57E11 moles H_2*68.3 kCal/mole H_2*4.1868 kJ/kCal*1PJ/1E12 kJ = 44.9 PJ

Table 36 summarizes the results obtained by Worrell, USMECS, and Battelle using a chlorine production rate of 11.1 Mtons/year. Table 35 presents PNNL calculations, and Table 36 compares these results with those of Worrell et al. and *U.S. Manufacturing Energy Consumption Survey* (USMECS). PNNL calculated the electricity needed for electrolysis, which is more in line with Worrell's results [9]. They also calculated the energy content of evolved hydrogen, which was 44.9 PJ (LHV). Worrell's report indicated that only 3.4 PJ of the 44.9 PJ evolved hydrogen was captured. This indicates that there is a significant opportunity for energy capture with the chlorine production industry. At 50% efficiency, fuel cells can generate 20.8 PJ electricity from the additional hydrogen captured, and with good heat exchange, some of the evolved heat can be used for cogeneration. The total electricity generated from hydrogen capture (50% of 44.9 PJ) corresponds to about 20% of total electricity use during electrolysis. By using the waste heat from the fuel cell, the overall system efficiency can be further increased. Clearly, the evolved hydrogen from chlor-alkali cells provides a major opportunity to capture and utilize this currently wasted energy source.

Since most chlor-alkali plants have an on-site cogeneration power plant, it is an ideal situation to use hydrogen as feed for a fuel cell. In order to fully utilize the heat from the power plant that generates the remaining power needed, it appears that SOFC or MCFC technology may be preferable. On the other hand, the temperature for the electrolysis cell more closely matches that of a PEM fuel cell. The pure hydrogen generated at the cathode can be used in any type of fuel cell.

Table 36. Summary of Worrell, USMECS, and Battelle Analysis for Electricity Required for Chlorine Production and Energy Content of Evolved Hydrogen

	Electricity PJ for Electrolysis	Energy Content (LHV) of Evolved Hydrogen (PJ)	Energy Content of Captured Hydrogen (PJ)	Opportunity for Energy Recovery from Evolved Hydrogen (PJ)
Worrell report	150		3.4	
USMECS	62			
Battelle calculation	124	44.9		**41.5**

Beaver et al. [10] performed a 5-level analysis (levels 0-4) of energy use at different degrees of energy recuperation, with the final level corresponding to the most optimized process. The energy requirement was calculated using:

- net power and hot utility needs
- net fuel consumed by process
- total energy consumed by process
- total energy consumed by the product chain (including the energy used to produce raw materials)

Level 0 was a baseline case. Level 1 was the benchmarked heat integration scenario. Level 2 was based on optimum heat integration of the process using pinch analysis. Stream matches were made between hot and cold streams above and below the pinch temperature. The study also analyzed opportunities to make temperature changes within the process (especially distillation, which is energy intensive) to improve heat integration. One opportunity was to use direct vapor recompression heat pumps, which compress vapors from a distillation column overhead and then condense the vapors in the column reboiler.

The Level 3 process redesign improved energy efficiency by focusing on:

- material selection – alternate catalysts, solvents, oxidizing agents
- unit operations – staged vs. single reactor, solvent extraction vs. distillation
- process integration – recycle of byproducts to reactor
- fluid handling – reducing process pressures to decrease energy needs

The Level 4 redesign calculated theoretical energy needs for a reaction in terms of standard enthalpies and represents the lower boundary of energy requirements.

Table 37 gives the results of this 5-level analysis for acetic acid production. In the carbonylation section, CO, methanol, and catalyst are fed. Unreacted gases are scrubbed. This appears to be a good location for energy capture from emissions. The energy for feedstock production has not been included, since it is not part of our analysis. There is a net savings of 9% of total energy using Level 3 process design and Level 2 heat integration improvements. Comparing Level 0 results with Level 4 indicates that fuel consumption for energy generation is quite high for this exothermic process. Therefore, there is a high potential for energy capture both in terms of heat and as chemical energy content of the emissions. The amount of raw materials fed is 35% in excess of the theoretical need. Recovery of byproducts such as propionic acid and emissions is very important. As a comparison, Table 38 provides the results of this 5-level analysis for maleic anhydride production.

Table 37. Energy Performance Levels (Btu/lb) for the Production of Acetic Acid

	Base Process	Heat Integration Improvements		Process Redesign	Theoretical Energy
	Level 0	**Level 1**	**Level 2**	**Level 3**	**Level 4**
Electricity	103	103	103	148	
Hot utility	1555	1555	1555	1391	
Hot utility credit	-363	-363	-363	-401	
Net Power & Hot Utility	1295	1295	1295	1138	
Fuel for electricity	333	333	333	476	
Fuel for steam/heat transfer fluid	2692	2692	2650	2275	
Total fuel energy	3025	3025	2982	2751	
Fuel energy credit	-572	-572	-572	-632	
Net fuel energy consumed	2452	2452	2411	2120	-867
Raw material energy	1173	1173	1173	1173	867
Total energy for process	3625	3625	3584	3293	0

Table 38. Energy Performance Levels (Btu/lb) for the Production of Maleic Anhydride

	Base Process	Heat Integration Improvements		Process Redesign	Theoretical Energy
	Level 0	**Level 1**	**Level 2**	**Level 3**	**Level 4**
Electricity	1421	1421	1421	1271	
Hot utility	2857	1312	901	1487	
Auxiliary fuel for incineration	3227	3227	3227	252	
Hot utility credit	-6698	-6698	-6698	-10263	
Net Power & Hot Utility	807	-738	-1149	-7253	
Fuel for electricity	4581	4581	4581	4097	
Fuel for steam/heat transfer fluid	5036	2249	1574	2711	
Auxiliary fuel for incineration	3227	3227	3227	252	
Total fuel energy	12844	10057	9382	7060	
Fuel energy credit	-12077	-12077	-12077	-19487	
Net fuel energy consumed	767	-2020	-2695	-12423	-5522
Raw material energy	15025	15025	15025	19812	5522
Total energy for process	15792	13005	12330	7389	0

Table 38 provides an example of using emissions from a chemical process for energy recovery. There is a 53% reduction in total energy used once the Levels 1-3 redesign is implemented. Use of a fluidized bed reactor in the Level 3 design lowers the yield to 46% (from 59% for baseline). The waste gas stream, which has a high butane concentration, is not incinerated, but is used as fuel to generate steam.

Glass Industry

The annual glass production is 20 MTons/year in the United States.[21] The emissions estimate for glass and glass fiber manufacture was determined using the approach described in the emission estimation technique manual prepared by the Queensland Department of Environment (Australia) [11]. Tables 39 and 40 give the gas emission factor (kg/ton) for glass manufacture. Table 39 provides glass production levels from various processes. Table 40 provides the emission factor and emission levels for glass fiber production, with the production level being 2.72 MTons/year. Production level for wool and textile are assumed to be 50:50.

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[21] http://www.eia.doe.gov/emeu/mecs/iab/glass/page6.html.

Table 39. Gas Emission (kg/ton) for Glass Production

Process	SO_2 (kg/ton)	Oxides (kg/ton) of Nitrogen	VOCs (kg/ton)	CO (kg/ton)	
Melting furnace container (uncontrolled)	1.7	3.1	0.1	0.1	
- with low energy scrubber	0.9	3.1	0.1	0.1	
- with venturi scrubber	0.1	3.1	0.1	0.1	
- with baghouse	1.7	3.1	0.1	0.1	
- with electrostatic precipitator	1.7	3.1	0.1	0.1	
Average	1.22	3.1	0.1	0.1	
Glass (Tons/year)	9.00E+06				
(kg/year)	1.10E+07	2.79E+07	9.00E+05	9.00E+05	
Emissions (Gg/year)	10.98	27.9	0.9	0.9	
Heat of combustion (PJ/Gg)	0.0014	0.00105	0.0505	0.01011	
Energy content (PJ)	0.015372	0.029295	0.04545	0.009099	
Melting furnace flat (uncontrolled)	1.5	4	0.1	0.1	
- with low energy scrubber	0.8	4	0.1	0.1	
- with venturi scrubber	0.1	4	0.1	0.1	
- with baghouse	1.5	4	0.1	0.1	
- with electrostatic precipitator	1.5	4	0.1	0.1	
Average	1.08	4	0.1	0.1	
Glass (Tons/year)	5.00E+06				
(kg/year)	5.40E+06	2.00E+07	5.00E+05	5.00E+05	
Emissions (Gg/year)	5.4	20	0.5	0.5	
Heat of combustion (J/Gg)					
Energy content (J)	0.00756	0.021	0.02525	0.005055	
Pressed and blown (uncontrolled)	2.8	4.3	0.2	0.1	
- with low energy scrubber	1.3	4.3	0.2	0.1	
- with venturi scrubber	0.1	4.3	0.2	0.1	
- with baghouse	2.8	4.3	0.2	0.1	
- with electrostatic precipitator	2.8	4.3	0.2	0.1	
Average	1.96	4.3	0.2	0.1	
Glass (Tons/year)	6.00E+06				
(kg/year)	1.18E+07	2.58E+07	1.20E+06	6.00E+05	
Emissions (Gg/year)	11.76	25.8	1.2	0.6	
Energy/Content (PJ)	0.016464	0.02709	0.0606	0.006066	
Total Emissions (Gg/year)	**28.14**	**73.7**	**2.6**	**2**	
Energy content (PJ)	**0.039396**	**0.077385**	**0.1313**	**0.02022**	
Total (PJ)					**0.268301**

Table 40. Emission Factor and Emission Levels for Glass Fiber Production

Source	SO_2 (kg/ton)	NO_x (kg/ton)	CO (kg/ton)	VOCs (kg/ton)	Phenolocs (kg/ton)	Phenol (kg/ton)	Formaldehyde (kg/ton)	(F kg/ton)
Glass furnace - wool								
Electric	0.02	0.14	0.025					0.001
Gas - regenerative	5	2.5	0.13					0.06
Gas - recuperative	5	0.85	0.13					0.06
Gas - unit melter	0.3	0.15	0.13					0.06
Average	2.58	0.91	0.1038					0.0453
(kg/year)	3508800	1E+06	141100					61540
(Gg/year)	**3.5088**	**1.2376**	**0.1411**	**0**	**0**	**0**	**0**	**0.0615**
(PJ/Gg)	0.0014	0.0019	0.0101	0.0505	0.033	0.0325	0.0188	
Energy Content (PJ)	0.00491	0.0024	0.0014					
Oven curing – wool		1	1.8	3.5				
(kg/year)		1E+06	2E+06	5E+06				
(Gg/year)		1.36	2.448	4.76				
Oven curing and cooling - textile		1.3	0.75					
(kg/year)		2E+06	1E+06					
(Gg/year)		1.768	1.02					
Energy Content (PJ)	0	0.0035	0.0103					
Rotary spin wool glass fiber manufacturing								
R-19					3.21	0.96	0.75	
R-11					6.21	0.92	1.23	
Ductboard					10.66	3.84	1.8	
Heavy density					0.88	0.53	0.43	
Average					5.24	1.5625	1.0525	
(kg/year)					7E+06	2E+06	1E+06	
(Gg/year)					7.126	2.125	1.4314	
Energy Content (PJ)	0	0	0	0	0.232	0.0691	0.0269	
Glass furnace - textile								
Gas-recuperative	1.5	10	0.25					1
Gas-regenerative	15	10	0.5					1
Gas - unit melter		10	0.45					1
Average	8.25	10	0.4					1
(kg/year)	1.1E+07	1E+07	544000					1E+06
(Gg/year)	11.22	13.6	0.544					1.36
Energy Content (PJ)	0.01571	0.0272	0.0055					
Total Emissions (Gg/year)	**14.7288**	**17.966**	**4.1531**	**4.76**	**7.126**	**2.125**	**1.4314**	**1.4215**
Total energy	**0.02062**	**0.0331**	**0.0172**	**0**	**0.232**	**0.0691**	**0.0269**	**0**
Total (Gg/year) from glass industry	**42.869**	**91.666**	**6.1531**	**7.36**	**7.126**	**2.125**	**1.4314**	**1.422**
Energy content (PJ)	**0.06**	**0.1105**	**0.0375**	**0.131**	**0.5**	**0.0691**	**0.0269**	**0**
Total Energy from glass industry (PJ)								**0.935**

Landfills

Landfills are not classified as industrial emissions for the purposes of this study. However, we have included a characterization of these emissions because landfills provide a significant opportunity for industries to recover emissions with chemical fuel value.

About 380 billion pounds (172.5 Mt/year) of waste are dumped into landfills every year in the United States [12]. This roughly agrees with EPA's estimated values of landfill wastes after accounting for recycling and incineration. Landfill gas is mainly composed of 50% CO_2 and CH_4, with a calorific value of 1800 kJ/NM^3. A quick verification of the calorific value indicated that for an exact 50:50 composition of CO_2:CH_4, the calorific value is 19887 kJ/NM^3. Since landfill gas also has trace amounts of SO_x, NO_x, and other gases, a calorific value of 1800 kJ/NM^3 seems reasonable.

In one study, Desideri [12] estimated the amount of biogas that evolves from landfills by using a factor of 0.35 NM^3 biogas/kg of urban solid waste. For 172 Mtons of waste per year, this corresponds to 60 billion NM^3 of biogas. We have found an alternative approach to estimating this value. According to the Energy Information Administration [2], the total landfill methane emissions for 2002 was 12.8 Mtons. We believe that this sum is probably the total taken from actual emissions data from various landfills. Of these emissions, 3 Mtons were recovered for energy, while 2.9 Mtons were flared. The net amount of landfill methane emissions that was not recovered or flared was 6.9 Mtons (12.8 – 3 – 2.9). This corresponds to a volume of 18 billion NM^3 of methane, using a density of 0.71 kg/NM^3. Assuming a 50:50 mix of CO_2 and CH_4, this corresponds to 36 billion NM^3 of biogas, which is actually 60% of the value estimated in the Desideri study. For purposes of this analysis, we will use the numbers provided by the EIA report [2].

To calculate the energy content of biogas, we used the EIA estimates and the calorific value of 18000 kJ/NM^3. From these values, we calculated the energy content to be 647 PJ or 179859 GWh. 24% of this energy, or 42300 GWh, is already being recovered. Currently, there are 1,858 landfills in the United States. Each site has an average gas generation rate of 19.4 million m^3/year and a calorific value of 348 TJ/year. This corresponds to a power of 11.1 MW from each landfill site. Assuming a net efficiency of 45% for a fuel cell, this corresponds to a generated power of 5 MW, with a 6 MW available as heat.

If the landfill is based on a bioreactor, the gases are released quickly and the energy content is available for use the same year. Clearly, the large fuel cell systems are needed to generate this power. The unused fuel can be used to heat the incoming fuel and air to the fuel cell, and also provide the energy for the endothermic steam reformer. Banks of MCFC or SOFC fuel cell systems appear to be ideal candidates to use the available fuel energy.

Desideri [13] did a feasibility study of using landfill gas in fuel cells. High-temperature fuel cells are especially compatible with methane as a source of fuel. By operating at the landfills, these fuel cells use the generated methane to reduce emissions and generate power. According to the EPA's Landfill Methane Outreach Program, landfill or biogas has been tapped at 140 landfills in the United States to provide methane gas directly to fuel cells through fuel processors referenced in http://www.siliconchip.com.au/cms/A_30527/article.html). After a successful demonstration test in 1992 at the Penrose Landfill in Sun Valley, California, fuel cells are operating at landfills in several states in America and in Japan. Groton Landfill in Connecticut, which has been operating since 1996, has been using fuel cells to produce 600,000 kWh of electricity a year, with a continuous net fuel cell output of 140 kW.

To validate our analysis, we compared our data with information from the Prometheus Energy Company (www.prometheus-energy.com). According to Prometheus, a U.S. landfill emits 19.4 NM^3 gas per year on average. This is of the same order of magnitude as the 7.57 NM^3/year number used in the above analysis, thus lending further credibility to the validity of our approach and results.

Another source of landfill gas emissions data is the EPA U.S. GHG report [1]. This report calculated the CH_4 emissions using the methodology that EPA describes in Annex Q of its report. For this report, the EPA modeled the amount of both municipal solid waste (MSW) and industrial waste disposed in U.S. landfills. They measured the methane emission rate for MSW landfills, assuming that methane emissions from industrial landfills were 7% of MSW landfill generation. The amount of methane recovered for energy and flaring and the amount oxidized in the soil was subtracted to yield the net emissions. The methane emissions in 2001 of 14.9 Mtons is close to the value of 12.85 Mtons for year 2001 in reference [2]. Appendix C has more comprehensive emissions data on landfill gas in the United States (see Table 41).

Table 41. Methane Emissions from Landfills (Gg)

Activity	1990	1993	1997	2001
MSW Generation	**11,598**	**12,510**	**13,802**	**14,954**
Large Landfills	4,534	4,927	5,663	6,439
Medium Landfills	5,791	6,223	6,699	7,016
Small Landfills	1,273	1,360	1,440	1,499
Industrial Generation	**812**	**876**	**966**	**1,047**
Potential Emissions	**12,410**	**13,386**	**14,768**	**16,001**
Emissions avoided	**1,190**	**1,915**	**3,790**	**5,263**
Landfill Gas-to-energy	732	892	1,452	2,396
Flare	458	1,023	2,338	2,867
Oxidation at MSW Landfills	**1,041**	**1,059**	**1,001**	**969**
Oxidation at Industrial Landfills	**81**	**88**	**97**	**105**
Net emissions	**10099**	**10323**	**9880**	**9663**

Source: [1].

Table 42 shows that the amount of methane recovered from landfills increased from 19% in 1990 to 40% in 2004. However, while the gas-to-energy conversion increased during this period, the amount of methane flared also increased significantly. This flared CH_4 presents an additional opportunity to capture 160 PJ. The flared CH_4 was included in our analysis as potential for energy capture from landfill emissions and, added to 538 PJ, yielded 698 PJ. The energy calculated in Tables 41 and 42 agree with the numbers in the general survey of industrial emissions. These numbers reveal that landfills can provide a significant source of energy.

Table 42. Energy Content of Methane Emissions from Landfills (PJ)

Activity	1990	1993	1997	2001
MSW Generation	**646**	**697**	**769**	**833**
Large Landfills	252	274	315	359
Medium Landfills	322	347	373	391
Small Landfills	71	76	80	83
Industrial Generation	45	49	54	58
Potential Emissions	**691**	**745**	**822**	**891**
Emissions avoided	**66**	**107**	**211**	**293**
Landfill Gas-to-energy	41	50	81	133
Flare	26	57	130	160
Oxidation at MSW Landfills	58	59	56	54
Oxidation at Industrial Landfills	5	5	5	6
Net emissions	562	575	550	538
% recovery	**19**	**23**	**33**	**40**

Cement Industry

The cement industry predominantly emits CO_2, but CH_4 and N_2O may also be released through combustion. The total emission depends on whether Portland cement or Masonry cement is produced. Portland cement is made with the addition of gypsum, which has no additional emissions. Masonry cement requires the addition of lime. In the U.S. inventory, emissions associated with lime manufacture are not included as cement production, but are included in lime manufacturing. Process-related emissions are defined as emissions created during chemical reaction converting limestone to CaO and CO_2. Combustion-related emissions result from combustion of fuel for heat and for generation of electricity. The emissions corresponding to the dry and wet processes are 224.2 and 249 kg C/short ton [14].

The U.S. GHG Inventory does not include combustion-related emissions separately as part of the emissions inventory. The annual cement production in the United States is 90 MMtons, or 90 Gg. The combustion-related CO_2 emission is 35.3 Tg, which corresponds to 3.7% of combustion-related emission in the industrial sector, while process-related CO_2 emission is 41.4 Tg CO_2.

Worrell and Galitsky [15] did a study of energy efficiency in the cement industry. According to their report, the energy costs for cement production is very high. There are significant opportunities to reduce these costs through energy capture of waste-derived fuels. Coal and coke are predominantly used as fuels, followed by natural gas and waste fuels. The role of carbon-intensive fuels, such as coal and coke, increased due to the higher prices of natural gas and crude oil. This increase in carbon intensity was offset by increased efficiency; therefore, the total carbon intensity actually dropped. From 1985-1999, use of waste-derived fuels for energy generation has risen from 0-17%, a very positive trend. Between 1970 and 1999, the primary energy intensity for cement production dropped from 7.3 MBtu/short ton to 5.3 MBtu/short ton, while the carbon dioxide intensity dropped from 0.31 tons C/ton cement to 0.26 tons C/ton cement.

The production of cement results in the emission of CO_2 from both fuel consumption and calcinations of limestone. The U.S. cement industry is made up of either cement plants that produce clinker and grind it to finished cement, or clinker-grinding plants that grind clinker produced in other plants. Clinker production consists of a high-temperature burn in a kiln of limestone with smaller amounts of siliceous, aluminous, and ferrous materials. More than 90% of cement produced in the United States in 1999 was Portland cement, while ~ 5% of cement production was masonry cement. There were 117 cement plants in the United States in 1999, distributed across 39 states and Puerto Rico, and owned by 42 companies. Production rates per plant varied from 0.5-3.1 million metric tons per year, with total production in 1997 ~ 86 Mtons. Clinker production from the wet process decreased from a 60% share in 1970 to a 25% share in 1999.

Raw materials production requires 25-35 kWh/tonne in the form of electricity. Unless electricity is generated in-house, emissions from this process cannot be addressed, since the electricity is generated in a remote utility. However, by using the process integration approach described in this report, thermal energy from other process streams can be captured to produce electricity in-house.

Clinker production (by pyro-processing in large kilns) accounts for > 90% of total industry energy use, and almost all of the fuel use. Most of the emissions occur in this process. These kilns evaporate water in the raw material, calcine the carbonate, and form cement minerals. Fuel consumption in a wet kiln ranges from 5.3-7.1 GJ/tonne clinker, while for a dry kiln, it varies from 3.2-3.5 GJ/tonne clinker.

Once the clinker is formed, it is cooled and transported to a finish mill to produce powdered cement by grinding with additives using roller or ball mills. This process is electricity intensive, using 50-70 kWh/tonne in older mills and 32-37 kWh/tonne in modern mills.

Table 43 provides an overview of energy consumption and emissions from the U.S. cement industry in 1999. The last column shows that the numbers match, when using 90MMT cement production with 26.6% being produced through the wet process.

Because most of the emissions from the cement industry are CO_2, there is not much opportunity to recover energy. However, there is significant opportunity to use CO_2 in tri-reforming of methane, or as feedstock for various chemicals.

Table 43. Energy Consumption and Emission in the U.S. Cement Industry in 1999

	Fuel (TBtu)	Elec (TBtu)	Primary Energy (TBtu)	Fuel SEC (MBtu/st)	Elec. SEC (kWh/st)	Primary SEC (MBtu/st)	CO_2 Emissions Energy Use (MMtCe)	CO_2 Emissions Calcination (MMtCe)	CO_2 Intensity (kgC/st)	Check, Using 90 MMT Cement 26.6% Wet Process
Wet Process										
Kiln feed preparation	0	4	13	0	27	0.3	0.2	0	4.4	7.58
Clinker Production	124	3	128	6	39	6.4	3.2	2.8	268.5	227.36
Finish Grinding	0	5	16	0	57	0.6	0.2	0	9.2	7.58
Total Wet Process	125	12	157	4.8	132	6.3	3.6	2.7	249	238.73
Dry Process										26.60
Kiln feed preparation	0	15	44.77612	0	38	0.4	0.7	0	6.1	9.61
Clinker Production	254	9	280.8657	4	45	4.5	6.7	7.9	231.7	200.50
Finish Grinding	0	12	35.8209	0	52	0.6	0.6	0	8.3	8.24
Total Dry Process	254	36	361.4627	3.6	150	5.2	8	7.9	224.2	218.35
Total all cement	379	48	518.4627	8.4	282	11.5	11.6	10.6	230.8	223.77
										73.40

Source: Table 1 of [15].

Table 44 provides a description of potential energy savings in cement production, and Tables 45 and 46 provide details for the dry process and wet process chemical plants, respectively. Following are the main opportunities for recovery energy.

- Regularly maintain motors, pumps, and compressors
- Ensure most efficient technology is in place for the process
- Fine-tune the efficiency of various processes in the plant
- Establish relationships with other industries to exchange energy/feedstock from plant emissions

Table 44. Partial Description of Potential Energy Savings in Cement Production

Process	Modification	Energy Savings
Transport of kiln feed and finished cement	Use of mechanical conveyors instead of pneumatic systems.	2 kWh/ton (note 1)
Blending of kiln feed	Use of gravity silos instead of compressed air or mechanical systems.	0.9-2.3 kWh (note 1)
Wet process	Replacement of tube mill with wash mill.	5-7 kWh/ton
Dry process	Use of roller mills instead of ball mills.	6-7 kWh/ton
Dry process	Avoiding vibration trips for vertical mills.	0.8-1.0 kWh/ton
Classifiers or separators for both raw material feed and finished product	Use high-efficiency classifiers or separators.	2.5-3.4 kWh/ton
Clinker production – all kilns, process control (note 2)	Better process control results in heat recovery, material throughput, lower emissions.	2.5-5% energy savings
Kiln combustion (note 3)	Improved combustion systems.	2-10% fuel savings and increase in output of ~ 5-10%
Firing system	Use of indirect firing.	Fuel savings of 130-190 kBtu/ton of clinker
Oxygen enrichment in kiln		Unlikely to result in energy savings
Seals	Upgrading of seals (Maihar cement, India).	Fuel savings of 10 kBtu/ton clinker
Kiln shell heat loss reduction	Use of better insulating refractories.	Reduce fuel usage by 100-340 kBtu/ton. Also improves reliability and reduces start-up energy needs
Kiln drives	Highest efficiencies for synchronous motors using single pinion drive with air clutch and synchronous motor.	Electricity savings of 0.5 kWh/ton clinker. Replacement of dc drive with ac results in ~ 1% reduction in electricity use.
Fuels	Use of waste derived fuels. – tires, carpet and plastic wastes, paint residue, dewatered sewage sludge, filter cake. (Note 4)	Energy savings of 500 kBtu/ton clinker
Cooling of clinker	Conversion to reciprocating grate cooler – large capacity, efficient heat recovery.	8% fuel savings, but extra electricity of 2.7 kWh/ton clinker
Clinker production, wet process	Conversion of wet process to semi-dry process by using slurry drier.	Reduce fuel consumption by 1.4 MBtu/ton clinker
Clinker production, wet process	Conversion of wet process to semi-wet process (filter press system).	Fuel savings 1MBtu/ton. Added electricity consumption of 3-5 kWh/ton.
Clinker production, wet process	Conversion of wet process to pre-heater/pre-calciner kiln.	Fuel savings of 2.7-2.9 MBtu/ton. High cost of conversion.

