BACKGROUND DOCUMENT A, ATTACHMENT 1

A Partial Life Cycle Inventory of Process and Transportation Energy for Boxboard and Paper Towels Submitted by Franklin Associates, Ltd.

			•
•			
•			
		26 ° 1	•
•			
		·	
•			
•			
			•
	$x \rightarrow x$		
·			
			•
		•	·
			•
		•	
•			
	·		
			•
	.		
÷			

A PARTIAL LIFE CYCLE INVENTORY OF PROCESS AND TRANSPORTATION ENERGY FOR BOXBOARD AND PAPER TOWELS

INTRODUCTION

This appendix presents the aggregated process and transportation energy used to manufacture boxboard and paper towels from virgin raw materials and from recycled mixed papers. Also included in this study are any process greenhouse gases emitted from these products or their raw materials.

Although they are not complete life cycle inventories, the energy profiles for each virgin material are based on life cycle inventory (LCI) practices. The process energy and transportation energy for most steps in the life cycle of the materials are included. The life cycle of each virgin material begins with the acquisition of raw materials, such as the harvesting of trees or the production of crude oil. The energy profiles for the virgin materials include raw materials acquisition through manufacture of the material or product specified.

For the recycled materials, the energy profiles represent a system which begins with the production of a first product (including mixed paper, newspaper, and corrugated boxes). Then, these products are collected and transported to a repulper and then to the production of the second product, which will be boxboard or paper towels in this study. The previous discussion represents a "two-product open-loop" recycling system. Open-loop recycling is discussed later in this report.

The following sections of this appendix present: 1) the data tables and flow diagrams illustrating the systems evaluated; 2) a discussion of the overall boundary conditions for the systems studied; 3) a discussion of the processes evaluated for each system, and 4) the data sources (references) for each process step in the models.

FLOW DIAGRAMS AND DATA TABLES

A flow diagram and data table are presented for the production of each material both from virgin and from recycled inputs. Each flow diagram shows the process steps that are included in the boundaries of the analysis. The data in the associated table show the aggregated energy to produce one ton of the material specified. The tables also present any greenhouse gas emissions produced during the process steps.

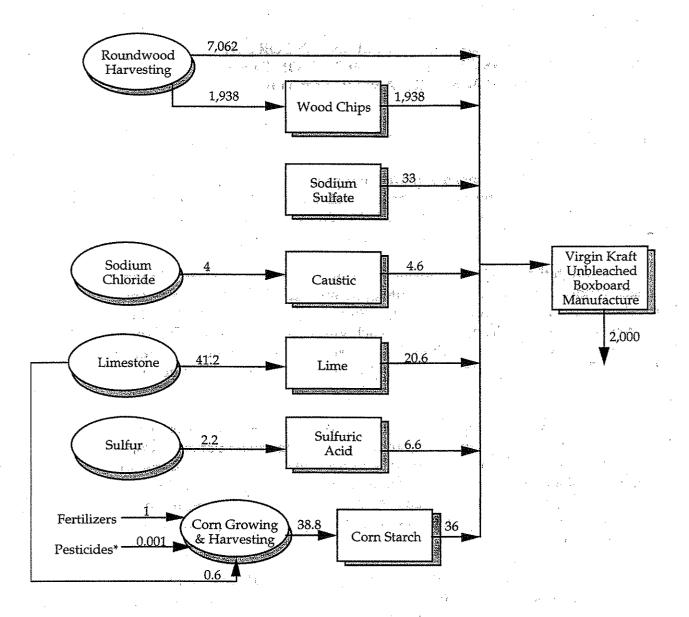


Figure 1. Flow diagram for the production of one ton of virgin kraft unbleached boxboard. All numbers represent pounds of materials.

^{*} This material is considered negligible in the model.

Table 1

DATA FOR THE PRODUCTION OF ONE TON OF VIRGIN BOXBOARD

Booker Box Down of Box Down of

	man and the second of the seco				
Energy Usage			Total Energy Thousand Btu		
Process Energy	4				
Electricity	154	kwh 11146	1 BH/WM 1,717		
Natural gas	2,509	cu ft	2,910		
LPG	0.0042	gal	0.45		
Coal	676	lb	7,747		
Distillate oil	0.0088	gal	1.39		
Residual oil	1.77	gal	304		
Gasoline	6.1E-04	gal	0.086		
Diesel	2.77	gal	[®] 439		
Wood	19,146	thousand Btu	19,146		
Total Process			32,264		
Transportation Energy					
Combination truck	1,126	ton-miles	•		
Diesel	10.6	gal	1,676		
Rail	302	ton-miles	• •		
Diesel	0.72	gal	115		
Barge	0.79	ton-miles			
Diesel	0.0016	gal	0.25		
Residual oil	6.3E-04	gal serge color	0.11		
Ocean freighter	2.40	ton-miles			
Diesel	2.4E-04	gal	0.038		
Residual	0.0043	gal .	0.74		
Pipeline-natural gas	0.098	ton-miles			
Natural gas	0.22	cu ft	0.26		
Pipeline-petroleum products	0.17	ton-miles			
Electricity	0.0036	kwh	0.041		
Total Transportation			1,792		

Environmental Emissions

Process Greenhouse Gas Emissions

Fossil Carbon Dioxide

16.5 lb

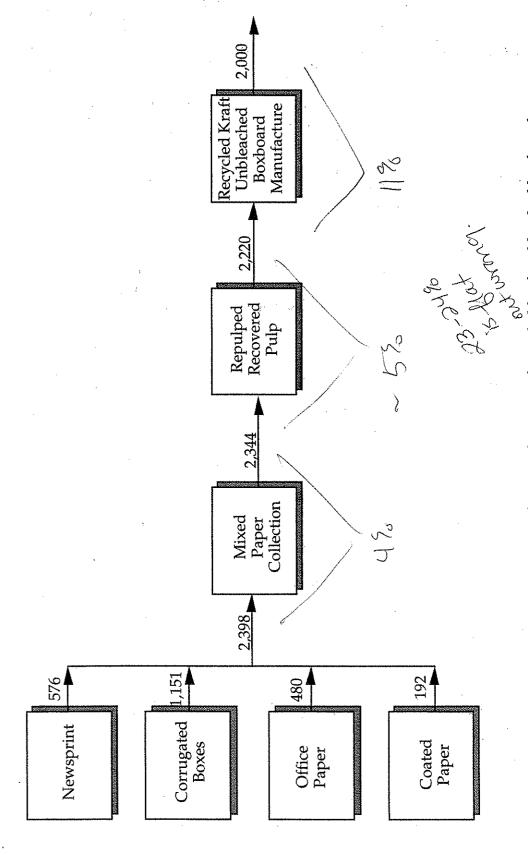
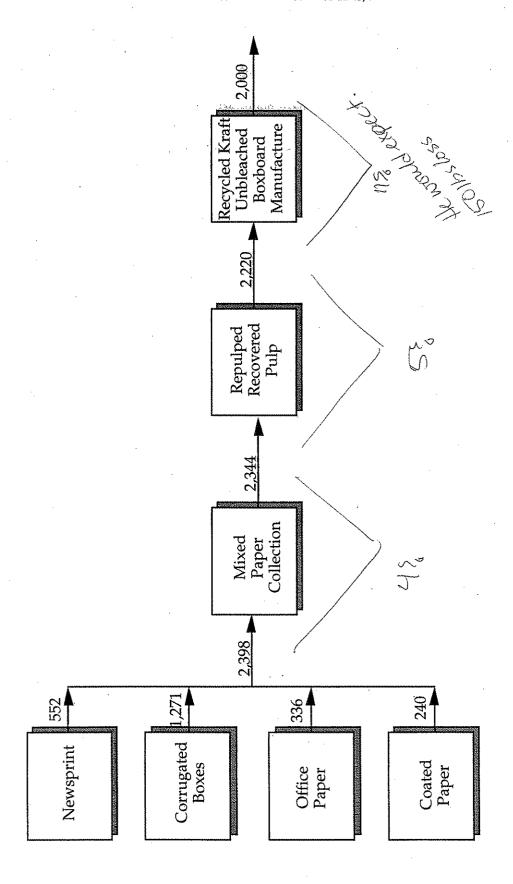


Figure 2. Flow diagram for the manufacture of one ton of recycled kraft unbleached boxboard using the broad definition of mixed paper. The weights include an 11% loss at the Numbers represent pounds of material. recycled boxboard manufacture.

Markey Cod DATA FOR THE PRODUCTION OF ONE TON OF BOXBOARD FROM RECYCLED PAPER

(Collection deinking, and recycled boxboard manufacture)

Energy Usage		,	Total Energy Thousand Btu
Process Energy			11/1 Zz BAYKWIN 15,199
Electricity	1,366	kwh	1\\Z>-\O\\ 15,199
Natural gas	1,409	cu ft	1,634
LPG	0.058	gal	6.24
Coal	479	lb	5,488
Distillate oil	0.028	gal	4.43
Residual oil	0.48	gal	82.1
Diesel	0.70	gal	111
Total Process		Ŷ	22,525
Transportation Energy			
Combination truck	188	ton-miles	
Diesel	1.76	gal	279
Single unit truck	23.4	ton-miles	
Diesel	0.62	gal	98.3
Tötal Transportation	4		377



using the single-family residential mixed paper. The weights include an 11% loss at the Figure 3. Flow diagram for the manufacture of one ton of recycled kraft unbleached boxboard Numbers represent pounds of material. recycled boxboard manufacture.

