New York Municipal Solid Waste

Senior Capstone Design Project Spring 2004

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EXECUTIVE SUMMARY

New York City is currently generating nearly 46,000 tons per year of municipal solid waste (MSW). With the closing of the Fresh Kills Landfill in 2001 and the population growth of nearly 9% per year, the MSW crisis continues to escalate as the city pays as much as \$75 per ton to dispose of waste in neighboring states.

The objective of this project is to provide a solution to the waste problem facing New York City. A more cost effective disposal method is accomplished through the development of a mathematical model that assists in the strategic planning of the New York waste management system. The model is to be used as an engineering tool that incorporates cost minimization of the waste management process from an economic perspective. This includes consideration of all possible investments, waste management disposals and technologies, locations, and amounts of waste processed.

The current mathematical evaluates pyrolysis as the waste management disposal method. This method was chosen over the alternative disposal methods of landfilling and incineration. Several end products were considered by the mathematical model including hydrogen, ammonia, and synthetic fuel. The model is capable of finding the optimal process and end product selection as well as providing the best processing route between transfer stations, plant locations, and consumer locations. The model also considers important factors and variables including capital investments, operating costs, revenue, waste amounts, and expansion.

The mathematical model currently selected hydrogen as the optimal product to be produced from pyrolysis. Of the thirteen possible plant locations, four were selected to startup in year 2010. These plants are located at Hempstead (NY), Babylon (NY), Huntington (NY), and Charles Point (NY). For a 20 year lifetime, the Total Capital Investment for all plants and expansions is \$2.1 billion with an annual plan operating cost of \$510 million. Revenue generated from the recovered scrap, waste disposal fee, and hydrogen production is predicted to be \$825 million annually. The total amount of waste processed per year is 3.8 million tons. This proposal provides NYC with a disposal fee of \$45/ton.

Presently, the model is set up to optimize the net present value in order to generate the largest profit. However, it is not a foregone conclusion that the solution to the MSW problem I sin the form of a private enterprise. If risk is too high or there exists no investors into a privately owned company, then the model possesses the capability to reverse course and determine the most cost efficient method to dispose of all the excess waste in the city. There does exist the possibility of managing some combination where a fraction or all of the profitable aspects of the proposal is privately owned and the remainder is run by the city of New York. For these reasons the potential market for this type of private enterprise in New York as well as possible forms of municipal investment and ownership must be further analyzed.

I. Introduction and Background

A. Municipal Solid Waste in the United States

In 2001, the United States generated 208.4 million tons of Municipal Solid Waste (MSW), or 5 pounds per person per day.¹ By weight, 15% is burnt, 30 % is recycled and 55 % is put into landfills.²

Municipal solid waste consists of product packaging, grass clippings, furniture, clothing, bottles, food scraps, newspapers, appliances and batteries. Materials such as construction demolition debris, municipal liquid waste (MLW) treatment sludges and non-hazardous industrial wastes are not considered MSW.² Institutional wastes, such as waste products from prisons, hospitals, and schools are considered MSW.

The composition and volume of MSW for the United States of America in the years' 1975 to 2001 are shown below in Table 1. The data is assumed representative of the composition and volume of MSW produced by New York City.

	1975 – Processed ³		2001 Process	 ed ⁴	
Component	TPD Wt %		TPD	Wt %	
Organic	1168	77.9	372,000	84.2	
Ferrous Metal	135	9.0	24,400	5.5	
Non-Ferrous Metal	14	0.9	7,900	1.8	
Glass	144 9.6		27,900	6.3	
Other	39	2.6	9,600	2.2	
Total	1500 100.0		442,000	100.0	

 Table 1: MSW Mass and Weight Percent Composition Data

The changes in composition over the past twenty-five years reflect changes in consumption trends in the United States as well as changes in the market. For example, plastics are more widespread in modern society than they were 30 years ago. Also, recycling levels have increased resulting in the decline of gross disposal volume in the last few years. Figure 1 shows the modern resulting trend.

B. Case Studies

Several locations were considered for a new disposal method of municipal solid waste. The decision was made based on: current disposal costs, trends in disposal costs, trends in waste production, population growth and the severity of the problem with current method of disposal. The four locations analyzed were New York City, New York; Los Angeles, California; Detroit, Michigan; and Hilo, Hawaii.



Figure 1: MSW Production and Disposal, 1960-2001

i. New York City, New York

New York City presently uses the method of landfilling. However, it has begun transporting its waste out of the city to several neighboring landfills. Everyday New York City and surrounding area generate approximately 47,303 tons of waste. The New York Department of Sanitation (DOS) manages 40% of this waste, and private corporations handle the other 60%. In the year 2000, 35% of the amount that the DOS managed was recycled, 34% was deposited at the Fresh Kills Landfill, and 31% was exported out of the city. However, the Fresh Kills Landfill closed in April of 2001. More recently, all non-recycled waste has been exported out of the state. On average, New York City pays an average \$63.30 per ton to landfill their municipal solid waste⁵.

New York City is experiencing a population growth of about $9.0\%^6$. The New York City metropolitan area had a population of 21,199,865 according to the 2000 census⁷.

ii. Los Angeles, California

The Los Angeles metropolitan area currently uses the method of landfilling to dispose of their municipal solid waste. Since Los Angeles is located on the west coast, the cost of using a landfill is not inordinately high. As of November 2003, Los Angeles had numerous landfills in use. The cost per ton to dispose of municipal solid waste at these landfills ranged from \$20.88 at the Puente Hills Landfill, to \$36.75 at the Downey Area

Recycling and Transfer Facility⁸. Based on the Los Angeles metropolitan area population and the MSW produced in the U.S., Los Angeles generated 36,535 tons per day of municipal solid waste.

Los Angeles' population is growing at a steady rate⁹. The Los Angeles Consolidated Metropolitan Statistical Area (CMSA) has a population of 16,373,645 according to the 2000 census¹⁰. This CMSA consists of the Los Angeles-Riverside-Orange County area. From 1990 to 2000 the city of Los Angeles' population increased from 8,863,000 to 9,519,000, an increase of $7.4\%^{11}$.

iii. Detroit, Michigan

Detroit uses the method of incineration for municipal solid waste disposal. In fact, Detroit is home to the largest incinerator in the nation. It is important to note that the state of Michigan does have many landfills. Michigan is the fourth largest receiver of imported waste in the U.S. Most of this waste comes from Canada¹². The incinerator processes 3000 tons per day of municipal solid waste¹³. Detroit and other communities sending their trash to the Detroit incinerator can be charged as much as \$130/ton, whereas the Wayne County landfill imports for only \$11/ton¹⁴.

Detroit has not experienced a large population growth in recent years. In fact, from 1980 to 1990 it experienced a population loss of 2.4%. The Detroit Metropolitan Area has a population of $5,456,400^{15}$. From 1990 to 2000, however, it experienced an increase an increase of $4.1\%^{16}$.

iv. Hilo, Hawaii

The big island of Hawaii on which Hilo is located also uses the method of landfilling. Currently, it is using the Hilo landfill at a cost of \$80 per ton as well as transporting MSW to Pu'uanahulu landfill at a cost of \$48.72 per ton. The Hilo landfill is reaching full capacity which is causing the high cost of disposal and will eventually be closed. When that occurs, an estimated increase in cost of \$70,000/yr will occur. This will cause the cost of disposal to be \$50.78 per ton. Based on the population of Hilo and the U.S. MSW production, Hilo produces 91 tons per day of MSW. Hawaii has limited space to develop new landfilling sites.

Hilo has a population of 40,759 from the 2000 census¹⁷. The big island of Hawaii has experienced an increase of 27.26% from 1990 to 2000^{18} . This is a high population growth, but relative to the small population, it results in an increase of only 11,111 people in ten years.

C. Location Choice

Although each location has significant problems processing municipal solid waste, New York City was selected based on the aforementioned criteria. It produces the largest amount of MSW per day, pays a high cost to dispose of its MSW, and it maintains a large population and population growth. The following discusses the comparative criteria.

The first and most influential reason for the choice of New York City us that it produces by far the largest amount of municipal solid waste at 47,303 tons per day. Los Angeles is a distant second at just 36,535 tons per day. Also, California has a successful recycling program that helps reduce the amount of MSW production. Hilo has such a low production of municipal solid waste per day that it can be dismissed despite lack of land to develop new landfills. The chart below compares each cities respective MSW production.



Figure 2: Amount of Municipal Solid Waste Produced per day

Furthermore, New York City pays the second highest disposal fees of any of the evaluated cities as shown in the comparison chart below. Detroit pays a higher cost to dispose, but was ruled out on because it only produces a fraction of the waste that LA and NYC produce.



Figure 3: Average Price to Dispose of Municipal Solid Waste

Finally, New York has the second highest population growth (Figure 3). Although Hilo has a higher population growth by percentage, the New York Metropolitan Area has 520 times the population of Hilo. New York has the highest population, with the Los Angeles CMSA following at about ³/₄ of New York's population. Detroit has the smallest population growth and about ¹/₄ of New York's population.



Figure 4: Population growth



Figure 5: Metropolitan Area Population from 2000 Census

D. MSW in New York City

i. Present Methods of Disposal

In New York City, approximately 10,500 tons of MSW need processing daily¹⁹. As previously mentioned, the amount not recycled is transported out of the city to several neighboring landfills. However, landfilling is a decreasing option for several reasons. In a high density area such as New York City, health problems stemming from landfill contamination have prompted the passage of state laws that prevent landfilling in the municipal area²⁰. The laws have long since placed a constraint on MSW disposal in the vicinity of New York City, particularly the state of New York.

The constraints are exemplified in a 2000 study by the Concerned Citizens of Cattaragus County (CCCC) where information provided by the New York State Department of Environmental Conservation confirmed that existing landfills in the state of New York do not have the capacity to hold the trash of New York City alone. New York currently has nine privately owned landfills and twenty-three publicly owned sites where the combined capacity is 60 million tons. Currently, 98 percent of New York's commercial landfill space is located in western New York State. If New York City sends all trash to state landfills, they would be filled to capacity within four years.

ii. Existing Contracts

As of February 5, 2003, 17 companies come to transfer stations around New York City and landfill the MSW as detailed in Tables 7 or 8. These companies have three-year base

Facility	Max. Capacity (tons/year)	Permit Issued	Permit Expires	Distance to New York City (miles)
Hempstead, NY	914,325	08/10/2000	06/30/2005	20.64
Islip, NY	177,025	11/25/1998	11/30/2003	46.23
Babylon, NY	273,750	05/16/1999	05/31/2004	38.85
Huntington, NY	350,400	04/06/2001	04/05/2006	33.58
Dutchess County, NY	164,250	08/11/1999	08/11/2004	79.47
Charles Point, NY	686,250	08/01/1996	07/31/2006	44.61
Adirondack, NY	152,500	05/30/2000	05/30/2010	241.12
Onondaga Cty, NY	361,350	11/16/2001	11/16/2011	272.98
Oswego County, NY	61,000	06/01/1994	06/01/2004	321.32
Niagara, NY	821,250	01/05/2000	01/15/2005	421.76

contracts with two 1-year extensions available if exercised. The average distance to each facility is 160 miles.

Table 2: Contracted landfills²¹

Facility	Capacity	Distance to	
	(tons/year)	New York City (miles)	
Belmont, NY	547,500	331.42	
Oxford, NJ	547,500	73.42	
Taylor, PA	547,500	144.88	

Table 3: Existing Landfills with open contracts

II. Possible Disposal and Processing Methods

There are three prevalent methods to dispose of municipal solid waste: landfilling, incineration, and pyrolysis. Figure 5 details the percentages for each method of waste management. Most recovery results from recycling, and combustion refers to both incineration and pyrolysis.



Figure 4: 2001 Waste Management Methods

A. Landfilling

According to the Environmental Protection Agency, the United States has over 3,000 active landfills and over 10,000 municipal landfills. The advantages of landfilling include small capital investment, little maintenance, and cheaper disposal fees, while the widespread disadvantages include environmental pollution and surround property being devalued. Methane and carbon dioxide generated from landfills of municipal solid waste are generated from anaerobic decomposition by the following reaction.

$$C_6H_{10}O_4 + \frac{3}{2}H_2O \rightarrow \frac{13}{4}CH_4 + \frac{11}{4}CO_2$$

The gas produced from this reaction is approximately 54% methane and 46% carbon dioxide in content.²² Leachate, a thick liquid formed from the decomposition of trash, is formed in landfill use. Leachate is an organic liquid that also contains heavy metals, and thus causes ground water pollution when it leaks. Newer landfills now have a plastic cap or liner to filter out the leachate, keeping it from contaminating the ground or groundwater. In addition, it should be noted that Fresh Kills Landfill in New York City did not have the appropriate liner to prevent leachate. Despite the use of liners, household chemicals in trash are known to rot away the liner and allow leachate to contaminate the ground and ground water.²³ The figure below shows a landfill, including its layers.²⁴ The importance of this figure shows the polyethylene liner that is designed to keep the leachate from penetrating into the ground and groundwater.



Figure 5: Layered cross-section of a landfill²⁴

Cities that use landfilling pay from \$15/ton to \$75/ton depending on the distance it must be transported. The average landfilling cost in New York City is \$63.30 per ton of municipal solid waste. Currently, landfilling is still being used, mostly in out-of-state landfilling locations such as New Jersey and Pennsylvania. An issue that seems to be of importance to New York is the distance to the existing landfills. Many of these sites are in the western part of the states, as many as 400 miles away from the in-state landfills. Private waste haulers can take it to the out-of-state landfills that they individually own; therefore allowing cheaper disposal.

According to the New York State Association for Solid Waste Management, the majority of New York State's county and municipally owned landfills currently ban trash from outside their own counties²⁵. In addition, continuing to export trash to landfills in nearby states cannot be done on a long-term basis since these surrounding states do not fully support this method. An article through the Earth Policy Institute states that a multi-state letter initiated by Pennsylvania has described New York City's policy of relying on trash disposal in other states as "not only unfortunate, but unacceptable."²⁶ Pennsylvania is currently seeking federal legislation on interstate waste that includes the following basic provisions:²⁷

- 1. Giving communities the ability to allow the disposal of imported waste through host community agreements, which would address concerns like operating hours, truck traffic, noise, and litter before permits are issued;
- 2. Imposing a freeze on waste imports immediately with a predictable schedule for reducing imports over time;

- 3. Allowing states to impose a percentage cap on the amount of imported waste that a new facility could receive;
- 4. Allowing states to consider in-state capacity as part of the permitting process;
- 5. Allowing communities to adopt waste flow control ordinances to protect existing bond debt.

B. Incineration

Presently in the United States, 15% of all municipal solid waste is incinerated. There are several advantages to incineration. It minimizes the volume required by landfills by up to 95% in some cases. This is especially desirable in areas where there is a limited land area. It is an efficient way to destroy combustible toxins and pathogenically contaminated material. Also, most modern methods allow some degree of energy recovery. One incinerator system even claims to be smokeless and odorless as well as being capable of taking in 3600 lbs/hr of waste while only discharging 1.56 lbs/hr²⁸.

Unfortunately there are several disadvantages to incineration. Building and operation costs are considerably high mainly because of the energy required. Disposal costs can range from \$120/ton to \$175/ton in some cities that use incinerators. The two biggest disadvantages, however, are the air emissions and toxic ash produced by incinerators. Studies have shown that 95% of environmental dioxins are due to incinerators burning chlorinated waste²⁹. Dioxins are a carcinogen, and one in particular (TCDD) has been described among the most toxic elements known to man³⁰. In addition, mercury, cadmium, nitrous oxide, hydrogen chloride, sulfuric acid, fluorides, and particulate matter small enough to lodge permanently in the lungs are all found in incinerator emissions. Thirty percent of incinerated waste is converted to toxic ash that consists of concentrated amounts of lead, cadmium, other heavy metals, dioxins, and other toxic chemicals³¹. Many times this ash is sent to landfills where it could penetrate the bottom of the landfills and cause contamination to the soil and groundwater. This is a possibility for many years after disposal.

In New York City, proposals have been made that tried to gain support for incineration as a solution to its MSW problem. None have had any success, and NYC residents point out the fact that a 3,000 tons/day incinerator with emission controls still releases about 2 million pounds of smog-forming nitrogen oxides into the air each day (similar to adding more than 300,000 cars to the road) as well as the fact that burning 5,000 tons per day of garbage could add about 300 pounds of mercury to NYC's air each year³².

The most promising modern incinerator, commonly known as a high temperature incinerator, was also investigated. It is an incinerator that emits effluent comparable in composition to ambient air. It eliminates many of the previously described drawbacks of incineration. The schematic below depicts a system that is designed to limit emissions in a variety of ways: pure oxygen feed instead of nitrogen diluent, a vacuum gas holding tank to prevent runaway reactions or effluent release, a catalytic carbon monoxide oxidizer, sub-stoichiometric oxygen feed to the primary chamber, heat integration, a high-temperature secondary chamber with excess oxygen to thermally dissociate the atoms of all compounds and several ash separators and effluent purification equipment.

The operating power requirements and cost for an oxygen plant of this scale are 140 MW. This does not take into account the duties of the reboilers because an assumption can be made that an air exchanger can be used for heat because the distillation takes place at cryogenic temperatures. Thus, a very conservative estimate of energy requirements leads to a net balance of 43 MW into the system – a theoretical maximum value – of combustion energy coming out of the system. This means that, assuming 0.05 \$/kWh, 19 million dollars per year of would have to be spent to keep the system operational. However, with no saleable products as well as the sequestration of carbon dioxide to consider, this method of municipal solid waste management is clearly infeasible.

C. Pyrolysis

Pyrolysis is the decomposition of organic material thermally in the absence of air^{33} . An intermediate option is gasification which is the degradation of organic matter in the presence of an inadequate air supply. The three major benefits of pyrolysis all have their root in savings that make it more marketable than the other options. The reduction of landfill volume – ranging from 85 to 92 % - makes landfill disposal of waste cheaper.³⁴ Transporting less material from the plant to the landfill will also be more inexpensive. The heat released while pyrolyzing may be used to make steam and generate electricity, a profit-making enterprise. Also, it is possible to produce synthetic gas which may then be used to process synthetic fuels, hydrogen, ammonia, alcohols, aldehydes, and carboxylic acids among other things.