Note 1: This does not decrease emissions in the plant, unless electricity is generated in-house.
Note 2: Several case studies listed – ABB LINKman system by Blue Circle Industries UK, Process Perfector of Pavillion Technologies Inc, fuzzy logic control systems by Krupp Polysius (Germany), Mitsui Mining (Japan), Ash Grove (Oregon, U.S.).
Note 3: Several case studies listed – Blue Circle Industries, Gyro-Therm Technology developed by University of Adelaide.
Note 4: Cement kiln efficient way to recover energy from waste. High temperature and long residence time destroy organics. Since 1990, > 30 plants gained approval to use tires.

Table 45. Energy Efficiency Measures in Dry Process Cement Plants

Energy-Efficiency Measure	Specific Fuel Savings (MBtu/ton cement)	Specific Electricity Savings (kWh/ton cement)	Estimated Payback Period (years)
Raw Materials Preparation			
Efficient transport system		3.2	> 10
Raw meal blending		1.5-3.9	
Process control vertical mill		0.8-1.0	1
High-efficiency roller mill		10.2-11.9	> 10
High-efficiency classifiers		4.3-5.8	> 10
Fuel preparation: roller mills		0.7-1.1	
Clinker Making			
Energy management & control systems	0.10-0.20	1.2-2.6	1-3
Seal replacement	0.02		< 1
Combustion system improvement	0.10-0.39		2-3
Indirect firing	0.13-0.19		
Shell heat loss reduction	0.09-0.31		1
Optimize grate cooler	0.06-0.12	-1.8 to 0	1-2
Convert to grate cooler	0.23	-2.4	1-2
Heat recovery for power generation		18	3
Low pressure drop suspension pre-heaters		0.5-3.5	> 10
Addition of precalciner or upgrade	0.12-0.54		5
Conversion of long dry kiln to preheater	0.36-0.73		> 10
Conversion of long dry kiln to precalciner	0.55-1.1		> 10
Efficient mill drives		0.8-3.2	1
Use of secondary fuels	> 0.5		1
Finish Grinding			
Energy management & process control		1.6	< 1
Improved grinding media in ball mills		1.8	8
High-pressure roller press		7-25	> 10
High-efficiency classifiers		1.7-6.0	> 10
Plant-Wide Measures			
Preventive maintenance	0.04	0-5	< 1
High-efficiency motors		0-5	< 1
Adjustable speed drives		5.5-7.0	2-3
Optimization of compressed air systems		0-2	<3
Efficient Lighting **0-0.5** **Product Change**			
Blended cement	1.21	-15	<1
Limestone Portland cement	0.30	3.0	<1
Use of steel slag in clinker	0.16		<2
Low-alkali cement	0.16-0.4		Immediate
Reduced fineness of cement for selected use		0-14	Immediate

Source: Table 3 of [15].

Table 46. Energy Efficiency Measures in Wet Process Cement Plants

Energy-Efficiency Measure	Specific Fuel Savings (MBtu/ton)	Specific Electricity Savings (kWh/ton cement)	Estimated Payback Period (years)
Raw Materials Preparation			
Slurry blending and homogenizing		0.1-0.6	<3
Wash mills with closed circuit classifier		10-14	> 10
High-efficiency classifiers		4.3-5.8	> 10
Fuel preparation: roller mills		0.7-1.6	
Clinker Making			
Energy management & control systems	0.14-0.27	1.0-2.0	<2
Seal replacement	0.02		< 1
Combustion system improvement	0.15-0.55		2-3
Indirect firing	0.13-0.19		
Shell heat loss reduction	0.09-0.30		1
Optimize grate cooler	0.06-0.13		1-2
Convert to grate cooler	0.24	-2.4	1-2
Conversion to semi-wet process kiln	0.9	-4	> 10
Conversion to semi-dry process kiln	0.8-1.2	-4 to -6	> 10
Efficient mill drives		0.7-2.7	1
Use of secondary fuels	> 0.5		1
Finish Grinding			
Energy management & process control		1.6	<1
Improved grinding media in ball mills		1.8	8
High-pressure roller press		7-25	> 10
High-efficiency classifiers		1.7-5.4	> 10
Plant-Wide Measures			
Preventive maintenance	0.04	0-5	< 1
High-efficiency motors		0-5	<1
Adjustable speed drives		5-7	2-3
Optimization of compressed air systems		0-5	<3
Efficient Lighting **0-0.5** **Product Change**			
Blended cement	1.21	-15	<1
Limestone Portland Cement	0.30	3.0	<1
Use of steel slag in clinker	0.16		<2
Low-alkali cement	0.16-0.4		Immediate
Reduced fineness of cement for selected use		0-14	Immediate

Source: Table 4 of [15].

While the U.S. GHG Inventory does not include combustion-related emissions, it does include process-related emissions. Process-related emissions (such as CO_2 generated during conversion of limestone calcium oxide) are calculated using the IPCC method ology outlined in the report [16]. Table 47 shows process-related CO_2 and combustion-related CO_2 for years 1994 and 2001 [16]. Using the combustion-related CO_2 emissions, the type of fuel used (mainly coal and coke), and the CH_4 emission factors for each fuel, we can also determine the amount of CH_4 evolved. A similar analysis can be carried out for N_2O emission.

Table 47. Combustion and Process-Related CO_2 Emissions from U.S. Cement Manufacturing

CO_2 Emissions MMTCO$_2$	**1994**	**2001**
Combustion-related CO_2	30.6	35.5
Process related CO_2	36.1	41.4
Total CO_2	66.7	76.9

At present, process-related emissions are estimated on the national level, while combustion-related emissions are accounted for in the national estimate of CO_2 emissions from fossil fuel combustion. The Hanle [14] analysis is particularly useful for this study since CO_2 emissions were calculated separately for the cement industry using appropriate CO_2 emissions factor for wet and dry processing facilities. The estimates in Hanle's study will be further refined in future studies by using available sources with facility-specific fuel data. The author points out that substitution of lower carbon-containing fuels for coal, coke, and petroleum coke will be useful for lowering CO_2 emissions. The author also cautions that using waste fuel (while lowering CO_2 emissions) could have an adverse environmental impact. Future reports from the EPA on this topic need to be closely watched.

Using a CO_2 emissions factor of 50 MMtons/Quad, the fuel energy corresponding to fossil fuel combustion of CO_2 with an emission of 35.5 MMtons CO_2 is 749 PJ. Using an emission factor for CH_4 of 5.7 g/GJ, this corresponds to methane emissions of 4.4 Gg, which has an energy content of 0.24 PJ based on the analysis described in Tables 23-26. Clearly, the methane energy content from fossil fuel combustion is negligible. However, the analysis in Tables 23-26 was necessary in order to ensure that potentially significant emissions during fossil fuel combustion are not missed.

Iron and Steel Industry

Table 48 lists the amount of energy used in the U.S. steel industry in 1994 (eia.doe.gov/emeu/mecs/iab/steel/index.html). About 2 Quads are used, which include losses due to transmission. This corresponds to 2.5% of energy use in the United States, and 8% of energy use in the U.S. manufacturing sector. Forty percent of total energy used is to chemically reduce iron ore to liquid ppig iron in the blast furnace. Twenty-five percent of the energy is used in process heating. Twenty-five percent of total emissions within the iron and steel industry are combustion related.

Table 48. Energy Used in 1994 in Steel Industry

Fuel	Energy Use TBtu	%
Coal	893	45
Natural gas	484	24
Electrical losses	344	17
Other	82	4
Fuel oil	42	2
Net electricity	148	7
Total	1993	100

Source: eia.doe.gov/emeu/mecs/iab/steel/page2a.html.

An analysis by Worrell et al. [17] lists the emissions from various processes within the iron and steel industry. As in their work on the cement industry, they also listed the various ways for increasing the efficiency and reducing emissions. According to this study, the manufacturing sector consumed 23 EJ of primary energy in the United States in 1994, nearly 25% of the total energy consumed. Within the manufacturing sector, primary metals, pulp and paper, cement, chemicals, petroleum refining need more energy than other industries. The iron and steel industry was analyzed at the aggregate level (SIC 331 and 332) which included blast furnaces and steel mills (SIC 3312), electro metallurgical products such as ferroalloys (SIC 3313), and gray and ductile iron foundries (SIC 3321). At a lower level, this study focused on blast furnaces and steel mills (SIC 3312). They also performed a detailed analysis of energy use and CO_2 emissions by process, and investigated specific energy efficiency technologies to reduce energy use and emissions.

Integrated steel mills produce ppig iron from raw materials (iron ore, coke) using a blast furnace and produce steel using a basic oxygen furnace. Secondary steel mills produce steel from scrap steel, ppig iron, or directly reduced iron using an electric arc furnace. The share of steel produced by secondary mills grew from 15% in 1970 to 40% in 1995. In 1997, there were 142 steel plants in the United States. Integrated steel mills using blast furnaces accounted for 20 plants, with steel production rates being 0.5-3.1 million metric tons per year. There were 122 secondary steel mills operating electric arc furnaces.

The energy use was 2.6 EJ in 1958, peaked at 3.9 EJ in 1973, and was 1.9 EJ in 1994. Unlike the cement industry, the share of coal and coke dropped from 75% to 57% between 1958 and 1994, while natural gas jumped from 10% to 28%. Between 1958 and 1990 improvements in process efficiency, increases in the use of natural gas, and the growing use of scrap-based electric arc furnaces led to a decrease in carbon intensity from 0.82 tons C/ton steel to 0.50 tons C/ton steel.

Figure 6 in the Worrell analysis indicated that the gap between actual and best practices data were much wider in the United States than in Germany, even though the United States had a higher production of secondary steel, which has a lower energy intensity. The authors explained that this was due to the high energy use in the blast furnace, in the basic oxygen furnace (due to lack of emissions recovery), in the reheating furnace, and in the hot strip mill. Table 49 shows the energy use and CO_2 emissions for U.S. steel production in 1994.

Table 49. Energy Use and CO_2 Emissions for U.S. Steel Production in 1994

	Fuel (PJ)	Electricity (J)	Final Energy (PJ)	Primary Energy (PJ)	CO_2 Emissions (MtC)	CO_2 Emissions (Tg CO_2)
Sintermaking	26	2	28	31	0.8	2.9
Cokemaking	74	2	76	81	0.6	2.2
Ironmaking	676	4	680	689	11	40.3
Steelmaking basic oxygen furnace	19	6	25	36	0.5	1.8
Casting	15	11	27	50	0.9	3.3
Hot Rolling	157	34	191	263	3.7	13.6
Cold Rolling and Finishing	43	15	58	89	1.3	4.8
Boilers (integrated steelmaking)	167	0	167	167	7.8	28.6
Cogeneration (integrated steelmaking)	101	-22	79	101	0.4	1.5
Total integrated steelmaking	1278	52	1331	1507	27	99
Electric arc furnace	6	62	68	197	2.8	10.3
Casting	1	4	5	12	0.2	0.7
Hot Rolling	102	22	124	170	2.4	8.8
Cold Rolling and Finishing	0	0	0	0	0	0
Boilers (secondary steelmaking)	42	0	42	42	2	7.3
Cogeneration (secondary steelmaking)	11	-2	9	11	0.04	0.15
Total secondary steelmaking 35.9 Mt	162	85	248	425	7.4	27.1
Total primary and secondary steelmaking	1440	137	1579	1932	34.4	126.1

Just as in the Lawrence Berkeley National Laboratory report on the cement industry, various energy-efficiency measures in the U.S. iron and steel industry were studied. Table 50 lists the energy savings options in the U.S. for integrated steel production.

Table 50. Fuel Savings for Energy-Efficient Technologies Applied to Integrated Steel Production in the U.S.

Option	Fuel Savings (GJ/ton)
Sinter plant heat recovery	0.12
Reduction	0
Increasing bed depth	0.02
Improved process control	0.01
Use of waste fuels in sinter plant	0.04
Coke Making	
Coal moisture control	0.09
Programmed heating	0.05
Variable speed drive coke oven gas compressors	0
Coke dry quenching	0.37
Iron Making - Blast Furnace	
Pulverized coal injection to 130 kg/thm	0.69
Pulverized coal injection to 225 kg/thm	0.51
Injection of natural gas to 140 kg/thm	0.8
Recovery of Blast Furnace Gas	**0.06**
Hot blast stove automation	0.33
Recuperator hot blast stove	0.07
Improved blast furnace control systems	0.36
Steelmaking - Basic Oxygen Furnace	
BOF gas + sensible heat recovery	0.92
Variable speed drive on ventilation fans	0
Integrated Casting	
Adopt continuous casting	0.24
Efficient ladle pre-heating	0.02
Thin slab casting	3.13
Hot charging	0.52
Process control in hot strip mill	0.26
Recuperative burners	0.61
Insulation of furnaces	0.14
Controlling oxygen levels and VSDs on combustion air fans	0.29
Waste heat recovery (cooling water)	0.03
Integrated Cold Rolling and Finishing	
Heat recovery on the annealing line	0.17
Reduced steam use (pickling line)	0.11
Preventive maintenance	0.43
Energy monitoring and management system	0.11
Cogeneration	0.03
Variable speed drive, flue gas control, pumps, fans	0

Source: Table 4 of Worrell report [17].

Table 51 lists the same options for secondary steel production. To keep within the scope of this report, only fuel savings have been listed, since this will directly reflect the energy savings for the plant.

Table 51. Fuel Savings for Energy-Efficient Technologies Applied to Secondary Steel Production in the U.S.

Option	Fuel Savings GJ/ton)
Steelmaking Electric arc furnace - scrap pre-heating	-0.7
Secondary Casting	
Efficient ladle pre-heating	0.02
Thin slab casting	2.86
Secondary Hot Rolling	
Process control in hot strip mall	0.26
Recuperative burners	0.61
Insulation of furnaces	0.14
Controlling oxygen levels on combustion air fans	0.29
Waste heat recovery from cooling water	0.03
General Technologies	
Preventive maintenance	0.09
Energy monitoring and management system	0.02

Source: Table 5 of Worrell report [17].

Gielen and Moriguchi [18] analyzed emission reduction potential in the Japanese iron and steel industry. As expected, proper choice of fuel is expected to decrease emissions significantly. As published in their study and elsewhere [19], coke oven gas, a byproduct of the coking process, consists of CO. No numbers for CO emission were provided. CO is also produced in a Basic Oxygen furnace. Overall, there appears to be significant opportunity to capture energy from CO emissions in the iron and steel industry.[22]

Natural Gas Systems

Natural gas systems in the United States emitted 5.8 Tg in 1990 and emitted 5.6 Tg of methane in 2001 (Table 52). Methane emission result in four stages – field production, processing, transmission & storage, and distribution. For each stage, fugitive emissions are the main reason for methane loss; therefore, capturing this energy can be difficult.

Table 52. CH_4 Emissions from Natural Gas Systems (Gg) [1]

Stage	Gg		PJ	
	1990	2001	1990	2001
Field Production	1445	1467	80.5	81.7
Processing	702	692	39.1	38.5
Transmissions & Storage	2223	1870	123.8	104.1
Distribution	1440	1559	80.2	86.8
Total	5810	5588	**323.5**	**311.1**

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[22] The potential energy content of this CO has not been included in the Executive Summary Table due to lack of data.

Petroleum Refining

Oil refining produces fuels for transportation, power generation, and heating. It also produces raw materials for the chemical industry. Oil refineries use various unit operations (such as distillation and extraction) and many chemical/catalytic processes. They also have processes for treating refinery off-gases [20], which is of primary interest in this report.

Some of the catalytic chemical processes used in the oil refinery are fluid catalytic cracking (FCC), hydrotreating, hydrocracking, catalytic reforming, and alkylation. In catalytic cracking, the feedstock is heavy oil fractions such as vacuum oil grease. Cracking is catalyzed by solid acids, which promote C-C bond rupture. Gasoline yields with current catalysts are 40-50 wt%. Because coke formation leads to catalyst poisoning, catalyst regeneration is done by combustion in air to generate CO/CO_2. Capturing this CO would be a good candidate for CO recovering energy. Also, coupling the exothermic regeneration reaction with the endothermic cracking process will increase overall process efficiency.

The FCC unit is very polluting, emitting both SO_x and NO_x. The feedstock is typically hydrotreated to yield H_2S. The evolved H_2S can be partially oxidized to form elemental S, giving off 444 kJ/mol, a significant energy content. The emission from the FCC unit is a good candidate for capturing energy both in the form of unreacted hydrogen and H_2S.

Exit gases from units such as fluid catalytic crackers and hydrotreaters contain significant amounts of hydrogen, which can be recovered for hydroprocessing if feeds and products or used as fuel. Recovery can be done using low energy processes such as adsorption of other gases or by membrane separation.

The total energy content of CH_4 emissions from petroleum production is 10 times that reported in Table 2-27 of [1] for years 1995-2001. It appears that this table does not include CH_4 emissions from production wells.

The emissions derived from petroleum transportation was 0.283 Bcf/year, which is 0.4% of the value obtained for petroleum production. The total energy content was 0.32 PJ. Since these emissions occur at various locations, this work will exclude these emissions from consideration for energy capture.

Tables 53-54 provide data on CH4 emissions from petroleum production and refining, while Table 55 summarizes these results, with the energy content of these emissions provided in Table 56.

Table 53. CH_4 Emissions from Petroleum Production Field Operations

Activity/Equipment	Emission Factor	Units	Activity Factor	Units	Emission (Bcf/yr)	Energy (PJ)
Vented Emissions					**48.18**	**54.45**
Oil Tanks	18	scf CH_4/bbl crude	1251	MMbbl/yr	22.52	25.45
Pneumatic device high bleed	345	scfd CH_4/device	142,872	# of high-bleed devices	17.99	20.33
Pneumatic device low bleed	35	scfd CH_4/device	265334	# of low-bleed devices	3.39	3.83
Chemical Injection Pumps	248	scfd CH_4/pump	28595	# of pumps	2.59	2.93
Vessel blowdowns	78	scf/yr CH_4/vessel	186546	# of vessels	0.01	0.02
Compressor Blowdowns	3775	scf/yr of CH_4/comp	2532	# of compressors	0.01	0.01
Compressor Starts	8443	scf/yr of CH_4/comp	2532	# of compressors	0.02	0.02
Stripper Wells	2343	scf/yr of CH_4/well	329434	# of stripper wells vented	0.77	0.87
Well Completion Venting	733	scf/completion	4731	Oil well completions	0.00	0.00
Well Workovers	96	scf CH_4/workover	40050	Oil well workovers	0.00	0.00
Pipeline Pigging	2.4	scfd of CH_4/pig station	0	# of crude pig stations	0.00	0.00
Offshore Platforms, Gulf of M	1283	scfd CH_4/platform	1832	# of oil platforms	0.86	0.97
Offshore Platforms, Other areas	1283	scfd CH_4/platform	23	# of oil platforms	0.01	0.01
Fugitive Emissions					**2.59**	**2.92**
Offshore Platforms, Gulf of M	56	scfd CH_4/platform	1832	# of oil platforms	0.04	0.04
Offshore Platforms, Other Areas	56	scfd CH_4/platform	23	# of oil platforms	0.00	0.00
Oil Wellheads (heavy crude)	0.13	scfd/well	14422	# of heavy crude wells	0.00	0.00
Oil Wellheads (light crude)	16.6	scfd/well	190144	# of light crude wells	1.15	1.30
Separators (heavy crude)	0.15	scfd CH_4/separator	10972	# of heavy crude seps	0.00	0.00
Separators (light crude)	14	scfd CH_4/separator	99858	# of light crude seps	0.51	0.58
Heater/Treaters (light crude)	19	scfd CH_4/heater	75716	# of heater treaters	0.53	0.59
Headers (heavy crude)	0.08	scfd CH_4/header	13929	# of heavy crude headers	0.00	0.00
Headers (light crude)	11	scfd CH_4/header	43183	# of light crude headers	0.17	0.20
Floating Roof Tanks (FRT)	338306	scf CH_4/FRT/yr	24	# of floating roof tanks	0.01	0.01
Compressors	100	scfd CH_4/comp	2532	# of compressors	0.09	0.10
Large Compressors	16360	scfd CH_4/comp	0	# of large compressors	0.00	0.00
Sales Areas	41	scf CH_4/loading	1764218	Loadings/year	0.07	0.08
Pipelines	0	scfd CH_4/mile pipeline	30467	Miles of gathering line	0.00	0.00
Well Drilling	0	scfd CH_4/pump	7437	# of oil wells drilled	0.00	0.00
Battery Pumps	0.24	scfd CH_4/pump	160200	# of battery pumps	0.01	0.02
Combustion Emissions					**6.41**	**7.24**
Gas Engines	0.24	scf CH_4/HP-hr	15950	MMHP-hr	3.83	4.33
Heaters note 1	0.52	scf CH_4/bbl crude	2117.4	MBbl/yr	1.10	1.24
Well Drilling	2453	scf CH_4/well drilled	7437	Oil wells drilled, 1995	0.02	0.02
Flares	20	scf CH_4/McF flared	492582	Mcf flared/yr	0.01	0.01
Offshore Platforms, other areas	481	scfd CH_4/platform	1852	# of oil platforms	0.33	0.37
Offshore Platforms, other areas	481	scfd CH_4/platform	23	# of oil platforms	0.00	0.00
Process Upset Emissions					0.56	0.63
Platform Emergency Shutdowns	256888	scfy/platform	1875	# of platforms	0.48	0.54
Pressure relief valves	35	scf/yr/PR valve	176866	# of PR valves	0.01	0.01
Well Blowouts Offshore	5	MMscf/blowout	2.25	# of blowouts/yr	0.01	0.01
Well Blowouts Onshore	2.5	MMscf/blowout	24.8	# of blowouts/yr	0.06	0.07
Total (excl stripper wells)					**57.18**	**64.61**

Source: Table H-1 of [1].

Table 54. 2001 CH_4 Emissions from Petroleum Refining

Activity/equipment	Emission Factor	Units	Activity Factor	Units	Emissions (Bcf/yr)	Energy (PJ)
Vented Emissions					**1.209**	**1.366**
Tanks	20.6	scfCH_4/Mbbl	1941	Mbbl/cd heavy crude feed	0.015	0.016
System Blowdowns	137	scfCH_4/Mbbl	15128	Mbbl/cd refinery feed	0.756	0.855
Asphalt Blowing	2555	scfCH_4/Mbbl	485	Mbbl/cd production	0.452	0.511
Fugitive Emissions					**0.091**	**0.103**
Fuel Gas System	439	McfCH_4/refinery/yr	153	Refineries	0.067	0.076
Floating Roof Tanks	587	scf CH_4/floating roof tank/yr	767	No of floating rood tanks	0.000	0.001
Wastewater Treating	1.88	scf/Mbbl	15128	Mbbl/cd refinery feed	0.010	0.012
Cooling Towers	2.36	scfCH^4/Mbbl	15128	Mbbl/cd refinery feed	0.013	0.015
Combustion Emissions					**0.092**	**0.104**
Atmospheric Distillation	3.61	scfCH_4/Mbbl	15352	Mbbl/cd refinery feed	0.020	0.023
Vacuum Distillation	3.61	scfCH_4/Mbbl	6875	Mbbl/cd feed	0.009	0.010
Themrla Operations	6.02	scfCH_4/Mbbl	2055	Mbbl/cd feed	0.005	0.005
Catalytic Cracking	5.17	scfCH_4/Mbbl	5194	Mbbl/cd feed	0.010	0.011
Catalytic Reforming	7.22	scfCH_4/Mbbl	3239	Mbbl/cd feed	0.009	0.010
Catalytic Hydrotreating	7.22	scfCH_4/Mbbl	1362	Mbbl/cd feed	0.004	0.004
Hydrorefining	2.17	scfCH4/Mbbl	1825	Mbbl/cd feed	0.001	0.002
Hydrotreating	6.5	scfCH_4/Mbbl	8382	Mbbl/cd feed	0.020	0.022
Alkylation/polymerization	12.6	scfCH_4/Mbbl	1065	Mbbl/cd feed	0.005	0.006
Aromatics/isomerition	1.8	scfCH_4/Mbbl	934	Mbbl/cd feed	0.001	0.001
Lube Oil Processing	0	scfCH_4/Mbbl	162	Mbbl/cd feed	0.000	0.000
Engines	0.006	scfCH_4/hp-hr	1467	MMhp-hr/yr	0.009	0.010
Flares	0.19	scfCH_4/Mbbl	15128	Mbbl/cd refinery feed	0.001	0.001
Total					**1.392**	**1.573**

Source: Table H-3 of [1].

Table 55. Summary of CH_4 Emissions from Petroleum Systems (Gg)

Activity	1990	1993	1997	2001
Production field operations	**1277**	**1180**	**1090**	**978**
Tank venting	558	486	409	345
Pneumatic device venting	525	507	495	460
Wellhead fugitives	26	24	25	22
Combustion & process upset	103	99	98	91
Misc. venting & fugitives	65	64	63	60
Crude Oil Transportation	**7**	**6**	**6**	**5**
Refining	**25**	**25**	**27**	**27**
Total	**1309**	**1211**	**1123**	**1010**

Source: Table H-5 of [1].

Table 56. Summary of Energy Content of CH_4 Emissions from Petroleum Systems (PJ)

Activity	1990	1993	1997	2001
Production field operations	**71.11**	**65.71**	**60.70**	**54.46**
Tank venting	31.07	27.06	22.77	19.21
Pneumatic device venting	29.23	28.23	27.56	25.61
Wellhead fugitives	1.45	1.34	1.39	1.23
Combustion & process upset	5.74	5.51	5.46	5.07
Misc. venting & fugitives	3.62	3.56	3.51	3.34
Crude Oil Transportation	0.39	0.33	0.33	0.28
Refining	1.39	1.39	1.50	1.50
Total	**72.89**	**67.43**	**62.53**	**56.24**

Source: Table H-5 of [1].

After unit conversion, there is a slight discrepancy between Table H-5 and Table H-1 in Reference 1. In H-1, the total CH_4 emission from vented emissions was 979 Gg, corresponding to 54.5 PJ. In Table H-5, these numbers correspond to total values for production field operations. Either H-1 or H-5 appears to have a slight error. The chances are that this error is in H-5, which underestimates emissions from production field operations.