Sugginted bake

DATA FOR THE PRO	Table 3 DDUCTION OF OM RECYCLEI ing, and recycle	ONE TON O	F BOXBOARD DING	rais Kabuza BDA)
Energy Usage		kwh Ness	Total Energy	sum.
Process Energy	Della	3.41	COV.	√ .
Electricity	1,366	kwh wes	15,199	
Natural gas	1,409	cu ft	1,634	
LPG	0.058	gal	6.24	
Coal	479	lb	5,488	
Distillate oil	0.028	gal	4:43	
Residual oil	0.48	gäl	82.1	
Diesel	₋ 0.70	gal	111	
Total Process	·		22,525	•
Transportation Energy		•		
Combination truck	188	ton-miles	The second section of the sect	
Diesel	1.76	gal 🤻	279	
Single unit truck	23.4	ton-miles		
Diesel	0.62	gal	98.3	
Total Transporta	rion		377	

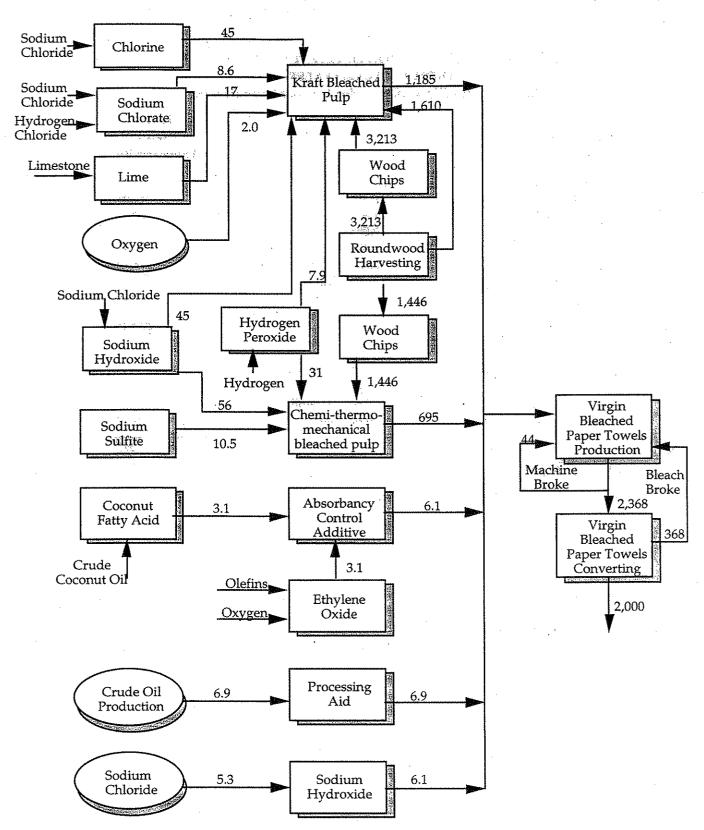


Figure 4. Flow diagram for the production of one ton of virgin bleached paper towels.

Many of the raw material and intermediate processes are not shown on this flow diagram for purposes of clarity. All numbers represent pounds of materials.

Table 4

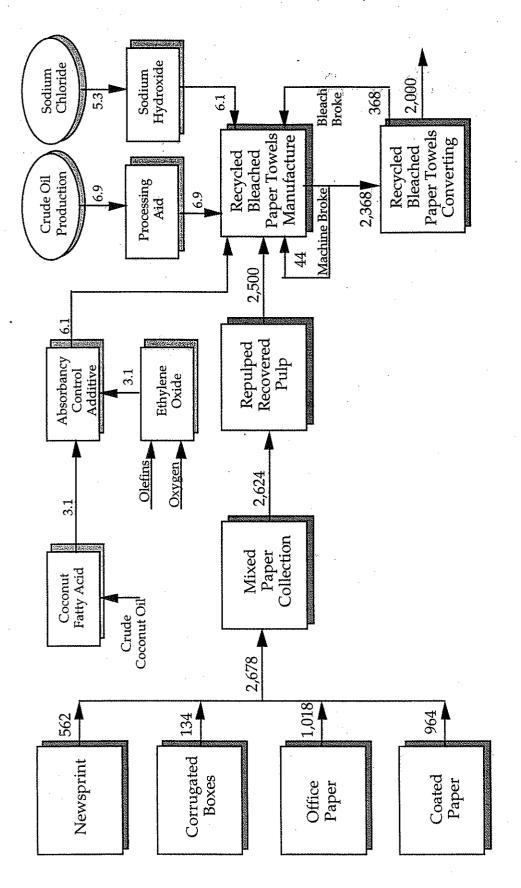
DATA FOR THE PRODUCTION OF ONE TON OF VIRGIN PAPER TOWELS

g ex	e e design		Total
Energy Usage		•* •	Energy Thousand Btu
Process Energy	201		1.5
Electricity	1,858	kwh 11125 B	√ 20,671
Natural gas	26,447	cu ft	30,679
LPG	0.0013	gal	0.14
Coal	188	lb	2,150
Distillate oil	0.046	gal	7.32
Residual oil	7.72	gal	1,320
Gasoline	0.0029	gal	0.41
Diesel	2.08	gal	329
Wood	18,281	thousand Btu	18,281
Total Process			73,437
Transportation Energy		·	. · ·
Combination truck	828	ton-miles	,
Diesel	7.79	gal	1,233
Single unit truck	0.068	ton-miles	
Diesel	0.0018	gal	0.28
Rail;	2,164	ton-miles	
Diesel	5.19	gal	822
Barge	5.08	ton-miles	
Diesel	0.010	gal	1.61
Residual oil	0.0041	gal	0.70
Ocean freighter	32.5	ton-miles	
Diesel	0.0032	gal	0.51
Residual	0.058	gal	10.0
Pipeline-natural gas	0.13	ton-miles	
Natural gas	0.30	cu ft	0.34
Pipeline-petroleum products	1.07	ton-miles	
Electricity	0.024	kwh	0.26
Total Transportation			2,069

Environmental Emissions

Process Greenhouse Gas Emissions

Methane 0.016 lb Fossil Carbon Dioxide 15.5 lb



using the mixed paper from offices. The weights include a 25% loss in the Flow diagram for the manufacture of one ton of recycled paper towels Numbers represent pounds of material. recycled paper towel manufacture. Figure 5.

Table 5

DATA FOR THE PRODUCTION OF ONE TON OF PAPER TOWELS
FROM RECYCLED PAPER

(Collection, deinking, and recycled paper towels manufacture and converting*)

Energy Usage			Total Energy
			Thousand Btu
Process Energy		•	
Electricity	1,688	kwh	18,775
Natural gas	24,572	cu ft	28,504
LPG	0.0013	gal	0.14
Coal	44.1	lb	506.
Distillate oil	0.010	gal	1.57
Residual oil	1.36	gal	233
Gasoline	0.0026	gal	0.37
Diesel	0.50	gal	78.7
Wood	3,587	thousand Btu	3,587
Total Process			51,685
Transportation Energy			
Combination truck	211	ton-miles	\$
Diesel	1.98	gal	313
Single unit truck	26,3	ton-miles	
Diesel	0.70	gal	110
Rail	3.11	ton-miles	
Diesel	0.0075	gal	1.18
Barge	0.40	ton-miles	
Diesel	8.0E-04	gal	0.13
Residual oil	3.2E-04	gal	0.054
Ocean freighter	32.5	ton-miles	
Diesel	0.0032	gal	0.51
Residual	0,058	gal	10.0
Pipeline-natural gas	0.13	ton-miles	
Natural gas	0.30	cu ft	0.34
Pipeline-petroleum products	1.07	ton-miles	
Electricity	0.024	kwh	0.26
Total Transportation		·	436

Environmental Emissions

Process Greenhouse Gas Emissions

Methane 0.016 lb Fossil Carbon Dioxide 1.71 lb

^{*} Also includes the production of the absorbancy additive, processing aid, and sodium hydroxide.

BOUNDARY CONDITIONS

Each materials flow diagram shows the process steps that are included within the system boundaries for each material analyzed. The data in the associated table(s) show the aggregated energy to produce one ton of the material specified, including the energy needed for each process step shown in the flow diagram. These tables also include any greenhouse gases produced as a process emission during the manufacture of the product or its raw materials.

If marketable coproducts or byproducts are produced in any process step in the system, adjustments have been made in the materials balance and energy requirements to reflect only the portion of each that is attributable to the product being considered. This is done based on the mass of each coproduct.

The first column in each data table shows the units of each fuel that are consumed in the process and transportation steps in the life cycle of the material. In the second column, these fuel units are converted to Btu values. The conversion factors include not only the energy content of the fuels but also the energy required to extract, transport, and process the fuels.

For electricity, precombustion energy calculations include adjustments for the average efficiency of conversion of fuel to electricity, and for transmission losses in power lines. Therefore, the kilowatt-hour (kwh) value shown on the tables is the aggregated amount of electricity used by the system. The Btu value shown in the second column accounts for the average mix of fuels used by utilities to produce electricity in the United States, in 1996. The Btu values also include the precombustion energy and efficiency factors.