The synthetic gas that can be burned has about a quarter of the heat of reaction of methane when burned with air³⁵. Economic constraints do not make transportation of the gas feasible, so the gases produced must be burned on site, doubly complicating facility stack emissions issues, unless the gas is processed. Therefore, a thorough investigation into possible by-products is necessary.

Unfortunately, pyrolysis does have many disadvantages. It shares similar disposal issues with incineration due to the emission of toxic compounds present in trace compounds in processed waste. These toxic products are released into the atmosphere and can potentially be leached into the groundwater by slag residue that must also be landfilled.³⁴ However, the emissions are considerably less than incineration and modern technology has indicated that new air exhaust filters can reduce toxic emissions even more significantly. The slag left over from the pyrolysis must be landfilled or can be used as an aggregate in asphalt. If the feed is screened well, stack gas scrubbing to remove toxic components may not have to be as intensive.

Gasification has been used in the U.S. commercially in the past; however, most of the facilities have closed.³⁶ This disposal approach has a bad track record, mainly due to trash/tires into oil schemes, and thus the public has been turned off to the concept of pyrolysis. Nevertheless, interest in alternative disposal scenarios is rising again as trash disposal costs increase and available disposal areas decline. With the integration of a separation process to keep pollutants out of the stack and facilitate recycling, the goal of this approach – reducing disposal fees while operating within EPA guidelines - is closer than simply implementing a nondiscriminatory waste disposal facility.

Pyrolysis is not compatible with composting as a waste processing option because the same organic materials that support biomass-processing organisms are those required to allow usable product derivation from pyrolysis. Pyrolysis, however, is believed to be the only option that is feasible in the New York City metro area because of restricted biomass processing rates and land constraints. In addition, the emissions from pyrolysis are considerably less than those of incineration as well as the possibilities of a valuable end product.

III. Pyrolysis Process Overview

Union Carbide Corporation (UCC) developed the PUROX pyrolysis system to convert solid wastes to syngas - a mixture of CO, CO₂ and H₂. A significant part of this development was pilot plant testing. A successful test report was published by the EPA regarding a 4.5 Mg/d facility built in Tarrytown, New York and another 181 Mg/d plant in South Charleston, West Virginia. This gas can be used as a medium value heating fuel, but because of the inefficient nature of using syngas for combustion, syngas will be used to develop another product such as ammonia, hydrogen, or synthetic fuel. Below is a figure depicting the general pyrolysis process.



Figure 6: Pyrolysis Process Overview

Pyrolysis complexities and issues comprise a long list. The major issue preventing the institution of a pyrolysis program, just like any other waste disposal plan, is the heterogeneity of modern waste. Components that are difficult to dispose of include needles, chemicals, other medical wastes, dead animals/feces, solvents and pesticides³⁷. A major component of making any disposal plan feasible is separation. The feed stream needs to be cleaned either before (shredding, etc...) or after (scrubbing) or both before and after pyrolysis. Glass, aluminum, lead, cadmium, chlorinated hydrocarbons and steel need to be recovered before pyrolysis³⁸. Tires, oil and circuit board scrap can be removed with established processes³⁹.

Consideration of the effect of the commercia Final and Ts-END mended; however, all construction companies are currently being phased into accountability to reuse and

GASIFIE

dispose of their own solid waste. There is no reason to believe that this trend will not continue regardless of possible MSW disposal methods. If industrial solid waste (ISW) must be handled, it would be easy to separate the dense material and pyrolize the remainder, requiring a minimal recalculation of the process involving material and energy balances.

Figure 7, below, details current MSW composition in terms of weight percentages.



Figure 7: MSW Proportions

PUROX unit testing by the EPA concludes that the facility is "technically capable of being installed in any community"⁴⁰. Emissions are negligible with the addition of a few key purification processes after gasification – namely, desulfurization. The process is scalable to allow the integration of several plants throughout a region. The optimization of a plant network that can meet the changing constraints of the New York City municipal area is one goal of this project. A secondary goal of the project is to keep material from being burned or landfilled.

The constraints on the facility follow: it must be large enough to handle the specified waste stream during the life of the project, it must be small enough to operate efficiently, and it must cost as little as possible. It must also have emissions control equipment - baghouses and desulfurization - and facility ambient air control equipment such as covered conveyors and ventilation leading to the baghouses.

Options for the process include the processing of sewage. This involves dewatering the sewage to 25% solids and adding this feed as 10% of the total feed to a pyrolysis unit⁴¹.

A. Background

Developing a method for the separation of heavy metal components - like lead in leadacid batteries and cadmium in nickel-cadmium batteries - from the gasifier feed is highly recommended. Although a desulfurization process may be able to precipitate these metals out of the vapor phase, a dry catalyzed desulfurization process may be poisoned quickly. Uncombusted portions would be encapsulated in glass slag and effectively inert.

A second eddy current unit to handle the aluminum in the light fraction should be modeled to achieve a higher recovery percentage than the heavy eddy current separator because of the lack of adhesive mixtures and heavy items resting on available aluminum scraps. This is an additional 16.8 - 20% of the total aluminum stream.

B. Front-End Design

It is necessary to include some separation before the pyrolysis reaction mainly because it is easier to separate the materials before reaction. Other reasons include that it facilitates recovery of salable products like aluminum that increase profit; it enhances product purity, which in turn increases sale prices; and it reduces problems with emissions controls. All of these things enhance the overall aesthetic of the process which in turn increases the community's acceptance of the operation.

Separation is accomplished with a set of equipment known as the 'front end'. The front end begins the process and follows the guidelines of the Parsons system design with two modifications: it only has one materials shredder and it includes an aluminum separator. A second shredder is reported by the EPA to be useless with regard to enhancing reaction conditions. Additionally, it does not make a significant impact on separation degree. It is simply a greater expense. The aluminum separator, however, is essential to the profit of the process because of the high price of recycled aluminum. This design is chosen because of the commercial availability of the components.

The front end is operated six days a week for two shifts – sixteen hours – a day. Because the gasifiers will be operated continuously, the average waste processing rates must be turned into hourly processing rates for the front end for accurate sizing and pricing. This is a rate of 1588 Mg/d or 98 Mg/h. Taking fluctuations into account means that the design capacity of the plant should be 108 Mg/h, or with two process lines 54 Mg/h per line. It is important that the front end have a day for maintenance because it is handling a coarse mixture of material.

i. Feed Composition and Its Effect on Production Rates

A refuse analysis for New York City is the best way to determine the composition of the feed, which dictates the performance specifications of the plant. However, these analyses cost millions of dollars and will be left as an itemized budget appropriation to be executed after the approval of the project. For the time being, the composition of New York City's MSW stream will be assumed to match that of the United States in the year 2001^{42} .

These stream specifications are handled in the same way with the addition of sewage, but an additional feed stream can be added to the gasifier. This feed stream will be characterized by energy requirements. An additional facility and corresponding utilities for dewatering will be taken into account. Municipal solid waste compositions for 1975 and 2001 are given in the table below. It is assumed that recycling will continue to increase after the implementation of this project, but the proposed facility will handle this material so the MSW values used are the all-inclusive values.

Component	1975	-	2001	-	2001-	
-	Processed ⁴³		Processed		All-Inclusive ⁴⁴	
	MgPD	Wt %	TgPY	Wt %	TgPY	Wt %
Organic	529.9	77.9	61.7	84.2	88.6	85.2
Ferrous Metal	61.3	9.0	4.0	5.5	6.1	5.9
Aluminum	6.4	0.53	1.3	1.5	2.1	1.4
Other Non-		0.3		0.3		6.1
Ferrous	65.3		4.6		5.7	
Glass	17.7	9.6	1.6	6.3	1.6	5.5
Other	680.6	2.6	73.2	2.2	104.0	1.5
Total	529.9	100.0	61.7	100.0	88.6	100.0

 Table 6: MSW Mass and Weight Percent Composition Data

These different compositions were used in simple mole and mass balances to recalculate the amounts of syngas produced per ton of MSW feed and the amount of slag produced per ton of MSW feed.

ii. Equipment: Functions and Capacity





The front end can be scaled in proportion to the plant in order to says eapital and allow the addition of fractional plant capacity. The major equipment components are included below to provide an overview of the separation process and provide an idea of the magnitude of costs. Itemized costs are discussed later.

a. Storage – Raw Feed, Metals and Processed Feed CONVEYOR

The plant must take in enough material to supply the gasifier for an entire week even though it only operates for six days. It is important to know how much waste is being accepted, so scales are installed to measure the trucks before and after they deliver their material. The loads are dumped onto the tipping floor, where front end loaders move it to one of two raw-refuse conveyors that take it to two equal capacity shredders.

The separated materials, ferrous and non-ferrous metals and pyrolizable matter, are conveyed to their respective storage bins. Trucks are notified to pick loads of the metals up when appropriate. The bins are elevated with bottom-dumping designs so that the metals can be collected easily.

The tipping floor and metal bins do not need to be scaled to weekly production, but the surge bin should be able to contain enough material to allow the pyrolysis plant to operate for one full day plus one shift (the third shift on the sixth day). This is a total of 32 hours. A safety margin leaves a surge bin capable of storing 36 hours of shredded, classified, and separated waste. Bins larger than this allow packing of the processed waste that interferes with its automated recovery when it is supposed to be sent to the gasifier. Because each pyrolysis module processes 317 Mg/d, the surge bins should hold (317*36/24=) 375 Mg.

AIR





b. Conveyors



The most reliable way to transfer feed automatically between equipment is via conveyor belts. There are some special belts like the electromagnetic belt and, later, the belt that collects the slag aggregate that must be underwater, but overall the belts are accepted as standard, sized and priced according to their transportation capacity and elevation changes. There is a single belt between each piece of equipment in the same process line, i.e., there are parallel lines of equal capacity equal to half the plant capacity running to parallel pieces of equipment. There are two parallel conveyors leading from the tipping floor to the shredders and from the shredders to the classifier. There are single belts that handle the high-density

Figure 9: Front-End Shredder

fraction from the classifier and the low-density fraction from the cyclone de-entrainer to the surge bin. There are multiple belts that run from the surge bin to the respective gasifiers.

c. Shredders

The shredders can process 54 Mg/h of material and produce material that is smaller than 20 centimeters on a side. Operating in parallel, they can process the appropriate amounts of material for the plant. This shredding facilitates separation and reaction later. These parallel shredded mixtures are conveyed to an air classifier that is tuned to separate light combustibles from glass, ferrous metals and the majority of aluminum.

d. Air Classifiers

The shredded MSW stream is conveyed to the top of the classifier, where it is blown into the top. It falls through a rising countercurrent air stream, which takes the light combustibles to a cyclone de-entrainer. The stream composed of higher-density materials falls to the bottom and goes to a magnetic separator. It is assumed that all of the steel and 80% of the aluminum cans are contained in the heavy fraction of the classifier.



Figure 10: Air Classifier 90 Mg/h

e. Cyclone De-entrainer

The light fraction is blown to a cyclone de-entrainer that uses centripetal forces to separate the light solids from the air. The heterogeneous mixture is blown into the cyclone (perpendicular and offset to the axis of the equipment), inducing rotation which throws the matter to the outside and forces the air to the inside.

f. Baghouse and Blowers

The air is sent to a baghouse that filters the dust before releasing it to the atmosphere. The baghouse also handles the air that circulates in the building. Blowers power the air movement, using approximately 315,000 scf/min.

g. Magnetic Separator



The magnetic separator consists of three conveyor belts. One picks up the heavy material from the classifier. Another is above the first and extends to the second with electromagnets that pick up ferrous components and transport them to a point where it drops them on the third belt. The nonferrous matter is

dropped from the first belt into a trommel for settling separation according to particle size.

Figure 11: Magnetic Separator

h. Trommel



Figure 13: Trommel

The trommel is a series of large rotating concentric drums whose axes are almost horizontal with the open side slightly raised and accepting the non-ferrous matter. There are holes in the sides of the drums, the inner drums have larger holes and the different drums feed different conveyors that either go to an eddy current separator or the surge bin, which leads to the PUROX unit. The small material (< 1.6 cm) is mostly glass, heavy hydrocarbons and other non-ferrous metals. It drops out and is conveyed to the surge bin. The mediumsized material (1.6 cm - 10 cm) is the aluminum-rich fraction. It passes through the trommel and is conveyed to the

eddy current separator. The large fraction (> 10 cm) is mostly wood and cardboard. It is conveyed to the surge bin along with the light fraction from the classifier.

i. Eddy Current Separator

The eddy current separator's intended use is to recover aluminum. It works by spinning in a sleeve at the end of a conveyor belt with alternating magnetic fields. This induces a current in electrical conductors (i.e., the non-ferrous metals in the heavy fraction), which in turn induces magnetism. The magnetic particles are repelled from the end of the conveyor, traveling farther than the



Figure 12: Eddy Current Separator

non-magnetized particles and thus able to be separated as illustrated in the figure to the right. The fraction of aluminum recovered, with respect to the raw MSW feed is specified at 67%. The air classifier is set to allow 80% of the aluminum fraction from the raw feed to fall out with the heavy feed.

j. Additional Equipment

An electrical conditioning plant is included to supply and protect the entire facility: front end, pyrolysis unit, desulfurization unit, oxygen production, UNOX wastewater treatment, compressors and controls. Steam generation is taken into account for climate control.

C. PUROX Pyrolysis Unit

The purpose of the PUROX system is to turn solid waste into a vapor that can be used for different synthesize different chemical products: ammonia, hydrogen, synthetic gasoline and synthetic fuel are a few options. Below is a figure depicting the PUROX system.



Figure 14: PUROX Pyrolysis Unit

The oxygen and trash are fed to the reactor with slag and syngas coming out. The basic reactions driving the production follow:

$C + O_2 \rightarrow CO_2$	$\Delta H = -405 \text{ kJ/mol} (1)$
$C + H_2 O \rightarrow CO + H_2$	$\Delta H = 13 \mathbf{O} \mathbf{F} \mathbf{f}_{m} \mathbf{G} \mathbf{A} \mathbf{S}$
$C + CO_2 \rightarrow 2CO$	$\Delta H = 17340\%$ (Water

The negative sign for reaction (1) indicates that it gives energy away as heat. Because this reaction gives away more than enough heat for the other reactions, the reaction is self-sustaining as long as the oxygen feed is present.

i. Moisture Content and Composition

Determining the moisture content of the feed is important because of the change in heat duty requirements with moisture content, potentially affecting the operating costs of the facility. Using both the composition information from the 2001 EPA US MSW report and information of the EPA UCC pilot plant results report, results for the moisture content and its effects on the energy balance of the system were determined and are shown below. Although the amount of high-moisture content paper in the waste stream has decreased in proportion to plastics and food waste, the overall content is relatively constant. The EPA UCC study indicates that, as long as the total moisture composition stays close to 25%, the results of pyrolysis are practically the same.

	1975		2001 - To	otal	2001 - Disposed	
	MSW %	wt% Moisture	MSW %	wt% Moisture	MSW %	wt% Moisture
Organic	79.10	25.32	85.16	24.67	84.20	24.92
Glass	9.80	0.29	5.49	0.16	6.32	0.19
Inorganic	1.50	0.05	1.53	1.53	2.17	0.07
Total	90.40	25.66	92.19	26.36	92.69	25.18

 Table 7: MSW Composition and Moisture Content

A more important implication of these changing compositions on the revenue stream is the relative proportion of the salable materials taken into the system. The amount of organic material available for recovery is tabulated below. The percentage of each component recovered or processed is assumed constant since the processes are identical with the exception of production volume. All other quantities are scaled using the 1975 and current raw total data. The differences between the salable product rates are in bold. Even small changes to increase the recovery of aluminum can have a great impact on the modern revenue of the plant because of the ease of its separation, the prevalence of aluminum in modern waste and the high recycling price aluminum commands.

	1975		2001	
Flow Rate or Composition	Mg/d or %	Total	Disposed	
Raw Feed	1361	2910	2050	
Mass % moisture	25.7	26.4	25.2	
Mass to Gasifiers	1240	2720	1920	

Mass Organic to Gasifiers	1060	2460	1716		
Mass % Org to Gasifiers	0.86	0.91	0.89		
Mass O ₂ to Purox	254	591	411		
Mass O ₂ to Unox	36.0	83.7	58.3		
Mass Off-Gas Production	1303	3030	2110		
Vol Purox Gas, Condensed	0.75	1.74	1.04		
Raw % Aluminum	0.59	1.40	1.49		
% Aluminum Recovered		67.50			
Mass Recovered Aluminum	5.40	27.4	20.6		
Raw % Ferrous	8.96	5.89	5.51		
% Ferrous Recovered	90.98				
Mass Recovered Ferrous	111	156	103		
Mass Char/Oil Production	32.0	74.4	51.8		
Mass Slag Production	222	142	161		
Air to O ₂ Plant	1450	3370	2350		
N ₂ Effluent - O ₂ Plant	1160	2700	18,800		
O ₂ Plant Air Compressor (MW)	4.06	9.44	6.57		
Vol. Cooling Water Tower	0.85	1.98	1.38		
Vol. C.W. Tower Makeup	0.02	0.047	0.032		
Dilution Water - Sewage	0.092	0.214	0.149		
Discharge Water - Sewage	0.096	0.223	0.155		
Recycled Spray Water (Scrubber)	0.013	0.030	0.021		

Table 8: Gasifier Stream Information – Composition and Utilization Rate (MGPD)

ii. Pyrolysis Equipment – Function and Capacity

a. Gasifier

The heart of the Purox system is a vertical column heterogeneous-phase gasifier. The UCC-standard reactor sizes can process up to 181 megagrams or 317 megagrams of waste feed per day. UCC indicates that these reactors need to process more than 67% of their full capacity in order to operate at optimum efficiency⁴⁵. The resulting design anticipates that plants will have either 4 or 8 reactors designed to process 312 Mg/d of waste 7 days a week.

The reactor operates continuously in order to maintain steady state operation, minimizing costly start ups and shut downs. This means that the facilities associated with the plant: electricity conditioning, oxygen production, water treatment and cooling also have to operate continuously or, in the case of the oxygen plant, operate with an excess stored in case of cyclic shutdown or emergencies.