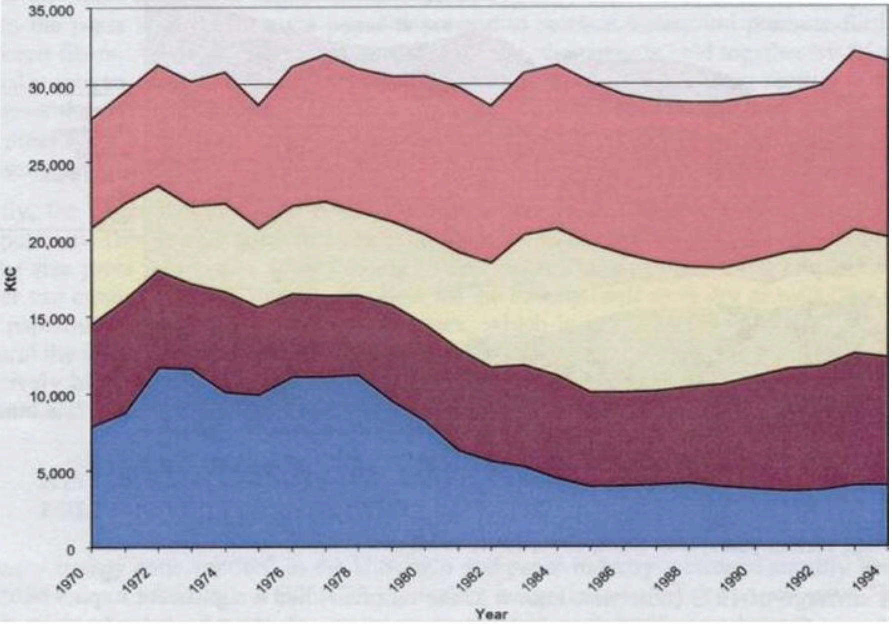
Forest Products Industry

There were 190 operating pulp mills and 598 operating paper and paperboard mills in the United States in 1996. About 58% of all paper/paperboard mills are located in the Northeast and the North central regions, close to final consumers. However, 56% of the paper/paperboard capacity and more than 70% of wood pulp capacity are located in the South Atlantic and South Central regions, close to the sources of fibers. Mills located in those regions are mostly large, integrated pulp and paper mills. More than 45% of all paper and paperboard and about 60% of all wood pulp are produced by mills with capacity over 450 tons per year (tpy). The average capacity of a U.S. paper/paperboard mill in 1995 was about 168 tpy. The average capacity of a wood pulp mill was about 330 tpy.

Paper production in the United States consists primarily of wrapping and packaging paper, paperboard, and printing and writing paper. These products made up about 80% of the U.S. paper production in 1994. The remainder is made up of newsprint, household and sanitary paper, and paper and paperboard not elsewhere specified, a catch-all category for such paper products as Kraft paper, blotting paper, and filter paper. Total U.S. paper production increased from 45.81 million tons (Mt) in 1970 to 82.46 Mt in 1994, an average increase of 2.5% per year. Growth has slowed slightly in recent years, though paper production still increased 2.2% per year between 1970 and 1980, and 2.7% per year between 1980 and 1994.

Primary energy consumption in the U.S. pulp and paper industry increased steadily between 1960 and 1994 from 1496 PJ to 3267 PJ, equivalent to an increase of 2.3% per year. Energy consumption (not accounting for electricity generation and distribution losses) grew at a rate of 2.1% per year. Primary energy consumption growth has slowed in recent years, evidenced by a 1.5% annual energy consumption growth rate between 1970 and 1994, and a 1.3% annual growth rate between 1980 and 1994. The composition of the fuel mix has also changed. Biomass and electricity grew more rapidly, increasing their shares from 35% and 5% in 1970 to 43% and 7.3% in 1994, respectively. Use of coal and coke, along with oil, decreased most rapidly in the paper sector, as coal and coke use fell from 21% to 11%, and oil use fell from 11.4% to 7%, between 1970 and 1994.

The paper industry's carbon dioxide emissions increased between 1960 and 1994 from 27.7 Mt to 31.5 Mt, at a rate of 1.4% per year, less than the increase in primary energy consumption which increased at 2.3% per year over the same period. Since 1970, the rate of growth of carbon dioxide emissions has been more gradual, 0.5%/year. This slower growth is due primarily to two major changes in the industry. First, there has been a significant increase in the use of biomass fuels over the past few decades. This results in lower carbon emissions per unit of energy consumed on an industry-wide basis. Secondly, there has been a significant increase in the use of waste paper and recycled pulp, which grew from 10.8 Mt to 28 Mt in 1994. Recycled pulp production is significantly less energy intensive, thereby reducing energy use as well as reducing CO_2 emissions. Carbon intensity, as measured by emissions per ton of product, has declined rapidly (3% per year) from 0.6 tC/T of paper in 1970 to 0.4 tC/t of paper in 1994.



Lawrence Berkeley National Laboratory 46141 (July 2000): page 16.

Figure 3. Carbon Dioxide Emissions from Fuel Consumption in U.S. Paper Production

The pulp and paper industry consumed 3114 TBtu of primary energy in 1998. In this same year, CO_2 emissions were estimated to be 118.4 million metric tons, or 8% of the total manufacturing emissions, despite the extensive use of biomass (as a byproduct of chemical pulping and wood waste use), which reduces the net CO_2 emissions. This total accounted for 36.32 million metric tons per quadrillion Btu of energy consumed, which was a decrease of 2.9% since 1991 and the lowest of the leading industry groups.

Table 57 provides a breakdown of the energy consumption and carbon emissions by fuel type from the U.S. pulp and paper industry. A carbon emission factor of 48.5 ktC/PJ is used for purchased electricity, reflecting the average carbon intensity in 1994 of U.S. public electricity production. It should be noted that Land-use and Forestry acted as a sink for CO_2, 1073 Tg CO_2 eq in 1990, and 838 Tg CO_2 eq in 2001.

Table 57. Energy Consumption, Carbon Emissions Coefficients, and Carbon Emissions from Energy Consumption in the U.S. Pulp and Paper Industry in 1994

Fuel	Energy Use (PJ)	Carbon Emissions Coefficient (ktC/PJ)	Carbon Emissions (MtC)
Electricity (Purchased)	235.3	48.5	11.4
Residual Fuel Oil	182.5	20.4	3.7
Distillate Fuel Oil	9.5	18.9	0.2
Natural Gas	605.6	13.7	8.3
LPG	5.3	16.1	0.1
Coal	323.9	24.3	7.7
Other (biomass & steam)	1416.6	0.0	0.0
Total Energy	2,779	N/A	31.5

U.S. Energy Information Administration, "Emissions of Greenhouse Gases in the U.S." Washington: Government Printing Office. 1997

Note: References for this section:
1. *Opportunities to Improve Energy Efficiency and Reduce Greenhouse Gas Emissions in the U.S. Pulp and Paper Industry*, Lawrence Berkeley National Laboratory-46141. July 2000.
2. *Energy Cost Reduction in the Pulp and Paper Industry.* Paprican. 1999.
3. Fapet Oy, Jyvaskyla. *Economics of the Pulp and Paper Industry.* Finland, 1998. Retrieved from http://ifcln1.ifc.org/ifcext/enviro.nsf/AttachmentsByTitle/gui_pulp_WB/$FILE/pulp_PPAH.pdf

Mining/Metal Processing Industry

The U.S. mining industries, which ran at peak performance following WWII, began a long-term decline starting in the 1960s. Today, the nation imports a major share of its industrial metals from foreign mines and smelters. Over half of metals, such as tin, tungsten, platinum, cobalt, chromium, zinc, and nickel, now come from foreign sources. Still, the U.S. minerals industry remains prosperous. In 1997, processed materials from the U.S. mining industries was valued at $413 billion and the value of raw non-fuel mineral production was estimated at $39.5 billion.

Non-fuel minerals in the United States are obtained by mining mineral reserves, importing mineral ores, or reclaiming minerals from secondary markets. Table 58 identifies several of the most common minerals consumed in the United States. In terms of production, the U.S. share of the world market for most metals has been declining over the past several decades. Still, the United States remains the western world's largest producer of refined aluminum, copper, and lead. Table 59 shows the United States' and the world's production of the most common, large-volume, non-fuel minerals.

Table 58. U.S. Mineral Reserves and Reserve Base

	Reserves	Reserve Base	% of World Reserve	% of World Reserve Base
Thousand Metric Tons				
Copper	45,000	90,000	14.5	14.8
Lead	8000	20,000	11.6	16.7
Molybdenum	2700	4,500	49.1	45.0
Zinc	16,000	50,000	11.4	15.2
Nickel	23	2500	0.05	2.3
Thousand Metric Tons of Ore				
Iron	16,000,000	25,000,000	10.6	10.8
Sulfur	140,000	230,000	10.0	6.6
Phosphate rock	1,200,000	4,400,000	10.9	13.1
Metric Tons				
Gold	5600	6100	12.2	8.6
Platinum Group metals	250	7800	0.4	1.2
Silver	31,000	72,000	11.1	17.1

U.S. Geological Survey. *Mineral Commodity Summaries.* Washington: Government Printing Office. 1996.

Table 59. U.S. and World Production of Selected Non-Fuel Minerals, 1996, in Metric Tons (Unless Otherwise Indicated)

Material	World Production	U.S. Production	U.S. Percent
Metals			
Arsenic	42,100	0	0
Aluminum	20,700	35803580	17
Cadmium	18,900	1530	8
Chromium	12,200,000	0	0
Copper	12,500,000	2,340,000	19
Gold (kg)	2,250,000	318,000	14
Iron (ore)	1,020,000,000	62,100,000	6
Lead	2920	436	15
Magnesium (primary)	341,000	133,000	39
Mercury	2890	Withheld	-
Nickel	1,080,000	1330	-
Silver	15,200	1520	10
Tin (smelter	207,000	11,000	5
Zinc	7,530,000	366,000	5
Industrial Minerals			
Asbestos	2,290,000	9550	-
Cement	1,480,000,000	80,800,000	5
Gypsum	99,700,000	17,500,000	18
Phosphate Rock	141,000,000	45,400,000	6
Silicon	3,200,000	412,000	13
Soda Ash	30,400	10,200	34
Sulfur	52,400	12,000	23

U.S. Geological Survey. *Minerals Yearbook, Metals and Minerals.* Washington: Government Printing Office. 1996.

The metalcasting industry is, by nature, very energy intensive. Metalcasting processes include melting, remelting, and heat-treating castings, which are very energy-intensive processes. The energy used by metalcasting facilities in the United States was determined to be 236 trillion Btu in the Manufacturing Energy Consumption Survey of 1998 at production volumes similar to 2003. Many studies have been undertaken during the last 15 years to determine the energy profile of the metalcasting industry, with varying results. Many casting facilities have other value-added processes in addition to the foundry operations. It is difficult to compare all of the energy usage associated with casting specific processes. Table 60 provides an estimate of the 2003 metalcasting energy uses and CO_2 emissions.

Table 60. Estimated 2003 Metalcasting Energy Usage and CO_2 Emissions

	Tacit Energy 10^6 Btu/Ship (Ton)	2003 Estimated Ship (Tons)	2003 Benchmark Tacit Energy 10^{12} (Btu)	Tons 10^3 CO_2
Gray Iron	29.7	5,477,808	162.6	11,187
Ductile (other than pipe)	26.0	2,016,128	52.4	3,494
Ductile Iron Pipe	7.8	2,000,000	15.7	1,160
Steel	36.5	1,257,660	45.9	2,993
Al High Pressure Die Casting	60.6	1,585,720	96.0	6,217
Al Permanent Mold/Sand	99.4	373,266	37.1	1,372
Al Lost Foam	81.9	304,014	24.9	1,613
Mg Die Casting	67.8	106,600	7.2	486
Zinc Die Casting	23.4	344,000	8.0	515
Copper-Base; Sand	37.3	311,600	11.6	780
Titanium	65.0	40,977	2.7	187
Other Non-Ferrous	22.5	86,227	1.9	353

Energy Use in Select Metalcasting Facilities. 2003.

The emission of CO_2 in million metric tons per quadrillion Btu of energy consumed in 2003 was 68.53, an increase of 0.5 from 1998. Table 61 shows total industry emissions.

Table 61. Estimated Total Emissions from the Mining and Metal Processing Industry

Industry Type	Gas Emissions	1990	2001
Ferroalloys	CO_2	2.0	1.3
Coal Mining	CH_4	87.1 (230 PJ)	60.7 (161 PJ)
Silicon Manufacturing	CH_4	-	-
Aluminum Production	HFCs, PFCs, SF_6	18.1	4.1
Mg Production & Processing	HFCs, PFCs, SF_6	5.4	2.5
Metals Manufacturing	NO_x, CO, VOC	2.6	1.3

U.S. Environmental Protection Agency. *U.S. Inventory of Greenhouse Gases*, Washington: Government Printing Office. April 15, 2003.

All values reported in Tg CO_2 Eq = Teragrams of Carbon Dioxide equivalent.

Coal Mining Industry

Table 62 provides CH_4 emissions for all coal mining activities in the United States as well as the additional formation of CO_2 through atmospheric CH_4 oxidation.

Table 62. Emission Breakdown of CH_4 from U.S. Coal Mining Industry, 1990 and 2001

Coal Mining Activity	1990	2001
Underground Mining	62.1	38.1
Liberated	67.6	54.2
Recovered & Used	(5.6)	(16.0)
Surface Mining	10.2	9.5
Post-Mining (Underground)	13.1	11.6
Post-Mining (Surface)	1.7	1.5
Totals	**87.1 (230 PJ)**	**60.7 (161 PJ)**
Formation through CH_4 oxidation	**11.4**	**8.0**

U.S. Environmental Protection Agency. *U.S. Inventory of Greenhouse Gases.* Washington: Government Printing Office. April 15, 2003.

All values reported in Tg CO_2 Eq = Teragrams of Carbon Dioxide equivalent.

Agriculture Industry

The agricultural industry generates emissions from a wide variety of sources, including enteric and manure management, soil management, and combustions processes. Table 63 shows the source of agricultural industry emissions. Table 64 shows a breakdown of the emissions by gas.

Table 63. Agriculture Industry Generated Emissions by General Source

Emissions Source	Gas	1990	2001
Enteric Fermentation	CH_4	117.9	114.8
Manure Management	CH_4	31.3	38.9
Rice Cultivation	CH_4	7.1	7.6
Field Burning of Ag. Residues	CH_4	0.7	0.8
Soil Management	N_2O	267.5	294.2
Manure Management	N_2O	16.2	18.0
Field Burning of Ag. Residues	N_2O, NO_x, CO	1.1	1.2
Fossil Fuel Combustion	CO_2	46.3	50.4

U.S. Environmental Protection Agency. *U.S. Inventory of Greenhouse Gases.* Washington: Government Printing Office. April 15, 2003.

All values reported in Tg CO_2 Eq = Teragrams of Carbon Dioxide equivalent.

Table 64. Agriculture Industry Generated Emissions by Gas Content

		1990	2001
Direct Emissions	CO_2	46.3	50.4
	CH_4	157.1 (416 PJ)	162.2 (430 PJ)
	N_2O	284.4	313.1
Electricity-Related	CO_2	23.8	20.2
	N_2O	0.1	0.1
	SF_6	0.4	0.1

U.S. Environmental Protection Agency. *U.S. Inventory of Greenhouse Gases.* Washington: Government Printing Office. April 15, 2003.

All values reported in Tg CO_2 Eq = Teragrams of Carbon Dioxide equivalent.

Table 65 shows that both enteric fermentation and manure management are primary contributors to greenhouse-gas-related emissions for the agriculture industry. Table 66 provides a breakdown of CH_4 and N_2O emissions from manure management.

Table 65. Detailed Breakdown of CH_4 Emissions from Enteric Fermentation

Livestock Type	1990	2001
Beef Cattle	83.2	82.7
Dairy Cattle	28.9	26.9
Horses	1.9	2.0
Sheep	1.9	1.2
Swine	1.7	1.9
Goats	0.3	0.2
Total	117.9 (312.6 PJ)	114.9 (304.7 PJ)

U.S. Environmental Protection Agency. *U.S. Inventory of Greenhouse Gases.* Washington: Government Printing Office. April 15, 2003.

All values reported in Tg CO_2 Eq = Teragrams of Carbon Dioxide equivalent.

Table 66. Detailed Breakdown of CH_4 and N_2O Emissions from Manure Management

Gas/Animal Type	1990	2001
CH_4	**31.3**	**38.9**
Dairy Cattle	11.4	15.1
Beef Cattle	3.4	3.3
Swine	13.1	17.1
Sheep	0.1	-
Goats	-	-
Poultry	2.7	2.7
Horses	0.6	0.6
Total	77.7 (206 PJ)	59.3 (157 PJ)
N_2O	**16.2**	**18.0**
Dairy Cattle	4.3	3.9
Beef Cattle	4.9	6.1
Swine	0.4	0.4
Sheep	-	-
Goats	-	-
Poultry	6.3	7.3
Horses	0.2	0.2

U.S. Environmental Protection Agency. *U.S. Inventory of Greenhouse Gases.* Washington: Government Printing Office. April 15, 2003.

All values reported in Tg CO_2 Eq = Teragrams of Carbon Dioxide equivalent.

Electronics Industry

Process exhaust systems are critical to microelectronic and semiconductor manufacturing facilities. Exhaust flow rates and compositions from the different microelectronics manufacturing processes vary. Effectively managing process exhaust to minimize emissions requires accurate knowledge of the quantities of each segregated exhaust, a characterization of the emissions, and an understanding of the constituents' physical and chemical properties. Due to the fact that conversion of reactants fed to tools is typically low, the majority of emissions are feed gases. Table 67 lists typical processes and resulting emissions from a small electronics facility.

Table 67. Typical Processes and Resulting Emissions from A Small Electronics Industry Fabrication Facility

Process or Area	Area (m^2)	Acid Exhaust Flow Rate (m^3/min)	Alkali Flow Rate (m^3/min)	VOC Flow Rate (m^3/min)	Typical Emissions
Epitaxy	1115				SiH_4, SiH_2Cl_2, $SiCl_4$, AsH_3, B_2H_6, PH_3, HCl, H_2
Acid Etch	186	113	583	497	NO, NO_2, HF, HNO_3, CH_3COOH
Cleaning/Wet Etch	2230	1473	58	1406	H_2SO_4, H_2O_2, HNO_3, HF, H_3PO_4, Cl_2, NH_4F, NH_4OH, IPA, MEK
Polyimide	558	294	934	83	CH_3COOH, IPA, Ethyl Lactate, NMP, Amines, TMAH
Photolithography	2320	332		331	$NH_{\backslash 4}OH$, NH_4Cl, NH_3, KOH, Organic Acid Salts
Dry Etch	1300	479	525	83	HDMS, NMP, TMAH, PGMEA, Xylene Ethyl Lactate, IPA
Implant	1860	1620			CL_2, BCl_3, C_2F_6, CF_4, CHF_3, C_3F_8, NF_3, SF_6, CH_3F, HF
CVD	930	1732			BF_3, AsH_3, PH_3, H_2
Diffusion	1115	442			SiH_4, $SiCl_4$, SiF_4, CF_4, B_2H_6, PH_3, N_2O, NH_3, NF_2, H_2, WF_6
Metals	558	294			SiH_4, N_2O, BBr_3, AsH_3, BCl_3, BF_3, B_2H_6, PH_3
TOTAL	14032	7000	2100	2400	SiH_4, BCl_3, $AlCl_3$, WF_6, TiF_4, SiF_4, BF_3, SF_6
IPA=Isopropyl Alcohol, MEK=Methyl Ethyl Ketone, NMP=N-Methyl-2-pyrrolidone, TMAH=Tetramethyl Ammonium Hydroxide, HMDS=Hexamethyldisilazane, PGMEA=Propylene Glycol Monomethyl Ether Acetate.					

U.S. Environmental Protection Agency. *U.S. Inventory of Greenhouse Gases.* Washington: Government Printing Office. April 15, 2003.

Table 68 lists the greenhouse gas emissions generated by the electronics industry. Although this data is incomplete, these figures indicate that fluorocarbon emissions are significant. However, energy content from these emissions appear minimal.

Table 68. Greenhouse Gas Emissions from the Electronics Industry

Semiconductor Manufacture	1990	2001
HFCs, PFCs, SF_6	2.9	5.5
All values reported in Tg CO_2 Eq = Teragrams of Carbon Dioxide equivalent.		

U.S. Environmental Protection Agency. *U.S. Inventory of Greenhouse Gases.* Washington: Government Printing Office. April 15, 2003.

Summary of Chemical Emissions with Residual Fuel-Value

The scope of this study was to determine the amount of energy in the emissions from industrial processes and identify technologies to capture the energy and redeploy it. Table 69 shows that about 2180 PJ, or 2.1 Quads (2066 TBtu) of emissions had residual chemical fuel value. Since landfills may not traditionally be considered industrial organizations, the industry component of the emissions identified that had residual chemical fuel value are 1482 PJ, or 1.4 Quads. This represents approximately 4.3% of the total energy usage in United States industry.

Table 69. Summary of Energy Content in Emissions from U.S. Industrial Processes

Industry	Gas	Emissions (Tg)	Energy	
			PJ	Trillion Btu
Mining	CH_4	2.89	161	153
Agriculture	CH_4	7.72	430	408
Landfill	CH_4	12.53[23]	698	662
Petroleum Systems	CH_4	1.01	56	53
Petroleum refinery	H_2	0.02	10	9
Natural gas Systems	CH_4	5.59	311	295
Chemicals (Cl_2 production)	H_2	0.29	42	40
Oil & Gas, Mining, waste combustion, industrial fossil combustion, miscellaneous industrial processes	CO	10.3	104	99
Total NMVOCs	NMVOC	7.27	368	349
Total energy content			**2180**	**2066**

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[23] Includes energy captured from CH_4 that is currently flared.

CHAPTER 2: SURVEY OF THERMAL EMISSIONS

Background

United States industry generates a large quantity of waste heat from industrial processes, combustion, and other process heating processes. The waste heat is produced in a wide variety of processes and is distributed in nature. This chapter evaluates some of the industrial processes that have the highest level of thermal emissions and evaluates the potential to recover these thermal emissions and convert them back into useful energy.

Energetics Incorporated quantified the amount of heat generated and rejected to the atmosphere in a study for the U.S. Department of Energy Industrial Technology Program (DOE-ITP). The Energetics report [34] studied the most energy-intensive U.S. industries in order to profile their energy supply and consumption. The report identified the major industrial processes that create waste heat, and included a summary of the largest opportunities to recover this heat. This section summarizes the major findings of Energetics report.

Summary of Thermal Emissions

Table 70 summarizes the five waste heat recovery opportunities identified by Energetics [34]. This summary shows that waste heat from industrial processes account for more than 10 Quads of energy consumption from industrial complexes. It also shows that an estimated 1.6 Quads of this energy has an opportunity to be recovered.

Table 70. Summary of Waste Heat Recovery Opportunities

Item #	Description of Opportunity Area	Estimated Energy Available (TBtu)	Estimated Recovery Efficiency	Estimated Recovery Opportunity (TBtu)	Economic Benefit if Realized, $ Billion (2005)
1	**Waste heat recovery** from gases and liquids in chemicals, petroleum, and forest products, including hot gas cleanup and dehydration of liquid waste streams	~7,000 (7400 PJ)	~12%	851 (898 PJ)	$2.15B
4	**Heat recovery from drying processes** (chemicals, forest products, food processing)	~3700 (3900 PJ)	~10%	377 (400 PJ)	$1.24B
10	**Waste heat recovery** from gases in metals and non-metallic minerals manufacture (excluding calcining), including hot gas cleanup	~1600 (1700 PJ)	~15%	235 (250 PJ)	$1.23B
18	**Waste heat recovery from calcining** (not flue gases)			74 (78 PJ)	$0.16B
19	**Heat recovery from metal quenching/cooling processes**			57 (60 PJ)	$0.28B
	Total	>10,000 (10,500 PJ)		1594 (1680 PJ)	$5.06B

Source: Energetics [34].

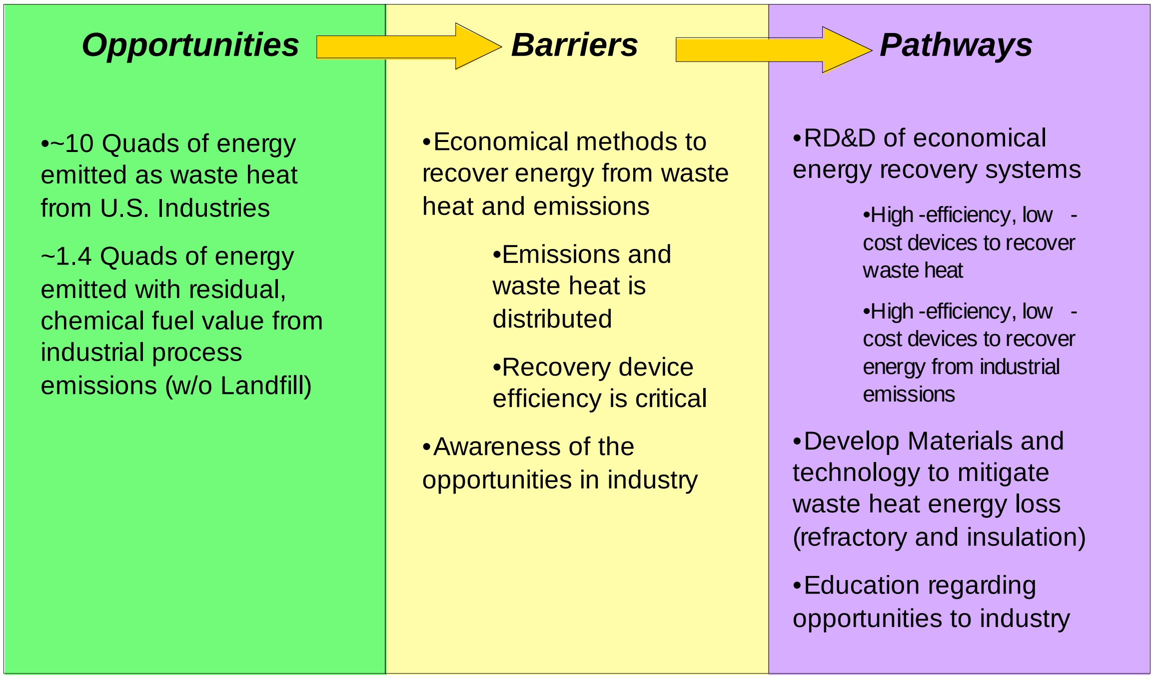
CHAPTER 3: OPPORTUNITIES-BARRIERS-PATHWAYS FOR RECOVERY

This report provides a detailed assessment of the chemical and thermal emissions from the U.S. industrial complex. It shows that the opportunities to recover chemical and thermal emissions are significant—with over 2 Quads (2180 PJ) of chemical emissions (1.4 Quads w/o landfills) and 10 Quads (10,500 PJ) of thermal emissions, representing 35% of the 32.5 Quads consumed by U.S. industry in 2003 [5]. (This is perhaps a conservative estimate given the number of conservative assumptions in both the chemical and thermal emissions survey.) Despite the numerous opportunities to recovering this energy, there are obvious barriers.