The data tables for each material system report energy data in the categories of **process energy** and **transportation energy**. Process energy is energy consumed in the various processes used to manufacture the material or product. Transportation energy describes the energy to transport the materials and components to the site of the next processing step. The Btu values shown for each fuel include precombustion and combustion energy.

Transportation energy is calculated by using the distance of transport (miles), mode of transport (truck, rail, barge, ship), and Franklin Associates (FAL) transportation database. The distance and mode of transportation are usually provided by specific companies or facilities from which materials are shipped. The FAL transportation database has been developed by FAL staff. It expresses fuel usage per ton-mile of goods transported by specific modes of transportation.

Franklin Associates assigns an energy of material resource to fossil fuels (i.e., petroleum, natural gas, or coal—materials that are normally used as fuels) when they are used as raw materials. The energy of material resource is the fuel energy equivalent of the material, i.e., the amount of energy that would be obtained through combustion of the designated quantity of fossil fuel material. In this analysis, this energy is included in process energy if the material is consumed in the process, thus creating carbon dioxide emissions. If the fuel material becomes part of the product, the energy of material resource is not included in the process energy. For example, the process energy for the virgin boxboard does include the energy content of natural gas and petroleum that are raw materials for fertilizer (a raw material for corn starch) because the oil and natural gas are consumed in the production of materials to make fertilizer.

Geographic Scope

With the exception of overseas transportation of crude oil to the United States, all energy data are for the United States.

Electricity

In general, detailed data do not exist on the fuels used to generate the electricity consumed by each industry. Electricity production and distribution systems in the United States are interlinked. Users of electricity, in general, cannot specify the fuels used to produce their share of the electric power grid. Therefore, the national average fuel consumption by electrical utilities is used for this study.

Electricity generated on-site at a manufacturing facility is not shown as electricity. Instead, the fuels used at the facility to produce self-generated electricity are represented in the process data.

Recycling

The materials in this analysis are considered to be recycled only once. In traditional life cycle studies, limited recycling is referred to as "open-loop" recycling, while repeated (theoretically infinite) recycling is called "closed-loop" recycling. The type of recycling depends not only on infrastructure, but to a large extent on the nature of the material. For example, paper fibers degrade with each reprocessing and cannot be recycled indefinitely, while aluminum can be remelted over and over.

In this study, each of the recycled materials systems is modeled as a two-product open-loop system. That is, the recycled product systems all begin with a first product produced, then collected and transported to a repulper, then manufactured into a second product. In this study, the first product is a mixture

of mixed paper (separated into four categories--newsprint, corrugated, office paper, and coated paper), newspaper, and corrugated boxes. The second products are the boxboard and paper towels.

Components Not Included

Capital Equipment. The energy associated with the manufacture of capital equipment is not included in the energy profiles. This includes equipment to manufacture buildings, motor vehicles, and industrial machinery. The energy associated with such capital equipment generally, for a ton of materials, becomes negligible when averaged over the millions of pounds of product which the capital equipment manufactures.

Space Conditioning. The fuels and power consumed to heat, cool, and light manufacturing establishments are omitted from the calculations. For most industries, space conditioning energy is quite low compared to process energy. Energy consumed for space conditioning is usually less than one percent of the total energy consumption for the manufacturing process.

Support Personnel Requirements. The energy associated with research and development, sales, and administrative personnel or related activities have not been included in this analysis.

Miscellaneous Materials and Additives. Selected materials such as catalysts, pigments, or other additives which total less than one percent of the net process inputs are not included in the assessment.

PROCESS DESCRIPTIONS

BOXBOARD PRODUCTION

The production of boxboard from virgin materials is estimated from the production of virgin unbleached kraft paperboard production. The following raw materials are input to produce the virgin boxboard:

- Roundwood
- Wood residues
- Salt mining
- Sodium hydroxide and chlorine production
- Sodium sulfate production
- Limestone mining
- Lime production
- Sulfur production
- Sulfuric acid production
- Corn starch production

Corn growing and harvesting

Fertilizer production

Pesticides manufacture

Corn starch production

Unbleached kraft paperboard production

Roundwood Harvesting

The technique of harvesting trees has become a highly mechanized process. Typically, trees are harvested by using a feller buncher to fell the wood. The wood is pulled to the roadside, where branches are removed and the wood is cut to manageable lengths for loading on trucks and delivery to the mill. After the wood is cleared from the forest, a variety of site preparations are used. On some sites debris is manually removed from the forest before replanting, while other sites are left to grow back naturally. Finally, some harvested sites are burned to remove any remaining debris before replanting. Emissions do result from clearing the site by burning, but this practice occurs infrequently compared to the mass of trees harvested. It is assumed that these emissions are negligible.

Trees harvested specifically for wood pulp production account for approximately 53 percent of the wood delivered to the paper mill. The remainder comes from wood residues (sawdust and chips) generated by lumber production or other wood processing operations.

Wood Residues Production

Wood residues used in the production of paper are either mill residues generated by lumber mills or other wood processing operations, or forest residues. It is estimated that mill residues make up about 90 percent of the wood residues used by paper mills, and forest residues make up the remaining 10 percent.

Typically the wood that a sawmill receives will already be delimbed and cut to manageable lengths. The roundwood is sorted by diameter and then sent to a debarker. After debarking, the logs are conveyed through a series of cutting and planing operations. Roughly 75 to 80 weight percent of the tree as received is converted to lumber, with the remaining 20 to 25 percent becoming wood chips and fines. The chips are sold to pulp mills, and the fines are either burned as an energy source or burned for waste disposal.

Forest residues are small diameter trees, limbs and cuttings which are turned into chips in the forest. In general, wood residues are generated on site or quite close to the mills.

Salt Mining

For the most part, salt-based chlorine and caustic facilities use captive salt from another process or use salt recovered from underground deposits in the form of brine. In solution mining, an injection well is drilled and pressurized fresh water is introduced to the bedded salt (Reference B-1). The brine is then pumped to the surface for treatment. Salt mines are widely distributed throughout the United States.

Sodium Hydroxide and Chlorine Production

Sodium hydroxide and chlorine are produced from salt by an electrolytic process. The aqueous sodium chloride solution is electrolyzed to produce caustic soda, chlorine, and hydrogen gas. For this analysis, resource requirement and environmental emission coproduct credit is allocated on a weight basis to each of the materials produced in the cell. The reason for giving coproduct credit on a weight basis is that it is not possible, using the electrolytic cell, to get chlorine from salt without also producing sodium hydroxide and hydrogen, both of which have commercial value as useful coproducts. Likewise, sodium hydroxide cannot be obtained without producing the valuable coproducts of chlorine and hydrogen. Furthermore, it is not possible to control the cell to increase or decrease the amount of chlorine or caustic soda resulting from a given input of

salt. This is determined by the stoichiometry of the reaction. The electrolytic cell is perceived as a "black box" with an input of salt and electricity, and an output of chlorine, sodium hydroxide, and hydrogen.

The electrolysis of sodium chloride is performed by one of two processes: the mercury cathode cell process, or the diaphragm cell process. About 83 percent of electrolyzed chlorine and caustic soda production comes from the diaphragm process, with the remainder coming from the mercury cell process (Reference B-2).

The diaphragm cell uses graphite anodes and steel cathodes. Brine solution is passed through the anode compartment of the cell, where the salt is decomposed into chlorine gas and sodium ions. The gas is removed through a pipe at the top of the cell. The sodium ions pass through a cation-selective diaphragm. The depleted brine is either resaturated with salt or concentrated by evaporation and recycled to the cell. The sodium ions transferred across the diaphragm react at the cathode to produce hydrogen and sodium hydroxide. Diffusion of the cathode products back into the brine solution is prevented by the diaphragm.

The mercury cathode cell process is described by:

NaCl + xHg
$$\Rightarrow$$
 1/2 Cl₂ + Na(Hg)x and
Na(Hg)x + H₂O \Rightarrow NaOH + 1/2 H₂ + xHg

Chlorine gas collects at graphite anodes. The chlorine gas from the anode compartment is cooled and dried in a sulfuric acid scrubber. The gas is then cooled further to a liquid for shipment, generally by rail and barge. Metallic sodium reacts with the mercury cathode to produce an amalgam, which is sent to another compartment of the cell and reacted with water to produce hydrogen and high purity sodium hydroxide. Mercury loss is a disadvantage of the mercury cathode cell process. Some of the routes by which mercury can escape are in the hydrogen gas stream, in cell room ventilation air and washing water, through purging of the brine loop and disposal of brine sludges, and through end box fumes.

Sodium Sulfate Mining and Processing

Sodium sulfate, which is referred to as salt cake by the pulping industry, is consumed in the kraft pulping process. The upper levels of Searles Lake, California, the Great Salt Lake in Utah, and the oil field brines of west Texas all contain sodium sulfate. Typically, sodium sulfate crystals settle out of the cooled brine. The crystals are then dissolved again and precipitated to achieve the desired purity.

Limestone Mining

Limestone is quarried primarily from open pits. The most economical method of recovering the limestone has been through blasting, followed by mechanical crushing and screening (References B-1 and B-3).