There are three regions within the reactor: the drying zone at the top, the pyrolysis zone in the middle, and the hearth zone at the bottom. The oxygen is fed to the hearth zone, and this is where combustion takes place. Organic solid waste, heavy non-metallic components and glass are fed into the top of the unit. As it falls it is heated until it is completely dry in the drying zone. After it is dry, it begins to char. In the absence of oxygen (it is all consumed in the lower zone of the reactor), the cellulose is pyrolyzed until it is reduced to char and oil. It continues to fall and settles on a grate. With oxygen blowing on it, all of its



Figure 15: Purox Gasifier

volatile components are vaporized and eventually it falls through, landing in the bottom of the reactor and mixing in with other molten waste such as glass. A slag aggregate forms and oozes out of the bottom of the reactor, falling into a quench tank.

The quench tank is essentially an underwater conveyor belt. When the slag hits the water, it shatters into little pieces, known as frit. It is collected on the conveyor and taken to an elevated frit container, which has a bottom-opening door for ease of loading onto trucks.

As the waste falls, it is dried by hot syngas coming from the pyrolized matter below it. Once the waste feed is completely dry, it begins to char and release the syngas. The char and residual oils that fall to the bottom ignite upon contact with the oxygen feed, providing heat for the reaction to continue. All of the oxygen is used up in this hearth zone, making carbon oxides, hydrogen gas, and hydrocarbon gases. The hearth zone is approximately 1650 °C, which is hot enough to melt the glass, which encapsulates the other heavy constituents. The drying zone is assumed to be at the dew point for the water vapor, taking into account the operating pressure and colligative properties of the vapor. Because of the lack of nitrogen in the feed streams, negligible amounts of nitrous oxides are released.

The slag coming out of the bottom is an aggregate of molten glass, tar, oil and ash. This slag is dropped into a water pool onto a conveyor, where the glassy mixture shatters. A conveyor belt takes the slag to an elevated holding bin with a drop door that facilitates truck shipment to customers. Because it is chemically stable and crystalline, the slag may be sold as chat or cinder block material.

b. Scrubber

The syngas leaving the reactor has water vapor, particulate emissions and sulfurous compounds in it. Because it is going to cool in ambient conditions, the dew point will be reached quickly and condensing vapor could be problematic when combined with other chemicals in the vapor if it is not removed promptly. EPA standards prevent any effluents have levels above those given in Table 4. That is why a scrubber is used. I scrubber cools the vapor to the point where the moisture drops out and some effluents are removed. The condensate from this process is very high in biochemical oxygen demand (BOD), and the EPA regulates these levels, too. The water is sent to a sewage treatment plant that utilizes the oxygen left over from the plant – not used in the pyrolysis.

c. KO Tank and Wet Electrostatic Precipitator

From the scrubber, the vapor passes through a knock out (KO) tank where solids and more liquid precipitate due to pressure drop. The gas moves on to a wet electrostatic precipitator. The electrostatic precipitator uses electrical fields in the moist vapor to collect and precipitate particles from the vapor. The electrical fields stimulate the formation of ions, namely ozone, that bond to everything that needs to be separated. When the vapor has the appropriate amount of moisture, the gas is then transported to the desulfurization facility.

d. Auxiliary Equipment

Storage tanks, coolers, pumps and condensers are all required to successfully execute the pyrolysis process. Because the vapor is being cooled, the heat transfer equipment needs a cool sink. A cooling tower is required, which requires conditioned water with makeup volume supplied constantly.

The off gas is saturated, with approximately 40% moisture by volume and 29.3% moisture by mass at a temperature ranging from 100 to 200°C. Depending on the material content of the refuse, the process efficiency is ~70% to 80%. This does not include the auxiliary processes. Approximately one-fifth ton of O_2 is needed in the reactor for every ton of waste pyrolyzed. One quarter of this is responsible for water vaporization for feed mixtures between 25% and 32%⁴⁶. Approximately 0.027 ton O_2 is needed in the waste treatment plant for every ton of waste pyrolyzed.

D. Oxygen Plant

i. Background

The composition of air is comprised of four main components: 78.084 % Nitrogen, 20.947 % Oxygen, 0.934 % Argon, and 0.033% Carbon Dioxide (all mole % compositions). The presence of argon makes the task of obtaining pure oxygen and nitrogen stream impossible from an air separation, or cryogenics, plant because argon is will be present in small amounts as an inert gas in the oxygen and nitrogen streams. However, this is not a significant problem because the use of oxygen will be for pyrolysis and wastewater treatment. In addition, the boiling point of argon is between the boiling points of oxygen and nitrogen causing it to act as an impurity in the product streams. Provided that the oxygen is at 99% purity, it may be used for these given processes.⁴⁷

280 TPD of 99% oxygen is required for every four purox reactors as well as the wastewater treatment plant. Also, if the plant expands, up to twice that number must are possible. The oxygen used in the Purox system and the wastewater treatment plant is produced in an on-site cryogenic oxygen plant where oxygen is separated from air. First, the air is compressed to liquefy it. Then, at temperatures below 90 K, the liquefied air is fractionally distilled to separate it into a top vapor nitrogen stream and a bottom liquid oxygen stream. Nitrogen, having a lower boiling point, is more volatile and rises to the top of the column, while the more dense liquid oxygen falls to the bottom of the column. The liquid oxygen can be stored or allowed to vaporize and used immediately. The nitrogen also has several uses. It is may be stored or used for purging reactors, and it is a critical to the plant safety program.

The major cost that is associated with the air separation process is the cost of electricity to compress the inlet air. This generally comprises the biggest change in the utility cost of the cryogenics plant, however, the cost of refrigerant for each of the columns is an expensive commodity. The goal of the design is to minimize the cost of compression.

ii. Equipment and Process Description

Plant Equipment				
C1	Feed Compressor	T1	Distillation Column 1	
E1	Heat Exchanger 1	T2	Distillation Column 2	
E2	Heat Exchanger 2			

Below is a table of the equipment needed in an oxygen plant.

Table 9: Plant Equipment



Figure 16: Process flow diagram of air separation system

In figure 18, a model of the cryogenic distillation of air, the process is details the compression of air in a double column separation system. Air enters the system and is compressed to a pressure of 9 atm. This air is then cooled to approximately 100 F in heat exchanger 1 (E1) with stream 2, a 99% composition of nitrogen at a temperature of 104 K. After passing through a second heat exchanger (E2) that cools this stream with cooling water, it then enters a column (T1) to separate the nitrogen and oxygen product. The nitrogen product from the top of T1 then is used to cool the heat exchanger E1 and the bottom product of oxygen is separated in the second distillation column (T2) to remove the carbon dioxide from the system. This further purifies the oxygen product, but more importantly, it removes the carbon dioxide product for possible use in the polycarbonate production process. The operation of this double-column system is similar to a single-column system, except that in this double-column system, air is compressed and carbon dioxide and water vapor are removed.

CONFRESSOR		
Total Direct Cost 42	Og7.9 Phillion	
Total Indirect Cost	\$2.9 million	
Fixed Capital Investment	\$10.2 million	
Working Capital	\$1.8 million	
Total Capital Investment	\$12 million	

3153.4 LBMOL/H 0.6 % Ar 99.0 % N₂ 0.3 % O₂

Table 10: Total Capital Investment for air separation plant

The total capital investment of this oxygen plant, or air cryogenics system, is \$12 million. The majority of this cost lies in the compressor because it must compress a high volume of air from 1 atm to 9 atm.

E. Wastewater Treatment Plant

Before wastewater from the solid-liquid separator can be released into the municipal sewage system, it must be treated to reduce Biochemical Oxygen Demand (BOD) and nutrient removal. This is done through a wastewater treatment plant which is provided by Union Carbide in the form of a UNOX plant. Following is a discussion on the reduction of BOD and nutrient removal.

i. Biochemical Oxygen Demand Reduction

The UNOX wastewater treatment system, developed by the Union Carbide Corporation, uses feed oxygen in a sludge process to reduce BOD. The feed of 40 tons per day of pure oxygen is provided to the microorganisms that remove the pollutants from the wastewater. If air were used instead of oxygen, these microorganisms would not receive enough oxygen to survive, and the pollutants would not be removed.

The wastewater treatment plant is a covered three-stage process that accepts wastewater and oxygen, and then discharges treated wastewater, off gas, and excess biomass, or sludge. The highest strength of wastewater is fed at the same time as the highest feed of pure of oxygen. The UNOX system is a high purity oxygen (HPO) activated sludge process as shown below⁴⁸.





The BOD level contained within the volume of waste water (70 gpm) purged from the PUROX plant is 50,000 mg/L. This BOD level must be reduced to an approximate value of 200 mg/dm³ before being discharged into the sewage lines. The UNOX wastewater plant releases discharge at a rate of 1530 GPM. Based on these values, a material balance can be completed to determine the flow rates of water, oxygen, and BOD through the UNOX system.

ii. Nutrient Removal

SURFACE AERATORS

Nutrient removal is also incorporated into this system. Specifically, phosphorous and nitrogen are the two nutrients focused on for removal. The reason for this is that phosphorous causes excessive plant growth in the receiving waters. Because of this algae blooms, odors, and dissolved oxygen depletion will occur, causing the microorganisms to die. The general requirement for phosphorous removal is a total of phosphorous no greater than 2 mg/l. Nitrogen in the form of unionized ammonia (NH₃-N) causes toxicity effects to aquatic life. The unionized ammonia increases as the temperature and pH of the water increases.⁴⁹

Unionized ammonia removal occurs through a process of oxidation in the presence of dissolve oxygen and bacteria as shown in the reactions $below^{50}$.

 $NH_3 + H_2O \rightarrow NH_4^+ + OH$

 $NH_{4}^{+}+O_{2}$ <u>Nitrosomomas</u> Bacteria <u>NO₂ + O₂ Nitrobacteria</u> NO₃

Nitrogen in the form of nitrate (NO₃-N) discharge must also be considered due to its contribution to algae growth in receiving water. Therefore, denitrification must occur prior to the wastewater treatment. The requirements for nitrogen removal are unionized ammonia must be less than 1 mg/l and the total nitrogen level must not exceed 9 mg/l⁵¹.

iii. UNOX Wastewater System

The UNOX wastewater system was initially used primarily for the removal of BOD and nitrification of wastewater. Now the HPO system has incorporated complete biological nutrient removal. The activated sludge process shown above in Figure 19 has a feed of oxygen gas. This allows secondary level biological wastewater treatment in an enclosed bioreactor followed by a clarifier⁵².

This system has several applications which make it suitable for this site. These applications include usage with medium to high strength wastewater and usage at locations with limited site area for new construction⁵³. A UNOX plant can be designed to handle a wide range of throughput of wastewater ranging from 1 to 500 million gallons per day. Our plant has a capacity of 81,100 gallons per day, which is well below the maximum capacity a UNOX wastewater plant can handle. A purchase of a fairly large wastewater plant allows for expansion of the PUROX pyrolysis plant without building a new site.

When designing the UNOX plant, environmental design factors must be taken into account such as temperature, dissolved oxygen, pH and alkalinity, substrate levels, and toxic materials. Nitrification must be completed within a temperature range of 5 to 30 C. Dissolved oxygen levels affect the nitrification rate; as DO level increases, the percent of nitrification increases and then becomes stable. At this point, the DO level is at least 6.0 mg/l. In the activated sludge system, carbon dioxide produced in the reactor is not released until the last reactor stage. An equilibrium relationship between the pH

alkalinity and percent CO_2 in the gas phase at atmospheric pressure exists and is described below:

 $ALK(mg/l) = [CO_2] * K_1/10^{-pH} 50/44$

In the equation above, ALK represents the alkalinity in mg/l as $CaCO_3$, $[CO_2]$ is the dissolved CO_2 in mg/l, K_1 is the bicarbonate dissociation constant at a given H₂O temperature.

Substrate removal is based on the effluent ammonia level used and is dependent on a plant's discharge permit. The presence of heavy metals and organic compounds affect the system selected⁵⁴.

Two systems exist for the HPO process: single and two step. Single step nitrification is used for low strength wastes with a BOD level less than 200 mg/l and when only seasonal nitrification is needed. Two step nitrification is used for high strength wastes and year round nitrification. Since our pyrolysis plant will produce high strength wastewater with BOD levels exceeding 200 mg/l and operate year round, two-step nitrification is the preferred. Several benefits exist for two step nitrification. First, it results in a reduction in retention time. Second, it results in greater sludge production and reduction in oxygen consumption. Finally, it has a greater resistance to toxic materials and organic surges. However, a two step process requires clarification before nitrification⁵⁵.

Phosphorous removal requires the addition of an anaerobic zone, which consists of 3-4 open tank compartments in series with small center mounted mixers. Nitrogen removal exists in the anoxic zones. The anoxic zone is a separate reactor stage following the anaerobic stage. Since phosphorous removal is not necessary in our plant due to negligible phosphorous in the wastewater, our wastewater process includes only the anoxic zone. The design of this process is shown below in Figure XX.

iv. Total Capital Investment

The total capital investment for a UNOX wastewater plant is determined based on the equipment cost of the plant. Four tanks are needed--one for nitrification and three for the activated sludge separation. The anoxic stage tank has a maximum capacity of 100,000 gallons. Also a clarifier is needed and three surface aerators must be considered. The anoxic tank price is based on Figure 12-52 in Peters and Timmerhaus for a mixing tank with agitator. Other tank prices are based on Figure 12-56 in Peters and Timmerhaus for carbon steel tanks with varying capacities from 1 to 25 million gallons of throughput⁵⁶. Below is a chart of the total capital investment for a UNOX wastewater plant with a capacity of 1 million gallons per day.

Direct Costs	Capacity	1,000,000.00
Purchased Equipment		
Front End Costs		
Process Equipment		
Covered Tanks (3)		\$300,000.00

Anoxic Zone Tank		\$200,000.00
Surface Aerators (3)		\$3,000.00
Clarifier		\$75,000.00
	Subtotal	\$578,000.00
Total Equipment Costs	100	\$578,000.00
Delivery	10	\$57,800.00
Installation	47	\$271,660.00
Instrumentation	36	\$208,080.00
Piping	68	\$393,040.00
Electrical Systems	11	\$63,580.00
Buildings	18	\$104,040.00
Yard Improvements	10	\$57,800.00
Service Facilities	70	\$404,600.00
Total Direct Plant Costs	370	\$2,138,600.00
Indirect Costs		
Engineering and Supervision	33	\$190,740.00
Construction Expenses	41	\$236,980.00
Legal Expenses	4	\$23,120.00
Contractor's Fee	22	\$127,160.00
Contingency	44	\$254,320.00
		<u> </u>
Total Indirect Plant Cost	144	\$832,320.00
Fixed Capital Investment	514	\$2,970,920.00
Working Capital	143	\$825,255.56
Total Capital Investment	571	\$3,301,022.22

Table 11:	Total Capital	Investment f	for the	wastewater	plant

The fixed capital investment can be projected for the various capacities of the UNOX wastewater plant in order to consider expansion of the PUROX plant. Below is a chart indicating the projection.



Figure 18: Fixed Capital Investment of Wastewater Treatment Plant

F. Desulfurization

i. Overview

The dry gaseous effluent from the pyrolysis unit after passing through the scrubber, electrostatic precipitator and condenser has the following composition as shown in Table 10. The gas is actually saturated with water vapor at 38 $^{\circ}$ C (100 $^{\circ}$ F).

Mole %		Contaminants		
H ₂	24.0		ppm	
CO	40.0	H_2S	300-600	
CO ₂	24.0	HC1	1	
CH ₄	5.6	PARTICULATE	15	
$C_2H_2, C_2H_4^{+2}$	5.4	NO _x	1	
$N_2 + Ar$	1.0	OIL	100	

Table 12: Dried, Clean Syngas Composition with Contaminants

The major problem with the contaminant composition is the sulfur concentration. Sulfur presence will poison catalysts if the concentration is far above 1 ppm, so the target removal of sulfur will produce a gas with less than 1 ppm sulfur compounds. Desulfurization is required to prepare the syngas for synthetic preparation. The removed sulfur can be used to produce sulfuric acid or elemental sulfur, both salable products.

The market for sulfur is currently saturated and expected to worsen. Market prices have been declining over the last five years to the current price \$55/ton while market volumes, comprised of 67% byproduct sulfur, have risen. Furthermore, new sulfur emissions standards on petroleum fuels imply that more sulfur will be available to market in the coming years. However, if the sulfur produced by the NYC MSW facilities can undersell
current producers, market share may be established. Sulfuric acid, on the other hand, is produced.

If a sulfur recovery unit were utilized to take out the stream sulfur, the amount of sulfur produced would be between 330 and 660 kg/d.

$$27.71 \cdot 10^{6} SCFPD \cdot \frac{28.1L}{CF} \cdot \frac{kgmol}{22,400L} \cdot \frac{300}{10^{6}} = 10.428 \frac{kgmol}{d} \cdot 32.1 \frac{kg}{kgmol} = 334 \frac{kg}{d}$$

At a sulfur selling price of \$55/ton, this means that the process will generate \$55 every three days. This is much less than the price of operating a desulfurization unit, so it can be deduced that another process will be essential.

An alternative available as an industry standard is the gas shift zinc oxide-hydrogen sulfide reaction below.

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

The zinc can be regenerated with oxygen gas.

$$2ZnS + 2O_2 \rightarrow 2ZnO + 2SO_2$$

According to an article in Oil & Gas Journal, regeneration can reduce sulfur levels in spent catalyst to below 1% and can recover over 95% of the available surface area.⁵⁷

Component	Amount
Fly Ash	125 ppm
Sulfur as H ₂ S	300-600 ppm
Sulfur as COS	< 1 ppm
Water	6 vol%
NO _x	1 ppm

Table 13: Cleaned Gas Contaminants

The catalysts can be regenerated in situ (on site) or ex situ (off site). The problems with in situ regeneration are predominantly low activity recovery of the ZnO, which increases operating costs and large SO_2 emissions. The SO_2 must be sequestered or scrubbed, requiring scrubbers, pumping equipment that resists corrosion, et cetera... This is expensive. Ex situ regeneration involves transportation of the catalyst to a company that specializes in regeneration. They can handle the awkward challenges of avoiding temperature fluctuations and channeling that can ruin the catalyst. Advantages and disadvatages of both methods are tabulated below.