The primary barriers appear to be the limitation of methods to economically recover this energy. This is true for two primary reasons: 1) the nature of the chemical and thermal emissions is distributed and 2) recovery device efficiencies and capital costs. The distributed nature of these emissions makes it difficult to focus recovery technologies. Chemical emissions appear to be dilute and distributed, and often occur with other emissions that have little or no residual fuel value (mainly carbon dioxide). Separating and concentrating the emissions so they are suitable for reuse is a major barrier to capitalizing on this opportunity. The thermal emissions have very similar circumstances, where much of the waste heat is distributed, and much of the heat could be low-grade (i.e., temperatures not sufficiently high to recover energy content using conventional technologies in an economic way). Another potential barrier to recovering this energy is the lack of awareness within the industry of the magnitude of this opportunity. These barriers are significant, but possible pathways to capitalizing on this opportunity do exist.

Generally, there are two methods to improve the energy efficiency of the industrial complex: 1) Develop new processes and facilities that do not generate these emissions, or 2) attempt to capture and re-employ these chemical and thermal emissions. Developing new processes and facilities (the first option) typically involves performing R&D on new manufacturing processes or process technology, demonstrating their effectiveness and reliability, and then convincing industrial organizations to purchase and deploy this new technology (capital investment). This appears to be the conventional primary approach to improving the energy efficiency of industrial manufacturing processes. However, this often requires large capital reinvestment in industrial equipment and infrastructure; and perhaps relies on abandoning industrial facilities with an extraordinarily high sunk cost (e.g., aluminum smelters, petroleum refineries).

The second option to improve the energy efficiency of the industrial complex includes research, development, and demonstration of economical energy recovery systems to capture, convert, or otherwise re-employ the chemical and thermal emissions from the current industrial complex into usable energy. This approach would enable substantial improvement in industrial process energy efficiency and reduce industrial GHG emissions without major recapitalization of the existing industrial infrastructure. These technologies would include both high-efficiency and low-cost devices. The pathways would include developing technologies to mitigate waste heat and emissions through better materials and process technologies. Figure 4 presents a consolidated view of the opportunities, barriers, and pathways associated with recovering energy from the chemical and thermal emissions from U.S. industry.



Opportunities

- ~10 Quads of energy emitted as waste heat from U.S. Industries

~1.4 Quads of energy emitted with residual, chemical fuel value from industrial process emissions (w/o Landfill)

Barriers

- Economical methods to recover energy from waste heat and emissions
  - Emissions and waste heat is distributed
  - Recovery device efficiency is critical
- Awareness of the opportunities in industry

Pathways

- RD&D of economical energy recovery systems
  - High-efficiency, low-cost devices to recover waste heat
  - High-efficiency, low-cost devices to recover energy from industrial emissions
- Develop Materials and technology to mitigate waste heat energy loss (refractory and insulation)
- Education regarding opportunities to industry

Figure 4. Opportunities, Barriers, and Pathways Associated with Recovering Fuel from Chemical and Thermal Emissions from U.S. Industry

Potential Recovery Technologies for Chemical Emissions

Conventional technologies for recovering energy from chemical emissions, such as combustion processes and fuel cells, are under further development to make them more cost-effective. However, chemical emissions are diverse in their origin and complex in their chemical composition. This complexity will likely pose challenges to the recovery of the energy content in these emissions.

The most conventional way to recover chemical emissions is through combustion processes that generate process heating or steam for turbine-based generation of electricity. This class of devices may include microturbine generators and similar distributed electricity generation devices. This is conventional technology, and may be the most robust and available means to recover energy. However, these technologies are capital intensive and require the addition of complex infrastructure to industrial facilities that are constantly striving to eliminate complexity and increase reliability. Efficient combustion also requires careful control of the fuel feedstock, which may be difficult using a chemical waste stream.

The emerging solution to recovering chemical emissions with residual fuel value is fuel cells. Fuel cells are solid-state devices that function like continuous operating batteries, where the energy is continually renewed with chemical energy. Fuel cells generally fit into two broad categories: solid-oxide fuel cells (SOFCs) and Proton Exchange Membrane (PEM) fuel cells. Even though these technologies have existed for some decades, they appear to be at the beginning in their commercialization life-cycle. The primary barrier to widespread application of fuel cells is the capital cost, which is projected to drop significantly in coming years. The SOFCs have some advantage over the PEM fuel cell in that they can tolerate a wider array of contaminants in their feed stock without fouling and failing over the long-term. However, all fuel cells must have controlled operating conditions with controlled chemical feedstock. The diverse and contaminated fuel feedstock of industrial emissions may prove to be a challenging feedstock.

The nature of the chemical emissions from U.S. industry is distributed, which makes it difficult to focus recovery technologies. Chemical emissions appear to be dilute and distributed, and often occur with other emissions that have little or no residual fuel value (mainly carbon dioxide). Separating and concentrating the emissions so they are suitable for reuse is a major barrier to capitalizing on this opportunity. Economic recovery of these chemical emissions may be predicated on robust separation and reformation technologies. However, even as these challenges prevail, several examples of chemical emission recoveries are apparent.

Examples of Chemical Emission Recovery Projects

This section describes the various technologies to capture the energy content of these chemical emissions. These are example applications that were identified while surveying the technical literature. These applications will be discussed briefly. Original references provide greater detail.

Biogas is rich in CH_4 and CO_2, and is obtained from animal/human waste or crop residues and landfills. Gasification of biomass also leads to production of biogas. After chemical treatment to remove sulfur and particulates, biogas can be used in fuel cells. The biogas can be fed to a MCFC or SOFC, with the exhaust from the fuel cell expanded in a gas turbine and then cooled in a heat recovery steam generator. Fuel Cell Energy recently showed that a coal gasifier can be used as a “reformer” for a MCFC. Bove et al [21] reviewed the status of this field, and presented some experimental results for biogas as fuel for MCFC. For fuel utilization of 80%, the current density was 0.12 A/cm^2, with a power density of 0.1 W/cm^2.

Pure Energy Corporation has developed a process to recover up to 90% of municipal solid waste (MSW). It can be used to process as much as 23 tons of MSW in each batch, converting MSW to sterilized organic (biomass) and inorganic materials such as ethanol and high-value chemicals. This process may also be used to process industrial landfill wastes.

The Plasma Enhanced Melter (PEM) developed by Integrated Environmental Technologies uses heating from plasma in a gasification system to convert wastes including industrial, municipal, and tires to valuable products such as roofing tiles, insulating panels and a hydrogen-rich gas to generate power by using fuel cells. These can be used in small units to process 4 tons of waste per day and generate 1-5 MW power in addition to the power to run the PEM system. Close integration of this process with an electricity-intensive process such as the chlor-alkali process has high potential.

As discussed earlier, CO can be used as fuel in MCFC and SOFC. However, it is poisonous to the PEM Pt electrode catalyst. In order to use hydrocarbons as fuel, after steam reforming, the CO has to be removed using water gas shift or preferential oxidation. Kim et al. [22] developed a method to extract energy from CO at room temperature using a reactor membrane made of gold nanotubes, which catalyze CO oxidation. The electrons extracted from CO are captured by polyoxometalates, which are then pumped to the fuel cell anode. While further development needs to be done, this offers a potential to capture energy from CO, which is one of the components of biogas.

The DOW Corporation petrochemical plant in Freeport, Texas, produces hydrogen byproduct, which will be fed to a PEM fuel cell system to be produced by GM. The PEM system will consist of 75-kW fuel cell stacks, with groups of 14 mounted on a trailer to give up to 1 MW power. Thirty-five trailers will be grouped to provide a total of 35 MW of power.

Methane is a byproduct in several industrial processes. Because of its inert nature, its oxidation requires a high temperature. Using a catalyst can lower this temperature considerably. Choudhary et al. [23] reviewed the various options for catalytic combustion of methane for use in gas turbines to generate power with reduced NO_x emission. Noble metal-based catalysts were very active, but had poor stability and were expensive. Perovskite-type metal oxides catalysts suffered from sintering and structure collapse, along with solid state reactions with the support. Further development is needed before low-temperature oxidation of CH_4 is viable for use in gas turbines.

Ford has developed a technology to capture energy from paint. Spray booth exhaust is directed to a concentrator and then to a regenerative thermal oxidizer. In an alternate system ("fumes to fuel"), volatile organic compounds (VOCs) from the painting process are concentrated in a fluidized bed. In the second stage, the VOCs are converted to hydrogen in a reformer, while in the second stage, the hydrogen is fed to a solid oxide fuel cell to generate electricity. This can be used to convert VOCs from various industries to a hydrogen-rich gas stream.

Process Integration and Optimization to Redeploy Emissions

A major portion of emissions from the various sectors is due to fossil fuel combustion, which is used to supply process heat. While capturing the energy content of emissions is expected to reduce fuel usage, and thus the emissions, better thermal management through efficient heat transfer would reduce the heat load for the process, as has been extensively documented. An area that still has room for considerable development is process integration, which can result in a significant amount of energy savings, as described below.

An example of process integration is the use of byproduct as feed for a different process [24]. In the production of vinyl chloride, chlorine is combined with ethylene to produce ethylene dichloride, which is pyrolyzed to produce vinyl chloride and HCI. One mole of HCl is produced for every mole of chlorine. The waste HCl is used as a raw material in the oxy-chlorination of ethylene to yield more vinyl chloride. This process would be more efficient if both processes operated together. By expanding this network to include other processes that use chlorine or HCl, the efficiency can be increased further. An example is isocyanate manufacturing, in which Cl_2 combines with CO to yield phosgene, which reacts with an amine to produce an isocyanate and HCl. This process sets up a Cl_2/HCl network. Cl_2 is fed to the isocyanate and vinyl chloride process. The HCl byproduct from the former is sent to the oxychlorination process.

The chemical process design engineers should understand their own processes and also processes that supply materials and use their byproducts. Byproducts from chemical processes can also be used as feedstock in other industries (HCl used in steel making) or byproducts from other industries can be used in the chemical industry (HCl from semi-conductor manufacturing).

The authors also provided an excellent example of a multi-industry network at Kalundborg, Denmark. An oil refinery, a sulfuric acid plant, a pharmaceutical manufacturer, a coal-burning power plant, a fish farm, and a gypsum board manufacturer form an industrial network. Steam, gas, and cooling water are exchanged between the power plant and refinery. Waste heat from the power plant is used for residential heating and in the greenhouses and fish farm. Ash from coal power plant combustion is used for cement manufacture, while calcium sulfate from the power plant is sent to the gypsum board facility. The refinery sends hot liquid sulfur from de-sulfurization of crude oil to a sulfuric acid manufacturer. In this approach, the power plant and oil refinery are the central facilities, with energy exchange originating or ending at these facilities.

In an eco-industrial park in North Texas, the central facility is a steel mill, which uses scrap cars as primary feed to the electric arc furnace. The furnace dust, which has zinc, lead, copper, manganese, zinc, is sent to a cement kiln.

One interesting point made by the authors was that about 100 Quads of energy is consumed annually in the U.S., out of which 33 Quads is used for electricity generation. About 22 Quads is lost as heat during electricity generation, which, if captured, can provide 22% of the total annual energy requirement. It should be noted that tri-forming of methane using power plant flue gas, as discussed earlier, is a good example of such use. Some of the new tools that are available for exchange of energy/reactants across various industrial processes are:

- Industrial Materials Exchange Tool – developed by Bechtel and owned by Nexant– not available to others. Has been used in several industrial eco-systems project.
- EPA's Designing Industrial Ecosystems Toolkit – helps users identify, screen, and optimize byproduct use opportunities at the regional scale.

Chevron recently completed an energy-efficiency assessment for DOE-ITP for its refinery in Salt Lake City, Utah, and found that > 25000 million Btu's could be saved annually by upgrading a debutanizer and completing a saturated gas plant project. Clearly, there are opportunities for energy capture using process integration.

The purge gases from a catalytic cracking unit consist of various olefins. British Petroleum, as part of a DOE-OIT program, developed a hybrid membrane/distillation system to separate these olefins, resulting in estimated energy savings of 150 GBtu/year.

In energy-intensive industries such as glass, oxygen-rich combustion can significantly reduce emissions and result in fuel savings, as determined by Praxair as part of a DOE-OIT program.

In an industrial process, fuels are consumed in the form of heat for producing process steam, raising temperature, generating electricity to operate processes and machinery, and feed-stocks. Unless the electricity is generated within the plant, the emissions from this process cannot be recovered. But the emissions from process heat and feedstocks can be recovered. Halmann et al. [25] summarized the various energy savings resulting from process optimization. Ceramic heat recuperators will recover per year an estimated 2 exajoules (EJ) of thermal energy currently wasted with corrosive and potential fouling high-temperature exhaust streams. Metallic recuperators will recover an estimated 1.6-3.2 EJ of process heat > 1000°F. New heat pump technology will upgrade an estimated 1-3 EJ of process heat from liquid and gas waste streams at 150-25-F, and bottoming-cycle engines for streams at < 700°F to a more useful temperature level. Development of organic working fluids will improve performance of organic Rankine cycle driven by low-temperature waste heat. Some examples of process optimization are given below:

- Energy cascading – placement of processes that need lower quality energy so each uses waste heat from preceding process.
- Combining process steam production with electricity generation in systems with high electrical to thermal output ratios – this applies only to cases where electricity generation is done within the plant. Data is still needed on which industries do this and how much electricity is generated within those industries in the plant.

- Apply catalytic separation/concentration technologies in chemical reaction and purification process in chemical, petroleum-refining, and pharmaceutical industries. Several physical separation techniques that avoid evaporation and freezing, such as membrane separation, have been developed that can improve efficiency. Potential energy savings from process flow optimization is estimated to be 2 EJ/year in the United States.
- Combustion is one way to capture energy of emissions from industrial processes. Improvements in combustion efficiency and use of advanced combustors are expected to save 30% in fuel.

Potential energy savings from process optimization is estimated to be 2 EJ per year in the United States. Additional examples of energy savings in industrial processes are given below:

- Industrial electric drives include pumps, compressors, conveyors, fans, machine tools – improvements in motors and other components are expected to save 33% of electricity consumed at present.
- Electricity is consumed in reduction on alumina or aluminum chloride to aluminum. The Alcoa process consumes 30% less energy than the Hall-Heroult process. Energy savings from improved technology is expected to cut energy required by 33%.
- In the iron and steel sector, electricity is mainly consumed by electric furnaces in the electric steel-making process. Furnace productivity can be increased by pre-heating the scrap, by operating at higher electric power levels, and by injecting oxygen. Energy consumption can be further reduced by direct rolling of continuously cast labs. These should save 25% of electricity by year end.
- Petrochemical feedstock – Petrochemicals such as synthetic fibers, plastics, and fertilizers are produced using fossil feedstock. Energy can be saved by a more efficient use of materials.

Potential Recovery Technologies for Thermal Emissions

Conventional technologies exist and are under development that could enable more cost-effective recovery of thermal emissions from the industrial processes. The two most obvious technology classes for this technology are process heat exchange and thermal energy conversion devices. However, thermal emissions from the industrial complex vary in the temperature gradients available and distributed nature of the thermal emissions. This complexity will likely require that different technology approaches be employed to recover thermal emissions depending on the quality of heat available and the nature of the ancillary processes and the ability to redeploy heat within the processes.

The most conventional method to re-use process heat is through heat exchangers. Heat exchangers permit the transfer of heat from one process fluid or gas to another. Heat exchangers can be used to transfer waste heat from process emissions to other locations that use it as process heat, thereby reducing overall energy demand. The ability to use these technologies is limited by the nature of the industrial process to re-use heat. Heat pipes, conventional heat exchangers, and more advanced, higher-efficiency heat exchangers (e.g., microtechnology-based heat exchangers) could recover process waste heat.

Solid-state devices are gaining attention as methods to convert thermal gradients to electricity. Thermoelectric and thermionic technologies are examples of these advancing technologies, which are largely based on semi-conductor materials. Appendix D provides a comprehensive description of these technologies, as well as several other technologies that might be deployed to recover thermal emissions from industrial processes.

There are other novel and experimental technologies that are being developed to convert thermal gradients into electricity. One example is piezoelectic power generators, which are being developed by Washington State University [36]. This system is based on MEMS technology. It uses a multilayer system to oscillate a thin film of piezoelectric material in the presence of a thermal gradient across the multi-layer system. This emerging technology appears to be capable of recovering low-grade thermal energy at higher efficiencies than other conventional solid-state devices, such as thermoelectrics. However, additional manufacturing process development will likely be required prior to introducing this technology to industrial applications.

Potential Treatment Options for CO_2

As discussed earlier, CO_2 is the main greenhouse gas emission from the various industries addressed in this report. While the heat of combustion for CO_2 is 0, it can be effectively used as feedstock for various petrochemicals and for fuel generation, as described in this section. Additional details for CO_2 utilization are given in Appendix A.

Chunshan Song [27] developed a new process known as tri-reforming for converting and using of CO_2 in flue gas from power plants (http://pubs.acs.org/isubscribe/journals/cinnov/ 31/i01/html/01song.html). This technique can also be used in any process that emits significant amounts of CO_2.

CO_2 is an important source of carbon for fuels and chemical feedstocks, and can be separated from gas mixtures by energy-intensive processes such as absorption, adsorption, or membrane separation. Tri-reforming is a 3-step reaction that can cost-effectively produce synthesis gas. While this does not directly result in energy recovery, it does fall within the scope of this work in terms of providing a pathway for recovery and productively using emitted CO_2, especially if the emission also contains CH_4. The reactions involved are the following:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \{\Delta H = 247.3\ \text{kJ/mol}\} \qquad (1)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \{\Delta H = 206.3\ \text{kJ/mol}\} \qquad (2)$$

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad \{\Delta H = -35.6\ \text{kJ/mol}\} \qquad (3)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \{\Delta H = -880\ \text{kJ/mol}\} \qquad (4)$$

Coupling CO_2 reforming and steam reforming can yield syngas with the desired H_2/CO ratio for methanol and Fisher-Tropsch synthesis, which require a 2:1 H_2/CO ratio, while steam reforming gives a 3:1 ratio. At present, two industrial processes (SPARG, Calcor) use this process.

It should be noted that with CO_2 reforming of methane, carbon formation is a big issue. Coupling with steam reforming mitigates this problem. In addition, introduction of air for partial oxidation of methane is also coupled with the above two processes to take advantage of the exotherm provided by the partial oxidation process. Any carbon formed is also oxidized. While tri-reforming has some disadvantages with respect to use of flue gas due to presence of various toxic substances, it appears to be a good candidate for emissions with CO_2 and CH_4 present in them.

Zhou et al. [26] investigated the use of dielectric-barrier discharge to convert CH_4 and CO_2 to synthesis gas at a low temperature and ambient pressure. For CH_4:CO_2 ratio of 20:80, a low H_2/CO molar ration was obtained, while for CH_4:CO_2 ratio of 80:20, H_2:CO ratio > 3 was obtained. This eliminates the need for separation of CO_2 from the flue gas and produces a valuable end product (synthesis gas).

CHAPTER 4: SUMMARY

United States industry consumed 32.5 Quads (34,300 PJ) during 2003, or 33.1% of total U.S. energy consumption [5]. This industrial complex and related energy consumption supports a multi-trillion dollar annual contribution to the gross domestic product and millions of jobs in the United States. However, beyond the valuable goods and products yielded by this nationwide enterprise, the manufacturing processes and related energy consumption also yields waste products in the form of chemical emissions and thermal emissions (waste heat). These waste products have residual energy values that are not routinely recovered. Recovering and reusing these waste products may represent a significant opportunity to improve the energy efficiency of the U.S. industrial complex. This report analyzed the opportunity to recover chemical emissions and thermal emissions from the U.S. industry and the barriers and pathways to more effectively capitalize on these opportunities.

A survey was conducted of publicly available literature to determine the amount of energy in industrial emissions and to identify technology opportunities for capturing and redeploying this energy. As shown in the table below, this analysis identified 2180 PJ, or 2 Quads of residual energy from chemical emissions. Since landfills are not traditionally considered industrial organizations, the industry component of the emissions that had residual chemical fuel value were 1482 PJ, or 1.4 Quads. This represents approximately 4.3% of the total energy used by U.S. industry.

Industry	**Gas**	**Emissions (Tg)**	**Energy**	
			PJ	**Trillion Btu**
Mining	CH_4	2.89	161	153
Agriculture	CH_4	7.72	430	408
Landfill	CH_4	12.53[24]	698	662
Petroleum systems	CH_4	1.01	56	53
Petroleum refinery	H_2	0.02	10	9
Natural gas systems	CH_4	5.59	311	295
Chemicals (Cl_2 production)	H_2	0.29	42	40
Oil & gas, mining, waste combustion, industrial fossil combustion, miscellaneous industrial processes	CO	10.3	104	99
Total NMVOC	NMVOC	7.27	368	349
Total energy content			**2180**	**2066**

Energetics Incorporated conducted a comprehensive study investigating the opportunity to reduce energy use and loss in industry [34]. This analysis summarizes these findings to quantify the thermal emissions from U.S. industry. As shown in the table on the next page, 10,500 PJ, or 10 Quads of thermal emissions, were identified from U.S. industrial processes. The table also describes the origin of these emissions. This represents approximately 30.8% of the total energy used by U.S. industry.

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[24] Includes energy captured from CH_4 that is currently flared.

Waste Heat Recovery Opportunities – from Energetics [34]

Item #	Description of Opportunity Area	Estimated Energy Available (TBtu)	Estimated Recovery Efficiency	Estimated Recovery Opportunity (TBtu)	Economic Benefit if Realized, $ billion (2005)
1	**Waste heat recovery** from gases and liquids in chemicals, petroleum, and forest products, including hot gas cleanup and dehydration of liquid waste streams	~7,000 (7400 PJ)	~12%	851 (898 PJ)	$2.15B
4	**Heat recovery from drying processes** (chemicals, forest products, food processing)	~3700 (3900 PJ)	~10%	377 (400 PJ)	$1.24B
10	**Waste heat recovery** from gases in metals and non-metallic minerals manufacture (excluding calcining), including hot gas cleanup	~1600 (1700 PJ)	~15%	235 (250 PJ)	$1.23B
18	**Waste heat recovery from calcining** (not flue gases)			74 (78 PJ)	$0.16B
19	**Heat recovery from metal quenching/cooling processes**			57 (60 PJ)	$0.28B
	Total	>10,000 (10,500 PJ)		1594 (1680 PJ)	$5.06B

The pathways to recovering the chemical and thermal emissions include research, development, and demonstration of high-efficiency, low-cost devices to recover chemical and thermal emissions. These pathways also include developing technologies to mitigate waste heat and emissions through better materials and process technologies. See Figure 4 for a consolidated view of the opportunities, barriers, and pathways associated with the chemical and thermal emissions from U.S. industry.

This report also discussed advanced materials (e.g., thermoelectric, thermionic, and piezoelectric) that might be employed to help recover thermal emission as well as solid oxide fuel cells and other technologies that appear to be the most promising technology to recover chemical emissions. Additional research and development as well as industry education may be required in order to make these technologies sufficiently cost-effective and widely commercialized.

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APPENDIX A: UTILIZATION OF CO_2

Opportunities for CO_2 Use

Energy utilization in modern society is based on combustion of fossil fuels – petroleum, coal, natural gas. The sources of CO_2 emissions include stationary, mobile, and natural sources. The stationary sources include fossil-fuel-based electric power plants, indepen dent power producers, manufacturing plants in industry, commercial and residential buildings, flares of gas in fields, military and government facilities.

Song et al [27] reviewed CO_2 emissions, conversion, and utilization. Several references were cited that described the synthesis of organic chemicals, chemical conversion of CO_2 over heterogeneous catalysts, CO_2 reforming of methane to produce gas polymer synthesis using supercritical CO_2, thermodynamics of chemical reactions, and various chemical reactions involving CO_2.

The U.S. CO_2 emission from fossil fuel corresponds to roughly 24% of the worldwide CO_2 emissions during the period 1980 to 1997. The U.S. CO_2 emissions from various sectors is listed in the table below. Note that the CO_2 emissions from electric utilities is already included within the emission numbers for each sector. By assuming that each sector uses 25% of electricity generated by utilities, it is estimated that the CO_2 emissions from the industrial sector was about 352 MMT carbon equivalent in 2004.

U.S. Emissions from Different Sectors (MMT of carbon equivalent)

CO_2 Emission Source	1980	1990	1997
CO_2 from Residential Sector	248.4	253.1	286.5
CO_2 from Commercial Sector	178.3	206.8	237.2
CO_2 from Industrial Sector	484.6	454.1	482.9
CO_2 from Transportation Sector	378.1	432.1	473.1
CO_2 from End-Use Total	1289.4	1346.1	1479.7
CO_2 from Electric Utilities	418.4	476.9	523.4
Estimated emissions from Industrial Sector Effluent	**380.0**	**334.9**	**352.1**

About 60% of U.S. industrial energy is consumed by a few energy-intensive manufactur ing sectors such as iron and steel, chemicals, petroleum refining, cement, and non-ferrous metals. The largest share of industrial energy consumption is for process heat. Mechan ical power and space heating require less energy. It is important that the emissions associated with generating process heat and mechanical power be included in this analysis. Fossil fuel is being burnt to provide process heat. In addition to the heat that can be captured from the effluent, this analysis should take into account the energy content of the effluent gases.

Reactions for CO_2 conversion are endothermic and require energy input. However, they can be used for various useful reactions such as pyrolysis of hydrocarbons for the manufacture of ethylene and propylene, dehydrogenation reaction for manufacture of petrochemicals such as styrene from ethylbenzene, and steam reforming of hydrocarbons for producing synthesis gas and hydrogen. The total U.S. demand for CO_2 for producing synthetic organic chemicals and polymer materials is 163 MMT CO_2. The U.S. production of liquid fuels in 1997 corresponds to a need of 513 MMT C, most of which can be met by utilizing CO_2 emissions.