Lime Production

Lime is never found in a natural state, but is manufactured by calcining (burning) high purity calcitic or dolomitic limestone at high temperatures. The calcination process drives off the CO₂, forming calcium oxide (quicklime). The subsequent addition of water creates calcium hydroxide (hydrated or slaked lime). The term lime is a general term that includes the various chemical and physical forms of quicklime and hydrated lime. Most of the lime produced in the United States in 1994 was quicklime (85%), with hydrated lime (13%) and deadburned dolomite (2%) accounting for the rest. The data in this section are for the production of quicklime (References B-4 and B-5).

Solid wastes generated during the manufacture of lime include impurities removed from the limestone, tailings collected in the lime production process, and lime kiln dust collected from particulate control devices on the lime kilns. Based on lengthy discussions with a representative of the National Lime Association and a confidential lime industry expert, it was assumed that all collected lime dust and tailings from lime production are either sold for various useful purposes, injected back into mines, replaced in quarries, or land applied on-site (Reference B-6 and B-7). This may not be true of a few smaller companies which are not close to their source of limestone.

Sulfur Production

Sulfur exists in nature as elemental sulfur and is also found in ores such as pyrite (FeS2). Sulfur is also recovered from hydrogen sulfide (H2S), a component of petroleum and natural gas. The Frasch process (recovery from limestone) accounts for approximately 25 percent of U.S. sulfur production, while the Claus process (recovery from petroleum and natural gas) accounts for approximately 75 percent. Descriptions of these two processes follow.

Sulfur Production from the Frasch Process. Sulfur is obtained from sulfur-bearing porous limestone primarily by the Frasch process. In this process,

a set of three concentric pipes are inserted into a well drilled into an underground sulfur dome. Injecting superheated water into the well raises the temperature of the sulfur-bearing rock above the melting point of sulfur. The molten sulfur is then forced to the surface by compressed air injected into the well. As all Frasch mines in the U.S. are near waterways, the sulfur is shipped by insulated barge or boat, or allowed to solidify and shipped as a solid (Reference B-1).

Sulfur Production from the Claus Process. Recovery of sulfur from sour natural gas and crude oil via the Claus process accounts for about 66 percent of the sulfur produced in the United States. Approximately 59 percent of the sulfur produced via Claus recovery is obtained from hydrogen sulfide recovered from petroleum refining, and the remaining 41 percent is recovered from natural gas sweetening (Reference B-1).

Hydrogen sulfide is recovered from natural gas or refinery gases by absorption in a solvent or by regenerative chemical absorption (Reference B-8). Hydrogen sulfide concentrations in the gas from the absorption unit vary. For this analysis, an industry average H₂S gas concentration of 85 percent is used (References B-9 and B-10). This concentrated hydrogen sulfide stream is treated by the Claus process to recover the sulfur. The Claus process is based upon the reaction of hydrogen sulfide with sulfur dioxide according to the exothermic reaction (Reference B-8):

$$H_2S + SO_2 \times 3S + 2H_2O$$
 (Reaction 1)

Sulfur dioxide for the reaction is prepared by oxidation of hydrogen sulfide with air or oxygen in a furnace using either the partial combustion process (once-through process) or the split-stream process. The partial combustion method is used when the H_2S concentration is greater than 50 percent and the hydrocarbon concentration is less than 2 percent. The split stream process is used when there is an H_2S concentration of 20 to 50 percent and a hydrocarbon concentration of less than 5 percent.

In the partial combustion method, the hydrogen sulfide-rich gas stream is burned with a fuel gas in an oxygen-limited environment to oxidize one-third of the H₂S to SO₂ according to the reaction (Reference B-10):

$$2H_2S + 2O_2 \varnothing SO_2 + S + 2H_2O$$
 (Reaction 2)

Sulfur is removed from the burner and the H_2S/SO_2 mixture moves to the catalytic converter chambers.

In the split stream process, one-third of the hydrogen sulfide is split off and completely oxidized to SO₂ according to the reaction:

$$2H_2S + 1.5 O_2 \varnothing SO_2 + H_2O$$
 (Reaction 3)

The remaining two-thirds of the H₂S is mixed with the combustion product and enters the catalytic converter chambers.

The H₂S and SO₂ mixture from either process is passed through one or more catalyst beds and is converted to sulfur, which is removed by condensers between each bed (Reference B-8). For this analysis, an H₂S concentration of 85 percent has been assumed; therefore, it is also assumed that the partial combustion process is used.

Although efficiencies of 96 to 99 percent sulfur recovery have been demonstrated for the Claus process, recovery is usually not over 95 percent and is limited by thermodynamic considerations (References B-8 and B-10). For this analysis, a sulfur recovery efficiency of 93 percent is assumed.

The energy generated from burning hydrogen sulfide to produce SO₂ is usually recovered and used directly to reheat the process stream in secondary and tertiary condensers, or recovered as steam for use in other processes (Reference B-10). Heat released from cooling the exothermic reaction to form sulfur is also recovered. The theoretical potential energy recoverable from the process is calculated from the overall sulfur production reaction:

$$H_2S + 0.5 O_2 \varnothing S + H_2O$$
 (Reaction 4)

The standard heats of formation, ?H $_{\rm f}$ $_{\rm 298}$, for the species in Reactions 4 are (Reference B-11):

```
?H f 298 (O_2 (g)) = 0 \text{ kcal mole}^{-1}

?H f 298 (S (s)) = 0 \text{ kcal mole}^{-1}

?H f 298 (H_2S (g)) = -4.93 \text{ kcal mole}^{-1}

?H f 298 (H_2O (g)) = -57.8 \text{ kcal mole}^{-1}
```

The standard heat of formation for Reaction 4 is therefore:

?H
$$_{\rm f}$$
 298 = [0 + -57.8 kcal/mol H₂O] - [-4.96 kcal/mol H₂S + 0] ?H $_{\rm f}$ 298 = -52.87 kcal/mole

For this analysis, a sulfur recovery rate of 93 percent has been assumed; therefore 1,073 pounds of H_2S are required to recover 1,000 pounds of sulfur. This equates to 14,315 moles of hydrogen sulfide. According to the above formation energy calculation, processing this amount of hydrogen sulfide could theoretically release 7.57×10^5 kcal, or 3.0 million Btu.

Industry sources report steam recovery from the sulfur recovery process of approximately 2,000 lb of steam per 1,000 lb of recovered sulfur. Assuming the heat value of 250 psia steam to be 1,200 Btu/lb (Reference B-11), this equates to 2.40 million Btu per 1,000 lb of recovered sulfur. The difference of 0.6 million Btu between the heat generated by the process and the heat recovered to produce steam is a loss of heat from the system. The fuel value of H₂S is not included in the total energy for the system because H₂S is not used as a commercial fuel. The system is also not given an energy credit for any steam exported from the system.

Included in this data set are the energy requirements for producing and refining crude oil to produce hydrogen sulfide-containing refinery gases and for sour natural gas production, processing, and sweetening to produce concentrated hydrogen sulfide gas.

Sulfuric Acid Production

Sulfur is burned with air to produce sulfur dioxide and heat. The heat is used to generate steam that is usually used in adjacent processing plants and to supply energy to the sulfuric acid plant. The energy import (as the calorific value) of sulfur and the energy export of steam cancel in the energy balance for this process. Thus, it is assumed here that there are no net fuel requirements. The sulfur dioxide gas is converted to sulfur trioxide and combined with dilute sulfuric acid to form the concentrated product.

Corn Starch Production

Corn starch is produced through the following steps:

Corn growing and harvesting
Fertilizer manufacture
Nitrogen
Phosphate
Potash
Pesticides manufacture
Corn starch production

Limestone, which is also added as a nutrient to the soil during corn growing, is discussed previously.

Corn Growing and Harvesting. Whole grain corn is composed of 71.7 percent starch (Reference B-30). To produce high corn yields, many factors must be considered. The most important of these factors include temperature, climate, and nutrients. Corn is a warm weather plant requiring a growing season of about 140 days with an average daytime temperature of 75°F with nighttime temperatures exceeding 58°F. Even in the U.S. central Corn Belt, temperatures are not considered ideal. Also needed for high yields is 16 to 26 inches of rainfall. Irrigation is used on most corn-growing farms to supplement inadequate rainfall. Finally, corn needs nitrogen, phosphorus, potassium, calcium, magnesium, and sulfur from the soil. Soil fertility is easily depleted, especially when the entire plant is harvested for silage. Fertilizer and limes are added to bring necessary nutrients to the soil. Pesticides are added to destroy insects, fungus, and any other pests that would hurt the plant.

Today, corn harvesting is mostly done by multi-row combines. The corn is then stored for drying. After drying, the corn is transported to customers. Corn used in the production of corn starch must be transported to a wet milling plant.

Fertilizer Manufacture. Most corn land receives applications of fertilizer, typically nitrogen, phosphate, and/or potash. Over half of all fertilizers are applied as single nutrient materials. USDA literature reports applications of nitrogen, phosphate, and potash fertilizers in terms of pounds of N, P_2O_5 , and K_2O (Reference B-12).