In Situ		Ex Situ		
Pro	Con	Pro	Con	
Small downtime	Unacceptable SO ₂	Removes chips,	Reactor downtime	
	emissions	fines and dust from	depends on	
		catalyst	company's process	

		time
SO ₂ removal	Better Activity	Difficult to remove
process necessary	Recovery	catalyst from reactor
Lower catalyst	Catalyst reusability	
activity recovery	and activity	
	evaluated	
	More precise, better	
	results	

Table 14: In Situ and Ex Situ Regeneration Comparison

ii. Reactor Operation and Design

Redundancy is critical for the reactor to function constantly since the catalyst must be regenerated. The process diagram is shown below.



Figure 19: Desulfurization Process

The syngas will exit the PUROX system at 38 °C, as mentioned before, but it should be close to 500 °C to be in the target range for oxidative regeneration. Zinc oxide, a Regenerative Oxide Catalyst (RCO) is appropriate for all products. Johnson Matthey Catalysts, previously has a complete Dycat that is tailored to handle methanol, ammonia, syngas and hydrogen production. They can also remove heavy metals such as mercury.⁵⁸ Synetix' Katalco 32-5 ZnO catalyst was used to determine system operation and design.

Size/shape	3 mm spheres	
Pore Volume	0.3 mL/g	
Density	86 lb/ft ³	
ZnO Wt%	92 ~	150°C

774 TPY

15,250 CF

Pick-up	31.2 lb/ft^3
% ZnO Converted	93

Table 15: Desulfurization Catalyst Specifications

Assuming continuous operation, a flowrate of 36 lb/h hydrogen sulfide in the Purox exit gas stream and the specified pick-up value and density indicates that 90 lb/h of catalyst will be needed. For continuous operation, this will amount to 400 tons of catalyst per year, or 9,300 ft³. The volume of catalyst needed, given 86 lb/ft³ and a void fraction of 0.29, will be 13,100 ft³, with a fluid volume of 3,800 ft³. Assuming an L/D of 5 gives a diameter of 9.89 ft and a length of 49.4 ft. This results in a velocity in the tank, assuming 28 million scfd, 4.2 ft/s.

Research by the University of Michigan indicates that the life expectancy of this catalyst is two to five years. A conservative estimate, given 75-95% regeneration, will find that the catalyst will last for two years.

iii. The Economics of Desulfurization

The synetix catalyst, available commercially, can be purchased for \$3/lb, while regeneration costs 0.50 - 0.60 /lb.⁵⁹ With two beds that can process one year's worth of hydrogen sulfide apiece, the costs are tabulated below.

Year	Bed 1	Bed 1 Cost	Bed 2	Bed 2 Cost	Action
	Activity	(MM\$)	Activity	(MM\$)	
1	Online	4.0	Offline	0	Fresh Catalyst Bed (FCB) 1

2	Offline	0.8	Online	4.0	FCB 2, Bed 1 Regenerated
3	Online	0	Offline	0.8	Bed 2 Regenerated
4	Offline	4.0	Online	0	FCB 1
5	Online	0	Offline	4.0	FCB 2
6	Offline	0.8	Online	0	Bed 1 Regenerated
7	Online	0	Offline	0.8	Bed 2 Regenerated
8	Offline	4.0	Online	0	FCB 1
9	Online	0	Offline	4.0	FCB 2
10	Offline	0.8	Online	0	Bed 1 Regenerated
11	Online	0	Offline	0.8	Bed 2 Regenerated
12	Offline	4.0	Online	0	FCB 1
13	Online	0	Offline	4.0	FCB 2
14	Offline	0.8	Online	0	Bed 1 Regenerated
15	Online	0	Offline	0.8	Bed 2 Regenerated
16	Offline	4.0	Online	0	FCB 1
17	Online	0	Offline	4.0	FCB 2
18	Offline	0.8	Online	0	Bed 1 Regenerated
19	Online	0	Offline	0.8	Bed 2 Regenerated
20	Offline	4.0	Online	0	FCB 1

 Table 16: Sorbent Bed Costs and Activity

For the lifespan of the 20 year project, each catalyst bed will cost \$150,000 with an average annual catalyst cost of 2.4 million with an additional cost in the first year of 2.6 million and in the second year of 2.4 million, yielding an average of 2.9 million. With fresh catalyst, ex situ regeneration (\sim 20% of catalyst price) will cost \$800,000.

Shipment of catalyst was quoted by Union Pacific at \$4800/boxcar with 100 tons/boxcar. Four cars will give \$38,400 per roundtrip cost each time the catalyst has to be regenerated. Because this happens every two years, the annualized cost is \$19,200 per year. The catalyst disposal fee is factored into this cost at \$100 per ton to give a total cost of \$20,000 per year.⁶⁰

	In Situ (MM\$)	Ex Situ (MM\$)
Capital	13	8.3
Operating	2	2.9

Table 17: Comparison of In Situ and Ex Situ Costs

From the table above, it can be seen that ex situ generation is the more economical option. To summarize, the cheapest way to remove 600 ppm sulfur particulates is with ZnO dry-bed absorption with ex situ regeneration and disposal every two years.

H. Environmental Regulations

Several environmental regulations from the Environmental Protection Agency must be taken into account when developing a pyrolysis plant. First, permits must be obtained and maintained under the following standards: meeting air quality requirements, byproduct classification and disposal, land use conflict resolution, biological resource disturbances, water usage – cooling towers; health impacts, traffic impacts, transportation impacts, odor impacts, safety impacts, hazardous materials leakage planning and the resolution of a disposal/generation method⁶¹.

Other regulations such as air emission standards must be met in accordance with the Clean Air Act of 1990. Gaseous effluents in a pyrolysis plant include H_2S , HCl, Particulate Matter, and NO_x .

In pyrolysis, the emission of H_2S is large. The current EPA limitation is 160 ppm. H_2S has a concentration of 600 ppm in contaminants; therefore a desulfirzation addition is needed. This is discussed previously in the pyrolysis section.

Pyrolysis also releases small amounts of HCl. The EPA limit is 25 ppm in concentration; however, the pyrolysis production releases only 1 ppm and is under the limit. Therefore, no precautions need be taken to remove HCl.

According to new rules implemented by the EPA in 1998, particulate matter (PM) 2.5 (fine particulates that are 2.5 microns in diameter or less) is now being regulated along with PM 10. This is of great importance since 90% of all smoke produced falls into PM 2.5^{62} . Particulate matter emissions for a combustion unit should not exceed 0.46 g/m⁶³. Our plant releases 15 ppm and is again under the limit.

Another gas released is NO. The EPA is very concerned with the emission of NO_x gases and is working to enforce stricter regulations on NO⁶⁴. The current EPA limitation for NO is 150 ppm. Again, the pyrolysis plant is at 1 ppm and well under the limit.⁶⁵

Fly ash is a visibility concern as well as an air pollution issue. The EPA states that visible emissions of fly ash must occur less than 5% of the time from ash transfer systems. The pyrolysis plant releases 125 ppm of fly ash. From the previously discussed pyrolysis plant, this again is under the limit.

I. Site Locations

When selecting locations to build a pyrolysis facility, there were several criteria were analyzed to optimize the project. First, the future expansion of the plant had to be incorporated into the original plans, so that it would be possible to expand with added trash over time. It is suggested that there be at least 30 m of clearance around the perimeter of the site and a 21.5 acre plot is ideal for a typical 1500 tpd plant. These 21.5 acres allows for room needed to bring trash into the plant and also for equipment needed to convert trash to useful product. In addition, this plant should be accessible by road in each direction so that the municipal solid waste can be supplied. The plant also must have electric power with capacity of 20,000 kV-A, 60 Hz, and 3 Phase, with at least 4,160 volts. A water supply for protection from fire of 3.78 m³/min and 2,271m³/day for normal plant usage must also be present. Finally, the sewage line of the plant must have the ability to handle 5.29 m³/min⁶⁶.

The locations selected were chosen using a mathematical model that optimized the best possible sites based on factors such as proximity to New York City from consumer locations and transfer station locations. Thirteen possible locations where landfills currently exist, including 11 in New York, 1 in Pennsylvania, and 1 in New Jersey were chosen for several factors. First, these sites already have existing roads where heavy trucks can have easy access to the plant. Second, zoning for these plants already exists in these sites. Finally, the capacity for each of these sites is currently known making it easy to know what is needed based on the trash produced in New York City. The table below gives the considered locations from the existing waste to energy plants including their maximum capacity, the permit issuing and expiration dates, and their distance to New York City. The table following the one below gives the considered locations that are currently existing landfills with their distance and capacity.

IV. CAPITAL COST ASSOCATED WITH PUROX PYROLYSIS PLANT

A. Cost Associated with Purox Pyrolysis System

All cost estimates are based on the 1978 EPA report by the Ralph M. Parsons Company that analyzes the Purox Pyrolysis facilities developed the Union Carbide Corporation⁵¹. The cost estimates are based on 1975 dollars so they are converted to 2004 dollars by using the Marshal & Swift cost equipment index.

Capital costs are broken up into the four categories shown in Table 7 below. Working capital is taken as 25% of the operating cost or 3 months.

Item	1975 \$ millions	2004 \$ millions
Construction	47.08	126.93
Interest during construction	4.30	11.59
Startup Costs	2.56	6.90
Working Capital	1.56	4.21
TOTAL	55.50	149.63

Table 18: Capital Cost Requirements for Purox System

B. Construction Cost

The construction cost used in the capital cost is detailed in Table 8. Because the land acquisition can change according to location, the construction costs do not yet take it into account. Contigency is taken as 10% of the sum of the remaining values in the construction cost. Contigency will also rise once land acquisition is added.

	1975	2004
Item	\$ (K)	\$ (K)

Taxes	0	0
Land Acquisition	X 75	X 04
Site Improvement	880	2,372
Front-end processing plant	10,066	27,137
Processed feed material s & h facilities	3,476	9,371
Purox Equipment (includes wastewater plant)	17,703	47,726
Purox Equipment installation	10,675	28,779
10% Contigency	4,280	11,539
TOTAL	47,080	126,925

Table 19: Estimated Construction Cost Summary

C. Land Acquisition

Land acquisition is dependent on the location of production plant and is net yet finalized. Table 17 details the cost of land at each respective possible location.

D. Site Improvement

Site improvement is detailed in Table 18. The suggested amounts are not considered allowances because actual costs can vary depending on location.

	1975	2004
Item	\$ (K)	\$ (K)
Clearing and Grubbing	40	108
Utilities	240	647
Earthwork (excavation, backfill, and disposal)	270	728
Fine Grading	40	108
Paving	200	539
Landscaping	40	108
Fencing	50	135
TOTAL	880	2240

 Table 20:
 Site Improvement Costs for Purox System

E. Front End Processing Plant

Table 19 details the front end processing plant for a purox system and is broken into two main categories, building and process equipment.

	1975	2004
ltem	\$ (K)	\$ (K)
Building:		
Piling allowance	330	890

Foundations	861	2,321
Structural	1,188	3,203
Architectural	461	1,243
Mechanical	1,306	3,521
HVAC (not including dust control)	440	1,186
Electrical	922	2,486
Subtotal	5,508	14,849
Process Equipment:		
Front-end loaders	208	561
Shredders	534	1,440
Conveyors	398	1,073
Air Classifier Systems	470	1,267
Magnetic separators	46	124
Trommel	85	229
Aluminum system conveyors	80	216
Aluminum separation unit	415	1,119
Material storage/truck loading bins (installed)	116	313
Ferrous and residue trailer/tractors	250	674
Pickup truck	5	13
Truck weighing scales (installed)	85	229
Dust Control Systems	1,140	3,073
Bridge crane (installed)	120	324
Subtotal	3,952	10,654
Equipment Installation (not already included)	448	1,208
Spare Parts & Tools	158	426
TOTAL PLANT COSTS	10,066	27,137

Table 21: Front End Processing Plant for Purox System

F. Feed Material Handling Equipment Cost for Use by Purox System

The equipment cost for the feed material handling is detailed in table 11.

	1975	2004
Item	\$ (K)	\$ (K)
Material Receiving Equipment		
Receiving conveyor (2		
installed)	192	518
Distribution		
conveyor	130	350
Traveling plow on distribution conveyor	26	70
Inclined	400	070
conveyor	100	270
Automatic conveyor sequencing control	6	16
Conveyor		
wiring	60	162
Subtotal	514	1,386
Material Reclaim Equipment		
Bin unloader assemblies (2 installed)	540	1,456
Bin discharge conveyor (2 installed)	202	545
Conveyor		
wiring	95	256
Subtotal	837	2,257
TOTAL FEED MATERIAL HANDLING EQUIPMENT	1,351	3,642

Table 22: Feed Material Handling Equipment Cost

G. Annual Operating Costs for Purox System

Table 12 summarizes the annual operating costs for the purox system. Labor is analyzed in the proceeding section.

	1975	2004
Item	\$ (K)	\$ (K)
Labor	2159	5,821
Power	2307	6,220
Heating fuel and miscellaneous	200	539
Process equipment & building maintenance supplies	840	2,265
Mobile Equipment (maintenance & replacement)	92	248
Mobile equipment fuel	28	75
Water & Sewer	250	674
Extra raw refuse hauling	56	151
Residue disposal	45	121
Insurance	289	779
TOTAL ANNUAL OPERATING COSTS	6266	16893

 Table 23:
 Summary of Annual Operating Costs for Purox System

H. Labor Costs

A reasonable estimate by payroll category for direct labor can be made based on plant size, type, location and operating schedule. The dollar amounts are based on figures from the Union Carbide Corporation.⁶⁷ These values are based on wages from 1975 so in order to compensate for increase and inflation, the Marshall & Swift Index was applied for scale-up purposes.⁶⁸ These rates from 1975 were determined on the basis of the U.S. Bureau of Labor Statistics are wage survey (Bulletin 1850-15).

The table below shows a chart of personnel by category, number required for each shift, hourly rate, and disposition by shift for the front-end processing plant. The disposition numbers are shown at the bottom the table.

Position	Basic	1 st	2 nd	3 rd	Total

	Pay (\$/hour)	Shift	Shift*	Shift**	(\$/position/hr)
Superintendent	\$25.48	1	0	0	\$25.48
Shift Supervisor	\$22.68	1	1	1	\$68.44
Process Operator	\$18.32	2	2	0	\$73.59
Heavy Equipment Operator	\$18.32	4	3	0	\$128.71
Equipment Monitor Front- End and Aluminum	\$16.18	1	1	0	\$32.51
Mobile Equipment Mechanic	\$18.32	0	0	1	\$18.57
Maintenance Mechanic	\$18.32	1	1	1	\$55.37
Maintenance Mechanic	\$18.32	1	1	1	\$55.37
Maintenance Welder	\$18.32	0	0	1	\$18.57
Maintenance Helper	\$16.26	1	1	1	\$49.18
Yardman	\$16.26	1	1	1	\$49.18
Laborer	\$14.78	2	1	1	\$59.52
Janitor	\$14.78	0	1	0	\$14.93
Records Clerk-Steno	\$12.74	2	0	0	\$25.48

*

2nd Shift, add \$0.15/hr 3rd Shift, add \$0.25/hr **

Figure 20: Personnel required for front-end processing plant

The following table illustrates the same information for the purox syngas unit.

Desition	Basic Pay	1 st	2 nd	3 rd	Total
rosition	(\$/hour)	Shift	Shift*	Shift**	(\$/position/hr)

Superintendent	\$25.48	1	0	0	\$25.48
Plant Engineer	\$24.08	1	0	0	\$24.04
Shift Supervisor	\$22.68	1	1	1	\$68.44
Process Operator	\$18.32	2	2	2	\$110.74
Heavy Equipment Operator (Residue)	\$18.32	1	1	1	\$55.37
Reactor Monitor	\$16.69	2	2	2	\$100.95
Feed Material Monitor	\$16.26	1	1	1	\$49.18
Product Compressorman	\$18.32	1	1	1	\$55.37
Maintenance Mechanic	\$18.32	1	1	1	\$55.37
Electrician	\$18.32	1	1	1	\$55.37
Maintenance Helper	\$16.26	1	1	1	\$49.18
Laborer	\$14.78	2	2	2	\$89.48
Instrument Technician	\$19.11	1	0	0	\$19.11
Water Treatment Plant Monitor	\$16.26	1	1	1	\$49.18
Water Treatment Plant Operator	\$20.13	1	1	1	\$60.80

* 2nd Shift, add \$0.15/hr

** 3rd Shift, add \$0.25/hr

Figure 21: Personnel required for purox syngas unit

The table shown below summarizes labor costs including a 50% hourly surcharge to cover fringe benefits and overhead costs (eg. payroll and accounting). An estimated overtime allowance of 3,300 hours per year will allow for development of a 6-day week operating schedule. In addition there are 6 standby personnel for vacation and sick leave fill-in and overtime shifts for front-end operators as follows: 1 process operator, 1 heavy equipment operator, 1 electrician, 1 mechanic and 2 laborers. These individuals are training for higher labor grade and are assigned to cover various positions while training. Finally, 5 standby personnel are added for the Purox plant operation to fill in for vacation and sick leave and overtime as follows: 1 reactor monitor, 1 maintenance helper, 1 water treatment plant monitor, and 2 laborers.

Regular Operating Positions	
Front-End Processing Plant	\$1,403,796.52
Syngas Plant	\$1,805,601.41

Standby Personnel	
Front-End Processing Plant	\$218,170.44
Syngas Plant	\$200,996.67
Overhead and Fringe Benefits (50%)	\$1,814,282.52
Overtime	
Front-End Processing Plant	\$86,533.95
Syngas Plant	\$57,979.81
Total	\$5,587,361.32

Table 22: Summary of labor costs for purox system

The PUROX plant will operate continuously so it is possible to develop a rotating shift schedule with an overtime allowance of 2,400 hours per year. To achieve this, 4 men are set to be assigned to each shift-day position in the PUROX syngas unit figure shown above. Annual labor cost for the complete facility is \$5,588,000.

I. Electricity Cost

Below is a table depicting the amount of electricity needed.