Most chemical processes are based on catalytic oxidation of hydrocarbons, which is the least selective of all reactions, thus contributing to CO_2 emissions. There is a significant opportunity to both increase reaction selectivity to reduce CO_2 emission and capture CO_2 from emissions.

The use of CO_2 as a raw material for the chemical and energy industry is increasing. Only four industrial processes based on CO_2 are on stream, two of which are very mature (urea synthesis and salicylic acid) and do not need catalysts. The other two, carboxylation of epoxides and methanol synthesis, need metal catalysts. It is clear that the development of CO_2-based processes require the discovery of new transition, metal-assisted, reactions. Understanding the behavior of carbon dioxide and organic substrates towards metal centers will play an important role in the chemical utilization of CO_2, with the production of the following products:

- Chemical industry – COOH, esters, lactones, -O-C-(O)O- organic carbonates, -N-C(O)O- carbamates, -N-C(O)- ureas, amides;
- Energy industry – energy-rich C1 molecules (HCOOH, CO, CH_3OH and Cn) hydrocarbons or their derivatives.

Most processes for recovering energy from CO_2 actually require a net input of energy. Capturing CO_2 with solar or another renewable energy is a viable option, contingent upon improved power density from these sources. The energy required to capture CO_2 from stack gas using mono-ethanolamine solvent is 0.27 kWh(e)/lb CO_2, or 2000 kWhe/ton carbon [25]. If fossil fuel is used to supply this energy, the power plant efficiency is reduced by 30%. Using nuclear power would require $300 billion to capture the total CO_2 emitted by power plants, which corresponds to 50% of the total CO_2 emitted in the U.S. in 1990 (1.33 G tons C/year). Using improved solvents and optimization of absorption/stripping is expected to decrease the energy requirements for CO_2 capture.

Solid adsorbents such as zeolites, silica, and molecular sieves can also be used to capture CO_2. It is estimated that 0.4 kWh(e)/lb CO_2 or 2900 kWh(e)/ton C is required for energy capture using molecular sieves. The efficiency of a coal-burning plant generating 0.56 kWh(e)/lb of CO_2 will be reduced by 70% if 0.4 kWh(e) is used to capture the CO_2. Hence, it is imperative that an energy-efficient process be found for CO_2 capture. In all calculations of energy recovered from emissions, the energy expended on capture/separation of these emissions needs to be accounted for.

Following are some options for re-using CO_2 [28] :

Gaseous CO_2

- Convert CO_2 to a fuel such as methane and methanol through a reaction with hydrogen using a non-fossil energy source such as solar energy.
- Decompose CO_2 to CO at a high temperature using solar energy, shift CO with water to CO_2 and H_2, then convert to fuels (this seems inefficient).
- React CO_2 with NH_3 to form urea fertilizer
- Use CO_2 for controlled photosynthesis in greenhouses
- Use CO_2 as feedstock for chemicals

Liquid CO_2

- Supercritical CO_2 solvent
- Displace crude oil from reservoir rock
- Vaporize and use as above

Solid CO_2

- Dry ice
- Sublime and use as above

Estimate of Current and Potential Uses of CO_2 [29]

	Actual Mt/y	Potential Mt/y
Technological uses	13.5	> 100 including EOR
Synthesis of urea	60	> 100
PC	0.04	
Polycarbonates	-	Several
Cyclic carbonates	-	Tens
Linear carbonates	-	Tens
Carbamates		Several
Acids		~ 10
Acids		> 100
Other chemical		> 100
Methanol	10	Tens

With these options, it is possible that the utilization of CO_2 can be increased tenfold to ~ 1Gt/y.

Production of Fuels from CO_2 by Chemical Reactions

CO_2 mitigation and fuel production deals with utilizing fossil fuels, coal, oil, and gas with reduced CO_2 emissions. In the chemicals industry, there is a capacity mismatch between gross CO_2 emission from some industries and the need for CO_2 in the smaller chemical products market. The Carnol process catalytically reacts CO_2 from coal-fired plants with hydrogen produced from the thermal decomposition of methane to produce methanol and higher oxygenated fuels. Using fuel cell engines reduce CO_2 emissions 80% compared to using conventional coal-fired power generating plants and gasoline-driven I_C engines. Availability of methane in the flue gas decreases the energy needs further. Integrating CO_2 recovery by absorption/stripping with the exothermic reaction of CH_4 and H_2 reduces the power needs further. Converting CO_2 from power plant flue gases to biomass reduces the total emissions to the same degree as the Carnol process.

Reducing CO_2 to useful compounds such as fuels and chemical intermediates involves several steps of electron and proton transfer. In the absence of an external energy source (electrochemical, photochemical, or radiation induced), CO_2 may be activated by reduced compounds such as hydrocarbons in the reforming reaction or by molecular hydrogen in the hydrogenation reaction. Catalysts are required to reduce the activation energy [25].

In order to reduce CO_2 to obtain new products, large amounts of additional energy, especially expensive hydrogen, is needed. H_2 for CO_2 hydrogenation can be replaced by a mixture of $CH_4 + H_2O$ over a nickel-based catalyst. This reaction is a major pathway to producing ethylene, propylene, methanol, ethanol, and high-quality gaseous and liquid fuels such as substituted natural gas and high-octane gasoline. These CO_2 conversion routes may lead to new energy usage cycles.

Biomass is produced through a reaction of CO_2 with water to produce plants and organisms. Biomass can be burned as fuel, or converted to hydrogen-rich fuel, regenerating CO_2, which is emitted to atmosphere. For a process using biomass, there is no net change in CO_2 emission. However, using biomass as an energy source is more expensive than fossil fuels. Co-processing biomass and natural gas for conversion to liquid and gaseous fuels can increase yields and economics of conversion of biomass and reduce CO_2 emissions. Converting agricultural crops to ethanol by a fermentation process has gained usage as motor fuel [25]. Co-firing fossil fuel with biomass and conversion of biomass to liquid fuel can reduce CO_2 emission.

The Carnol process was developed to remove CO_2 from power plant flue gas, and to utilize CO_2 to produce alternative fuel. H_2 is generated by thermal cracking of methane and sequestering the carbon. The CO_2 is captured from power plant stack flue gas. The CO_2 and H_2 are catalytically combined to form methanol. Since this is exothermic, the heat from this reaction is used to capture CO_2.

H_2 is produced by steam reforming of saturated hydrocarbons, especially natural gas or methane on supported Ni catalyst at 1170K.

$CH_4 + 2H_2O = 4H_2 + CO_2$ 165 kJ/mol
$CO + H_2O = H_2 + CO_2$ -41 kJ/mol
$CH_4 + H_2O = 3H_2 + CO$ 206 kJ/mol

Hydrogen can also be produced by the CO_2 reforming of methane, using Ni-Ce_2O_3-Pt catalyst with Rh addition [30]:

$CH_4 + CO_2 = 2H_2 + 2CO$ 248 kJ/mol

By using available process heat for flue gases containing both CH_4 and CO_2, fuel can be produced for feeding to a SOFC or MCFC, thus converting two GHGs to useful product: methane. Steam reforming gives a product with a higher H_2:CO, which inhibits HC chain growth, and enhances methanation reaction. Hence CO_2 reforming also leads to lower concentration of CH_4, resulting in high purity syn gas, which is a building block for various chemicals such as methanol, ethanol, ethylene, acetic acid, formaldehyde, phosgene, and acetone. By using a H_2 permeable membrane, the conversion of CH_4 can be increased to 95%, much higher than the equilibrium conversion of 40%. H_2 removal also prevents the reverse water gas shift reaction, thus increasing H_2 selectivity to 99%. Plasma can be used to overcome the energy barrier for the endothermic CO_2 reforming of methane.

The CALCOR process is an example of a commercial application of CO_2 reforming. It consists of a multi-stage process of reacting dry CO_2 with natural gas, LPG, and syngas to produce high-purity CO (syn gas) that contains < 0.1% methane.

By using a combination of partial oxidation and CO_2 reforming of methane, the exothermicity of CH_4 partial oxidation is compensated for by the endothermicity of reforming reactions, and the $H_2/(CO+CO_2)$ ratio lowered to 2, which is desired for methanol and Fisher-Tropsch synthesis.

In instances where methanol is the preferred fuel of choice (such as a laptop), the hydro genation of CO_2 and CO to provide methanol could be viable, especially of process integration allows capture of the evolved heat for hydrogen generation.

$CO_2 + 3H_2 = CH_3OH\ (l) + H_2O\ (l)$ delta H 298K = -131 kJ/mol
$CO + 2H_2 = CH_3OH\ (l)$ delta H = -128 kJ/mol

Reforming of natural gas, followed by hydrogenation of mixtures of CO and CO_2 to methanol on various transition element catalysts is one of the most important processes in petrochemical industry.

Gasification of carbon by CO_2 by the following reaction leads to production of CO, which can be used as feed to a SOFC or MCFC. This reaction requires moderate energy input, which can be provided by capturing heat content of the flue gas.

$CO_2 + C = 2CO$ delta F 298K = 172.5 kJ/mol
$C + CO_2 = 2CO$ delta H = 171.5 kJ/mol

Gaseous fuel can be produced by thermo-chemical reactions of CO_2. Thermal splitting of CO_2 at high temperatures could be an attractive means for converting concentrated solar energy to gaseous fuel.

$CO_2 = CO + 1/2O_2$ delta G = 0 at 3350 K.

The reaction may be shifted to right by withdrawing one of the products.

Dissociation of CO_2 to surface-adsorbed CO and O can also be achieved at lower temperature (500K) at surface defect sites on clean rhodium surfaces.

The fixation of CO_2 by algae is also a promising area, with potential of aquatic bio-mass to be used as fuel source.

Electroreduction of CO_2

High coulombic efficiency in CO_2 and CO reduction is difficult to achieve due to competing side reactions such as hydrogen evolution. Another problem is their low solubility in aqueous media. The following are the equilibrium potentials vs. NHE electrochemical reduction of CO_2 [25]:

$CO_2 + 2H^+ + 2e \rightarrow HCOOH$ (Eo = -0.61 V)
$CO_2 + 2H^+ + 2e \rightarrow CO + H_2O$ (Eo = -0.52 V)
$CO_2 + 4H^+ + 4e \rightarrow HCHO + H_2O$ (Eo = -0.48 V)
$CO_2 + 6H^+ + 4e \rightarrow CH_3OH + H_2O$ (Eo = -0.38 V)
$CO_2 + 8H^+ + 8e \rightarrow CH_4 + 2H_2O$ (Eo = -0.24 V)

These multi-electron reductions require less energy per electron transferred than the direct monoelectronic reduction of CO_2 to CO_2 - (-2.1 vs. SCE). Therefore, it is advantageous to do the multi-electron transfer. Water can be used as a proton source for electrochemical reduction of CO_2. The reduction of aqueous CO_2 to formic acid corresponds to 89% -85% faradaic yield.

Metals with high and moderate hydrogen overvoltage such as Sn, In, Bi, Sb, Zn, Cu, Pb, Ga, Ag, Au, Ni, Fe, W, and Mo and glassy carbon are good candidates for CO_2 reduction. The nature of the electrode material strongly affected product composition as shown below:

- Cd, Hg, In, Sn, Pb – reduction selectively produced formic acid.
- Au, Ag, Zn – selectivity towards CO formation.
- Cu – hydrocarbons (mainly methane and ethane), aldehydes, alcohols produced.
- Al, Ga, Pt, Fe, Ni and Ti have little activity for CO_2 reduction.

For economic viability, high current density is necessary. Carbon dioxide reduction in aqueous solutions is enhanced by elevated CO_2 gas pressure, which provides increased solubility. Note that formic acid produced in water, and oxalic acid/CO in aprotic solvents.

The solubility of CO_2 is much higher in methanol than in water. Electro-reduction of CO_2 in electrolyte containing methanol may be a good option for recovery and conversion of CO_2 released from various processes.

High-temperature electrolysis of CO_2 to CO and oxygen using solid ceramic oxide electrolyte has been investigated [25]. At high temperature, the free energy for this process decreases, since thermal energy becomes a more significant portion of the reaction enthalpy increase. Because the CO generated can be used as fuel, the system can be run as a regenerative fuel cell.

$CO_2 = CO + ½ O_2$

Using a proton conducting solid electrolyte such as $SrZrO_3$ or $CaZrO_3$, CH_4, and CO_2 from flue gases can be fed to the anode of a high temperature fuel cell (with air feed to the cathode) to generate power, as shown below.

$CH_4 + CO_2 = 2CO + 4H+ + 4e$ nickel anode
$O_2 + 4H+ +4e = 2H_2O$ Pt cathode
$CH_4 + CO_2 + O_2 = 2CO + 2H_2O$

Electro-reforming of CH_4 can be carried out by running the above cell as an electrolysis cell (with no air feed to the cathode). H_2 is electrochemically pumped from the anode to the cathode.

$CH_4 + CO_2 = 2CO + 4H+ +4e$ Ni anode
$4H+ + 4e = 2H_2$ Pt cathode
$CH_4 + CO_2 = 2CO +2H_2$

Using the same cell, by feeding CO_2 to the cathode and CH_4 to the anode, power is generated, as shown below:

$2CH_4 = C_2H_6 + 2H^+ + 2e$ Ag anode
$CO_2 + 2H^+ + 2e = CO + H_2O$ Pt cathode

$2CH_4 + CO_2 = C_2H_6 + CO + H_2O$

Photocatalytic Reduction of CO_2

As seen above, the electro-reduction of CO_2 requires a high overpotential. With semi-conductor materials as electrodes, the electrochemical reduction of CO_2 may be achieved at lower bias potentials than in the electrochemical reduction, since light is more energetic than the bandgap of these materials. Some of the overpotential required for CO_2 reduction may be obtained by the photo-potential produced.

Pollutants in the air can be treated in a photo-catalytic reactor in the gas phase or in a liquid phase [31]. The reaction rates for some compounds are orders of magnitude faster in the gas phase than in aqueous media. One problem with gas-phase photocatalysis is the slow degradation in the photocatalyst activity due to depletion of chemisorbed water at the semi-conductor electrode/gas interface. Air-borne pollutants such as ozone and CO_2 have been treated after partitioning into the liquid phase to yield energy rich fuels.

It was first demonstrated that CO_2 could be photoreduced at p-GaP photocathodes. Semiconductor particles of various sizes have been used, with the efficiencies for formic acid formation increasing with particle dimension in the 3.4-5.3 nm range. Catalysts such as crown ethers have been found to assist in the photoelectrochemical reduction of CO_2 on *p*-GaP in lithium carbonate electrolytes.

Some of the design issues for photocatalytic reactor are:

1) Use of suspended or supported photocatalyst
2) Solar or UV light
3) Concentrated or non-concentrated sunlight

The low pressure drop for slurry reactors is an advantage. Slurry reactors have outperformed supported photocatalyst reactors by a factor of 2. UV photocatalysis is preferable if electricity is cheap. Concentrated solar collectors are more compact, while non-concentrated collectors can collect diffused sunlight along with direct radiation.

The efficiency for photosynthetic reduction of CO_2 with H_2O to produce CH_4 and CH_3OH depends on the type of photocatalyst used. When the particle size of TiO_2 decreases, band gap between conduction and valence band becomes larger, making it suitable for CO_2 reduction. At 275K, UV irradiation of powdered TiO_2 catalysts in the presence of a gaseous mixture of CO_2 and H_2O led to evolution of CH_4 into gas phase. The yield increased with UV-irradiation time, while no products were detected in dark conditions.

Heterogeneous photoreduction of CO_2 requires presence of sacrificial hole traps (or electron donors) such as n-propanol, tertiary amines, or EDTA in order to get high yield. These compounds are more valuable than the CO_2 reduction products. However, sulfide or sulfite ions are available as waste products. **In the petrochemical and metallurgical industries and from fossil-burning fuel stations, huge amounts of H_2S or SO_2/SO_3 are released.** The oxidation of these compounds are beneficial environmentally. Hence, use of these as hole scavengers can lead to a high-yield photocatalytic process for CO_2 reduction.

High Energy Radiation Decomposition of CO_2

Irradiation of CO_2 with high energy radiation (gamma, electron, and other fission fragments) decomposes it to CO and O_2. Further irradiation of CO reduces it to C_3O_4, which is a polymer and can be used as a building block for various organic compounds [25]. However, 12,400 MW(t) of nuclear power is estimated for a 1000 MW(e) coal-fired plant. This does not appear to be cost effective or practical. UV generation from a solar power plant can be used for photochemical decomposition of CO_2 to CO and O_2. For a 1000 MW(e) fossil-fuel plant, 180,000 MW(t) is required. Improvement in energy efficiency is needed before this becomes viable. Thermal decomposition of CO_2 to CO and O_2 is not considered viable due to the extremely high temperature (2500C) required.

Synthesis of Chemicals from CO_2

As discussed earlier, several chemicals can be synthesized using CO_2 as a building block. Some examples are given below [25], [30]:

- DMC synthesized from methanol and CO_2 over zirconia catalysts with the addition of H_3PO_4 – DMC can be used as a fuel additive.
- Utilization of CO_2 for direct, selective conversion of methane to ethane and ethylene with Ca-based binary catalysts. Reaction for oxidation with CO_2 –
- Copolymerization of CO_2 with epoxides (carboxylation) such as propylene oxide to yield poly-ether-carbonate, avoiding use of a more toxic compound such as phosgene. Since CO_2 is relatively un-reactive, an effective catalyst is needed. The worldwide demand for polycarbonates is growing worldwide by >10% per year. Using these compounds instead of metals/cement for building materials will mitigate CO_2 release to the atmosphere, since the metal and cement industry is highly energy intensive.
- CO_2 reduction by natural gas using multi-functional catalysts to yield methanol, ethanol, light olefins, gasoline.
- Styrene produced by dehydrogenation of ethylbenzene over iron oxide catalysts in presence of large excess of steam is energetically wasteful. Dehydrogenation of ethylbenzene in excess CO_2 yields styrene with considerably less energy.
- Toluene reforming by CO_2 to benzene, CO, and H_2.
- Decomposition of propane by CO_2 on chromium oxide and ZnO catalyst to yield propene, CO, and water.

Treatment of Miscellaneous Gases

H_2S is produced in large amounts during de-sulfurization of fossil fuels and in coal gasification and liquefaction processes. H_2S gas is frequently released to the atmosphere above the waste water in sewers, where it can accumulate, oxidize to sulfuric acid, and corrode pipes. Electrochemical alternatives to the Claus process for H_2S treatment have been tested with H_2S removal of 99% [32]. Heating H_2S to yield H_2 to be fed to a SOFC is an option. Using a Na-S cell, hydrogen can be generated from H_2S effluent from various process streams such as crude oil or natural gas. The hydrogen generated can be fed to a fuel cell for current generation. Electrical coupling of the fuel cell with the Na-S cell would result in high process efficiency.

Some other examples of treatment of effluents are given below:

- Reduction of NO and SO_2 to N_2O, N_2 etc. Thermodynamically favorable reduction of NO to produce NH_3, HA, and N_2O – electro-generative process can be used to react NO in cell, with H_2 feed, thus behaving like a fuel cell.
- N_2O – H_2 fuel cell using Pd-Pt (1:1) catalyst provides OCV of 1V, and is a viable option for generating power.
- Mixed ioninc and electronic conductors (MIEC) such as perovskites transfer ions and electrons simultaneously perovskite type mixed oxides suitable for this. This can be used to decompose NO_x. Similar schemes have been proposed for H_2S decomposition.
- Electrochemical decomposition of CFCs by metal-supported gas diffusion electrodes.
- NO_x catalyzed partial oxidation of CH_4 to yield syngas, HCHO, CH_3OH.
- Partial reduction of SO_x by CH_4 and waste biomass inside coal-fired boiler.
- Catalytic conversion and combustion of methane.

APPENDIX B: CALCULATION OF METHANE EMISSIONS FROM VARIOUS TECHNIQUES

(details for Table 23)
Source: P. 20 of EIA-2002 1998 data [2] (EMC: emission coefficient)
Estimation of energy consumed in each industry sector

Industry Sector	SIC Code	CO_2 Emissions MMT	CO_2 EMC MMT/Quad Consumed	Quads Energy Consumed	Quads Electricity	Non-Electricity Related Quads
Petroleum	29	320.4	45.26	7.08	0.51	6.57
Chemicals	28	319.2	45.84	6.96	2.25	4.71
Metals	33	251	68.17	3.68	1.49	2.19
Paper	26	118.4	37.4	3.17	1.22	1.95
Food	20	90.4	59.05	1.53	0.71	0.82
Glass	32	82.9	67.76	1.22	0.36	0.86
Other manufacturers		303.6	55.2	5.5	4.02	1.48
Total		1485.9	50.91	29.19	6.54	17.11

Petroleum SIC 29					CH_4 EMF g/GJ*	CH_4 Emitted Gg
	CO_2 Emissions	**% Energy**	**Quads Used**	**GJ Used**		
Fuel						
Petroleum	174.8	58.8	3.86	4074547061	2	7.74
Natural gas	53.2	17.9	1.17	1240079540	5	5.58
Coal	0	0.0	0	0	10	0
Other	69.5	23.4	1.54	1620028723	30.0	43.74

Chemicals SIC 28					CH_4 EMF g/GJ*	Gg CH_4
	CO_2 Emissions	**% Energy**	**Quads Used**	**GJ Used**		
Fuel						
Petroleum	56.5	26.2	1.23	1300338133	2	2.47
Natural gas	127.7	59.1	2.79	2938994328	5	13.22
Coal	26.9	12.5	0.58	619099040.1	10	5.88
Other	4.9	2.3	0.11	112772687.6	30.0	3.04
	216	100.0	4.71	4971204188		**24.62**

Metals SIC 33					**CH_4 EMF g/GJ***	**Gg CH_4**
	CO_2 Emissions	**% Energy**	**Quads Used**	**GJ Used**		
Fuel						
Petroleum	3.6	2.4	0.053	55713657	2	0.11
Natural gas	47.9	32.1	0.70	741301159	5	3.34
Coal	94.3	63.2	1.38	1459388294	10	13.86
Other	3.4	2.3	0.05	52618454	30.0	1.42
	149.2	100.0	2.188646032	2309021564		**18.73**

Paper SIC 26					**CH_4 EMF g/GJ***	**Gg CH_4**
	CO_2 Emissions	**% Energy**	**Quads Used**	**GJ Used**		
Fuel						
Petroleum	15.1	20.7	0.40	425949197.9	2	0.81
Natural gas	31.1	42.7	0.93	986408937.3	5	4.44
Coal	25.8	35.4	0.78	818307092.6	10	7.77
Other	0.8	1.1	0.024	25373863.34	30.0	0.69
	72.8	100.0	1.95	2053582888		**13.71**

Food SIC 20					**CH_4 EMF g/GJ***	**Gg CH_4**
	CO_2 Emissions	**% Energy**	**Quads Used**	**GJ Used**		
Fuel						
Petroleum	3	6.1	0.05	52945003	2	0.10
Natural gas	31.8	64.6	0.53	561217034	5	2.52
Coal	13.6	27.6	0.23	240017348	10	2.28
Other	0.8	1.6	0.01	14118668	30.0	0.38
	49.2	100.0	0.82	868298053		**5.29**

Glass SIC 32					**CH_4 EMF g/GJ***	**Gg CH_4**
	CO_2 Emissions	**% Energy**	**Quads Used**	**GJ Used**		
Fuel						
Petroleum	6.7	11.5	0.10	104316706	2	0.20
Natural gas	23.4	40.0	0.35	364329988	5	1.64
Coal	27.7	47.4	0.41	431279515	10	4.10
Other	0.7	1.2	0.01	10898760	30.0	0.29
	58.5	100.0	0.86	910824970		**6.23**

Other Manufacturing					**CH_4 EMF g/GJ***	**Gg CH_4**
	CO_2 Emissions	**% Energy**	**Quads Used**	**GJ Used**		
Fuel						
Petroleum	10.4	12.7	0.19	199011704.3	2	0.38
Natural gas	59.7	73.2	1.08	1142403726	5	5.14
Coal	10	12.3	0.18	191357408	10	1.82
Other	1.5	1.8	0.03	28703611.2	30.0	0.77
	81.6	100.0	1.48	1561476449		**8.11**

Summary Table of Methane Emissions Gg for Year 1998

Industry	**SIC Code**	**Fuel**				
		Petroleum	**Natural Gas**	**Coal**	**Other**	**Total**
Petroleum	29	7.74	5.58	0	43.74	57.06
Chemicals	28	2.47	13.23	5.88	3.04	24.62
Metals	33	0.11	3.34	13.86	1.42	18.73
Paper	26	0.81	4.44	7.77	0.69	13.71
Food	20	0.10	2.53	2.28	0.38	5.29
Glass	32	0.20	1.64	4.10	0.29	6.23
Other manufacturing	no code	0.38	5.14	1.82	0.77	8.11
		11.80	35.89	35.71	50.34	**133.75**

The above results were obtained from using CO_2 emission coefficient to determine energy consumed by each industry. The CO_2 emission from electricity generation within each SIC code was available. This value was used to estimate the energy associated with electricity generation. The energy associated with electricity generation was subtracted from the total energy consumed within each sector. The CO_2 emission data for each fuel type within each industry was used to calculate the energy related with that emission. This could have been done using the CO_2 emissions coefficient for the particular industry. However, this emission coefficient is a function of fuel type used. In order to keep things simple, the energy associated with each fuel type within an industry was assumed to be proportional to CO_2 generation.

*Source: Lisa Hanle, U.S. Environmental Protection Agency, Washington, D.C.

The values for 1990, 1995, and 2001 were calculated using CO_2 emission data for these years (Table 8 of [2]), assuming an average CO_2 emission coefficient to calculate the fuel consumption, and then using the CH_4 emission coefficient to determine CH_4 emissions. The average CO_2 emission coefficient was calculated by weighting the CO_2 emission coefficient for each sector with the CO_2 emission data for each sector in the Year 1998 (the only year for which this data was available) from p. 20 of the same report. As a check, the CH_4 emissions for year 1998 was 100 GJ, while the result using actual data for year 1998 was 133 GJ. This discrepancy is due to the errors associated with the estimation of the CO_2 emission coefficient.

Estimation of energy consumed in each industry sector. (p. 29, Table 8 of [2]).