Nitrogen. Nitrogen as a single nutrient is commonly applied in the form of anhydrous ammonia. The following steps are included in this data:

Natural gas production Natural gas processing Ammonia production Nitrogen fertilizer production

Natural Gas Production. Natural gas is extracted from deep underground wells and is frequently co-produced with crude oil. Because of its gaseous nature, it flows quite freely from wells which produce primarily natural gas, but some energy is required to pump natural gas and crude oil mixtures to the surface. Atmospheric emissions from natural gas production are primarily due to line or transmission losses and unflared venting. The waterborne waste pertains to the portion of natural gas that is produced in

combination with oil. These combination wells account for approximately 25 percent of all natural gas production.

Natural Gas Processing. Light straight-chain hydrocarbons are normal products of a natural gas liquids processing plant. The plants typically use compression, refrigeration and oil adsorption to extract these products. Heavy hydrocarbons are removed first. The remaining components are extracted and kept under controlled conditions until transported in high-pressure pipelines, insulated rail cars or barges.

If the natural gas has a hydrogen sulfide content of greater than 0.25 grain per 100 standard cubic feet, it is considered "sour." Before it can be used, the gas must undergo removal of the hydrogen sulfide by adsorption in an amine solution, a process known as "sweetening."

The primary pollutants from the natural gas stream are volatile hydrocarbons that leak into the atmosphere. Additional sources of pollutants are natural gas-fired compressor engines. Emissions will also result from the gas sweetening plants if the acid waste gas from the amine process is flared or incinerated. When flaring or incineration is practiced, sulfur dioxide is the major pollutant of concern.

Ammonia Production. Ammonia is produced primarily by steam reformation of natural gas. Natural gas and steam are fed into a tubular furnace where the reaction over a nickel reforming catalyst produces hydrogen and carbon oxides. The primary reformer products are then mixed with preheated air and reacted in a secondary reformer to produce the nitrogen needed in ammonia synthesis. The gas is cooled to a lower temperature and subjected to a water shift reaction in which carbon monoxide and steam are reacted to form carbon dioxide and hydrogen. The carbon dioxide is removed from the shifted gas in an absorbent solution. Hydrogen and nitrogen are reacted in a synthesis converter to form ammonia (References B-13 and B-14).

Nitrogen Fertilizer Production. Nitrogen fertilizer is applied in the form of anhydrous ammonia, which is 82 percent by weight N.

Phosphate. Phosphate fertilizer applied as a single nutrient is most commonly in the form of superphosphate, with 16 to 20 percent available P₂O₅, or triple superphosphate, with 44 to 51 percent available P₂O₅. Superphosphates are produced by the action of sulfuric acid on phosphate rock, while triple superphosphates are made by adding phosphoric acid to phosphate rock (References B-15 and B-16). The data are based on half of the phosphate applied as superphosphate and half as triple superphosphate. The following process steps are required for the manufacture of the phosphate fertilizers:

Superphosphate

Phosphate rock mining
Crude oil production
Crude oil refining
Natural gas production
Natural gas processing
Sulfur production
Sulfuric acid production
Superphosphate production

Triple superphosphate

Phosphate rock mining Silica mining and processing

Coal mining

Coal coke production

Elemental phosphorus production

Oxygen production

Phosphorus pentoxide production

Phosphoric acid production

Triple superphosphate production

Phosphate fertilizer production

Natural gas production and processing, sulfur production, and sulfuric acid production are discussed elsewhere in this appendix.

Phosphate Rock Mining. Phosphate is mined as a natural rock containing mostly calcium phosphate. Large deposits are contained in the United States, North Africa, and the former Soviet Union (Reference B-16).

Crude Oil Production. Oil is produced by drilling into porous rock structures generally located several thousand feet underground. Once an oil deposit is located, numerous holes are drilled and lined with steel casing. Some oil is brought to the surface by natural pressure in the rock structure, although most oil requires some energy to drive pumps that lift oil to the surface. Once oil is on the surface, it is separated from water and stored in tanks to await transportation to a refinery. In some cases it is immediately transferred to a pipeline that transports the oil to a larger terminal.

There are two primary sources of waste from crude oil production. The first source is the "oil field brine," or water which is extracted with the oil. The brine goes through a separator at or near the well head in order to remove the oil from the water. These separators are very efficient and leave minimal oil in the water.

According to the American Petroleum Institute (API) it is estimated that 21 billion barrels of brine water were produced from crude oil production in 1985 (Reference B-17). This quantity of water equates to a ratio of 5.4 barrels of water per barrel of oil. The majority of this water (85 percent) is injected into separate wells specifically designed to accept production-related waters. This represents all waters produced by onshore oil production facilities which are not permitted to discharge "oil field brine" to surface waters (Reference B-18). The remainder of the produced water is from offshore oil production facilities and is assumed to be discharged to the ocean. Therefore, the waterborne wastes represent the brine wastes present in this 15 percent of brine water (Reference B-19). Because crude oil is frequently produced along with natural gas, a portion of the waterborne waste is allocated to natural gas production (Reference B-17).

The second source of waste is the gas produced from oil wells. While most of this is recovered for sale, some is not. Atmospheric emissions from crude oil production are primarily hydrocarbons. They are attributed to the natural gas produced from combination wells and relate to line or transmission losses and unflared venting.

The transportation data assume a mix of foreign and domestically produced crude oil. According to the **Petroleum Supply Annual**, **June 1994**, 49 percent of the crude oil used in the United States is imported.

Distillation, Desalting, and Hydrotreating. A

petroleum refinery is a complex combination of processes that serve to separate and physically and chemically transform the mixture of hydrocarbons found in crude oil into a number of products. Modern refineries are able to vary the different processing steps through which a charge of crude oil passes in order to maximize the output of higher value products. This variation of processing steps can change according to the make-up of the crude oil as well as the economic value of the products. Because of this variation, it is necessary to make certain assumptions about the refinery steps to which crude oil is subjected in order to produce petrochemical feedstocks.

For this analysis, it is assumed that crude oil used to produce feedstocks for olefins production goes through the following refinery operations: desalting, atmospheric and vacuum distillation, and hydrotreating. Due to a lack of facility-specific data, literature sources were used to estimate the energy requirements for these refining steps. A number of literature references were used, most of which showed similar energy inputs (References B-20 through B-24).

Crude desalting is the water-washing of crude oil to remove water-soluble minerals and entrained solids (Reference B-25). For this analysis it is assumed

		•	•		* * * * * * * * * * * * * * * * * * * *
•		•			
•		<u>.</u>			
			a		
			6	• *	
		4		* .	
·	,		•		
			•		
			•		
			·		
			. *		
			ı		
			•		
•					
	•				
		•			
	·	*			
		·		· -	
			,		
				,	
		•		•	
	•				
•	•				•
		,		•	
·			5.	•	
•					

that all of the crude that enters a refinery passes through the desalting step (References B-23 and B-25).

Crude oil distillation separates the desalted crude oil into fractions with differing boiling ranges. Atmospheric distillation is used to separate the fractions with a boiling point less than 650° Fahrenheit (References B-23, B-24, and B-25). At temperatures greater than 650° Fahrenheit thermal cracking of the hydrocarbons starts. Fuel gas or still gas that is liberated from the crude during distillation is further processed into liquefied petroleum gas or natural gas, depending on the carbon chain length. This gas is sold or used in the refinery to generate heat. About 52 percent of the non-electrical energy used in a refinery for direct heating or steam production comes from fuel gas (Reference B-26). Coproduct credit is given on a mass basis for the gas fractions not used for energy in the refinery. Fuel gas or still gas used as an energy source in refining is assumed to have the same composition as natural gas and is shown as process energy, not as raw material.

The residue from the atmospheric distillation unit passes to a vacuum distillation unit where separation of the various fractions can be accomplished at lower temperatures than would be required at atmospheric pressure. The residue or bottoms of the vacuum distillation unit is a valuable coproduct that is further processed to make usable products. Coproduct credit is given on a weight basis for this residue. It is assumed that all of the crude used to produce olefins feedstock passes through atmospheric distillation, while only 46 percent of the initial crude oil charge passes through vacuum distillation (References B-20, B-21, and B-25).

Hydrotreating is a catalytic hydrogenation process that reduces the concentration of sulfur, nitrogen, oxygen, metals, and other contaminants in a hydrocarbon feed. These contaminates can poison or foul catalysts used in catalytic crackers and contribute to air emissions if the hydrocarbon is used as a fuel. It is assumed that all of the feedstock for olefin cracking passes through hydrotreatment. Sulfur and metals removed from crude are separated and sold as coproducts (References B-20 and B-23). Coproduct credit is given for these materials on a mass basis.

Energy requirements for petroleum refineries are usually listed in literature sources as Btu of fuel, pounds of steam, and electricity per 42 gallon barrel of crude processed. For this analysis, a conversion of 3.385 barrels of crude per 1,000 pounds was used. Steam inputs were converted to Btu requirements using a conversion of 1,200 Btu per pound. Btu inputs for steam were added to the Btu inputs listed as fuels, and the total was converted to quantities of fuels using the combustion energy values listed in Appendix A and the following refinery fuel mix: residual oil and residues (coke), 22 percent;

purchased natural gas, 24 percent; LPG, 2 percent; and fuel gas or still gas, 52 percent (Reference B-27). Negligible quantities of coal and distillate oil are also used in the "average" refinery.