Total Amount Needed	14800 KW
KWh/ton raw refuse	237
Average Cost per KW consumed	\$0.05
Average Cost per ton of Refuse	10.902
Annual Raw Refused Processed	547500 Tons
Total Annual Power Cost	\$5,968,845.00

Table 24: Electricity Cost

V. Product Selection

A. Methanol

Methanol has many uses in the chemical industry. It is used in making formaldehyde, acetic acid, and methyl tertiary butyl ether (MTBE). MTBE is primarily used in gasoline to increase octane levels. In 1990, the U.S. Congress passed a new Clean Air Act which caused an increase in usage of MTBE. MTBE reduces smog and air pollution resulting from vehicular exhaust. However, many states that were previously large consumers of MTBE are now banning the use of it due to MTBE being released in small concentrations to ground water sources⁶⁹.

The United States is the largest consumer of methanol and in 2001, the U.S. consumed more than 8 million tons of methanol. Before 2000, the U.S. had 18 functioning methanol plants, but by the beginning of the decade, 8 had been closed. The methanol

market is expected to continue to decline due to the decrease in use of MTBE. Currently, methanol sells for 0.66/scf or $254/ton^{70}$.

Methanol production is a complicated design including many pieces of equipment. The production of methanol takes place in two different sections: compressing and converting, and distillation. Prior to the first stage, water, hydrogen, carbon monoxide, and carbon dioxide is passed through a shell and tube heat exchanger. Steam is released, and the remaining gases are taken to the compression and conversion phase. Carbon monoxide, carbon dioxide, and water leaving the heat exchanger are compressed and then joined by the carbon dioxide, carbon monoxide and hydrogen stream and this is passed through a converter. Another heat exchanger is used and the exit stream is put through two methanol separators. The top stream from this is compressed again and recycled back through. The bottoms streams from both methanol separators are then put through the distillation process. This distillation process consists of two distillation columns. The final products are water, byproducts, and methanol. The water and the byproducts are put back through the process and the methanol is sent to storage.

The main reactions in the production of methanol are as follows:

 $CO + H_2O < -- > CO_2 + H_2 \quad (1)$ $CO + 2H_2 < -- > CH_3OH \quad (2)$ $CO_2 + 3H_2 < -- > CH_3OH + H_2O \quad (3)$

Because of the ratio of hydrogen to methanol in these reactions, the production of hydrogen is more profitable. The rate of hydrogen used is 3 to 1 for the production of methanol. Hydrogen sells for almost ten times as much as methanol. Although methanol production creates hydrogen which could eventually be used in fuel cells, the high percentage of methanol use in MTBE will keep the market from fully recovering. For this reason, methanol production is not a logical choice for an end product⁷¹.

B. Methanol Products

i. Acetic Acid

Acetic acid is useful as an industrial solvent used during the production of polyethyl terephthalate (PET), the material from which carbonated drink bottles are made. This is the impetus for the current 4.5% growth in acetic acid demand. Other uses for this acid include photographic films, vinyl acetate and vinegar – although the vinegar is usually restricted to fermentation processes. Food-grade and container-grade acetic acid is available for sale at 960 \$/T with a market volume of 5660 TPY.⁷² Historical data indicates that this is ahead of the current market trend, which places the actual worth of acetic acid at 740 \$/T. Industrially-produced acetic acid availability is correlated with energy prices. Increases in natural gas prices – the major reactant used to form acetic acid industrially – increase price and decrease production of acetic acid because of the shifting profit margins.⁷³ Recent trends have inflated prices and demand indicates that this will continue.



METH

RFAC

Figure 23: Acetic Acid Facility

The mechanism of acetic acid formation from synthesis gas involves methanol carbonylation.

$CH_3OH + CO \rightarrow CH_3COOH$

Older methods required extreme conditions for production, in excess of 200 atm, but current methods using rhodium-based catalysts allow production at 1 atm.

The enthalpy theoretically recoverable from the reaction above to make acetic acid is 3.4 MJ/kg, calculated in the chart below (changes in standard enthalpies of formation). These calculations assume that subsequent changes in enthalpy are negligible in relation to the reaction enthalpies.

	MW	$\Delta_{\rm f} { m H}^0 ({ m MJ/kg})$
Acetic Acid	60	-8.1
Methanol	32	7.5
Carbon Monoxide	28	4.0
Total		3.4

Table 25: Synthesis	Gas Com	ponent and	Product F	Properties
2		1		

The maximum theoretical amount of acetic acid from syngas without a gas shift reaction is limited by the amount of hydrogen gas available (24 vol%). The overall mole balance requirements of a syngas-to-acetic-acid process are:

$$2H_2 + 2CO \rightarrow CH_3COOH$$

NOTE – this is not a reaction. This balance implies that the theoretical limit of acetic acid mass production approaches the sum of the total hydrogen production

$$21,200 \frac{kgmol \ syngas}{d} \cdot 24 \frac{vol\%H_2}{100} \cdot (100-40) \frac{vol\%moisture}{100} \cdot 2 \frac{kgH_2}{kgmolH_2} = 6100 \frac{kg}{d}$$

plus the total carbon monoxide production (note -40 vol% CO is available, but the reaction is limited by hydrogen availability):

$$21,200 \frac{kgmol \ syngas}{d} \cdot 24 \frac{vol\%H_2}{100} \cdot (100-40) \frac{vol\%moisture}{100} \cdot 28 \frac{kgCO}{kgmolCO} = 85,500 \frac{kgCO}{d}$$

Both of these add up to 91,600 kg = 101 TPD = \$75,000 per day. This will clearly be profitable, but what about practical concerns such as equilibrium limitations, power consumption and capital costs?

More practically, an equimolar feed of hydrogen and carbon dioxide has been demonstrated to have a 55% equilibrium CO_2 conversion.⁷⁴ Due to the expense of separation, the best way to get acetic acid is to reform the gas so that there are only the components of the reaction present, then put the gas through a water gas shift reactor so that the components approach equilibrium, then reacting the equilibrated vapor through to form acetic acid. Kinetic information for the methanol formation⁷⁵ and the acetic acid formation⁷⁶ was provided by the National Institute of Standards and Technology. The acetic acid can be precipitated out of the effluent when it is cooled. Consequently, the vapor is recycled – after heat recovery – and sent back to the gas-shift reactor to make more of the necessary reactants. This should increase the concentration of carbon dioxide and hydrogen in the reactor, which will allow a practical total conversion of all of the hydrogen and oxygen to acetic acid. The ideal conversion of the reaction would allow the largest amount of each reactant to be turned into acetic acid. With a recycle stream setup, this could produce, at each reactor – a reformer to get rid of other hydrocarbons, a water gas-shift reactor (WGSR) to optimize the potential for making the acid, and an acetic acid reactor (AAR) – the amounts and fractions of each chemical shown in the table below.

	Reforme	er Outlet	WGSR Outlet		MR Outlet		AAR outlet	
	kgmol/s	mol%	kgmol/s	mol%	kgmol/s	mol%	kgmol/s	mol%
СО	49.4	25.9	39.5	20.7	18.8	24.4	0.0	0.0
H ₂	29.6	15.5	39.5	20.7	0.0	0.0	0.0	0.0
CO ₂	29.6	15.5	39.5	20.7	39.5	51.2	39.5	67.7
CH ₃ OH	0	0.0	0	0.0	18.8	24.4	0.0	0.0
H ₂ O	82.3	43.1	72.4	37.9	0	0.0	0	0.0
AA	0	0.0	0	0.0	0	0.0	18.8	32.2
Total	190.9	100	190.9	100	77.1	100	58.3	100

Table 26: Acetic Acid Molar Flow Rates and Percentages

Note that water is removed after the water gas shift reaction via condensation and carbon dioxide must be compressed and cooled after leaving the facility. The amount of acetic acid produced is 18.8 kgmol/s, which is equivalent to 1130 kg/h, 30 TPD at 740 /T - 22,000 /D. This cost is less the price of CO₂ sequestration and water processing. The annualized cost of a Selexol facility that will handle 39.5 kgmol/s CO₂ is 758,000 /Y, or 2,100 /D, leaving a conservative 19,000 /D, assuming that the steady state acetic acid

reactor can approach equilibrium. With hydrogen, the actual modeled potential is \$160,000/d, clearly superior on the basis of weight waste processed.

ii. Formic Acid

Also known as methanoic acid, formic acid is the simplest carboxylic acid. It is a strong reducing agent, and is used in fumigants, animal feed additives, commercial paint strippers, hide tanning products and textile dyes.⁷⁷ The first step in the formation of formic acid is the carbonylation of methanol to produce methyl formate. The formic acid synthesis step takes place via the electrolysis of the methyl formate.

 $CH_3OH + CO \rightarrow HCOOCH_3$ $HCOOCH_3 + H_2O \rightarrow HCOOH + CH_3OH$

Industrially, this reaction is performed in the liquid phase at elevated pressure. Typical reaction conditions are 80°C and 40 atm. The most widely used base is sodium methoxide. Hydrolysis of the methyl formate produces formic acid:

iii. Dimethyl Ether

Dimethyl ether (DME) is being considered as a potential fuel gas to be blended with diesel for cold weather conditions and enhanced performance characteristics in all operation⁷⁸, in addition to use as a fuel substitute in developing countries. The high volatility of the ether, in conjunction with its clean burning characteristics, is what makes it attractive as a fuel source.

Reference values for the DME market are difficult to come by, in addition to the complications due to flux due to its loss in competition as a fuel additive to ethanol. Enthalpies of combustion for chemicals that are produced with similar processes and that have similar heating values (in MJ/L): methanol (-18.0⁷⁹), ethanol (-24.1⁸⁰) and DME (-18.9⁸¹). The latest annual-averaged prices of methanol and ethanol (\$/gal) are 0.51 and 1.50, respectively.⁸² A simple assumption that there is a proportional linear relationship between heating value and price for the products gives a price of 0.68 \$/gal. Theoretically, the greatest amount of DME that could be made from the purox off gas, determined by mole balance, is limited by the number of hydrogen gas molecules that enter the system, 29.6 kgmol/s from the gas and 82.3 kgmol/s from water, if it can be shifted to yield gas. Altogether, this is 111.9 kgmol/s of hydrogen gas, which can go to make 37.3 kgmol/s DME, which would be 1720 kg/h DME or 45.5 TPD at 109 \$/T, yielding 4,960 \$/D, or a fifth the selling value of acetic acid. This is still well short of acetic acid and hydrogen.

C. Ammonia

Ammonia is a product used in such applications as fertilizers, refrigeration, and processing. In fact, over 80% of all ammonia produced is used for fertilization. The demand at this time indicates that it is not a stable product for marketing, but that there is always demand as long as ammonia is being produced.

The Haber process was examined as a possibility to produce ammonia for an end product. At this time, the ammonia market is still stable; however, its growth has slowed over the past few years. The following reaction is used to produce ammonia.

$$N_2 + 3H_2 \rightarrow 2NH_3$$

There are other methods for the production of ammonia as a product, however this is the method considered based because of these components that are available, that is the nitrogen and hydrogen.

The nitrogen from the air cryogenics plant is combined with hydrogen from the syngas to produce ammonia, based on this reaction. This is modeled in PRO-II® simulation series and conversion is roughly 99%. This conversion rate is achieved at a pressure of 15 atm and a temperature of 800 F.

In the model of ammonia production, the process is modeled using the standard 3:1 reaction ratio of hydrogen to nitrogen in a Gibbs Reactor (used in PRO-II® due to lack of kinetic data). Both Nitrogen and Hydrogen enter the system at atmospheric pressure and room temperature. The reaction produces a product of ammonia that is almost 100% pure, and a catalyst at high temperature and pressure is required to make this reaction occur. This product is then cooled with a heat exchanger system using nitrogen as a coolant where the nitrogen and hydrogen fall off making ammonia of a near pure composition. This is explained by the boiling points of nitrogen and hydrogen and how the hydrogen boiling point is lower than the nitrogen causing it to fall off in the cooling process.

The production of ammonia is based on the process of reacting nitrogen and hydrogen from the hydrogen to sell on the market as a product. The molecular weights for each of the compounds involved are as follows: Nitrogen has a molecular weight of 14.0067 g/mole and hydrogen a molecular weight of 1.00794 g/mole. Based on a per-mole basis using the ratio's of these reactions, the maximum amount of ammonia that can be produced can be figured from the model.

Energy Balance (kJ/mole)

- $(0 \text{ kJ/mol of } H_2) - (0 \text{ kJ/mol of } N_2) + 2 \text{ x} (-45.8873 \text{ kJ/mol of } CO_2) = -91.8 \text{ kJ/mol}$

This energy balance, shown above indicates the amount of energy needed to produce 1 mole of ammonia. Based on this energy balance, cost of energy needed for this process can be estimated to aid in the calculation of capital investment.

Based on the mole balances, mass balances, and energy balance for this reaction to make ammonia, the process is profitable enough to look at as a product. The current market price of ammonia is approximately \$200 per metric ton, with the market suggesting a growth of about 2 % per year in selling price. This trend has held and the price of ammonia at this time is down as well as the market demand is low. The total capital investment for an ammonia plant also includes the cost of a hydrogen plant, bringing an amount to approximately \$25 million.

Currently, the ammonia market is still increasing though not at as high of a rate as in the past years.⁸³ The cost of hydrogen production makes this relatively costly in that almost all of the total capital investment is the production of the hydrogen. In addition, it must be noted that the basis of this argument lies in the idea that the hydrogen market will take off at this rate, even though the actual value of hydrogen is used in this estimation.

Also, because of the decision of hydrogen based on a hopeful demand, nitrogen was looked at as a possible end product and should be discussed at this time. The current market price of nitrogen is approximately \$160/ton.⁸⁴

D. Polycarbonates

The production of polcarbonates was a process that was examined for a possible end product from the waste generated from the purox system. This is a relatively new process where companies like Dow Chemical Company currently occupy the market with plants around the world in a growing market⁸⁵.

Polycarbonate is produced from three different reaction processes. Carbon dioxide is combined with hydrogen gas in the water gas shift reaction to produce carbon monoxide and water. The amount of carbon monoxide produced is determined by the hydrogen that is used in this reaction. This carbon monoxide is then combined with sodium chloride to produce phosgene. Finally, the phosgene produced is combined with bisphenyl-A to produce the products of polycarbonate resin and hydrochloric acid. These three reactions are shown below in a mole balance.

 $CO_2 + H_2 \leftrightarrow CO + H_2O$

 $CO + 2NaCl \rightarrow Phosgene + 2Na$

 $Phosgene + bisphenyl - A \rightarrow Polycarbonate + 2HCl$

Combing mole and mass balances along with the product amounts from the syngas that produces the necessary products, in addition to the products that are needed to purchase, the process can be examined for feasibility both actual and economically.

The raw materials needed are sodium chloride and biphenyl-A and are currently available on the market at a value of \$100,000/ton and \$470,000/ton respectively. The current market value of the products polycarbonate and hydrochloric acid are \$950,000/ton and \$5,000/ton respectively. Also factored into the equation, before even the capital cost, is the cost of energy at \$4/MM BTU. The overall energy needed to produce one day's product is 1385.73 kJ per mole of product bring the total energy cost of the reaction process to \$74,229/day.

The fact that this process is relatively new and that at this point in time, could not compete with the business that is turned out by Dow Chemical Company® and others, would eliminate this as a possible product. In addition, with the hydrogen market projected to do as well as it is, polycarbonate production should not be considered as a possible end product.

E. Synthetic Fuel

i. Overview

Synthetic fuels can be produced from natural gas or synthetic gas. For the purposes of processing the municipal solid waste, the route of converting synthetic gasoline to synthetic fuel was investigated. Synthetic fuels from synthetic gas can be achieved using Fischer-Tropsch (F-T) chemistry. With the synthetic gas already being produced upstream (from the pyrolysis), the major cost in the production of synthetic fuel is already eliminated. The production of synthetic fuel from synthetic gas consists of synthetic gas purification, Fisher-Tropsch (F-T) synthesis, and product upgrade.

The products produced from Fischer-Tropsch technology can compete with traditional petroleum products. The principal products are clean-burning and premium grade diesel, naphthas, and waxes. These products are free of sulphur, aromatics, nitrogen, and heavy metals that are typically found in crude oil. Of the products produced from Fischer-Tropsch synthesis, the diesel fuel fraction is the most appealing and offers many advantages. First and foremost, the diesel fraction produced from F-T synthesis requires very little processing as it can be used in existing diesel engines without altering its infrastructure or modifying vehicle engines. Since it contains virtually no sulfur or aromatic compounds, this synthetic diesel can lead to lower vehicle emissions and maximum efficiency of fuel use (diesel uses 20-25% less fuel than gasoline engines of the same power).⁸⁶ Naphthas are lighter hydrocarbons compared to diesel. These products are appealing to manufacturing processes for paint, ink, polish, adhesives, perfumes, and glues due to their low toxicity and lower aromatic content (compared to other naphthas). Waxes produced can be useful in hot-melt adhesives, inks, and several other wax-based products. The market is high for waxes, but demand is very limited. Due to this limited demand, these waxes can be hydro-cracked to yield additional diesel fuel.

Fischer-Tropsch synthesis converts the hydrogen and carbon monoxide from synthetic gas to the wide range of hydrocarbon products by way of the reaction presented below.

$$nCO + 2nH_2 \rightarrow (CH_2)_n + nH_2O$$

Different types of F-T reactors have been designed to carry out the highly exothermic reaction listed above. Such reactors used in industry (by companies such as Sasol, Shell, ExxonMobil, Syntroleum, and Rentech) include fixed bed, fluidized-bed, slurry bubble columns, and circulating-fluidized bed reactors. Recent development in gas-to-liquid

technology of the F-T process has focused on slurry bubble column reactors. Most F-T processes utilize use of an iron catalyst or cobalt catalyst. For this study, an iron-based catalyst is used due to its ability to process a wide range of H_2/CO ratios in the synthesis gas. This is important as the pyrolytic synthetic gas is comprised of a low H_2/CO ratio. The iron-based catalyst promotes an internal shift in the F-T reaction above by using the water produced from the F-T reaction to produce more H_2 . As a result, high H_2/CO ratio synthetic gas can be achieved from a low H_2/CO ratio synthetic gas (see process below for details), which is important in the quality of products produced.

ii. Synthetic Gas to Synthetic Fuel Plant Design

The type of F-T plant chosen produces synthetic diesel fuel from a slurry bubble column and iron-based catalysts. Figure 24 below illustrates a schematic diagram of producing synthetic diesel from pyrolytic synthetic gas using a Fischer-Tropsch plant. The plant consists of a reactor section and the product recovery section. In the figure, the pyrolytic synthetic gas is sent to the F-T slurry reactor. The heat of reaction that takes place in the slurry reactor is removed by steam generation, with the heat exchange elements of the slurry reactor connected to steam drums. Due to the high heat of reaction, the product stream from the slurry reactor is cooled by a heat exchanger prior to entering the product recovery section.