Year 1990

Industry	CO_2 Emissions MMT	CO_2 EMF MMT/Quad	Quads	GJ Used	CH_4 EMF g/GJ	CH_4 Emitted g	CH_4 Emitted Gg
Petroleum	380.3	52.75	7.21	7605497277	2	1.445E+10	14.45
Natural gas	432.9	52.75	8.21	8657427744	5	4.112E+10	41.12
Coal	249.5	52.75	4.73	4989670183	10	4.740E+10	47.40
Total	1062.7	52.75	20.14	21252595203			102.98
			20.14				

Year 1995

Industry	CO_2 Emissions MMT	CO_2 EMF MMT/Quad	Quads	GJ Used	CH_4 Emission Factor g/GJ	CH_4 Emitted g	CH_4 Emitted Gg
Petroleum	365.5	52.75	6.93	7309516841	2	1.389E+10	13.89
Natural gas	490.5	52.75	9.30	9809351602	5	4.659E+10	46.59
Coal	224.3	52.75	4.25	4485703495	10	4.261E+10	42.61
Total	1080.3	52.75		21604571938			103.10

Year 1998

Industry	CO_2 Emissions MMT	CO_2 EMF MMT/Quad	Quads	GJ Used	CH_4 Emission Factor g/GJ	CH_4 Emitted g	CH_4 Emitted Gg
Petroleum	387	52.75	7.34	7739488420	2	1.471E+10	14.71
Natural gas	495	52.75	9.38	9899345653	5	4.702E+10	47.02
Coal	201.2	52.75	3.81	4023734031	10	3.823E+10	38.23
Total	1083.2	52.75		21662568104			99.95
Adjust emissions factor such that CH_4 emitted = value calculated from p. 21 data for 1998.							
Use this adjusted emissions factor for years 1990, 1995 and 2001 for p. 29, Table 8.							

Year 2001

Industry	CO_2 Emissions MMT	CO_2 EMF MMT/Quad	Quads	GJ Used	CH_4 Emission Factor g/GJ	CH_4 Emitted g	CH_4 Emitted Gg
Petroleum	410	52.75349	7.771998	8199458016	2	1.5579E+10	15.57897023
Natural gas	441.5	52.75349	8.369115	8829416375	5	4.194E+10	41.93972778
Coal	192.7	52.75349	3.652839	3853745267	10	3.6611E+10	36.61058004
Total	1044.2	52.75349		20882619659			94.12927805

APPENDIX C: CALCULATION OF EMISSIONS FROM LANDFILLS

3.796E+11	lbs/year	of waste in	Landfill/year	Source [12]
=1.725E+11	kg/year			
=172545454.5	tons/y			
=172.54	Mt/y			

50% CO_2, 50% CH_4 Landfill gas composition

Calorific value 18000 kJ/Nm3

0.35 N m3/kg of urban solid waste [12]

Hence amount of biogas evolved =	6.022E+10	Nm3		
Value from Table 19 of [2] (bottom of this page) =	3.60E+10	Nm3	Use this value, since EIA values are expected to be closer to actual emission data	
Energy content = Calorific value * Nm3/year	=6.47E+14	kJ		
	=647	PJ	179859	GWh
Amount being captured	152	PJ		
Potential for capture	495	PJ		

Assume the gases are released in one year (bioreactor)

Hence annual rate of gas evolution =	36E9	Nm3/year
There were 1858 landfills in the US in 2001		
Gas generation from each landfill	19E6	Nm3/year
Calorific value of gas generated/year	3.5E+11	kJ/year
Power	11	MW

Assume net efficiency of 45% for fuel cell

Hence generated power	**5.0**	MW
Thermal power to be captured = 4.32-1.95 =	**6.1**	MW

Hence large fuel cells are needed in order to use the evolved biogas as fuel.

The largest PAFC is 200 kW. It appears this is more suitable for MCFC or SOFC technology

The CO_2 captured could be used for synthesis, photocatalytic energy generation, and CO_2 reforming of methane

EIA / Voluntary reporting of GHGs 2002 [2]

Landfill methane emission	6.90E+06	tons
Methane recovered	3.0E+06	tons
Methane flared	2.87E6	
Total landfill methane	1.28E+07	tons
Methane density	0.71	kg/m3
Volume of methane	1.8E10	Nm3
Total biogas volume	**3.6E10**	Nm3

Use this number, since this is probably closer to actual methane evolved.

APPENDIX D: TECHNOLOGY SOLUTIONS FOR ENERGY RECOVERY

Technology Solutions to Minimize Industry Energy Usage Incorporating Waste Heat and Effluent Utilization

Introduction

This analysis describes the leading technologies for utilizing waste heat and gas emission from U.S. industry. The first section, Cross-Cutting Technologies, applies to all industries; the following sections present several industry-specific opportunities.

1.0 Cross-Cutting Technologies

A. Thermoacoustic Air Conditioning

Thermoacoustic air conditioning is a rather new cooling technology. The process involves the ingestion of waste heat via forced convection or electricity (which is much less efficient). Cooling is provided through conversion of the waste heat to sound waves. The process is environmentally benign, as it uses inert gases. This technology is reversible in that it can be used to heat as well as cool.

Thermoacoustic cooling systems use high-amplitude standing sound waves to pump heat through inert gasses. No toxic, ozone-depleting, or global warming gases are used as working fluids. The thermoacoustic heat transfer process is relatively simple, requiring few moving parts, no sliding seals, and minimal lubrication. At the present time, the efficiency thermoacoustic refrigerators is 20-30% lower than their vapor compression counterparts. Current thermoacoustic refrigerators are inefficient due to technical immaturity. With time and research, improvements in heat exchangers and other sub-systems should narrow the gap. The efficiency in many applications, such as thermoacoustic refrigerators, will improve because these applications can handle “proportional control.” That is, the thermoacoustic refrigerator continually adjusts for varying load conditions. This could lead to higher efficiencies than conventional vapor compression chillers that are only capable of binary control. Proportional control avoids losses due to start-up surges in conventional compressors and reduces the inefficiencies in the heat exchangers, since the proportional systems can operate over smaller temperature gaps between the coolant fluid and the heat load.

The heat transfer process for an electrically driven thermoacoustic refrigerator starts when a prime mover (speaker) sets up an acoustic standing wave in a resonator. The working fluid (inert gas) begins vibrating in the direction of the resonator axis. The sound wave produces pressure, which causes the gas molecules to both move and change temperature. A porous solid material called a “stack” uses this adiabatic temperature difference to move heat, creating a heat-pumping action. The length of the stack puts various molecules of gas in series, shuttling heat from one side to another. Heat exchangers at either end of the stack complete the process. The cold-side heat exchanger circulates fresh water producing chilled water for either direct cooling of electronic equipment or air conditioning. The hot-side exchanger pulls the heat out of the stack, which can be dumped to the other appropriate heat sinks or used for heating other parts of the system.

A thermoacoustic engine can be used to generate sound from heat. By combining two acoustic engines, it is possible to generate cooling from waste heat. Gas turbine exhaust and/or waste heat could power this heat-driven thermoacoustic chiller and then be used to provide supplemental cooling wherever it is needed.

B. Thermoelectric Devices

The thermoelectric effect operates by the direct application of electrical energy to create a temperature difference across a thermoelectric couple (see figure below). This phenomenon was discovered by Peltier in 1834 and is sometimes referred to as Peltier cooling. The search for better thermoelectric materials continues today. Thermoelectric performance is determined by the material properties figure of merit, a dimensionless number, defined by the equation:

$$ZT = \frac{\alpha^2 T}{\mathrm{K}\rho} \qquad (1)$$

where: α is the Seebeck coefficient, ρ is electrical resistivity, T is absolute temperature, and *K* is thermal conductivity.

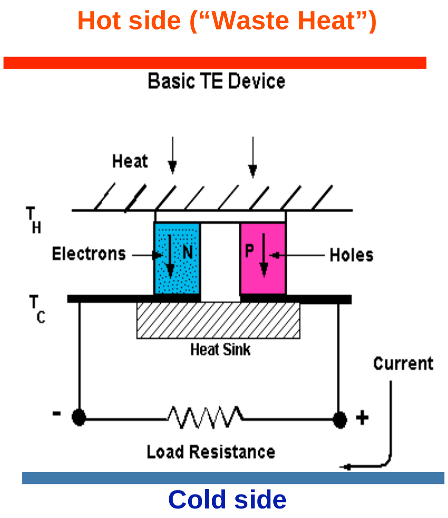

Figure D.1: Thermoelectric device principle.

Many individual thermoelectric couples can be packaged together into a module arranged so that one side becomes cold and the other becomes hot when a current is applied. The thermoelectric module is, in essence, a solid-state cheat pump with no moving parts. The advantages of such a cooling system are very low noise, low vibration, and adaptability to many configurations. The amount and direction of the current applied across the thermo electric junction control the direction and the magnitude of cooling.

Current air conditioning modules use Bismuth Telluride as their thermoelectric material. The efficiency of these systems have a COP up to 1.2. For material quality to improve (i.e., larger Z), it is generally agreed that the thermal conductivity (*K*) and electrical resistivity (ρ) of semiconductor materials must decrease. Generally, when thermal conductivity is lowered, the electrical resistivity of a material rises. It has proven very difficult to lower both *K* and ρ at the same time. The K/ρ relationship has been the principal limiting factor toward higher conversion efficiency in both thermoelectric devices.

Recent developments in advanced thermoelectric material research could lead to much higher figure of merit values, which correspond to efficiencies approaching those of current vapor compression air conditioning systems. Developments in Quantum-Dot Superlattice (QDSL) thermoelectric material indicate that with further optimization, QDSL TE materials could propel TE cooling systems into mainstream air conditioner applications.

Thermoelectric modules can also be used to produce DC current from a waste heat source. Presently, efficiencies of power generating systems are as high as 14%. Better TE materials are required to go much beyond this performance level. In addition, it may be possible to combine decentralized cooling and waste heat electrical generation. The thermoelectric materials used for power generation are optimized to work at higher operating temperatures than those used for cooling systems.

Thermoelectric power generators are configured as shown in Figure D.2. The heat source provides the high temperature and the heat that flows through the thermoelectric converter to the heat sink. The heat sink is maintained at a temperature below that of the source. The temperature differential, $T=T_1 - T_0$, across the converter produces direct-current electrical power to a load R (ohms), having a terminal voltage *V* (volts), and provides a current *I* (amperes). There is no intermediate conversion process. For this reason, thermoelectric power generation is classified as direct power conversion. The amount of electrical power generated, W (watts), is I^2R_L, or alternatively *VI*. The non-thermoelectric quantities must also be identified before a thermoelectric device can be appropriately described. They are Joule heating and thermal conduction. Although a thermoelectric device is made up of many *p*-type and *n*-type semiconductor legs, its behavior can be discussed using only one couple.

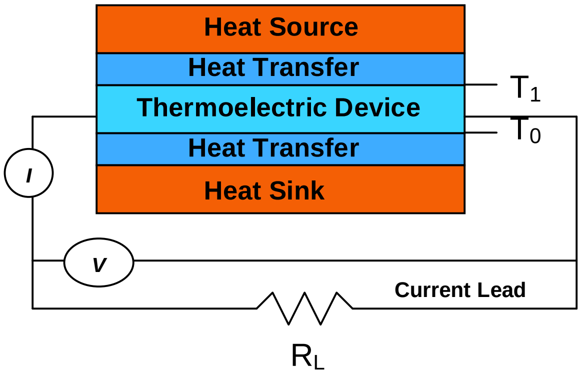

Figure D.2: Thermoelectric power generator configuration.

Figure D.3 shows a p-type and n-type semiconductor leg coupled to a heat source, heat sink, and an electrical power consuming load. The leg geometry affects operation. The leg length is L and the base area a. Under the condition that p- and n-type semicon ductors are similar in their measured properties, average value parameters can be used to analytically describe the couple. The heat flow (H) through the couple at T_1 is given by:

$$H = 2\alpha IT - I^2\rho\left(\frac{L}{a}\right) + 2K\left(\frac{a}{L}\right)\Delta T \quad (2)$$

where temperature is in kelvin, r is the electrical resistivity in ohm-cm, *K* is the thermal conductivity in watts per centimeter kelvin, *a* is the Seebeck coefficient in microvolts per Kelvin, and L/*a* is in centimeters^{-1}. In this equation, the first term results from the reversible Peltier effect that generates heat at the top junction. The second term reflects loss due to irreversible Joule heating (one half of the total amount generated). The last term is the irreversible heat loss due to thermal conductivity in each leg.

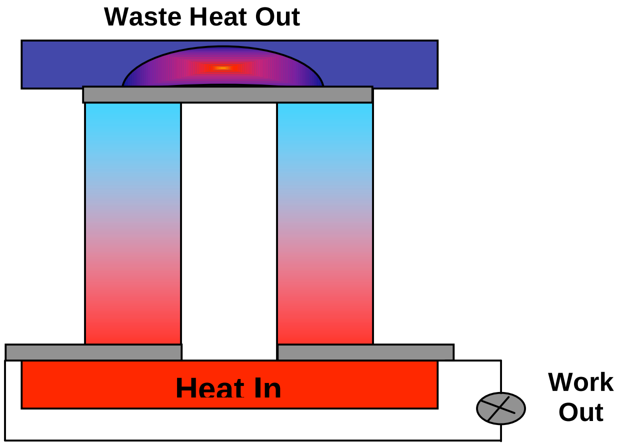

Figure D.3: A *p*-type and *n*-type semiconductor leg coupled to a heat source, heat sink, and an electrical power-consuming load.

In a thermoelectric power generator, a temperature differential between the upper and lower surfaces of two legs of the device generates power. If a power-consuming load is not attached to the generator (open-circuited), the applied heat source (*H*) results in a temperature differential (T) of some value dictated only by the thermal conductivity of the *p*- and *n*-type semiconductor legs. Since no current would flow in the thermoelectric device, no power would be generated. Because of the Seebeck effect, however, a voltage would be present at the output terminals, just like in an unconnected battery. When a load is attached, current will flow through the load. The Seebeck voltage $V_\alpha=\alpha\Delta T$ is divided between two terms: the internal device voltage drop IR_{int} due to the internal resistance $R_{int} = 2\rho(L/a)$ (for the couple), and the external voltage drop IRL. It is the Seebeck voltage and these two resistances that dictate the flow of current (and the generated output electrical power) given by:

$$I = \frac{2\alpha\Delta T}{\left(R_{\text{int}} + R_L\right)} \tag{3}$$

This same current pumps heat within the thermoelectric device due to the Peltier effect, which lowers the initial temperature differential when the current is zero. Part of the heat energy, H, through the Seebeck-generated current, is converted to Joule heating within the legs of the thermoelectric device. The efficiency, *n*, for a power generator is the output power, I^2R_L, divided by *H*. It can be shown that

$$\varepsilon_{\max} = \left(\frac{T_1 - T_0}{T_1}\right)\left(\frac{\sqrt{1+Z\overline{T}} - 1}{\sqrt{1+Z\overline{T}} + \frac{T_0}{T_1}}\right) \tag{4}$$

where the first term is the Carnot efficiency. The second term contains T, which is the average temperature of the leg. The Z is the figure of merit of the semiconductor legs; it represents a “quality factor” of the material to perform as a thermoelectric device.

Recent Developments in Thermoelectric Materials

Thermoelectric materials are of interest for application as heat pumps and power generators. The performance of thermoelectric devices is quantified by a figure of merit, ZT, as previously described. A material with a figure of merit of around unity was first reported over four decades ago, but since then – despite investigation of various approaches – there has been only modest progress in finding materials with enhanced ZT values at room temperature. In 2001, Rama Venkatasubramanian and co-workers at the Research Triangle Institute in North Carolina reported that thin-film thermoelectric materials demonstrate a significant enhancement of ZT at 300 K, compared to bulk Bi_2Te_3 alloys. This amounts to a maximum observed factor of 2.4 for p-type Bi_2Te_3/Sb_2Te_3 superlattice devices. The enhancement is achieved by controlling the transport of phonons and electrons in the superlattices. High atomic weight reduces the speed of sound in the material, and thereby decreases the thermal conductivity. Although it is possible in principle to develop bulk semiconductors with $ZT > 3$, there are no candidate materials on the horizon. Preliminary devices exhibit significant cooling (32 K at around RT) and the potential to pump a heat flux of up to 700 W/cm^2; the localized cooling and heating occurs some 23,000 times faster than in bulk devices.

Most commercial thermoelectric devices are for cooling. Venkatasubramanian’s group has found a way to greatly increase the amount and speed of heating or cooling using superlattices: stacks of very thin films of two alternating superconducting materials. It is reported that the material properties, as measured by ZT, are 2.5 times better than the current state of the art, have been verified by more than one method, and are useful at room temperature. Previously, it had been widely assumed that a thermoelectric “barrier” existed with a ZT = 1.

Another encouraging development has been by Hsu et al., in a report describing $AgPb_mSbTe_{2+m}$ with a ZT ~2 at 800 K for $m = 18$. Although the temperature may be too high for refrigeration, it is appropriate for power generation. What is interesting, however, is the discovery that this material contains regions 2 to 4 nm in size that are rich in Ag-Sb and are epitaxially embedded in a matrix that is depleted of Ag and Sb. Presumably, the electronic band structure and vibrational properties of these nano-regions are different from those of the surrounding material, suggesting quantum confinement. Several questions remain: Are there quantum effects in these nanostructures and, if so, do they play any role in raising the *ZT* of the material? Is the acoustic impedance of the nanodots very different from that of the matrix and, if so, do they scatter acoustic phonons and thereby reduce thermal conductivity? How does the structure and size depend on *m*, and are there ways to maximize *ZT*? What are the thermoelectric effects and efficiencies of other metal-Group V-VI elemental compounds?

Seen historically, this is a huge jump over an extremely short period (see Figure D.4). What is the underlying science? In semiconductors, electrons and holes carry charge, whereas lattice vibrations or phonons dominate heat transport. Electrons (or holes) and phonons have two length scales associated with their transport–wavelength, λ, and mean free path, ℓ. By nanostructuring semiconductors with sizes comparable to λsharp edges, peaks in their electronic density of states are produced whose location in energy space depends on size. By matching the peak locations and shape with respect to the Fermi energy, one can tailor the thermopower *S*. Furthermore, such quantum confinement increases electronic mobility, which could lead to high values of σ. Hence, quantum confinement allows manipulation of $S^2\sigma$ that is otherwise difficult to achieve in bulk materials.

It is entirely possible, though, that the increase of *ZT* may be less dependent on quantum confinement of electrons and holes, and more on phonon dynamics and transport. For example, if the size of a semiconductor is smaller than the mean free path of phonons and larger than that of electrons or holes, one can reduce thermal conductivity by boundary scattering without affecting electrical transport. Although charge transport in thermoelectricity is almost monoenergetic (energy levels within a few *kT* around the Fermi energy), heat transport by phonons is broadband over the Brillouin zone. Many bulk thermoelectric materials are alloys because alloy scattering of the short-wavelength acoustic phonons suppresses thermal conductivity without substantially altering $S^2\sigma$. However, the mid- to long-wavelength phonons remain largely unaffected and conduct heat in alloys.

Can researchers beat the alloy limit? It is possible that embedded nanostructures in semiconductor alloys could scatter the mid- to long-wavelength phonons as well because of the similarity in sizes, and thereby reduce the thermal conductivity below the alloy limit. Given all these possibilities, it is unclear which effect can be exploited most readily to increase *ZT*. What is clear, though, is that if researchers must increase *ZT* beyond 3, it is imperative that they understand how charge and heat transport occur in semiconductor nanostructures.

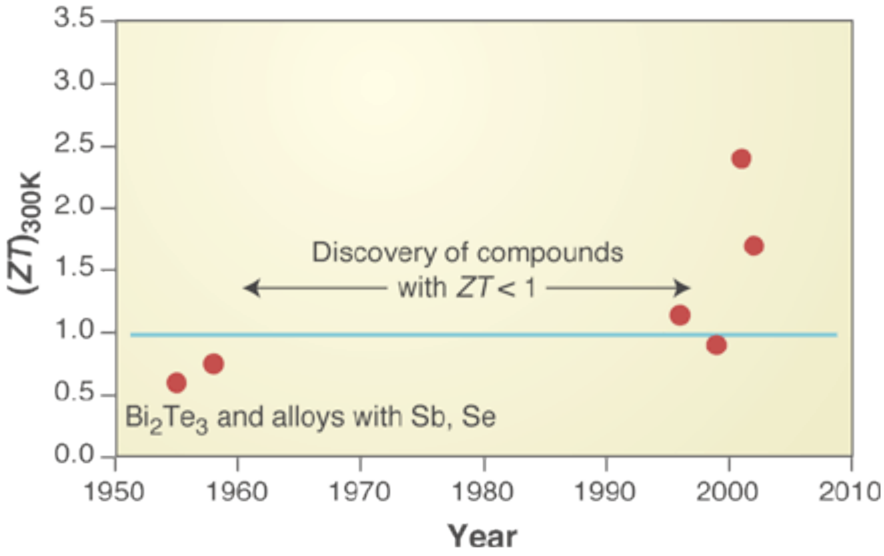

Figure D.4: History of thermoelectric figure of merit improvement, ZT, at 300 K. Since the discovery of the thermoelectric properties of Bi_2Te_3 and its alloys with Sb and Se in the 1950s, no bulk material with $(ZT)_{300K} > 1$ has been discovered. Recent studies in nanostructured thermoelectric materials have led to a sudden increase in $(ZT)_{300K} > 1$. Source: Science, Vol 303, Issue 5659, 777-778, 6 February 2004.

Potential commercial markets for thermoelectric devices include:

- Power generation from high and low temperature waste sources.
- Replace conventional cooling and refrigeration systems.
- Cooling for High temperature semiconductors, microprocessors, and multi-chip modules.
- Power for hybrid electric vehicles.
- Alternator replacement.
- Self-powered engine pre-heaters.
- Self-powered gas furnaces and heaters.
- Remote power sources.

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C. Thermo Photo Voltaic (TPV) Generator

The TPV generator is composed of three primary sections: a thermal radiator, a thermal radiation filter, and a semiconductor diode. In many instances, the thermal radiation filter is incorporated into a semiconductor diode, called a TPV cell. Photovoltaic (PV) cells face an emitter element and convert radiation from the emitter element into electricity. Spectral filters are intended to pass only radiation at wavelengths that can be converted to electricity by PV cells and reflect the remainder back to the central emitter where it is reabsorbed (Figure D.5).

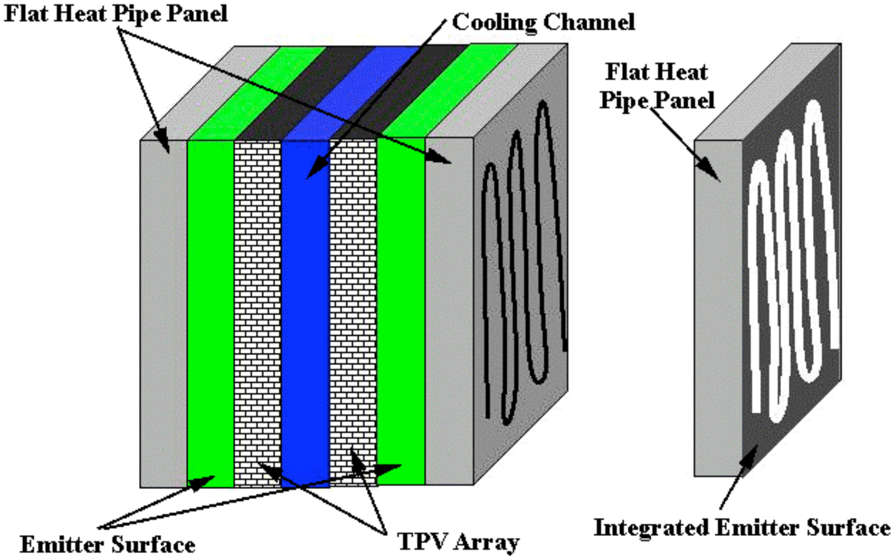

Figure D.5: Schematic of symmetrical TPV conversion system. On the left, a heat pipe radiator is located on the outside of the stack with a selective emitter inside powering TPV cells cooled by a fluid channel. On the right, a flat heat pipe with an integrated emitter surface.

Photovoltaic cells work most efficiently when they absorb only radiation (photons) with energies slightly above the bandgap energy of the cell. Photons with energies below the bandgap energy of the cell are not absorbed and do not create an electron-hole pair with the useful electrical current a PV cell can deliver to a load proportional to the number of electron-hole pairs. Photons with energies greater than the bandgap energy can be absorbed but create only one electron-hole pair regardless of the excess photon energy. Phonons (lattice vibrations) are emitted as the electron rapidly relaxes back to the conduction band edge and the hole relaxes back to the valance band edge in a process referred to thermalization. After thermalization, the electron and hole are separated by only the bandgap energy of the p-n junction and any excess energy has been lost as heat in the semiconductor. This effect alone limits the maximum achievable to approximately 44% for single junction PV cells (Coutts, T.J. et al., 1998).