Superphosphate Production. Superphosphate is produced by the addition of sulfuric acid to phosphate rock. This superphosphate is a mixture of gypsum and calcium phosphate.

Silica Mining and Processing. Silica is obtained from glass sand, a high purity quartz sand with high silica content and typically less than one percent of iron oxide, chromium compounds, and alumina, calcium, or magnesium oxides. In general, the U.S. consumption of glass sand is met by U.S. production, but some high purity glass sand is imported. Glass sand deposits exist in New Jersey in the form of unconsolidated sand banks, and as sandstone found in the Alleghenies and the Mississippi Valley. The east-west belt of states running from Pennsylvania to Illinois has rich resources for glass sand.

Mining operations vary depending on the nature of the deposit at each location. Open pit excavation and dredging are the two basic mining methods, each requiring a combination of many types of equipment including crushers, screens, washers, classifiers, and grinding mills.

Coal Mining. Coal may be obtained by surface mining of outcrops or seams that are near the earth's surface or by underground mining of deposits. In strip mining, the overburden is removed from shallow seams, the deposit is broken up, and the coal is loaded for transport. Generally, the overburden is eventually returned to the mine and is not considered as a solid waste in this analysis.

After the coal is mined, it goes through various preparation processes before it is used. These processes vary depending on the quality of the coal and the use for which it is intended. Coal preparation usually involves some type of size reduction and partial removal of ash-forming materials.

Metallurgical Coke Production. The two proven processes for manufacturing metallurgical coke are known as the beehive process and the byproduct process (Reference B-28). The primary method for manufacturing coke is the byproduct method, which accounts for more than 98 percent of U.S. coke production. For this analysis, it is assumed that all metallurgical coke is produced in the byproduct oven.

In the byproduct method, air is excluded from the coking chambers, and the necessary heat for distillation is supplied from external combustion of some of the gas recovered from the coking process (Reference B-28). Coking 1,000

pounds of coal in the byproduct oven is assumed to produce the following: coke, 774 lb; tar, 37 lb; water, 32 lb; benzene, 11 lb; and coke oven gas, 147 lb (Reference B-29). Coproduct credit is given on a weight basis to all of the byproducts from the oven, except water. It is assumed that about 40 percent of the coke oven gas (59 pounds) is used as a fuel for underfiring the coke oven (Reference B-28). Therefore, coproduct credit is given for the remaining 88 lb of coke oven gas. The energy content of the coke oven gas is accounted for in the energy of material resource for the coal used as a feedstock for the coke oven. While it is recognized that the gas is actually used as a fuel in the coke oven, the methodology used in this study accounts for the energy derived from materials used as feedstocks on the basis of the energy content of the material that is extracted from the ground to produce the raw material.

Elemental Phosphorus Production. Elemental phosphorus is produced from phosphate rock by a reaction with coke and silica in an electric furnace. Elemental phosphorus is one of several materials resulting from this process.

Oxygen Production. Oxygen is manufactured by cryogenic separation of air, a technique by which air is liquefied, and the oxygen is collected by fractionation. The oxygen is produced in the form of a liquid which boils at 300°F below zero at normal atmospheric pressure. Therefore, it must be kept under stringent conditions of temperature and pressure for handling. Most oxygen plants are located near their point of consumption to minimize transportation difficulties, although there is a small amount of long-distance hauling in insulated rail cars.

Phosphorus Pentoxide Production. Oxidation of the elemental phosphorus produces phosphorus pentoxide.

Phosphoric Acid Manufacture. Finally, hydration of the phosphorus pentoxide yields phosphoric acid.

Triple Superphosphate Production. Triple superphosphate is produced by the addition of phosphoric acid to phosphate rock. It has three times the amount of available phosphate as in superphosphate and contains no gypsum.

Phosphate Fertilizer Production. Phosphate fertilizer is applied in the form P_2O_5 . The superphosphate is applied with 20 percent available P_2O_5 and the triple superphosphate with 50 percent available P_2O_5 .

Potash. Potash fertilizer is generally applied in the form of potassium chloride (KCl), which is sold in various agricultural grades, containing

60 to 62 percent K₂O, 48 to 52 percent K₂O, or 22 percent K₂O. The following process steps are needed:

Sylvinite mining and processing KCl production
Potash fertilizer production

Sylvinite Mining and Processing. Most of the U.S. supply of KCl produced from sylvinite ore is mined from deep deposits in the Carlsbad, New Mexico region. Sylvinite mining and processing is assumed to be similar to soda ash mining and processing.

KCl Production. KCl is obtained from sylvinite ore and purified by fractional crystallization or flotation. It is also extracted from salt lake brines and purified by recrystallization (References B-15 and B-16).

KCl is prepared from sylvinite ore by passing hot liquor through a series of steam-heated turbomixer dissolvers countercurrent to a flow of crushed ore. KCl and a small amount of NaCl go into solution. When the solution is cooled from its boiling point, KCl separates out. Tailings from the process, largely NaCl, are carried out of the plant to waste storage. A large part of the process liquor is decanted to be used again (Reference B-15).

KCl is also produced by extraction from the brines of Searles Lake, California. This brine, containing various salts, is carbonated with flue gas from the boiler plant. Sodium bicarbonate separated by this reaction is calcined and converted to dense soda ash. Crude borax is crystallized from the carbonated end liquor by cooling under vacuum. The filtrate is returned to the lake. Soda ash, KCl, borax/boric acid, and salt cake are produced by brine extraction (Reference B-15).

Potash Fertilizer. The potash fertilizer analyzed in this study is based on application as KCl containing 50 percent K₂O. Seventy-five percent of the KCl is assumed to be produced from sylvinite and 25 percent from brine extraction.

Pesticide Manufacture. Pesticides applied to corn include a variety of herbicides, insecticides, defoliants, and desiccants. Fungicides, miticides, and growth regulators may be applied as well. A wide variety of pesticides have been formulated to address the varying needs and conditions of each region; thus, the types and quantities of pesticide applied to corn acreage vary widely. As a result, the effects of individual pesticides on the environment also vary.

Once the pulp is produced, it is sent as a water slurry to the paperboardforming section of the mill. To form the paperboard, the fiber suspension drains
onto a finely woven plastic or wire mesh belt which allows the water to drain
through and retains the fiber. Approximately 98 percent of the water is removed
by draining and pressing the fiber web between hard machine rolls. Paper
(wood) fibers have a natural affinity for themselves and coupled with the
mechanical interweaving and chemical additives, the web becomes a structure.
The final water is evaporated by passing the web of paperboard over a number
of steam-heated drums. The paperboard is then wound onto rolls.

Corn Starch. Corn starch is produced from corn by wet milling. The corn is soaked in steeping tanks containing a solution of 0.3 percent sulfur dioxide in water to soften the kernel and dissolve inorganic components. This steep liquor is later concentrated for sale as a coproduct. The softened corn is lightly milled to free the germ from the kernel. The germ is then processed for oil removal. The remaining corn fraction, mostly starch, protein, and hulls, is then heavily milled. The starch is washed from the hulls, and the resulting starch slurry is separated, refined, washed, and dried.

Starch is a surface sizing material which fills in surface voids and therefore, reduces the rate of liquid penetration in the dry paper (Reference B-31).

Unbleached Kraft Paperboard Production

Kraft pulp is the most widely used type of wood pulp in the United States today, accounting for 70 percent of the total wood pulp produced. It is used in either an unbleached or bleached form.

The kraft pulping process is based on chemical digestion of wood which has been previously debarked and chipped. The digester is a closed container which holds the wood chips and digestion liquors. The liquor is mainly an aqueous solution of chemicals including sodium sulfide and sodium hydroxide.

In order for digestion to take place, heat and pressure are applied to the mixture of wood and liquor. The digestion process delignifies the wood and removes other chemical components from the wood, leaving only the wood fiber.

One of the features of the kraft process is that the used digestion liquor, called black liquor, is burned. Because the liquor contains a high percentage of flammable wood components, it burns readily. The remaining digestion chemicals, called green liquor, are removed and reacted with salt cake and lime. The resulting white liquor is returned to the digester.

Combustion of black liquor and the bark removed from logs entering the mill often provides sufficient energy to operate a pulp mill. Thus, there are only small amounts of fossil fuel requirements for the pulp-making process, although additional energy from fossil fuel sources is used in the paper-forming steps that immediately follow pulp making. The black liquor that is burned in the recovery furnace is treated as fuel for the process.

After the wood pulp is "blown" from the digester by the steam used in the process, the pulp is washed free of the chemicals, screened and refined for entry into the paperboard-forming section of the mill.