Figure 24: Fischer-Tropsch Schematic

The product recovery section is composed of the separation, filtration, and recovery units. The product separation and filtration units are composed of catalyst/reactor wax separation units, with a slurry filtration system that utilizes cake handling. (Cake filtration can operate at high capacity with low labor costs and good washability.) From the separation and filtration, the product stream leaving the reactor is separated into two streams, one comprised of lighter hydrocarbons to be processed downstream, and the other comprised of the heavy slurry. The heavy slurry has a high catalyst concentration and is recycled back to the slurry reactor to maximize use of the catalyst. The light product stream consists of a broad range of hydrocarbons that require fractionation and processing. This stream is therefore extracted using a series of distillation columns (hydrocarbon recovery section) to separate the light hydrocarbons into four streams: $H_2O/oxygenates$, naphtha (C5 to C9), diesel (C10 to C19), and waxes (C20+). The naphtha can be blended into petrol, and the diesel (as discussed previously) does not require any more processing and represents a high quality diesel fuel. The waxes are hydro-cracked to form diesel. Any un-reacted hydrogen gas is separated from the permanent gases and the light hydrocarbon gases, to be recycled back to the synthetic gas feed.

iii. Capital and Operating Cost

A report from ACTED Consultants on gas-to-liquid technology discussed various Fischer-Tropsch technologies used in industry for the production of synthetic fuels. It reports the capital costs (to build a plant) for gas-to-liquid projects to be between \$20,000 and \$30,000 per daily barrel of capacity. (The capital costs for refineries are between \$12,000 and \$14,000 per daily barrel.) Also, Sasol uses Fischer-Tropsch technology with slurry reactors, similar to the process designed for the production of synthetic fuels from pyrolytic syngas. Sasol claims that their plant producing 10,000 bbls/day can be built at a cost of \$250 million. From these two references, a capital of \$25,000 per daily barrel of capacity was used to determine estimates of capital costs. In addition to the total capital investment, the fixed capital investment and working capital were determined. Material balances confirmed that from a raw material feed of 28 million ft³/day of synthesis gas (from 1500 tons/day waste), 939 barrels per day of synthetic diesel fuel can be produced. All capital cost and operating costs were therefore based on this operating capacity.

Direct Costs	Costs
Equipment Costs	\$3,958,685
Equipment Installation	\$1,860,582
Instrumentation	\$1,425,126
Piping	\$2,691,906
Electrical Systems	\$435,455
Buildings	\$712,563
Yard Improvements	\$395,868
Service Facilities	\$2,771,079
Total direct plant costs	\$14,251,265
Indirect Costs	
Engineering and Supervision	\$1,306,366
Construction expenses	\$1,623,061
Legal expenses	\$158,347
Contractor's fee	\$870,911
Contingency	\$1,741,821
Total indirect plant costs	\$5,700,506
Fixed-Capital Investment	\$19,951,771
Working Capital	\$3,521,250
Total Capital Investment	\$23,475,000

Table 27: Capital Costs for Synthetic Fuel Fischer-Tropsch Plant

Equipment costs for a Fischer-Tropsch plant total \$4.0 MM. The bulk of this price comes from the costs of a slurry reactor, product separators, slurry filtration and activation systems, compressors, and distillation towers. (The slurry reactor chosen was chosen to have a diameter of 5 m and a height of 22 m, with a maximum operating capacity of 2500 bbl day. The distillation towers were 12 feet X 100 feet each.) Total capital investment is \$23.5 MM, with a fixed capital investment of \$20.0 MM and working capital of \$3.5 MM. Additional direct plant costs are included in the table above.

For production costs, an USA Energy assessment of a hypothetical gas-to-liquid project estimated the cost to produce F-T fuel at \$25/barrel. From the \$25/barrel estimate, \$12/bbl was estimated for taxes, \$5/bbl was estimated for operating costs, and \$8/bbl was estimated for the cash cost of production. These were helpful in providing a basis for comparison when determining the costs of producing F-T diesel, listed below.

Variable Operating Costs	Costs
Raw Materials	
Syngas	\$0
F-T catalyst	\$694,650
Operating Labor	\$564,279
Operating Supervision	\$84,642
Utilities	
Water (\$.08/1000 kg)	\$736,780
Electricity (\$.045/kWh)	\$1,105,171
Maintenance and Repairs	\$552,408
Operating Supplies	\$82,861
Total Variable Production Costs	\$3,820,791
Fixed Operating Costs	
Taxes	\$3,526,884
Insurance	\$276,204
Total Fixed Charges	\$3,803,088
TOTAL PRODUCT COST	\$7,623,879

Table 28: Annual TPC to produce synthetic diesel fuel using a Fischer-Tropsch plant.

iv. NPW for Total Plant

When considering the net present worth of producing synthetic fuel from pyrolytic syngas, the total capital investment and operating oosts were considered for the entire process. This includes capital and operating cost of the pyrolysis purox process and the F-T process to produce synthetic diesel fuel. The project lifetime was assumed to be 20 years, with straight-line depreciation used in determining cash flow and net present worth. Synthetic diesel prices were predicted using a forecast of world oil prices supplied by the Department of Energy. A low price projection was used to be conservative, where the price of diesel was assumed relatively constant (before inflation). The net present worth for the entire process producing synthetic diesel fuel is -\$5.4 MM, thereby an indication of a non-profitable process.

v. Outlook

Alternative fuels have been attracting more attention in recent years. The development of cleaner fuels for the transportation industry has been encouraged by the changes in environment law and the addressing of the limited supply of oil and natural resources. The Clean Air Act Amendments of 1990 and the Department of Energy's (DOE) Ultra-Clean Fuels program were implemented to pioneer a new generation of clean transportation fuels to reduce vehicle emissions. The Ultra-Clean Fuels program has funded extensive research in the area of alternative fuels. Also, in 1992 the Energy Policy Act (EPAct) was passed by Congress. The purpose of the act was to promote use of alternative fuels (non-petroleum) to decrease our dependence on foreign oil and increase homeland energy security. This has come as a result of the increasing pressure put on the world's economy (restricting petroleum production and controlling the cost) by the Organization of the Petroleum Exporting Countries (OPEC).⁸⁷

Synthetic fuels have emerged as a solution to relieve some of this pressure by offering an affordable fuel that is cleaner and safer. Synthetic fuels have been investigated and researched by the U.S. Department of Energy as well as other petroleum companies in the energy industry, and are considered a more secure supply source than other competing alternative fuels. The cost to produce synthetic fuels from synthetic gas (when compared to producing petrochemicals such as methanol and ammonia) are cheaper to transport, market, and distribute to large markets⁸⁸. With crude oil prices exceeding \$34 per barrel (as of April 2004), the possibility of synthetic fuels are attracting more and more attention and can be expected to compete with crude petroleum fuels.

It is projected that from the increasing pressure on the energy industry from governments, environmental organizations, and the public, synthetic fuels are expected to grow rapidly at roughly 5.5% per year for the next five years. The global demand in the transportation industry is already over 11MM barrels per day, and the demand outlook remains positive over the next decade and beyond. Also, diesel will continue to dominate as the universal fuel as diesel engine technology continues to lead to advancements in cleaner, better burning fuel. The government is already offering incentives to encourage consumers to use ultra clean alternative fuels through tax credits, making the price for premium fuel more attractive.⁸⁹

vi. Tax Credits

The process above appears very unattractive when evaluating the net present worth. However, with the push to develop alternative fuels, the federal government has added incentives. The Internal Revenue Service offered a tax credit of \$1.083 per MMBtu of alternative fuel sold under Section 29 of the Internal Revenue Code. The F-T synthetic diesel produced has a heating value of 0.1375 MMBtu/gal.⁹⁰ This equates to about \$.15 per gallon of synthetic diesel sold.

This credit offered by the IRS was enacted in 1980 after the Arab embargo in an attempt to make the United States less dependent on oil and gas from the Middle East. It has been estimated that over \$3 billion dollars per year are awarded in tax credits from the IRS. Without the tax credits, production of synthetic fuel would not be economical. Of course, there are stipulations to qualify for this tax credit. Three primary conditions must be met to qualify for the credits:

- 1) There must be a significant chemical change in product from the feedstock
- 2) The product must be sold to a non-affiliated party
- 3) The production facility must have been placed in service before July 1, 1998

In regard to the last condition, no new projects could qualify for credits. In addition, these credits could only be claimed through 2007 as the credits expire on December 31, 2007.

Recently, the Bush administration passed the Energy Tax Policy Act of 2003. This bill is an extension to Section 29 of the Internal Revenue Code (1979) and allows production facilities in service before July 1, 1998, to claim the credit above. The bill also extends credits to new projects, including synthetic plants, for qualified fuels produced and sold until December 31, 2009. At this time the credits expire. However, if Congress follows tradition, the credits will be extended past this date. The tax credit is \$3/bbl produced (\$.07/gal), which is considerably lower than the Section 29 credit. However, with tax credits, synthetic fuel production is a profitable process with a net present worth of \$4.8 MM (compared to -\$5.4 MM with no tax credits).

F. Hydrogen Processing Plant

The production of hydrogen from synthetic gas involves four major systems: steam reformation, water-gas shift conversion, carbon dioxide removal, and pressure swing adsorption. Steam reformation converts the 11 molar percent composition of hydrocarbons in syngas to hydrogen and carbon dioxide. The next phase uses the water-gas shift to further convert carbon monoxide and steam to hydrogen. Then, Selexol solvent selectively absorbs most of the remaining CO_2 and H_2O . Finally, a pressure swing adsorption purifies the hydrogen to industrial quality levels.



Figure 29: Hydrogen Processing Plant Overview

i. Steam Reformation

In order to maximize hydrogen production, a steam reformation process is used to separate the hydrogen from the hydrocarbons by way of a nickel oxide catalyst. The overall reaction consists of methane and steam reacting endothermically to form carbon dioxide and hydrogen. Below, figure 30 shows the steam reformation process. There are only two pieces of equipment, the reformer furnace and a compressor.



Figure 30: Steam reformation system

The unprocessed synthetic gas has an 11 molar percent dry composition of hydrocarbons. If a steam reformer system were not used, the hydrogen from these hydrocarbons would pass through the entire processing plant unreacted and thus wasted. In the reformation reactor, the following reactions can potentially occur.

(1)

Compressor

$CH_4 + H_2O \rightarrow 3H_2 + CO$	
$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$	
$\rm CO + H_2O \rightarrow CO_2 + H_2$	
$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$	
$CO + H_2 \leftrightarrow C + H_2O$	
$CH_4 \leftarrow \rightarrow C + 2H_2$	
$2CO \leftrightarrow C + CO_2$	



Any pair among the first four reactions is adequate for representing equilibrium compositions, and it has been customary to select the first and third reactions⁹¹. For carbon not to be present at equilibrium as well as to deter the disintegration of the catalyst, the steam to methane ratio must be at least in the 3 to 5 range. The steam to methane ratio of this particular reformer is 8 because that is the ratio at which it arrives from the purox pyrolysis plant. So within this range of ratios, any carbon formed will react to form the bottom three reactants and the overall reaction will be:

 $\begin{array}{l} CH_4 + 2H_2O \twoheadrightarrow CO_2 + 4H_2 \\ \Delta H_{RX} = 84,000 \; Btu/lb_{mol} \end{array}$

Of the 11 molar percent hydrocarbons, half is comprised of ethylene and acetylene. However, hydrocarbons other than methane are rapidly converted to methane near the inlet by hydrocracking (ibid).

The reactor must be capable of handling pressures up to 30 atm's and temperatures up to 2000 F. Energy is saved by operating the reformer at elevated pressures, but the negative effects of the high pressure on the forward progress of reaction 1 is overcome by increased temperatures and high steam to methane ratios (ibid). The high temperatures are necessary for an operating range of 17,000 to 21,000 Btu/hr*ft². Although kinetics and mechanism have been studied and it is known that the reaction path involves

alternate oxidation and reduction of the active nickel centers, it has been established that in this heat flux operating range, the rapid reactions are controlled by the rate of heat transfer (ibid).

The reformer furnace specifications are as follows. The coal-fired furnace generates a heat load of 140 MM Btu/hr. A 40 feet long tubular catalytic reactor consisting of 170 5-inch diameter tubes passes through it. Also, before the tubular reactor, the syngas feed must first pass through the reformer without catalyst to bring it up to nearly 1600F so that it reacts upon arrival to the catalytic reactor.

The catalyst is nickel oxide consisting of 15% Ni, 0.03% S, and 0.2 SiO₂, and is in the form of 5/8in by 5/8in by 3/16in Rasching rings with a bulk density of about 50 lb/ft³. The process requires about 380,000 lbs of catalyst that must be replaced every five years.

As previously mentioned, the syngas must enter the reformer at about 20 atm's. Therefore, a compressor is necessary prior to introduction into the reformer furnace. It compresses the syngas from 1 atm to 19.7 atm and at a duty of 0.57 MM Btu/min.

Below, figure 31 details the effects of steam reformation on a syngas from the purox pyrolysis plant on a dry gas basis. Next, syngas is sent to the shift conversion system.





Below, the equipment costs for steam reformation are tabulated. The Microsoft Excel Worksheet file entitled "Waste to Hydrogen Processing Plant" details each piece of equipment sizing and costs for the Steam Reformation.

Steam Reformation	Compressor	\$5,727,400
	Steam Reformer	\$2,000,000
Total Equipment Costs		\$7,727,400

 Table 32: Total Reformer Equipment Costs

ii. Water-Gas Shift conversion

After steam reformation, the syngas enters the water-gas shift conversion system. Carbon monoxide and steam react exothermically to produce carbon dioxide and additional hydrogen in four high temperature catalytic reactors. The resulting product stream is then

condensed and passed through a flash drum to remove the remaining water. Below, figure 33 shows the shift conversion process. The main pieces of equipment are the four catalytic tubular reactors, two heat exchangers, and a flash drum.



Figure 33: Water-Gas Shift System

The four tubular catalytic reactors are central to this process. About 620 more lb_{mol}/hr of hydrogen is produced in the adiabatic reactors by what is known industrially as the watergas shift. In the water-gas shift, carbon monoxide and steam react to form carbon dioxide and hydrogen over a chromia promoted iron catalyst. The reactor specifications were decided by the reaction temperature, the steam to carbon monoxide molar ratio in the feed, the necessary amount of catalyst, and the amount of feed.

 $\begin{array}{c} \text{CO} + \text{H}_2\text{O} \bigstar \textbf{O}_2 + \text{H}_2 \\ \text{dH}_{\text{rx}} = \textbf{-37.2 kJ/mol} \end{array}$

The reaction is both exothermic and reversible. The percent yield of hydrogen is a **Tubular Rea** function of temperature and the steam to carbon monoxide molar table. But G **Tubular Rea** graphically illustrates the CO molar percentage as a function of temperature and molar steam:CO ratio. Lower temperatures and higher steam:CO molar ratios both favor a higher yield of hydrogen. The minimum temperature for an iron oxide catalyst to operate efficiently, 600F, was chosen for a reactor temperature. A steam:CO ratio of 8 was selected because a higher ratio results in impractical catalyst weights and subsequent reactor volumes. Figure 35 shows that the resulting CO molar percentage is 1.5%. A small amount of steam must therefore be added prior to the reactors in order to increase the steam:CO ratio from about 4 to 8.



Figure 34: Adiabatic plot for shift conversion at various steam:CO ratios¹

Taking all the necessary specifications into account as well as the kinetic reaction data, a simulation was set up on the chemical engineering equipment simulation software, PRO/II. The simulation allowed the calculation of volumetric capacity. There are four stainless steel tubular reactors 36 feet long. Each reactor has 100 tubes that are 3.25 inch outside diameter or 3 inch inside diameter. The required catalyst weight for all four reactors is 300,000 lbs of an iron oxide catalyst with a bulk density of 70 lbs/ft³. The catalyst must be replaced every five years.

The process requires two heat exchangers. In order to prepare the syngas for the watergas shift conversion reactors, it must first be passed through a heat exchanger to cool it from 1600F to 600F (as previously discussed the lowest temperature for the catalyst to operate is 600F). The preliminary heat exchanger has a cooling area of 700 ft² and a cooling duty of 1.8 MM Btu/min. The second heat exchanger is used to initiate a phase change from steam to water. The syngas exits the tubular reactors at about 705F and is cooled to 77F. The cooling area is 1650 ft² with a cooling duty of 2.4 MM Btu/min.

After the final heat exchanger, the vapor-liquid stream is sent to a 10,000 gallon adiabatic flash tank to separate the mixture into each phase where the near dry syngas is sent on to the CO_2 removal system, and at 77F the water may be introduced into the municipal water system.

Below, Figure 35 details the inlet and outlet stream conditions. Hydrogen will not be further produced- the remaining processing systems are only concerned with hydrogen purification mainly by the removal of CO and CO₂.



Figure 35: The effects of the water-gas shift system on the syngas.

Below, the equipment costs for the water-gas shift conversion system are tabulated. The Microsoft Excel Worksheet file entitled "Waste to Hydrogen Processing Plant" details each piece of equipment sizing and costs for the Water Gas Shift systems.