A theoretical blackbody radiation spectrum at 1250 K can be converted into useful electrical energy by an infrared-responding GaSb PV cell with bandgap energy of 0.73 eV (Figure D.6). The convertible portion of the spectrum for a Si cell with bandgap energy 1.12 eV is included for comparison. Power radiated is proportional to T4 by Stefan-Boltzmann Law (Halliday et al., 1978) for an identical body that explains why the area under the blackbody curves (total energy) increases rapidly for small temperature increases.

$$P = \sigma A T^4 \tag{5}$$

P is the power radiated, σ is Stefan's constant (5.67 e10^{-8} W$m^{-2}K^{-4}$), A is the surface area (m^2), and T the temperature of the body (K). Stefan's law illustrates the magnitude that temperature has on power generation and accentuates the scientific challenge in developing materials for energy conversion at relatively low exposure temperatures. An emitter with a "blackbody" emissive power spectrum radiates the theoretical maximum amount of power at a specific wavelength, P (λ, T), at a given temperature T as described by Planck's Law (Kreith et al., 1980):

$$P = \frac{2\pi h c^2 \lambda^{-5}}{\exp(hc/\lambda kT - 1)} \tag{6}$$

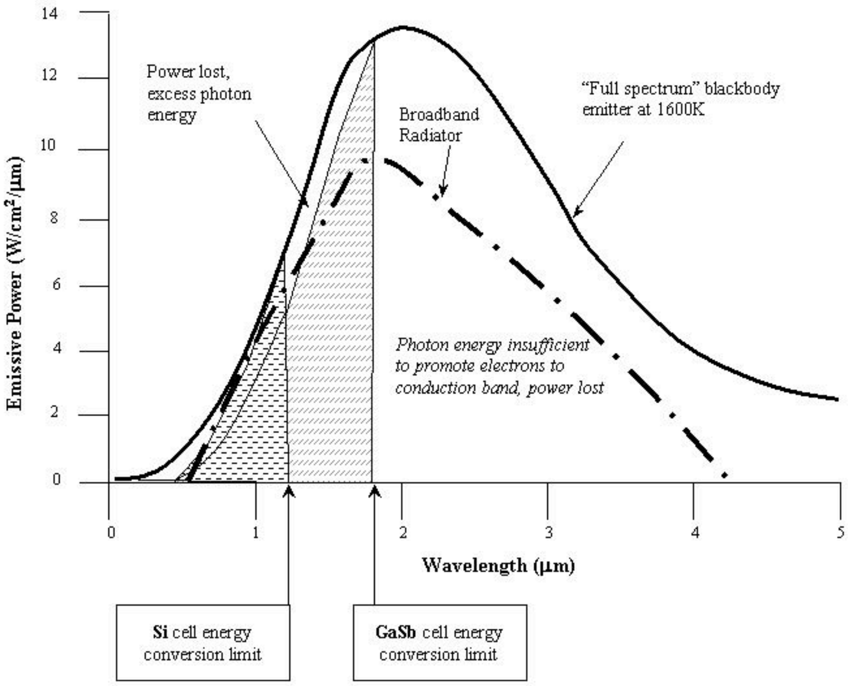

Figure D.6: Emissive power spectrum for 1600K-blackbody emitter with shaded portion where energy conversion is possible with Si and GaSb photovoltaic cells. For comparison, the emissive power spectrum for a broadband radiator is included. Note that beyond 1.7 µm, photon energy is insufficient to promote electrons to the conduction band; thus, no power conversion takes place (Coutts, T.J. et al., 1998).

One detriment to TPV conversion stems from the radiating source to PV cell proximity dictating performance. Conversion efficiency is minimized due to energy losses resulting from convection and conduction of heat from the thermal generator. Broad spectrum or near-blackbody type emitters, such as silicon carbide (SiC), are used in most conventional TPV systems. The problem of spectral control is a challenging design requirement. SiC is an attractive material for high-temperature TPV emitter applications due to its high thermal shock resistance and an ability to resist decomposition in air atmospheres up to approximately 1600ºC (Ferguson, L.G. et al. 2001).

Broad-spectrum emitters can work efficiently with PV cells if infrared filters can be devised to effectively reflect nearly all of the non-convertible radiation back to the emitter. The primary reason no TPV generator with efficiency over 10% exists is due the lack of practical infrared filters that can perform under the traditional TPV generator environment. Low conversion efficiencies stem from the decreased emitter temperatures that result when non-convertible radiation is not contained and recycled by the spectral filters. Inadequate filters can also lead to extremely high heat loads on PV cells, filters, insulating materials, and other components.

Selective Emitter Development

Spectrally selective emitters take advantage of the ability of certain rare earth oxides, including erbium oxide and ytterbium oxide, to radiate in a relatively predetermined wavelength range when thermally excited at a specific temperature range. Early attempts at rare earth oxide selective emitters were met with excessive radiation in non-convertible wavelengths as well as mechanical failure due to thermal stress. Subsequent efforts to produce rare-earth oxide high-temperature emitters in small diameter fibrous form were met with higher thermal tolerance but were difficult to handle and had the inherent disadvantage of exhibiting only narrow "line-type" emissions at convertible wavelengths where emissive power should be maximized. Efforts to increase emissions utilizing multi-dopant selective emitters with a mixture of erbia and holmia rare-earth oxides produce high emittance peaks at 1.55 µm for erbia and 2.01 µm for holmia, which is outside the emission range for low-cost GaSb PV cells and more applicable to complex ternary InGaAs or quaternary GaInAsSb PV cells.

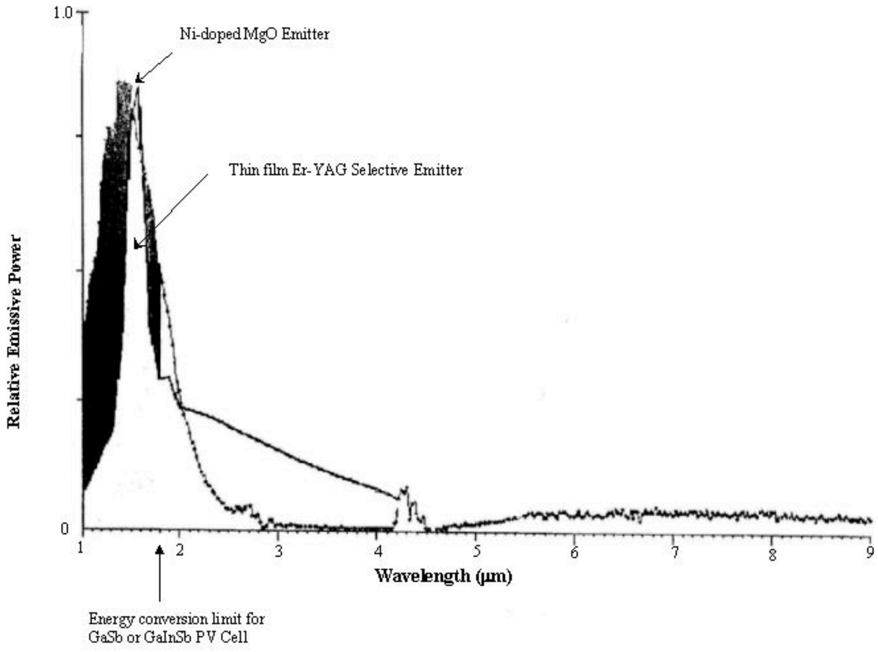

Figure D.7: Relative emissive power as a function of wavelength with Ni-doped MgO and Er-YAG emitter effective regions. Note the energy conversion limit for GaSb and GaInSb photovoltaics are at approximately 1.8 μm.

Charge Transfer and Bandgap Theory

Multiple theories have been advanced to explain interactions between matter and radiation and the resulting spectral behavior. Ionic models, energy band models, crystal field and ligand field theories, and molecular orbital theory are but a few. No single theory adequately describes the entire radiation spectrum of transition-metal doped selective emitters. Figure D.8 is a qualitative diagram of the high-temperature emittance of a selective ceramic oxide emitter with a small percentage (~1 at %) of Co or Ni transition-metal impurities. Each component of the spectrum is identified with a dominant underlying radiation mechanism.

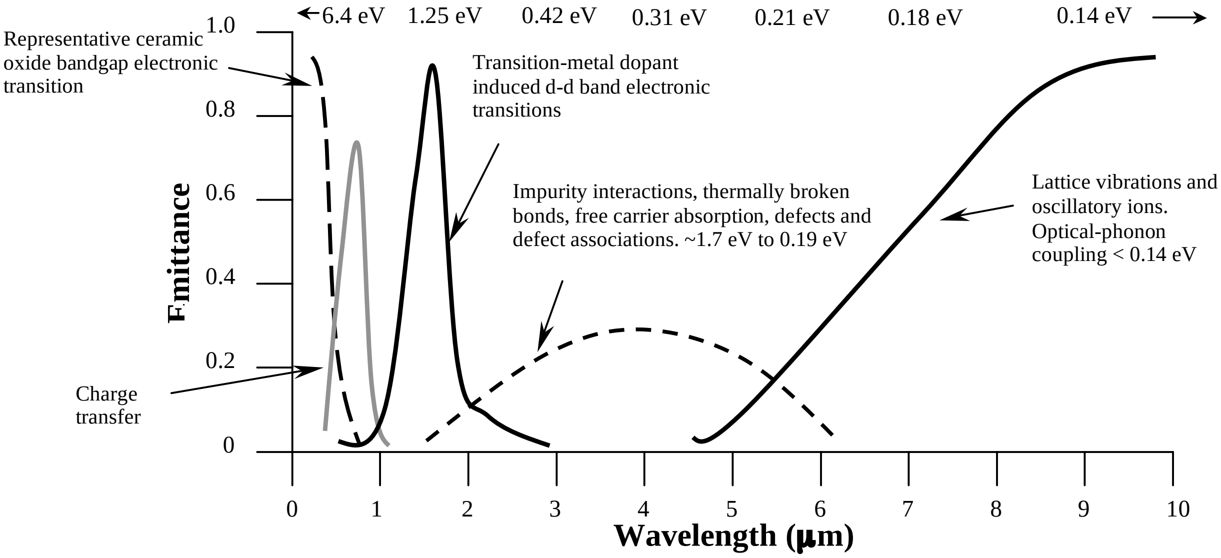

Figure D.8: Emittance for a generalized "matched emitter" showing spectral components with probable radiation mechanisms.

A highly stoichiometric, ionic solid such as pure NaCl may be classified as a closed-shell insulator because each Na atom donated one electron from its outer 3s orbital to create a closed $2p^6$ shell around the Cl atom. Similarly, for MgO each Mg atom donates 2 electrons from its outer $3s^2$ orbital to create a $2p^6$ shell around the O atom. An energy bandgap is created between a filled band having bonding orbitals with predominately 2p character, and an empty "metal cation" band for anti-bonding orbitals. It is typical of highly stoichiometric oxides where the cation has a fixed valence (1) that the defect concentration is low and that (2) intrinsic atomic defects are relatively insignificant (until temperatures approach the material melting point) and have little influence on the radiative properties of the host ceramic oxide emitter material.

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D. Microturbines

Microturbines are high-speed devices, usually rotating over 40,000 rpm. They come in several physical configurations, which represent tradeoffs in cost and performance. The engine can be a single-shaft machine, which reduces cost, or a split-shaft machine, which is more complex but allows for direct drive of a generator, thus avoiding the need of an inverter. Another design consideration is choice of bearings. Air bearings, which have emerged as a technology of choice, reduce the cost of the microturbine, but oil bearings offer longer life and are more rugged.

The simple-cycle microturbine is less efficient than a recuperated and/or intercooled machine, and is also less expensive. Simple cycle microturbines are projected to have an efficiency of 26-30%; but, with heat recovery, the efficiency could approach 40%. When used in a cogeneration or combined heat and power (CHP) system, the fuel conversion efficiency can approach 80%.

Microturbines could play a large roll in manufacturing because they can be deployed to generate a portion of a plant’s electricity needs onsite, reduce demand during peak periods, and support premium power applications (e.g., microelectronics manufacturing). Microturbines are even more efficient when operated as part of a CHP system, which can meet some of the facility’s thermal requirements as well. However, microturbines will have to compete with reciprocating engines and fuel cells to gain a stronghold in this market.

One of the promises of microturbines is greater reliability and a lower operating cost than reciprocating engines. However, field experience with microturbines has been limited, and because the technology is evolving rapidly, reliable information about performance is not readily available. Another area in need of improvement is environmental emissions, in particular NO_x. While manufacturers have raised hopes that microturbine emissions would be much lower than emissions from other technologies, current rates are similar to those for low-emissions gas engines.

Current projections for operating costs are for $90 per kWyear, falling to $75 by 2020. These compare favorably with reciprocating engines today and appear even more attractive in the future. Realizing these performance goals require further product development with deployment of advanced materials and operating experience.

E. Thermoionics

Thermionics or Direct Energy Conversion is the process by which energy is converted from one form of energy to another form without the benefit of a prime mover. A study conducted at MIT in the mid-1990's involved an investigation of using thermionics to eliminate the prime mover and enable a fully electric drive system. While this is the main function of thermionics, other applications may include energy storage and cooling. One of the primary drawbacks of thermionics at present is the fact that it is only effective at input temperature of 1000ºC or above. At this temperature level, it could only be used at nuclear power plants or in the space program. The capability of this technology needs to be developed to fulfill requirements of advanced power electronics or waste heat conversion before this concept may be applied.

Solid state thermionic devices could, however, capture waste heat energy and convert it into electricity without creating additional pollution. The technology also can be reversed to provide an efficient means of cooling. Current thermoelectric technology can convert only 10 percent of the heat it absorbs. However, new thermionic technology is capable of 35% conversion efficiency of the Carnot limit. MIT, with the Salt Lake City-based company ENECO, has developed a semiconductor technology that efficiently and affordably converts heat into electricity using solid state thermionics, a combination of thermoelectrics and thermionics. Recent interest in solid state thermionics has spurred ENECO scientists to combine the two sciences to produce a single, solid state device that exhibits the best features of both technologies, namely higher conversion efficiencies at lower operating temperatures than previously achieved by either technology. Utilizing InSb and HgCdTe based materials, recent technology advances have demonstrated high heat-to-electricity conversion from 100ºC to 300ºC, temperatures typical to waste heat. What is not known at the present time is the magnitude of the technology's ability. Significantly higher efficiencies and operating temperatures are predicted as materials are optimized.

ENECO's device is a sandwich of three layers of semiconductor. One of the outer layers is heated and the other is kept at RT. The middle layer is an insulator that maintains the temperature difference. The heat causes electrons to eject, generating an electrical current. Originally developed under a DARPA grant in 2000, testing is being conducted under follow-on DARPA funding. The company claims the technology produces low acoustical and electrical signatures which, if proven true, may be useful for thermal management for future weapon systems.

F. Thermorestrictive Materials

Recent developments indicate that it is possible to bond bulk $Gd_5Ge_2Si_2$ with PZT to directly convert thermal energy to electrical energy[1,2]. $Gd_5Ge_2Si_2$ undergoes a coupled magnetic and structural phase change near room temperature that can be induced by either a magnetic field or a temperature change. The strains induced are on the order of 1% and can be induced both by an increase and decrease temperature. When this "thermostrictive" material is bonded to a piezoelectric such as PZT, it is possible to create a new type of material, referred to as a "compound thermoelectric."

Initial measurements[2] show a Seebeck coefficient of 1800 V/K, which is very large compared to conventional thermoelectric materials. The transition temperature and the width can be modified by an external magnetic field, and by sample composition. Other materials, can also be used as the "thermostrictive" material such as NiTi. It is believed that the conversion efficiencies for compound thermoelectrics prepared as thin films can greatly exceed that of current solar cells for producing hydrogen by electrolysis. Initial (best scenario) estimates indicate that efficiencies up to 36% are possible, which would be an improvement by a factor of 3 over conventional thermoelectric materials. It is also possible to consider other sources of waste energy to harvest, such as car engines or hot asphalt, which are available even when the sun is not shining. The basic concept of the $Gd_5Ge_2Si_2$/PZT compound thermoelectrics has been filed as a provisional patent by LLNL and UCLA[1].

The basic concept is that solar or other “free” sources of thermal energy would be converted to electricity using a thin-film compound thermoelectric material operated at high thermal cycling frequency. This electricity would be used to produce hydrogen by electrolysis, in a standard manner. Figure D.9 illustrates one potential operating mode of the compound thermoelectric based on the bimorph principle. When the thermostrictive material is in the low-temperature phase, the laminate is at the unstressed state and is in contact with the heat source (or T_{hot}). When the material is sufficiently heated to undergo a phase transformation to the high-temperature phase, it strains, causing the laminate to bend. This breaks the contact with the heat source and establishes contact with the heat sink (or T_{cold}). Once the material is sufficiently cooled, the thermostrictive material returns to the low-temperature phase and the laminate re-establishes contact with the heat source. This process is repeated as long as the difference between T_{hot} and T_{cold} is larger then the temperature hysteresis associated with the phase transformation.

The goal is to design the structure using thin-films and appropriate microstructures to allow thermal cycling in the kilohertz regime, which will in turn increase the power output (being directly proportional to frequency). Such frequencies are attainable because at the micro scale the thermal mass is greatly lowered. This high frequency of operation will in turn increase the power output (P = W*f, where W is the work and f is the frequency of operation) of the system.

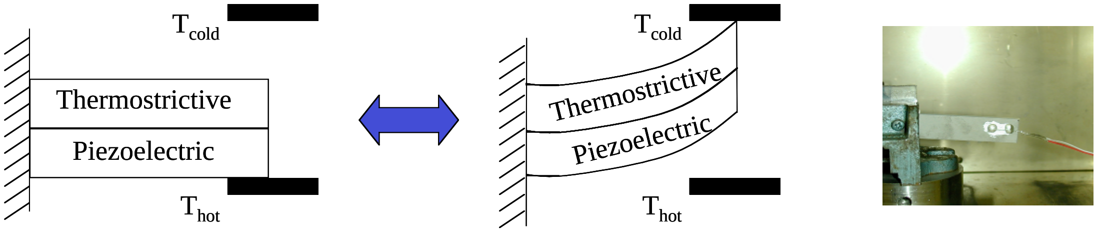


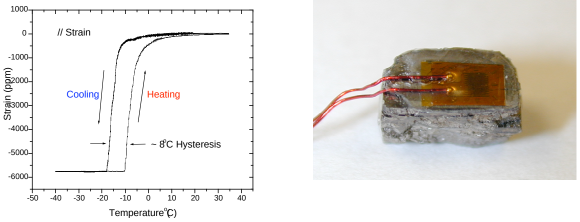
Figure D.9: Thermoelectric laminate.

Table D.1: Daily Efficiency Comparison of a solar cell and compound Thermoelectric laminate. Note: Daily efficiency calculated based on 8 hours of sunlight.

	Solar Cell	Compound Thermoelectric (Estimate for Gd5Ge2Si2/PZT)
Efficiency	**~8-30%**	**~36%**
Actual Daily Efficiency	**~3-10%**	**~36%**

How Thermostrictive Materials Work

Thermostrictive materials such as $Gd_5Ge_2Si_2$ undergo a phase transition, which coverts thermal energy into strain energy. Materials such as $Gd_5Ge_2Si_2$ involve a coupled magnetic and structural phase transition that occurs near room temperature (260 K). The phase transition can be induced by a change in magnetic field, which represents a volume magnetostriction, or by a change in temperature. Large strains are produced over the narrow range in temperature as shown in Figure D.10 for a bulk material, or with magnetic field as shown in Figure D.11 for a single crystal. The induced strain values are similar for both the magnetostrictive and thermostrictive aspects of the transition. It is also possible to modify the location of the thermostrictive transition by altering the chemical composition and by the application of magnetic fields. The huge Seebeck coefficient of 1800 V/K in the $Gd_5Ge_2Si_2$/PZT laminate has its origin in the very large (1%) strain observed in the thermostrictive material over a very narrow temperature range of 10 K. At all temperatures outside of the phase transition region, the Seebeck coefficient would be zero.



Material strains ~0.6% over a temperature range of 8°C

Figure D.10: Thermally induced strain.

$Gd_5Ge_2Si_2$ is well known as a magneto-caloric material, which has been characterized by Ames Laboratory[3]. We have recently demonstrated its usefulness as a volume magnetostrictive material using samples obtained from Ames, and have characterized its performance in the useful form of a polymer composite[4]. The material has a layered structure as shown in Figure D.12, and undergoes a coupled magnetic and structural phase transition. The hysteresis in going up and back in temperature can be seen in Figure D.12.

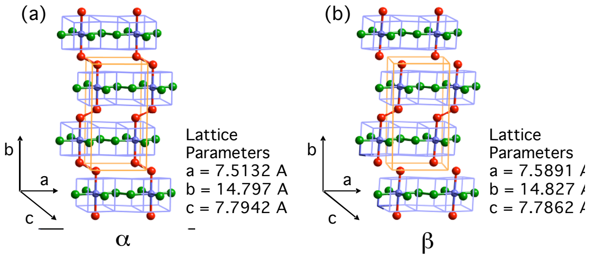


Figure D.11: Structure of $Gd_5Ge_2Si_2$.

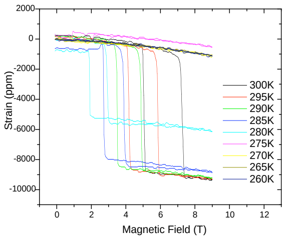


Figure D.12: Single Crystal – Measured along a-axis, field along c-axis.

Other Potential Materials

There are a number of materials that can be considered as the thermostrictive component for compound thermoelectrics. Potential thermostrictive materials for this application other than $Gd_5Si_2Ge_2$ include $La(Fe_{0.88}Si_{0.12})_{13}$, $MnFeP_{0.5}As_{0.4}Si_{0.1}$ and FeRh. The transition (Curie) temperatures and associated strains for these materials are shown in Figure D.13.

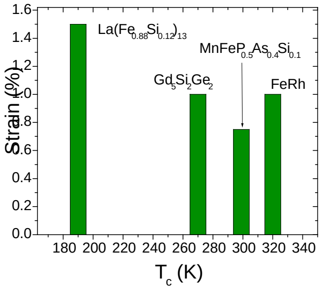


Figure D.13: Potential thermostrictor materials including their saturation strain and Curie temperature.

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2.0 Metal Processing

In this synopsis, several areas where efficiency can be improved will not be addressed such as motors, compressed air systems and controls. Opportunities for process insertion/research & development include the following:

- Energy Management Systems and Programs
- Combined Heat and Power
- Direct Heating
- Alternative Fuels
- Boiler – Recover Heat from Flue Gas

Energy Management Systems (EMS) and Programs

Changing or implementing an overall energy management system is often the most successful and cost-effective way to bring about energy-efficiency improvements. Energy management systems can include sub-metering and monitoring systems, control systems, and/or changes in staff behavior through a feedback registration system. The U.S. EPA Energy Star Program is working with the industrial sector to develop strategic Energy Management Systems.

Combined Heat and Power (CHP)

For industries that have process heat, steam, or cooling and electricity requirements, the use of combined heat and power systems can save energy and reduce pollution. Cogeneration plants are significantly more efficient than standard power plants because they take advantage of what are losses in standard plants by utilizing the waste heat. In addition, distribution losses are minimized when CHP systems are located at or near the assembly plant. For systems requiring cooling, absorption cooling can be combined with CHP to use waste heat to produce cooling power.

For example, in the vehicle manufacturing industry, hot water is used for process functions, such as washing and degreasing vehicle components, and maintaining paint at correct temperatures for spraying, while electricity is used to power the motors, pumps, and compressors. In addition to the energy savings, CHP also has comparable or better availability of service than utility generation. Typical CHP units are reported to have been online for 95 to 98% of planned operating hours. For installations where initial investment is large, potential multiple small-scale CHP units distributed to points of need could be used cost effectively.

Innovative gas turbine technologies can make CHP more attractive for sites with large variations in heat demand. Steam-injected gas turbines (STIG, or Cheng cycle) can absorb excess steam (due to seasonal reduced heating needs) to boost power production by injecting the steam in the turbine. The typical size of STIG's start around 5 MWe. STIG's are found in various industries and applications, especially in Japan and Europe.

CHP can be combined with absorption cooling. Absorption chillers are cooling machines that use heat as the primary source of energy for driving an absorption refrigeration cycle. These chillers require very little electric power (0.02 kW/ton) compared to electric chillers that need 0.47 to 0.88 kW/ton, depending upon the type of electric chiller. Absorption chillers have fewer and smaller moving parts and are thus quieter during operation than electric chillers.

Commercially available absorption chillers can utilize one of the four sources of heat: steam, hot water, exhaust gases or direct combustion. Because absorption cooling produces cooling power using heat, it increases heating demand and decreases electricity demand. For this reason, it is best when combined with CHP. All absorption chillers, except those that use direct combustion, are excellent candidates for providing some, or all, cooling load in a CHP system for a building. Modern absorption chillers can also work as boilers for providing heating during winter and feature new electronic controls that provide quick start-up, automatic purge, and greater turndown capacity than many electric chillers.

These chillers are also environmentally friendly in that they use water as a naturally benign refrigerant. The coolant is based on a mix of water and a salt, such as LiBr or LiCl, which is capable of absorbing water very efficiently. District heating or a locally produced low-temperature heat source replaces electricity as the primary energy source for the cooling. Absorption cooling plants should have a minimum size of 500 kW in order to be cost effective.

Absorption cooling installations using CHP are currently used mainly for large buildings, campuses, or industries throughout the U.S. for continuous operation or for peak shaving. Payback periods vary between half a year to over 5 years, depending on local circumstances and utility billing structure.

Direct Heating

District heating systems use a central plant in an urban area to supply heat to multiple buildings and complexes. Several plants operated by Ford Motor Company are supplied by district heating. For example, Ford-Werke AG headquarters (DE) uses district heat and saves 73,500 tons of coal and 3,500 tons of fuel oil, while reducing CO_2 emissions by 60% annually.

Alternative Fuels

Some industrial metal processes produce waste products that can be incinerated exothermically to provide an ideal fuel for the boiler. The energy saved by using some of these waste streams (particularly chemical waste streams) must be balanced with the potential release of environmental toxins into the atmosphere. At the Orion Assembly Plant (MI) in 1998, in affiliation with the U.S. EPA Landfill Methane Outreach Program, General Motors replaced the coal burned in their boilers with landfill gas from a nearby landfill, reducing coal use by 60,000 tons on an annual basis (roughly equivalent to 1.5 TBtu, or 30% of the fuel used for heating the plant). In addition, the new plant reduced sulfur dioxide emissions by 40% and nitrogen by 46%. The EPA estimates that more than 700 landfills across the U.S. could install economically viable energy recovery systems; however, plants must be located near viable landfills to implement the measure.

Boiler – Recover Heat from Flue Gas

The motor vehicle industry in the U.S. spends about $3.6 B on energy annually. Over 70 assembly plants currently produce ~13 million cars and trucks each year. According to the vehicle manufacturing industry, heat recovery from the flue gas is the best opportunity for heat recovery in the boiler house. Heat from flue gasses can be used to preheat boiler feed water in an economizer. While this measure is fairly common in large boilers, there is often room for more heat recovery.

The limiting factor for flue gas heat recovery is that the economizer wall temperature must not drop below the dew point of acids in the flue gas. Traditionally, this has been done by keeping the flue gases exiting the economizer at a temperature significantly above the acid dew point. In fact, the economizer wall temperature is much more dependent on the feed water temperature than the flue gas temperature because of the high heat transfer coefficient of water. As a result, it makes more sense to preheat the feed water to close to the acid dew point before it enters the economizer. This allows the economizer to be designed so that the flue gas exiting the economizer is just barely above the acid dew point. 1% of fuel use is saved for every 45^{o}F reduction in exhaust gas temperature. Since exhaust gas temperatures are already quite low, but can still take advantage of using the higher temperature feed water mentioned above, an estimated 1% savings is possible.

1. “Energy Efficiency Improvement and Cost Saving Opportunities for the Vehicle Assembly Industry,” Galitsky, C. and Worrell, E., LLNL, 2001.