Boxboard References

- B-1 U.S. Bureau of Mines. Mineral Yearbook. Volume 1. 1989.
- B-2 North American Chlor-Alkali Industry Plants and Production Data Report - 1995. Pamphlet 10. The Chlorine Institute, Inc. April, 1996.
- B-3 U.S. Department of the Interior, Bureau of Mines. Mineral Facts and Problems. 1984.
- B-4 Lime, Minerals Yearbook 1995, USGS.
- B-5 Emission Factor Documentation for AP-42, Section 11.15, Lime Manufacturing. US EPA, April 1994.
- B-6 Discussions between Franklin Associates, Ltd. and Eric Malias of the National Lime Association, January, 1998.
- B-7 Discussions between Franklin Associates, Ltd. and confidential industry sources, January, 1998.
- B-8 Riegel's Handbook of Industrial Chemistry. Ninth Edition. Edited by James A. Kent. Van Nostrand Reinhold. New York. 1992.
- B-9 Franklin Associates, Ltd., based on confidential information supplied by industry sources.
- B-10 Gary, J. H., and G. E. Handwerk. **Petroleum Refining, Technology and Economics**. Second Edition. Marcel Dekker, Inc. New York. 1984.
- B-11 Handbook of Chemistry and Physics. 63rd Edition. CRC Press Inc. Boca Raton, Florida. 1983.
- B-12 Agricultural Resources: Inputs Situation and Outlook. Resources and Technology Division, Economic Research Service, U.S. Department of Agriculture, Washington DC. Report AR-29. February 1993.
- B-13 Welch, R.O., et al. Study of Environmental Impacts of Disposables versus Reusables. Prepared for the U.S. Environmental Protection Agency by Midwest Research Institute and Franklin Associates, Ltd. April, 1977.

- B-14 Midwest Research Institute. Resource and Environmental Profile Analysis of Plastics and Competitive Materials. Prepared for The Society of the Plastics Industry, Inc. February, 1974.
- B-15 Shreve, Norris. Chemical Process Industries. McGraw-Hill, Inc. 1967.
- B-16 Sax, N. Irving and Richard J. Lewis, Sr. Hawley's Condensed Chemical Dictionary. Eleventh Edition. Van Nostrand Reinhold. 1987.
- B-17 **Oil and Gas Industry Exploration and Production Wastes.** Prepared by ERT for American Petroleum Institute. Document #471-01-09. July, 1987.
- B-18 Personal communication between Franklin Associates, Ltd. and L. Gibson. U.S. Environmental Production Agency. NPDES Permits Branch. Dallas, Texas.
- B-19 Energy Information Administration. **Petroleum Supply Annual 1993.** Volume 1. June, 1994.
- B-20 Energy and Materials Flows In Petroleum Refining, ANL/CNSV-10. Argonne National Laboratory. February 1981.
- B-21 Hydrocarbon Processing- Refining Handbook '92. November, 1992. Volume 71. Number 11.
- B-22 **1989 Industrial Process Heating Energy Analysis**. Gas Research Institute. May, 1991.
- B-23 Gary, James H. and Glenn E. Handwerk. Petroleum Refining-Technology and Economics. Marcel Dekker, Inc. 1984.
- B-24 Meyers, Robert A., ed. Handbook of Petroleum Refining Processes.

 McGraw-Hill Book Company. 1986.
- B-25 **Riegel's Handbook of Industrial Chemistry.** Ninth Edition. Edited by James A. Kent. Van Nostrand Reinhold. New York. 1992.
- B-26 Manufacturing Energy Consumption Survey, Consumption of Energy 1988. DOE/EIA-0512(88). Energy Information Administration. May, 1991.
- B-27 AMOCO/U.S. EPA Pollution Prevention Project, Yorktown Refinery, Refinery Release Inventory. PB92-228550. United States Environmental Protection Agency. June, 1992.

- B-28 The Making, Shaping and Treating of Steel, 10th Edition. United States Steel Corporation. Published by the Association of Iron and Steel Engineers. Pittsburgh, PA. 1985.
- B-29 Loison, Roger. **Coke- Quality and Production.** Buttersworth Books. London. 1989.
- B-30 Watson, Stanley A. and Paul E. Ramstad, eds. Corn: Chemistry and Technology. 1987.
- B-31 Smook, G. A. Handbook for Pulp and Paper Technologists. TAPPI. 1987.

PAPER TOWEL PRODUCTION

Virgin paper towels are usually made with a combination of kraft pulp and chemical-thermomechanical pulp being fed into a paper making machine. The following steps in the production of paper towels are discussed in the sections below:

- Bleached kraft pulp
 Hydrogen production
 Sodium chlorate production
 Hydrogen peroxide production
 Bleached kraft pulp production
- Bleached chemi-thermomechanical pulp (CTMP)
- Absorbency control additive
- Processing aid
- Paper towel production and converting

Some processes were discussed in the boxboard section above and are not repeated here. These include:

- Roundwood harvesting
- Wood chips
- Salt mining
- Caustic soda and chlorine production
- Oxygen production
- Limestone mining
- Lime production

Bleached Kraft Pulp

Hydrogen Production. Hydrogen and carbon dioxide are coproducts in the production of synthesis gas. Synthesis gas is primarily produced from natural gas by steam-methane reforming. Natural gases, or other light hydrocarbons, and steam are fed into a primary reformer over a nickel catalyst to produce hydrogen and carbon oxides, generally referred to as synthesis gas. About 70 percent of the hydrocarbon feed is converted to synthesis gas in the primary reformer (Reference PT-1).

The effluent from the reformers is fed into carbon monoxide shift converters where the carbon monoxide reacts with water to form carbon dioxide and hydrogen. The effluent from the shift converters is cooled, and condensed water is removed. The carbon dioxide and some excess hydrogen are also removed from the synthesis gas as coproducts.

The ratio of carbon monoxide to hydrogen in the synthesis gas differs depending on the specifications for the synthesis gas, and therefore the amounts of hydrogen and carbon dioxide coproducts differ also. Synthesis gas is a raw material for many different processes, each with specific requirements. Because of this difference in requirements, it is difficult to show an accurate material balance for this process. The data for hydrogen production are estimates of the synthesis gas production. Raw material inputs for hydrogen are based on the conversion of methane to carbon monoxide and hydrogen.

Sodium Chlorate Production

Sodium chlorate is used to produce chlorine dioxide at the pulp mill site. The chlorine dioxide is used for bleaching. Sodium chlorate is produced from electrolysis of salt brine similar to the production of caustic and chlorine, except that the chlorine and caustic are not separated, but are instead allowed to mix (Reference PT-2). Hypochlorite forms first, followed by the formation of sodium chlorate.

Hydrogen Peroxide Production

Hydrogen peroxide can be produced by several electrochemical or organic routes. This study characterizes hydrogen peroxide from the oxidation/reduction of an anthraquinone—the predominant commercial route to hydrogen peroxide.

An anthraquinone in an organic solvent is first catalytically hydrogenated. This material is then oxidized with oxygen taken from air back to anthraquinone, with hydrogen peroxide being produced as a byproduct. The hydrogen peroxide is water extracted from the reaction medium and the solvent and anthraquinone are recycled.

Bleached Kraft Pulp Production

Kraft pulp is the most widely used type of wood pulp in the United States today, accounting for 70 percent of the total wood pulp produced. It is used in either an unbleached or bleached form.

The kraft pulping process is based on chemical digestion of wood which has been previously debarked and chipped. The digester is a closed container which holds the wood chips and digestion liquors. The liquor is mainly an aqueous solution of chemicals including sodium sulfide and sodium hydroxide.

In order for digestion to take place, heat and pressure are applied to the mixture of wood and liquor. The digestion process delignifies the wood and removes other chemical components from the wood, leaving only the wood fiber.

At this point the pulp is bleached using one or a combination of the following: chlorine, caustic, oxygen, ozone, chlorine dioxide, hydrogen peroxide, and others (Reference PT-3). Chlorine dioxide, generated on-site from sodium chlorate, is most commonly used. A mixture of the bleaching agents based on an average of the mill data collected has been used.

One of the features of the kraft process is that the used digestion liquor, called black liquor, is burned. Because the liquor contains a high percentage of flammable wood components, it burns readily. The remaining digestion chemicals, called green liquor, are removed and reacted with salt cake and lime. Salt cake (sodium sulfate) is generated as a byproduct of chlorine dioxide manufacture, so purchased salt cake is not required (Reference PT-4). The resulting white liquor is returned to the digester.

After the wood pulp is "blown" from the digester by the steam used in the process, the pulp is washed free of the chemicals, screened and refined for sale.

Bleached Chemi-Thermomechanical Pulp (CTMP)

The bleached CTMP process uses steam heat, pressure, and mechanical means to separate fibers. Bleaching of the fibers is accomplished by chemical inpregnation of the chips with hydrogen peroxide.

The fiber source for most CTMP operations is wood chips delivered from a sawmill or other wood product manufacturer. At the CTMP mill, various types of wood chips are mixed together in order to obtain the best properties in the end product. The wood chips are steamed and washed to both soften and remove foreign matter. Next, they are screened to get rid of irregular sized chips. For the remainder of the pulp mill processing steps, either metering screws or centrifugal pumps are used to deliver the pulp from one stage to the next.

To both soften and increase brightness, the chips are impregnated with sodium sulfite. The sulfite also aids in separation of the fibers. After sulfonation, the fiber bundles are further separated by a series of refining operations (mechanically breaking down the fiber bundles). The refining operation consists of forcing the chips under great pressure between the surfaces of two metal disks, one stationary and one that rotates, which are separated by a small gap. The combined pressure and friction cause any remaining fiber bundles to be

separated. After two or three refining operations, the consistency of the wood fiber has been converted from chips to pulp. After the refining operations, several stages of screening, cleaning, and filtering are needed to separate undesirable particles from the pulp.