Water-Gas Shift	High Temp. Reactor X 4	\$1,029,776
	Heat Exchanger 2	\$30,000
	Heat Exchanger 1	\$10,500
	Flash Drum	\$112,000
Total Equipment Costs		\$1,182,276

 Table 36: Total Water-Gas Shift Equipment Costs

iii. Carbon Dioxide Removal

Carbon dioxide removal is expensive in large part because of capital investment and because of heat transfer requirements associated with phase change systems that afford high purity separations. A low vapor pressure solvent that selectively absorbs and releases carbon dioxide forms the basis of a system that will avoid most of the high costs associated with phase changes and heat transfer. The Selexol process of CO_2 capture recovers lost pressure work but does not use extensive heating processes, yielding a low overall operation cost. Regression analyses of performance and capital cost information have been developed with extensive Aspen simulations. Correlations have been developed that will allow sizing and cost information, given feed composition, temperature and pressure information, in addition to the fraction carbon dioxide that must be removed from the stream.

The removal of CO_2 from the effluent stream takes place after the synthesis gas stream is shifted and cooled with the process flow diagram shown below.



SLUMP

TANK

Selexol is a solvent composed predominantly of dimethyl ether and polyethylene glycol. It has a very low vapor pressure, low viscosity and low heat of absorption. It is non-corrosive and non-toxic. The selection dioxide in Selexol at 230 psia is 0.485 SCFCO₂/US gal. The solubility of carbon dioxide in Selexol at ambient pressure is a function of temperature an Shas Net Atemined to be the result of PATE and T7 °F)

 $\chi = 0.0908 - 0.0008$ T (°F)

The best temperature for absorption in this range is 30 °F. However, the colder the solvent is, the more energy it will cost to cool so an optimal value must be determined. Because the absorbance varies with temperature, accurate sizing and costing of the system may require that the temperature of the solvent in the absorber be determined, so a check will be determined once the flow rate is specified. The glycol solvent's relevant properties are tabulated below.

Cost	1.96 \$/gal
CO ₂ Solubility 25°C, 230 psia	0.485 SCF/US gal
CO_2 Solubility 25°C, 4 psia	0.0375 SCF/US gal
Solubility of H_2 25°C	0.00049 SCF/US gal
Vapor Pressure 25 °C	0.00073 mmHg
Viscosity 25 °C	5.8 cp
SG 25 °C	1.03
MW	280
C _p 25 °C	0.49 Btu/lb °F

Table 37: Selexol Solvent Properties

Figure 39 summarizes the effects of the CO_2 removal on the syngas. In summary, the system will handle a throughput of 4,960 lbmol/h input synthesis gas and 2,050,000 (US) gal/h Selexol, removing 99.99% of the 1743 lbmol/h carbon dioxide input. The selexol is assumed to circulate every twelve minutes and new Selexol must be purchased every five years - \$180,000/y.

The total capital cost of the system will be 4.18 million dollars, Results are tabulated below and calculated in Appendix B.

	Power	Capital	
	hp	\$1000	
Stripper		1,640	
Turbine		312	
Slump		88	
C 1	657	1,070	
C 2	54.6	106	
C 3	229	278	
Refrig	213	504	
ΣF		63	
Pump	556	114	
TOTAL	1,710	4,175	

Table 38: Power and Cost Requirements of Selexol System

Equipment costing procedures are available for verification, taken from generalized correlations based on Aspen simulations.⁹²



Figure 39: The effects of carbon dioxide removal on syngas

iv. Pressure Swing Adsorption

A Pressure Swing Adsorption (PSA) system is used to further purify the hydrogen stream after using a CO_2 removal system. Pressure swing adsorption adsorbs impurities such as CO_2 , N_2 , etc. onto a fixed bed of adsorbents at a high pressure⁹³. Pressure swing

adsorption can result with a hydrogen stream in excess of 99.999% purity. Below, the PSA system for the hydrogen process is detailed. The equipment needed for a pressure swing adsorption system include two compressors, a heat exchanger, two packed bed reactors, and seven valves.



Hydrogen Pu

Heat Exchanger 1

Figure 40: Pressure Swing Adsorption System

A hydrogen enriched stream enters the pressure swing adsorption at a flowrate of 3203 lbmol/hr. A compressor is used to increase the pressure from 230 psia to 460 psia or 30 bar, where the PSA will operate. From there, the stream is passe **Officients Decised** bed reactor where the contaminants including CH₄, CO, N₂, CO₂, and H₂O are adsorbed onto the bed. The fixed bed of adsorbents used for this process is Zeolite 5A. Zeolite is chosen because it is typically used in hydrogen purification processes with these particular contaminants⁹⁴. Also, the adsorbent bed type of zeolite 5A is most often used in PSA systems.⁹⁵

Eventually, the adsorbent bed becomes saturated and no longer removes the contaminants efficiently. At this time, the packed bed reactor is depressurized to remove the contaminants that are adsorbed on the bed in an offgas. The offgas is sent to the offgas drum.

Through a ratio analysis, our process only needs to operate one packed bed reactor to handle all of our hydrogen production. However, since the packed bed reactor must periodically be depressurized, a second packed bed reactor is required to operate the PSA continuously, i.e. allowing for the continuously of the continuously is used for this switch.

Compressor 1

After passing through the packed bed reactor, the hydrogen has a purity of 99.999%. Before being sold, it must be compressed to 2000 psia which causes a drastic increase in the temperature. The temperature must be brought down to ambient temperature; therefore a heat exchanger is needed. From the heat exchanger the hydrogen is sent to a series of 12 tanks where it can be stored up to 3 days before being shipped and sold. Below, figure 41 summarizes the effects of the PSA system on the hydrogen rich stream.



Figure 41: PSA system effect on the purification of hydrogen

I he equipment costs are tabulated below in table 4.
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Equipment	Quantity	Individual Cost	Total Cost
Compressor	1	362400	362400
Valve	7	1000	7000
Packed Bed			
Reactors	2	837000	1674000
Offgas Drum	1	9800	9800
Compressor	1	1403600	1403600
Heat Exchanger	1	1500	1500
		Total Equipment Cost	\$3 458 300 00

Table 42: Equipment Cost for PSA System

v. Hydrogen Processing Plant Capital and Operating Costs

Table 43 and 44 detail the operating cost and total capital investment, respectively, of the hydrogen processing plant including those of all four systems. The Microsoft Excel Worksheet file entitled "Waste to Hydrogen Processing Plant" details each piece of

equipment for the Steam Reformation and Water Gas Shift systems. Also, the chemical engineering software, PROII, was used to simulate equipment sizes and all utilities. Each PROII file and the Excel file can be found in the folder "Hydrogen Plant Simulations, Capital & Operating Costs". Utility analysis for CO₂ removal and PSA are found in Appendix asdfa and asdf, respectively.

			Rate or	Cost per	Calavilated
			Quantity	Rate of Quantity	Calculated
			per Year	Unit	Values
Raw Materials					n/a
Operating Labor				268.21	\$2,059,246
Operating Supervision		0.15	of Operating La	bor	\$308,887
Utilities					
Water	Disposal		326904	0.53	\$173,259
	Cooling		56.386156	10,000	\$563,862
Steam					
Coal			1190424.432	0.350000	\$416,649
Electricity			14.676024	394,461.57	\$5,789,127
Maintenance and Repa	irs	0.07	of FCI		\$7,779,584
Operating Supplies		0.15	of Maintenance	and Repairs	\$1,166,938
Laboratory Charges		0.15	of Operating La	bor	\$308,887
Royalties		0.04	of TPC without	Depreciation	\$1,541,062
Catalysts and Solvents					\$532,633
Total Variable Produc	tion Cost	5			\$20,640,133
Depreciation					
Taxes (Property)		0.02	of FCI		\$2,222,738
Financing (Interest)		0.05	of TCI		\$6,538,114
Insurance		0.01	of FCI		\$1,111,369
Rent		0.00	of FCI		\$0
Fixed Charges (Witho	ut Deprec	iation)			\$9,872,222
Plant Overhead Costs		0.10	of TPC without	Depreciation	\$3,852,655
Administrative Costs		0.15	of Operating La	bor	\$308,887
Distribution and Market	ing				
Costs		0.05	of TPC without	Depreciation	\$1,926,328
Research and Develop	ment	0.05	of TPC without	Depreciation	\$1,926,328
Total General Expenses				\$8,014,197	
Total Production Cost (Without Depreciation)/year				\$38,526,553	

Table 43: Hydrogen Processing Plant Operating Costs
Direct Costs		
I otal Equipment Costs		\$22,050,976
Steam Reformation	Compressor	\$5,727,400
	Steam Reformer	\$2,000,000
Water-Gas Shift	X 4	\$1,029,776
	Heat Exchanger 2	\$30,000
	Heat Exchanger	\$10,500
	Flash Drum	\$112,000
CO2 Removal	Stripper	1694000
	Turbine	\$312,000
	Slump Tank	\$88,000
	Compressor X 4	\$1,454,000
	Flash Drum X 3	\$63,000
	CO2 Storage Tank	\$0
	Pump	\$114,000
	Refrigerator	\$504,000
PSA stuff	PSA	\$2,201,000
Storage/Production	Compressor	\$3,000,000
	Heat Exchanger	\$1,500
	Off Gas Drum	\$9,800
	Storage Tanks X 12	\$3,700,000
Installation		\$10,363,959
Instrumentation/Controls		\$7,938,351
Piping		\$14,994,663
Electrical systems		\$2,425,607
Buildings		\$3,969,176
Yard Improvements		\$2,205,098
Service Facilities		\$15,435,683
	Total	\$79,383,512
Indirect Costs		
Engineering/Supervision		\$7,276,822
Construction expenses		\$9,040,900
Legal expenses		\$882,039
Contractor's fee		\$4,851,215
Contingency		\$9,702,429
	Total	\$31,753,405
Fixed Capital Investment		\$111,136,917
Working Capital		\$19,625,368
Total Capital Investment		\$130,762,286

 Table 44: Hydrogen Processing Plant Capital Costs

G. End Product Comparison

After examining several different end product possibilities from the purox plant, hydrogen was chosen based on its revenue per ton of MSW (see Figure 45). Hydrogen was estimated to sell for \$107 per ton of MSW processed. The synthetic fuel was approximately \$72 per ton of MSW, with an additional income from government tax credits. Assuming there exists a market to sell all or most of the hydrogen produced, hydrogen will be the most profitable end product. Synthetic fuel production is the next best option.



Price (\$/ton MSW)

Figure 45: Price Comparison with Price and Revenue for products considered

VI. Transportation

A. Transportation to PUROX Plant

The feasibility of purchasing municipal solid waste garbage/dump was evaluated. A garbage truck by Heil was found to have a 3 cubic yard rear end loader with an 18 cubic yard volume. It had a capacity for 1000 pounds per cubic yard or a total of 9 tons available capacity⁹⁶. The cost of these trucks in the New York City area has been on average \$135,000 a piece⁹⁷. These trucks get an average of 6 miles per gallon. Because of the capacity, numerous trucks would be needed to handle the MSW produced by New York City.

Because of the large number of trucks needed and high purchase cost, semi trucks with dump trailers were also evaluated. The cab for this truck has a cost of approximately \$95,000.00 and is a Sterling LT9500 model. The dump trailer has a capacity of approximately 15 tons and a cost of \$30,000⁹⁸.

The price per ton-mile to transport the municipal solid waste from a transport station to the plant site was 27.46 cents. This amount was then taken and multiplied by the number of miles to give the price of transportation per ton of Municipal Solid Waste⁹⁹.

B. Transport of Synthetic Fuel

Synthetic fuel can be transported in tankers with no insulation, unlike Hydrgoen. However, the trucks have to be prepared for possible electrical fire. Therefore, the tank and tank truck's must be coupled in order to ensure electrical conduction; the tank must have a grounding plug and electrical wiring encased in plastic tubes¹⁰⁰.

The tanker model found is a 2004 Beall 4 Compartment Semi tanker with a capacity of 9,500 gallons. The cost of this tanker is $70,000^{101}$. A cab and chassis is also needed for this tanker, and also has a cost of 95,000.

C. Transport of Hydrogen

Liquid hydrogen should be transported with special double-walled insulated tanks to prevent boil-off. Some of the tankers also use liquid nitrogen heat shields to cool the outer wall of the liquid hydrogen vessel in order to further minimize heat transfer. Tank trucks can carry approximately 260-4,300 kg (800-9,500 lb) of liquid hydrogen. Railcars have even greater capacities and can carry 2,300-9,100 kg (5,000-20,000 lb) of hydrogen. However, railcars are not being considered due to the lack of railways in the area¹⁰².

Another mode of transportation that can be considered is through insulated pipeline. In the case of transporting hydrogen, the liquid hydrogen would act as a refrigerant for the superconductor and would allow long distance transportation of electricity without high current losses of conventional power lines. The main problem with liquid hydrogen transport deals with specialized insulating requirements, losses from pumping, and recooling the liquid hydrogen along the way.

The major operating cost for hydrogen pipelines is compressor power and maintenance. Some hydrogen losses may occur in the piping network, but for natural gas piping systems, these losses are less than 1%. An estimate of the cost of piping hydrogen from North Africa to Central Europe (3,300 km or 2,050 miles) was 0.48 per lb, which includes compression costs. For the United States, another estimate put the cost at 0.14 per lb¹⁰³. It is important to consider the cost of piping, however, economically this is not the most desirable mode of delivery for small amounts of hydrogen over long distances.

The capital costs of liquid hydrogen transport will consist mainly of the insulated tank trailer, plus the cost of the cab for truck transport. The price to transport liquid hydrogen was estimated to be 0.95 per ton mile and this multiplied by the number of miles to get the amount of transportation per ton¹⁰⁴. The cost of the tanker for the transport of hydrogen is found to be 350,000. The cost of the truck and chassis is found to be 90,000.

VII. The Mathematical Model

A. Introduction

A mathematical model was developed to be used as an engineering tool that assists in the logistic planning of the New York City waste management system. The model incorporates cost minimization of the waste management process by evaluating all possibilities from an economic perspective. This includes consideration of all possible investments, waste management disposals and technologies, locations, amounts of waste processed, and ownership options. The deterministic model developed for this project was designed to incorporate the following objectives:

- Implement and control the most efficient and cost-effective flow of materials in relation to time
- Account for current MSW disposal contracts
- Encompass transport of MSW and final products
- Execute the right number, location, and capacity of plants
- Incorporate expansions in relation to time, money, and the amount of trash available



- Evaluate ownership options

Figure 46: Schematic of input/output of deterministic mathematic model.

To better quantify the importance of the mathematical model for a project of this complexity and magnitude, consider a few of the variables incorporated in the model. A few of the main variables for the system include the transfer stations to collect waste from, the amounts of trash to collect from each transfer station, the plant locations, and the consumer locations. A total of 13 possible transfer stations, 13 possible plant

locations, and 6 possible consumer locations were entered into the model. For this example, when one just considers the optimal processing route between transfer stations, plant locations, and consumer locations, there are over 2.8 X 10^{22} different possible processing routes! This does not even consider all other variables for the process. The model can be used to evaluate several different options or objectives, by maximizing, minimizing, or constraining variables such as capital investments, operating costs, revenue, waste amounts, expansions and savings. From these results, ownership and business strategies for the process can be evaluated and developed, and an optimal processing route to manage, dispose, and convert the municipal waste can be obtained. What could take years of investigating, researching, and calculating to reach the most efficient and economic route can be performed by a mathematical model in a time efficient manner.

B. Scale Up of Pilot Plant Data

In order to formulate the mathematical model, it is necessary to extrapolate data from the already developed pilot processing plants. The pilot plants were all quoted for a MSW processing capacity of 1500 TPD because they are based on the 1975 EPA reportⁿⁿⁿ that used the same capacity. This information may be scaled up in order to accurately represent the processing capacities that are required of each individual location. The following graphs may be considered a rough estimate for the entire New York MSW processing system.

The front end capital costs and operating costs are shown in Figure 47. The slope of the line was used to model the expansion capabilities and costs for each individual location. The model was programmed to account for the increasing capital investment and operating cost associated with expansion. Also, the model was programmed to take into account the fact that it needs one front end for every 4.66 purox reactors. Basically, if the model must take in more than 1500 TPD, it will build another purox reactor and thus it must build another front end plant. On a broader scale, Figure 47 gives a rough estimate of the amount it will cost with respect to front ends to process the entire city of New York's waste. However, the model will determine the final, accurate number for the total capital investment.



Figure 47: Front End Fixed Capital Investment and Operating Costs

The oxygen plant and wastewater treatment capital costs and operating costs for the entire processing system are shown in Figure 48 and Figure 49, respectively. Each location must build an oxygen plant and wastewater treatment plant, however, expansion is unnecessary due to the fact that each oxygen/wastewater plant can support up to eight purox reactors. Because expansion is unnecessary, the capital and operating costs are predetermined as reflected in Figure 48 and Figure 49.



Figure 48: Oxygen Plant Fixed Capital Investment and Operating Costs



Figure 49: Wastewater Treatment Plant Fixed Capital Investment and Total Production Costs

The purox reactor capital costs and operating costs are shown in Figure 50. Again, the slope of the line was used to model the expansion capabilities and costs for each individual location. The model was programmed to account for the increasing capital investment and operating cost associated with expansion. The purox reactors were most crucial in the operation of the model because they were used as base unit for each process. In other words, expansion for each system of the entire processing plant was input with respect to one purox reactor which, as described previously, process 350 TPD of MSW.



Figure 50: Purox Reactors Fixed Capital Investment and Total Production Costs

The hydrogen plant capital costs and operating costs are shown in Figure 51. Similar to the front end, the slope of the line was used to model the expansion capabilities and costs for each individual location. The model was programmed to account for the increasing capital investment and operating cost associated with expansion. Also, the model was programmed to take into account the fact that it must have one hydrogen plant for every 4 purox reactors. Basically, if the model must take in more than 1500 TPD, it will build another purox reactor. For each purox reactor, the hydrogen plant needs one water-gas shift reactor, but it must build a new CO₂ removal system and a new PSA system. On a broader scale, Figure 51 gives a rough estimate of the amount it will cost with respect to hydrogen plants to process the entire city of New York's waste. However, the model determines the exact number for the total capital investment.



Figure 51: Hydrogen Plant Fixed Capital Investment and Total Production Costs

Finally, Figure 52 provides a broad estimate for the entire processing plant if it were to process the entire city of New York's municipal solid waste. Figure 52 will support the final results of the model.