3.0 Forest Products

The pulp and paper industry accounts for over 12% of total manufacturing energy use in the U.S., contributing 9% to total manufacturing carbon dioxide emissions. In the last 25 years, primary energy intensity in the pulp and paper industry has declined by an average of 1% per year. The estimated primary energy consumption is 2,970 TBtu. Of this, 1,348 TBtu of biomass is used in boiler plant facilities to produce steam for various paper manufacturing processing.

A large number of technologies and measures exist that can reduce energy intensity (i.e., electricity or fuel consumption per unit of output) of the various process stages of pulp and paper production. Advanced technology energy-efficient measures projected for future pulp and paper application include alcohol-based solvent pulping, black liquor gasification, pre-treatment of incoming pulp into drying section, and several new drying technologies including infrared, impulse, airless, press, air impingement, and steam impingement drying.

Process Description of Conventional Paper Making

In conventional paper making, the fiber is mixed with about 100 times their weight of water, then the water is removed. The processes in a conventional, non-integrated paper mill can be categorized into three sequential clusters: stock preparation, paper machine, and finishing operations. In the stock preparation, pulp and waste paper are screened and de-inked and then mixed with water. Fibers are refined and additives brought in. The mixture is called the stock. The percentage of dry solids (ds), also called the consistency of the sheet, is about 1%. The operations in the paper machine are conducted in three steps: forming, pressing, and drying. The forming process disperses the stock over a wire screen to form a sheet, and subsequently removing most of the water by gravity and suction. The consistency of the sheet at the end of the forming section is about 20% ds. Next, the consistency is increased to 40-45% ds; water is removed by passing the sheet, supported by a felt, through three or four pairs of press cylinders. Finally, when no more water can be removed mechanically, the sheet is passed over 40-50 steam-heated cylinders (drying section), the final consistency being about 90-95% ds. Finishing operations are calendaring to smooth the paper surface, winding on wheels, cutting, etc.

Main Production Parameters in Paper Making

For each new technology, the impact on the production rate, the runnability, and the paper quality should be considered. The production rate of modern paper machines ranges from lower than 1000 m/min for board to 1600 m/min for newsprint. The production rate is determined largely by the drying rate in the drying section, expressed in kg water removed per m2 contact surface between paper and heated surface per unit of time. Increasing the drying rate makes it possible to increase the production rate without having to extend the drying section. The drying rate in a traditional drying section with 55 drying cylinders operating at a speed of 1500 m/min is about 15-30 kg water/m2h.

The term runnability is used to indicate how the paper goes through the paper machine. A technology with poor runnability decreases the reliability of the process. Important aspects are: does the paper stick to the supporting felt, how easily is the transfer from one cylinder to the next, does much paper get damaged, and is the paper dried equally over the whole surface? The main parameters to determine paper quality are the basic weight (in g/m2), the thickness, the optical properties (brightness, color, opacity, transparency, and gloss), stiffness, moisture content, and strength (tensile, burst, and tear). These parameters are determined largely by the types of fiber, the machine speed, the pressing load, and the drying temperature.

Enthalpy and Energy Analysis

In the paper-making process, heat is required mainly in the form of low-pressure steam. When heat and electricity are produced in a cogeneration plant, it is common to generate high pressure steam first, and let this expand to low-pressure steam in a back pressure turbine to generate electricity. Paper drying consumes about 90% of the steam demand. Some steam and hot water is used in stock preparation. In some paper mills a small amount of steam is used by steam showers in the press section. The electricity demand is more evenly distributed over the various unit operations than the steam demand. Electricity is used to drive the pumps that handle the huge flows of water and the fans for removing the damp air from the paper machine, and to drive the paper machine. Furthermore, refining the fibers also requires electricity. During the numerous wet processes the temperature of the process, water increases by 10-20°C.

Table D.2: Based on material, enthalpy, and energy flows in a standardized paper mill, the energy balance to produce one kilogram of paper is listed.

INPUT (MJ)				OUTPUT (MJ)			
Material	**Mass (kg)**	**Enthalpy (MJ)**	**Energy (MJ)**	**Material**	**Mass (kg)**	**Enthalpy (MJ)**	**Energy (MJ)**
CHP-Unit							
Natural Gas	0.27	10.80	10.20	Electricity		3.60	3.60
Air	7.11	0.10	0.00	Steam (7 bar, 140C)	1.80	4.80	1.50
Water/Condensate	0.00	0.00		Exhaust (105C)	7.38	1.50	0.20
				Heat Loss (500C)		0.20	0.00
				Energy Balance		0.90	0.00
Stock Preparation							
Steam	0.19	0.50	0.20	Wet Pulp	103.33	19.80	24.40
Pulp/waste	1.03	19.80	24.40	Condensate (100C)	0.19	0.10	0.00
Paper							
Water	102.30	0.00	0.00	Energy Balance		1.30	0.00
Electricity		0.90	0.90				
Paper Machine							
Wet pulp	103.33	19.80	24.40	Paper	1.00	18.10	22.00
Steam	1.61	4.30	1.30	Broke	0.05	1.00	1.20
Electricity		0.90	0.90	Lost	0.05	1.00	1.20
Atmospheric Air	6.82	0.10	0.00	Water	101.21	0.00	0.00
				Damp air (55C)	7.84	3.20	0.20
				Condensate	1.61	0.50	0.10
				Energy Balance		1.30	0.00

Total energy loss for a kg of paper is shown in Table D.3, divided into internal and external losses. The largest internal energy loss occurs in the CHP unit and is caused by the conversion of a high-quality fuel to low-quality steam. The steam used in a typical mill has an energy factor of 0.3, whereas the energy factor from a high-quality fuel (NG) is about 1. The energy loss in the paper machine is about 35% of the total energy loss. About one third of this loss is caused by lost fibers. The energy of the steam and electricity is largely lost internally in the process; a small amount is found in damp air and the condensate.

Table D.3: Total energy loss for a kg of paper.

Unit Operation	Internal	Energy Loss External	Total
CHP Unit	4.9	0.2	5.1
Stock Preparation	1.1	0.0	1.1
Paper Machine	1.9	1.5	3.4
TOTAL	**7.9**	**1.7**	**9.6**

The relationship between energy use and the amount of water removed in the three processes occurring in the paper machine are quantified, with the bulk of the water removed in the forming section using the smallest amount of energy. Table D.4 indicates that drying uses by far the most energy per mt of water removed.

Table D.4: Energy requirements for water evaporation of paper.

	(GJ/mt of paper) Ingoing Consistency	(% ds)	(GJ/mt of water evaporated)
Minimum Energy requirement for:	40%	45%	
Heating and evaporation of water, from 50C to 100C	3.25	2.63	2.46
Heating of fibers from 50C to 100C	0.07	0.07	0.07
Desorption Heat	0.02	0.02	0.02
TOTAL	**3.34**	**2.27**	**2.55**

There are various technologies available to address energy usage in the drying process including dry sheet forming, press drying, condensing belt frying, impingement drying, and airless drying.

Specific Paper Process Energy Savings/Conversion Opportunities

Black Liquor Gasification

Boiler plants that burn biomass materials are primarily located at Kraft pulp mills, which currently account for nearly 80% of the pulp produced in the U.S. In standard integrated Kraft mills, the spent liquor produced from de-lignifying wood chips (called black liquor) is normally burned in a large recovery boiler, named that because the black liquor combustion is used to recover the chemicals used in the delignification process. Because of the relatively high water content of the black liquor fuel (usually combusted at a solids content of 65-75 percent), the efficiency of existing recovery boilers is limited. Electricity production capacity is also reduced since recovery boilers produce steam at lower pressures for safety reasons.

Black liquor gasification is used to produce gas from spent pulping liquor. This gas can be used in a traditional boiler, or may in the future be used in conjunction with gas turbines. There are two major types of black liquor gasification: low temperature/solid phase and high temperature/smelt phase. Today, black liquor gasifiers are used as an incremental addition in chemical recovery capacity in situations where the recovery boiler is a process bottleneck. In the future, gasifiers may be able to provide fuel for gas turbines and lime kilns by means of a standard combined cycle power generation system (made up of a gas turbine, heat recovery system, steam turbine, and electricity generators). The success of turbine-based technology depends on making a turbine that can use low energy gas (produced by an air blown gasifier) or the creation of more efficient oxygen blown gasifier.

Gasification produces a fuel gas that needs to be cleaned to remove unwanted impurities for the power system and to recover pulping chemicals. Low-temperature gasification is based on a fluidized bed at atmospheric pressure and a temperature of approximately 700ºC or lower, below the melt point of inorganic salts that comprise most of the char from black liquor. Sodium carbonate is used as the bed material and is precipitated out and reused. High-temperature gasification occurs at 2.5 MPa and above the melt point of the inorganic salts (950ºC) or higher, and the chemicals are recovered in a smelt. Higher temperatures lead to higher carbon conversion rates but also may lead to more corrosion in the reactor vessel. The synthesis gas is water quenched to produce steam and cleaned before being fired in the turbine.

Energy savings estimates for this technology vary, but are potentially significant. Existing recovery boilers consume roughly 27 MBtu of black liquor and other biomass per air dried ton of chemical pulp with power production efficiencies using steam turbine systems of 10%. While increased fuel inputs are required for gasification systems, and increased electricity inputs are required, power efficiencies are much higher thereby allowing for significant primary energy savings. Based on an electricity production capacity of 2,000 kWh/ton, which represents an average of the range of outputs from the various systems, a primary energy savings potential of 6 MBtu/ton pulp is expected.

Currently, there are no full-scale gasifier/combined cycle plants operating—although the opportunities for this technology are quite large. A majority of the recovery furnaces and conventional power boilers in existing pulp and paper plants are 20 to 30 years old and more than half of them will need to be replaced or upgraded in the near future. The gasification systems also are expected to improve environmental performance, with fewer particulates and nitrogen oxides than in conventional systems. However, additional research and demonstration are needed before gaining market acceptance. Some key areas include: developing adequate clean up systems for the medium Btu gas, improving refractory reliability, demonstrating cost-effective chemical recovery (especially sulfur separation), and demonstrating overall system integration.

Alcohol-based Solvent Pulping

Alcohol-based solvent pulping offers a potential advantage to traditional Kraft pulping in that it can produce high-yield, high-quality pulps in shorter cooking times. The process also produces a sulfur-free lignin that is extracted at a much faster rate than the Kraft process. Wood chips and the ethanol-water solution is processed in a batch digester at 200C and 392 psi. The combination of alcohol and high-pressure releases about 75% of the lignin; most of the remaining lignin is removed with secondary extraction liquor and recycled alcohol-water. Steam stripping is used to recover residual alcohol from the pulp; lignin is recovered from the black liquor in a proprietary process. A drawback is the high cost of solvents that can be cost prohibitive.

Impulse Drying

Impulse drying involves pressing the paper between one very hot rotating roll (1150-500C) and a static concave press with a very short contact time. The pressure is about 10 times higher than that in press and Condebelt drying. Impulse drying tremendously increases the drying rate of paper and the energy savings can be significant; estimates of steam consumption savings are as high as 75%, although electricity requirements increase between 5-10%. Impulse drying subjects the paper web to very high temperature at the press nip in order to drive moisture out of the web. This technology promises to bring reduced capital costs, increased machine productivity, reduced fiber use, reduced energy use, and improved physical properties to the paper.

Heat Recovery – Enclosed Hoods

In the paper drying section, steam-filled rollers dry paper through the evaporation of water in the web. In a typical drying machine, there may be 40-50 steam heated drying cylinders. Heat recovery technologies are primarily directed at this initial stage of the drying section. There is a strong link between pulp consistency and steam demand on the drying section. Here, pulp enters with a consistency of 40-45 percent and paper exits the machine with a consistency of 90-95%. Typically, 2 kg water is evaporated per kg of paper and 6.7 kg of air is required to remove 1 kg of water vapor. In the paper making process, the heat, which is in the form of low-pressure steam, is transferred to the web via the steam-injected cylinders. As the water vapor exits the web, carried away by pre-heated air, and the web is dried, saturated low-pressure steam is released. The goal of more advanced waste recovery systems is to convert the lower quality steam into more useful heat. There are opportunities to devise system solutions that combine closed hoods, heat regeneration, and sensor control technology to optimize the system via control logic algorithms.

4.0 Agriculture

Opportunities for process insertion/research & development include the following:

- Agriculture waste gasification
- Low-Temperature Heat Recovery in the Food Processing Industry
- Cooling and Storage

Most dairy farms have concentrated supplies of manure waste that are used as fertilizer on crops grown for animal feed. However, economic and logistic constraints often require farm operators to purchase additional feed and fertilizer rather than using the supplies that are available on the farm. Because of this practice, many farms struggle with a manure surplus. It has been shown that cow manure wastes can be an excellent bioenergy fuel; a portion of the dairy farm waste can be used as feedstock in an energy production system, the extra nutrient flow difficulties would be alleviated and the farm's energy cost could be offset. Collected manure is first separated into liquid and solid portions, using a commercial auger press. While liquid manure is returned to the field and used as a fertilizer, solids can be used as a fuel for the gasifier. The fuel gas produced by the gasifier is used on the farm for power and heat generation, or sold for other uses.

In addition to waste reduction and farm energy production advantages, there are three other opportunities worth noting. First, the biomass waste fuel will not contribute significantly to a net increase in CO_2 emission when burned. Secondly, this renewable source of energy could potentially displace fossil-fuel-derived energy. Third, unlike some other farm-based energy conversion processes, the availability of the manure fertilizer, the liquid portion in the case, is maintained.

The gasification process and the components for gasification are described in Figure D.14. Solid fuels (coal and/or wastes) are gasified using high temperature, preheated air in a reactor vessel to produce a flammable raw synthetic gas. The inorganic ash residue from the gasification reactions is extracted from the gasifier either as a molten slag or an ash, depending upon the selected operating temperature of the gasifier. Upon exiting the gasifier, the fuel gas is cooled in a heat recovery boiler and then cleaned, using conventional gas cleanup technology. A small fraction of the product gas is diverted to the pre-heater where it is used to heat the gasification air. Depending on the intended application of the plant, the rest of the cleaned fuel gas is utilized for a variety of possible downstream processes. For power plant applications, the fuel gas can be used for driving gas or stream turbines for utility and industrial power production or for use in manufacturing of chemicals and fertilizers.

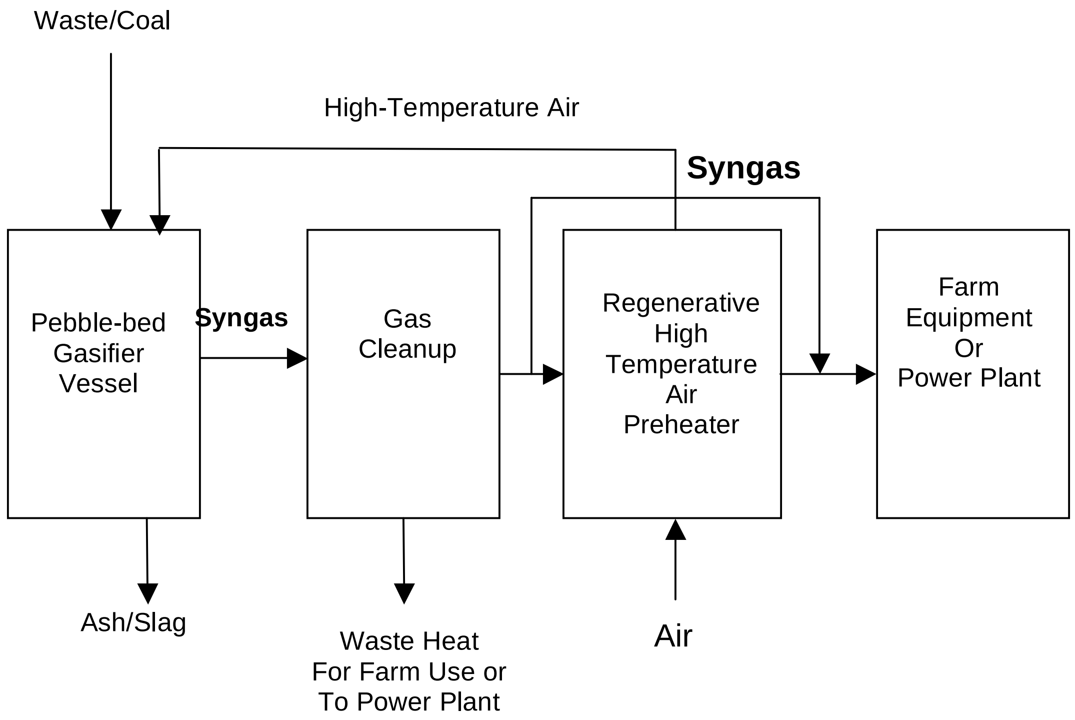

Figure D.14: Schematic of gasifier for agriculture waste.

The gasifier vessel consists of two sections: an entrained flow section followed by a particulate removal section (Figure D.15). The coal/waste feedstock is gasified in the entrained-flow section to produce a flammable raw synthesis gas consisting primarily of CO, H_2, and N_2. Several actions occur simultaneously in this region of the gasifier: the thorough mixing of the fuel particles with the high-temperature gas, the rapid heating of this mixture to an elevated temperature, and the stabilization of the volatiles evolved from the fuel particles.

In a multi-staged gasifier, the gasification temperature is maintained above the fluid temperature of the slag, typically 1350-1400ºC, and a high-temperature ceramic pebble-bed filter is used for particulate removal, as shown in Figure D.15. During operation, the gasifier internal temperature is controlled by varying the fuel/air ratio. As the fuel gas flows through the packed bed, molten slag particles are collected onto the surface of the pebble balls via inertial impact separation. The accumulated slag is extracted through a slit at the bottom of the pebble bed into a slag receiver where it is quenched and then removed from the gasifier. The use of high-temperature air in the process increases the yield of the gasification process. This occurs for two reasons. One is that the preheated air increases the heating rate of the incoming fuel with the volatile yield from the fuel particles greatly enhanced under these high-temperature, rapid-heating conditions. Another reason for the increased yield is that higher caloric-valued syngas can be obtained from a given biomass fuel when high-temperature air is used as the gasifying agent. By using higher preheat temperatures, the gasifier can be operated at more fuel-rich conditions to achieve the given gasification temperature (~1400°C for slagging operation and ~900ºC for non-slagging operation). As the gasifier fuel-to-air ratio increases, the resulting concentrations of CO and H_2 increase, leading to higher caloric-valued product gas.

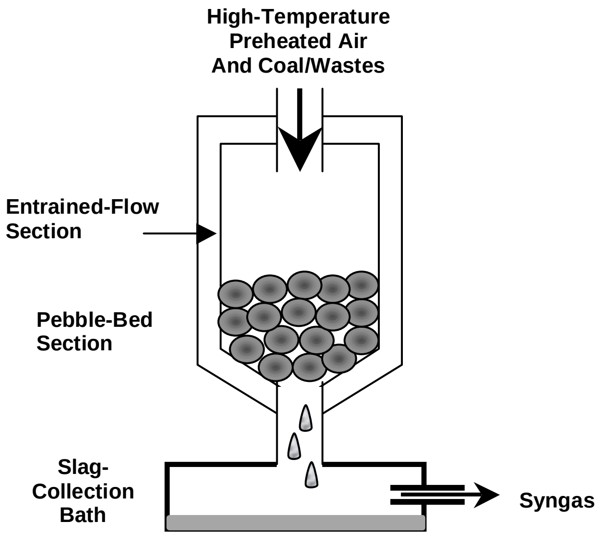

Figure D.15: Schematic diagram of the multi-stage extraction gasifier, slagging configuration.

The use of high temperature preheated air is especially advantageous for the gasification of biomass fuels, such as dairy-farm wastes. Biomass feedstocks are usually modest in heat content (usually ~45% Carbon, 5.8% Hydrogen, 38% Oxygen, 2% Nitrogen, 0.3% sulfur, and the remainder ash). If such fuels are used in conventional, air-blown gasification processes, the energy released during the gasification process is often insufficient to provide the necessary temperature for complete gasification of the fuel, leading to poor conversion efficiencies and low caloric-valued fuel gas. Such fuel gas would have limited economic value. As a result, oxygen must be used in such a conventional biomass-fired gasifier to increase the heat value of the product gas.

Pebble-bed filters of the slagging multi-stage extraction gasifier can consist of several layers of alumina spheres, the consistency based on the coal/waste fuel characteristics. There is much room for development in this area. A biomass gasifier coupled to an advanced gas turbine can generate electricity with much higher efficiency and lower pollution than direct combustion. Additionally, there is the potential that new biological and enzymatic processes can greatly boost the efficiency of ethanol production.

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Low-Temperature Heat Recovery in the Food Processing Industry

Food processing industries play a vital role in the U.S. economy and in foreign trade. This industry accounts for a large portion of the U.S. industrial energy use, ranking as the fifth largest energy-using industry after petroleum refining, chemicals, primary metals, and paper manufacturing. Unlike other energy-intensive industries, the food industry does not produce a homogeneous output and operates at significantly lower temperatures. Therefore, energy consumption in food industries comes from a wide range of production activities such as roasting, baking, cooking, frying, freezing, drying, refrigeration, pasteurization, evaporation, and distillation. There are also energy demands for supplying buildings with heat, light, and air conditioning. In 1994, roughly two-thirds of final energy demand for the food industries was fuel for boilers to provide steam and heat to various processes.

There are many opportunities to take advantage of heat recovery in food processing, achievable by using all or part of the exhaust gas from one process as the inlet gas to another process. Alternatively, heat exchangers can capture heat in the exhaust and transfer it to another flow of gas or liquid. Energy savings from heat recovery in the food industry depends upon finding applications where heat recovery is economical and improves the process.

Case studies illustrate there are many potential applications for cost-effective heat recovery applications in the food industry. In some of these projects, excess heat from one energy-intensive process step was used in another process step. These have been demonstrated in bakeries, vegetable processing plants, beverage facilities, drying of grains, drying of malt for breweries, and pulp drying in the sugar processing industry. Most of these applications utilize heat exchangers constructed from steel, except in caustic applications where the material of choice is nickel, nickel-steel alloy, or titanium.

It is estimated that the food industry energy consumption in 2015 will be approximately 1700 TBtu of primary energy. Roughly 50 percent of this will be fossil fuel for boilers meeting steam demand for food processing. Another 15 percent of this will be fossil fuel used directly in processes. Thirty-five percent will be fuels consumed to meet the food industry’s electricity demand. Of the total energy consumed for steam demand, 20 to 25 percent is lost due to boiler inefficiencies. The use of heat recovery systems can lower the boiler systems to 12 to 16 percent in industries where there are opportunities for heat recovery. Assuming that 20% of energy use falls into this category and is retrofit for heat recovery by 2015, 14 TBtu of energy savings can be attained. Given that 16% of food industry energy is used for drying, and that potential savings from heat recovery systems for drying range from 10 to 50 percent, and assuming 20% drying energy demand is appropriate for heat recovery and retrofit by 2015 with an average dryer demand reduction of 25%, energy consumption will be lowered by 9.5 TBtu.

Cooling and Storage (Food)

Refrigeration in the food sector is a large energy consumer and is mainly used for freezing or cooling of meat, fruit, vegetables, as well as for frozen products. Refrigeration in industry is mostly done by means of compression cooling and in some cases by absorption cooling. Electricity use for refrigeration in the food and beverages industry is estimated at 11.1 TWh, mainly used by compressors.

Many options exist to improve performance of industrial refrigeration systems. System optimization and control strategies combined show a large potential for energy efficiency improvement of up to 30 percent. Opportunities include system design, component design, adjustable speed drives, process control systems, adsorption heat pumps, gas-engine-driven adsorption cooling, new working fluids (e.g. ammonia, CO_2) and alternative approaches (e.g. thermal storage). Many of these opportunities already exist; insertion is what is needed to realize up to 40% efficiency savings.

5.0 Steel

Gas and Heat Recovery at Basic Oxygen Furnace

The iron and steel industry is one of the largest U.S. industrial energy consumers. The U.S. iron and steel industry is made up of integrated steel mills that produce pig iron from raw materials (iron ore, coke) using a blast furnace and steel using a basic oxygen furnace (BOF) and electric arc furnace steel mills that produce steel from scrap steel, pig iron, or direct reduced iron (DRI) using an electric arc furnace. In 1994, 2,180 TBtu (about 11% of manufacturing primary energy use) was consumed in the production of about 100 Mton of crude steel products. Within steelmaking, the largest energy use is required to reduce iron ore in the integrated mills to re-melt steel scrap in electric arc furnace mills. Primary steel is produced using the BOF. In the BOF process liquid pig iron, scrap and limestone are mixed. Oxygen is injected to reduce the carbon content of the hot metal from about 5% to less than 2%. Steel contains less than 2% carbon. The BOF process replaced the last open hearth furnace in the U.S. by 1992 due to its greater productivity and lower capital costs.

Fuel and electricity consumption in the BOF is estimated at 18TBtu and 1.7TWh, respectively, in 1994. Energy intensity for this process step in 1994 was 0.30 MBtu/short ton fuel and 27 kWh/short ton steel. In the U.S., no BOF gas seems to be recovered at this time. According to the EPA, the BOF-process is an important source of CO emissions, emitting 617,000 tons in 1992, or equivalent to 21 lb/short ton liquid steel.

Carbon in the hot metal reacts to carbon monoxide, which is emitted as BOF gas. The BOF gas has a heating value of 7.4 and 9.1 MJ/Nm^3. By reducing the amount of air entering over the converter, the CO is not converted to CO_2. The BOF gas can be recovered and used as fuel gas in the steel plant or for steam and power production. The hot off-gases must be cooled before gas cleanup, and the heat can be recovered by generating steam and hot water. BOF gas combined with sensible heat recovery is the single most energy-saving improvement in the process step, making the BOF process a net energy producer. Repressed combustion is very common in integrated steel plants in Europe and Japan as an efficient means of energy recovery, emission control, and dust recycling. Repressed combustion reduces CO and dust emissions and, since the metal content of the dust is high, about 50 percent of the dust can be recycled in the sinter plant or in the steel plant.

The amount of gas recovered depends on the hot metal charge in the BOF as the main source of carbon. Assuming a hot metal charge of 1800 lb/ton liquid steel, approximately 2860 cu. ft. of BOF gas can be recovered, accounting for flaring and air leakage into the system. This is equivalent to 607 kBtu/ton. Steam recovery can be up to 120 lb/ton of steel. Assuming a steam recovery of approximately 100 lb/ton, equivalent to 130kBtu/ton, total fuel savings are equivalent to 737 kBtu/ton with increased power consumption of 2 kWh/ton.