To produce bleached CTMP, hydrogen peroxide and sodium hydroxide are added to the unbleached pulp as it is passed through a series of two towers. After bleaching, the pulp is mechanically dewatered by the use of both filters and roll presses. The final pulp drying operation involves passing the dewatered pulp through a series of columns that circulate hot air over the pulp. The pulp reaches a consistency of approximately 80 percent solids. By the time the pulp is baled and packaged to be sent to the converter, it has reached a consistency of 90 percent solids.

Absorbency Control Additive

An alcohol ethoxolate is assumed for the absorbency control additive in the paper towels manufacture in this study. This is produced by ethoxylating coconut fatty acid. The reaction is very exothermic and requires cooling. The ethylene oxide used is completely reacted.

Processing Aid

A refining product from crude oil is used as a processing aid in the paper towels manufacture in this study. An initial distillation is used to remove the lighter portions from the crude leaving a residue consisting of raw materials for fuel oil, lube grease, and asphalt. This residue is processed through a vacuum distillation column to isolate the raw materials for lubricating oil manufacture. Then, this raw feed is hydrotreated to produce technical and medicinal grade white oils.

Paper Towel Production and Converting

The purchased fiber products are brought into the stock storage chest where they are mixed with water and combined with other pulps to form a suspension which is ready to be made into paper. Washing and bleaching operations can also be part of the stock prep operation depending upon the furnish source and desired characteristics of the end product. Dyes and additives may also be blended with the furnish in the stock prep area. Dyes are not included in this study. Some additives were included. The dry strength additive data were not available. Due to the small amount of this additive, it is considered negligible and should not affect the outcome of the results.

From the stock prep, the furnish is fed into the headbox. With the use of pressure, the headbox deposits the furnish in a regulated fashion onto a plastic mesh wire. From the headbox, the plastic wire mesh moves over a series of vacuum boxes where the sheet is mechanically dewatered.

Next, the furnish sheet is transferred from the wire to a plastic fabric. It carries the furnish over vacuum boxes and predryers, which remove additional water from the sheet. The predryers remove the moisture by thermal (dry heat) transfer of hot air which is blown through the web. A pressure roll transfers the web (furnish) to a large, steam-heated drum cylinder, which is enclosed in a hot air hood. This operation is the final drying operation for the sheet.

Once the fiber has passed through the final drying operation, the fiber has now entered the "dry end" of the papermaking operation. The paper is scraped off the dryer, passed through calendar rolls to soften and smooth the paper, and wound onto a large, bulk size reel (parent roll). As the fiber passes through the papermaking process, scrap or broke that is created is fed directly into the holding chest underneath the machine to be repulped and sent back to the headbox. This internally recycled scrap is referred to as machine broke.

From papermaking, the parent rolls are taken to the converting line for processing into the finished consumer product. In general, paper scrap created subsequent to the parent rolls leaving the papermaking operation is called bleach broke as compared to machine broke.

The parent rolls are loaded on unwind stands. To produce two-ply paper towels, two parent rolls are unwound simultaneously. An adhesive is applied laminating the two sheets. Decoration and printing of rolls may be done at this point, but were not included in this study. The continuous sheet of paper is next wound onto a paperboard core, which is also not included in this study. This winding process determines the sheet count and consumer size roll diameter. During this winding operation, the paper is perforated into individual sheets. The individual rolls are then cut. (Reference PT-5)

Paper Towels References

- PT-1 Riegel's Handbook of Industrial Chemistry. Ninth Edition. Edited by James A. Kent. Van Nostrand Reinhold. New York. 1992.
- PT-2 Smook, G. A. Handbook for Pulp and Paper Technologists. TAPPI. 1987.
- PT-3 1993 North American Pulp and Paper Fact Book. Miller Freeman, Inc. 1992.
- PT-4 Jentzen, Carl. Jentzen Associates, Inc. 1993.
- PT-5 Discussions between Franklin Associates, Ltd. and confidential industry sources. 1991-1992.

RECYCLED PULP SOURCES

Recycled boxboard and paper towels are made from a variety of wastepaper grades, including mixed paper (See Figures 2, 3, and 5). The scenarios for the mixed paper portion of the raw materials are taken from the October 13, 1997 paper, "Mixed Paper Scenarios." Three scenarios for mixed paper were offered in this paper, as there is no broadly recognized average mixed paper scenario. For the boxboard, a "broad definition mixed paper" scenario and a "single family residential mixed paper" scenario are considered. For the paper towels, a "mixed paper in offices" (or file stock) scenario is the only alternative considered.

These scenarios are shown in Table RP-1 as percentages of newspaper, corrugated boxes, office paper, and coated paper. Some detailed categories from "Mixed Paper Scenarios" did not fit into these four categories, so surrogates from the four categories were used in their place.

Newspapers were used as the surrogate for recycled folding boxes and set-up boxes because they contain large amounts of repulped newsprint. Newspapers were also the surrogate for uncoated groundwood paper because it is mechanically produced, as is most newsprint. Kraft boxes, bags, sacks, and wrapping paper were included in office paper, as they are produced by chemical pulping.

The "recipes" for producing recycled boxboard and paper towels were based on data in **Capacity and Fiber Consumption**, published by the American Forest and Paper Association. In this document, amounts of newsprint, corrugated boxes, and mixed paper going into new products are shown. The end product "tissue" was assumed for the paper towels, and "Other recycled paperboard" was assumed for boxboard. The mixed paper percentage from this document was multiplied by the different mixed paper scenarios shown in Table RP-1 and added to the newspaper and corrugated percentages from the AF&PA document to come to the final recipes for boxboard and paper towels shown in Table RP-2.

Discussions for the collection of mixed paper and the manufacture of recovered pulp are shown below.

Recovered Paper Collection

Collection of recovered paper, whether from an industrial or consumer setting, involves separation of the various grades of recovered paper, baling the discards for ease of shipment, and delivery to a repulping operation.

Table RP-1
SUMMARY OF MIXED PAPER SCENARIOS USING NEWSPAPER, CORRUGATED BOXES,
OFFICE PAPER, AND COATED PAPER

Paper Grade	Broad Definition Mixed Paper	Single-Family Residential Mixed Paper	Mixed Paper in Offices
Newsprint (1)	16.4	13.7	7.9
Corrugated Boxes (2)	0	15.1	0
Office Paper (3)	60.1	42	47.5
Coated Paper (4)	23.5	<u>29.2</u> 100	<u>44.6</u> 100

⁽¹⁾ Includes newsprint, uncoated groundwood paper, recycled folding boxes, and set-up boxes

Source: "Mixed Paper Scenarios." Prepared by Franklin Associates, Ltd. for EPA. October 13, 1997.

Recovered Pulp Manufacture

The following discussion describes the production of repulped market pulp from recovered fiber sources, either industrial scrap or postconsumer. For many paper products, repulped recovered paper can be used as a raw material substitute for wood pulp.

The most common method of preparing recovered paper for reuse begins with repulping the fiber sources. During the repulping step, large sized contaminants are separated from the fiber. Immediately following pulping, smaller sized contaminants are screened for removal. If inks are present, a portion of the inks are washed from the fiber during the screening process and may result in sufficient deinking for some applications, such as for recycled paperboard. This process also removes some coatings and fillers from the recovered paper.

⁽²⁾ Includes virgin and recycled corrugated boxes

⁽³⁾ Includes uncoated free sheet paper, cotton fiber paper, bleached bristols, unbleached kraft folding boxes, bleached kraft folding boxes, bleached bags and sacks, unbleached bags and sacks, and unbleached wrapping paper.

⁽⁴⁾ Includes coated free sheet paper and coated groundwood paper.

Table RP-2

RECYCLED BOXBOARD AND PAPER TOWELS RECIPE
(%)

Paper Grade	Boxboard using the Broad Definition for Mixed Paper	Boxboard using Single-Family Residential for Mixed Paper	Paper Towels using Office Paper for Mixed Paper
Newsprint (1)	24	23	21
Corrugated Boxes (2)	48	53	5
Office Paper (3)	20	14	38
Coated Paper (4)	8	10	36
	100	100	100

⁽¹⁾ Includes newsprint, uncoated groundwood paper, recycled folding boxes, and set-up boxes

Sources: (1) "Mixed Paper Scenarios." Prepared by Franklin Associates, Ltd. for EPA.
October 13, 1997.

(2) "Capacity and Fiber Consumption" American Forest and Paper Association. 1997.

When higher brightness is needed in the final product, a washing and/or flotation process involving chemical digestion "cooking" is required to further remove inks, fillers and coatings. This intensive digestion process often results in a significant weight loss of fiber in terms of both cellulosic fines and ash. These losses end up as deinking sludge. Chemicals, such as detergent, are used in the deinking process. The deinking process is not included for the recycled pulp used in boxboard or paper towels.

The recycled pulp is then dried or partially dried and prepared for delivery to a paper mill. The partially dried pulp, referred to as wet lap, has an average moisture content of 50 percent.

⁽²⁾ Includes virgin and recycled corrugated boxes

⁽³⁾ Includes uncoated free sheet paper, cotton fiber paper, bleached bristols, unbleached kraft folding boxes, bleached kraft folding boxes, bleached bags and sacks, unbleached bags and sacks, and unbleached wrapping paper.

⁽⁴⁾ Includes coated free sheet paper and coated groundwood paper.