Figure 52: Entire Plant: Fixed Capital Investment and Total Production Costs

C. Analysis of Private Ownership with Strategic Planning

Note: Detailed results in regard to all capital investments, operating costs, taxes, number of puroxes per plant, amount of waste processed, revenues, profits, number of MSW trucks, number of H2 trucks, and cumulative cash position can be found in the Appendix and in the respected GAMS files.

The model was built to incorporate the private aspect of ownership for the disposal and processing of New York MSW. The private model incorporated Mixed Integer Programming (MIP) to achieve the optimum objective solution. The objective was not to process the maximum amount of MSW available, but to select the optimal amount of MSW to maximize the net present worth (NPW) over the lifetime of the 20 year project. Therefore, the model sifted through all possible processing routes between transfer stations, plant locations, consumer locations, and amounts of MSW and products, to arrive at the maximum NPW possible. As discussed previously, the end product chosen to be employed in the mathematical model was hydrogen.

Several disposal fees to the city of New York were evaluated. It was determined that it would be in the best interest of the company to offer a fee to the city that would ensure the option to process as much waste as the company desires, to maximize the objective function. The offer should be low enough to beat out competitors, but high enough to not sacrifice the goal objective of maximizing the net present worth. The current average price of disposal that the city of New York pays is \$63.30 per ton. A disposal fee of \$45/ton of MSW was chosen in order to be well below the average disposal fee. This price offers the freedom and reality to select and win bids on available contracts from the city, to process this optimal amount of MSW from the desired transfer stations.

Thirteen possible plant locations were input into the model as listed below:

- 1) Belmont, NY
- 2) Oxford, NJ
- 3) Taylor, PA
- 4) Islip, NY
- 5) Charlespoint, NY
- 6) Hempstead, NY
- 7) Babylon, NY
- 8) Huntington, NY
- 9) Dutchess County, NY
- 10) Adirondack, NY
- 11) Onondaga County, NY
- 12) Oswego County, NY
- 13) American Ref-Fuel Niagara

Of the above 13 possible plant locations, the model selected 6 plants to be built over the lifetime of the project. The locations chosen by the model are depicted in the figure below. All cities were in the New York City vicinity, with closeness to the respective consumer locations. Six consumer locations were entered into the model, all of which were used. The six consumers were refineries in New Jersey (no refineries are in the

state of New York), which were chosen since the main consumers of hydrogen, at this time, are refineries. These refineries are as follows:

- 1) Port Reading, NJ (Amerada Hess Corp)
- 2) Perth Amboy, NJ (Chevron USA Inc.)
- 3) Paulsboro, NJ (Citgo Asphalt Refining Co.)
- 4) Westville, NJ (Coastal Eagle Point Oil Col)
- 5) Linden, NJ
- 6) Paulsboro, NJ



Figure 53: Plant locations for private. The state depicted above is New York.



Figure 54: Waste processed by each plant in relation to time for private ownership

The figure above depicts the amount of waste processed by each plant in relation to time. The years included in the figure represent the years where major changes occurred in total processing capacity, either through additions of new plants or expansions to existing ones. From the figure it can be seen that two plants start-up in year 2007 and by 2013 all six plants are operating at full capacity. Figure 55 below compliments the above figure, illustrating the amount of total MSW processed by all plants in relation to time of the project. Also depicted in the figure is the amount of waste available from all transfer stations (including those not free from contracts). As seen below, the amount of MSW processed increases as the number of contracts expire, where the company is assumed to be able to pick up the contract from the city. By the year 2013, the company is handling 86% of the amount of MSW handled by the NY Department of Sanitation. Over the lifetime of the project, the company processes about 78% of the waste available. At this fee of \$45/ton, processing 78% of the waste available over the lifetime of the project saves the city an average of \$54.7 million (MM) per year. This calculation assumes that the remaining 22% of the MSW is disposed of at the average fee of \$63.30/ton.



Figure 55: Waste processed by all plants: time, expansions, and available waste

The model was also programmed to determine the number of MSW semi-trucks needed to transport waste from the transfer stations to the 6 plants (see equation below).

$$\#Trucks_{MSW} = \frac{(w)}{(\#trips)(capacity_{truck})}$$

where,

w = the amount of waste processed (tons/day)

#trips= the number of trips that can be made by a truck between a given transfer station and plant location in one day. This figures in the time to travel the given distance to and from, as well as loading and unloading times (assumed 1 hour ea.) capacity_{trucks}= capacity of MSW truck in tons

The first year of operation requires 35 MSW trucks. As more plants are added and expansions take place, more trucks are required. By 2007, 197 trucks are needed between all six plants to handle the MSW. The table below shows the distribution of the number of trucks needed at each of the plants, based on the equation above.

Location	No. MSW Trucks
Oxford,NJ	20
Hempstead,NY	33
Islip, NY	36
Babylon, NY	36
Huntington, NY	36
Charlespoint, NY	36

Table 56: MSW trucks from transfer stations to plant.

The total revenue from the disposal fee, metals recovered, and hydrogen end product is illustrated in Figure 57, showing it's relation to processing capacity with time. Also in

the figure, revenue is compared to the operating costs as plants are added and expanded onto existing plants. The operating costs includes all operating costs of the purox plant, the front end, the oxygen and water plant, the hydrogen plant, and all transportation costs. It can be seen that both the revenue and operating cost are in direct relation to the amount of waste processed (above). At the start-up in 2007, there is a revenue of \$175 MM and an operating cost of \$137 MM. As the total operating capacity increases to over 9,000 tons of wastes per day, the gap between the revenue generated and the operating costs increases. By 2027, an operating cost of about \$790 MM is needed, and a revenue of \$1.1 billion is generated.



Figure 57: Revenue and operating costs during project lifetime for private enterprise

The number of trucks needed to transport all the hydrogen was determined just as the MSW trucks were calculated, in relation to the amount of product to be transported between plant and consumer, the number of trips that can be made in one operating day per truck, and the capacity of each truck. As seen from the table below, at full capacity, 508 hydrogen trucks are needed.

Location	No. H2 Trucks
Oxford,NJ	45
Hempstead,NY	99
Islip, NY	90
Babylon, NY	90
Huntington, NY	94
Charlespoint, NY	90

Table 58: H₂ trucks

Over the 20 years of the lifetime of the project, the total capital investment of all plants and trucks totaled \$2.0 billion. The cumulative cash flow is illustrated in the figure below, and includes the capital investment for each year as plants are built and expanded on. The cash can be represented by the equation below.

Cumulative Cash (t) = Cumulative Cash (t-1) +Revenue(t-1) - Operating Costs(t-1) - Capital Investment (t) - Dividends(t-1)

Also included in the diagram below are the dividends, which represent 10% of each year's profits. According to the results from the model, the project breaks even between 2015-2016. By 2027, a total cumulative cash of \$4.1 billion is predicted by the model. A net present worth over the 20 years is \$198 million, with a favorable return on investment of 12.5%.



Figure 59: Cumulative Cash over project lifetime for private enterprise.

D. Analysis of Private Ownership with Strategic Planning

A model based on public ownership was also built for investigation. The major difference between the public model and the private model is that the public model has the added constraint that all the MSW should be processed. To account for the money needed for investment of the project, bonds were added to the model. The equations below are the basic equations added to the model to account for the issuing of bonds.

Cumulative Cash (t) = Cumulative Cash (t - 1) + Revenue(t - 1) - Operating Costs(t - 1)
- Capital Investment (t) -
$$\sum_{b=1}^{b=3}$$
 Bond Repayment10(t, b) + $\sum_{b=1}^{b=3}$ IssuedBond10(t,b)
- $\sum_{b=1}^{b=5}$ Bond Repayment5(t, b) + $\sum_{b=1}^{b=5}$ IssuedBond5(t,b)

Bond Repayment n (t, b) = Issued Bond n (t - 10) * $((1+0.04)^n)$ where n = 5 or 10 (depending on lifetime of bond—5 or 10 years)

As illustrated above, equations were added to give the model options to issue 10 year bonds or 5 year bonds, or a combination of the two types over the lifetime of the project. Additional limitations were added to the model on the number of bonds for each type that could be issued, where the maximum number of ten year bonds was set at 3 during the lifetime of the project, and the maximum number of five year bonds was set at 5 during the lifetime of the project. The interest rate for both bonds was assumed to be at 4%, a common interest rate for municipal bonds. The model's purpose was to choose the amount of bonds needed and for what years they should be issued, to prevent the cumulative cash from going negative during the lifetime of the project.

Unfortunately, when trying to force the model to take all the MSW available, the model faced difficulties in converging to a solution. Therefore, to understand and demonstrate the process of how the public ownership would be executed with the issuing of bonds, a model run was recorded and analyzed that did not process all the waste of New York. The analyzed results are summarized below.

Similarities between the two models were achieved in some results. The plant locations chosen were the same as those chosen for the private business. However, the amount of waste processed, as well as the amount processed at each plant and expansions, etc. were different. A disposal fee of \$35 per waste ton was chosen as the lowest fee that the city of New York could charge to its people without losing money. This fee would be charged by the city to its residents through taxes.



Figure 60: waste processed by all plants: time, expansions, and available waste

The figure above illustrates the amount of MSW processed by all plants during the project. Figure 61 below shows how much each individual plant processes in relation to time and shows what years plants were built or expanded. By the year 2015, the company is handling 84% of the amount of MSW handled by the NY Department of Sanitation (compared to 86% by the year 2013 for the private). When comparing the numbers from the public ownership to those found in the previous section over private ownership, it is easy to see that less waste is processed over the lifetime of the project. In comparison to the private ownership, the public option processes approximately 69% of the MSW available over the lifetime of the project (private processes over 79%). Obviously, from the public perspective, this is not acceptable as it is desirable to process all the waste available.



Figure 61: waste processed in relation to time for public ownership

The number of MSW semi-trucks was found using the same equations as those for the private. The first year of operation requires 24 trucks. After other plants are built and expansions take place, more trucks are required. By 2027, 195 trucks are needed between the six plants. Table 62, below shows the distribution of the number of MSW trucks needed at each plant. Similarly, the number of trucks needed to transport all the hydrogen was determined. As seen from Table 63, at full capacity, 492 hydrogen trucks are required.

Location	No. MSW Trucks
Oxford,NJ	36
Hempstead,NY	33
Islip, NY	36
Babylon, NY	18
Huntington, NY	36
Charlespoint, NY	36

Table 62: MSW trucks transfer station to plant

Location	No. H ₂ Trucks
Oxford,NJ	81
Hempstead,NY	99
Islip, NY	90
Babylon, NY	45
Huntington, NY	87
Charlespoint, NY	90

Table 63: H₂ trucks transfer station to customer

The total capital investment of all plants and trucks totaled \$2.5 billion over the 20 years of the lifetime of the project. The cumulative cash flow is illustrated in the figure below, and includes the capital investment for each year as plants are built and expanded on. As discussed earlier, complications arose when running the public model. Therefore, results from the model were analyzed in Excel to determine the time and amount of bond to be issued during the project. The cumulative cash used for this analysis can be represented by the equation below. Notice that it is the same equation as that given at the beginning of this section without the bond payments and bond revenue.

Cumulative Cash (t) = Cumulative Cash (t - 1) + Revenue(t - 1) - Operating Costs(t - 1) - Capital Investment (t)



Figure 64: Cumulative cash over project lifetime for public ownership - No Bonds

Figure 64 was therefore used to determine the years and amount of bonds needed. The blue lines above represent the amount of each bond needed throughout the project. As illustrated, three bonds are needed. All three bonds were 10 year bonds at 4% interest. The cumulative cash without bonds (using the above figure's data) was then used to determine the amount of bonds needed to keep the cumulative cash positive over the life of the project. Once the amounts for each bond were determined, a new cumulative cash can be generated to represent the cash with bonds as shown in Table 65. Notice from the table that Bond 1 is issued in 2007 for \$974 million, Bond 2 in 2011 for \$136 million, and finally Bond 3 in 2014 for \$30 million. The bonds are paid as listed in the table in

	Cumulative Cash w/out		New Cumulative Cash Including Bonds
year	Bonds(\$MMM)		(\$MMM)
2007	-\$0.23	Bond 1 issued	\$0.75
2008	-\$0.40	\$974,000,000.00	\$0.57
2009	-\$0.54		\$0.44
2010	-\$0.97		\$0.00
2011	-\$1.02	Bond 2 issued	\$0.09
2012	-\$1.09	\$136,000,000.00	\$0.02
2013	-\$1.11		\$0.00
2014	-\$1.02	Bond 3 issued	\$0.12
2015	-\$1.14	\$30,000,000.00	\$0.00
2016	-\$0.79		\$0.36
2017	-\$0.43	Pay Bond 1	-\$0.73
2018	-\$0.07	\$1,442,000,000	-\$0.37
2019	\$0.29		-\$0.01
2020	\$0.65		\$0.35
2021	\$1.02	Pay Bond 2	\$0.52
2022	\$1.39	\$201,000,000	\$0.89
2023	\$1.75		\$1.25
2024	\$2.12	Pay Bond 3	\$1.57
2025	\$2.50	\$44,500,000	\$1.95
2026	\$2.88		\$2.33
2027	\$3.27		\$2.72

years 2017, 2021, and 2024. The amount paid back on the each bond includes the interest generated over the 10 year payback period.

Table 65: Cumulative cash over project lifetime with bonds and repayment

The above table was then used to generate a new plot representing the new cumulative cash over the project, including the bonds and the repayment of bonds. This is represented in Figure 66 below. The cumulative cash does go negative again in year 2017. However, no additional bond is taken out to cover this since this it is due to paying off the first bond. By 2020, positive cash is again achieved, and by 2027 the cumulative cash reaches over \$2.72 billion. A total of \$1.14 billion is issued in bonds to cover a capital investment of \$2.48 billion (profit pays for remainder of capital investment not paid for by bonds). The bond repayment totals \$1.69 billion between the 3 bonds after a payback period of 10 years for each bond. All taxes were taken out of the model as the public enterprise is exempt.



Figure 66: Cumulative cash over project lifetime with bonds and repayment.

Sensitivity Analysis

Sensitivity analysis was performed on the model for the disposal fee charged to the city of New York, as well as the selling price of hydrogen to the consumers. The model therefore has the freedom to vary such things as the amount of waste processed and the plant locations to reach a new optimal solution to maximize the net present worth (for private ownership). The model's results to such changes are discussed below. Varying one variable at a time, the hydrogen selling price was set at \$2500/ton when varying the disposal fee, and the disposal fee was set at \$45/ton when varying the hydrogen selling price.

Varying Disposal Fee



Figure 67: Profit of private ownership with varying disposal fees

Varying the disposal fee was conducted to inform the private company of their limitations and expectations when compromising on a disposal fee with the city of New York. For the case of varying the disposal fee, the same plant locations were selected by the model. Instead of comparing the operating cost and revenue for each case, the profit was compared, which evaluates both at the same time. Figures 68 and Table 69 illustrate the profit as the disposal fee is varied, as well as the optimal amount of MSW that the model chose to process between all six plants. As expected, the profit is a direct correlation to the disposal fee charged to the city. Figure 68 and Table 69 below illustrate that the optimal amount of waste that would be processed for a disposal fee of \$50/ton is very similar to that of the fee of \$63.3/ton. Nearly the same amount of MSW is processed each year of the project for both cases. A disposal fee of \$50/ton processes 86% of the MSW over the lifetime of the project, compared to 87% using a disposal fee of \$63.30/ton.



Figure 68: Optimal amount of waste in relation to the varying disposal fee

Obviously, charging the city a disposal fee of \$63.3/ton serves the city of New York no advantage from what they are currently paying, and they are very unlikely to agree to such a contract. Therefore, it is in the best interest of the city to therefore lock on to a disposal fee of \$50/ton (compared to \$45/ton), to process more waste at a price \$13/ton lower than the current disposal fee of \$63.30/ton. It is also in the best interest of the company to offer the city this fee to achieve a profit and net present much higher than that for the \$45/ton. For both disposal fees at \$45/ton and \$50/ton, the return on investment is very similar.

Table 69: Effect of disposal fee on the optimal amount of waste to be disposed, total capital investment, return on investment, and net present worth.

Disposal Fee	Lifetime % of waste Disposed	тсі	ROI	NPW
(\$/ton)		(\$MM)		(\$MM)
\$45	77.52%	\$1,995	12.53%	\$198
\$50	86.30%	\$2,439	12.27%	\$314
\$63	87.91%	\$2,446	14.80%	\$574

Table 69: Summary of MSW Solid Waste

Varying Demand/Price of Hydrogen

To account for demand changes for hydrogen, the selling price of hydrogen was varied at three prices: \$3000/ton, \$2500/ton, and \$2000/ton. The \$3000/ton represents the selling price with a high demand market for hydrogen, while \$2500/ton and \$2000/ton represent the selling prices of hydrogen with a normal and low market for hydrogen.



Figure 70: Profit of private ownership varying H₂ selling prices/demands

The hydrogen demand does have a large impact on the economics and the amount of waste processed for the project. As with varying the disposal fees, no changes in plant locations were chosen by the model in the cases of \$3000/ton and \$2500/ton. However, for the case of \$2000/ton only one plant was chosen (Hempstead, NY). This is explained as at low market, the project is not feasible so the model chooses to minimize the amount of waste, to minimize the losses. As demonstrated in the table below, for the low demand market scenario, the process disposes only 18% of the MSW handled by the New York Department of Sanitation, to yield a poor return on investment of 7.41%, and a negative net present worth (over 20 years).

Selling Price H2	Lifetime % of waste Disposed	тсі	ROI	NPW
(\$/ton)		(\$MM)		(\$MM)
\$2,000.00	18.33%	\$438	7.41%	-\$50
\$2,500.00	77.52%	\$1,995	12.53%	\$198
\$3,000.00	73.90%	\$2,398	17.61%	\$1,022

Table 71: Effect of hydrogen demand on the optimal amount of waste to be disposed, total capital investment, return on investment, and net present worth

The project remains very feasible and profitable for cases when the hydrogen demand is normal or high. As illustrated by Figures A and B and Table A, the economics are very favorable and the amount of waste processed is very attractive to the city of New York. For the case of normal hydrogen demand, a total capital investment of \$2 billion dollars is required over the lifetime of the project, to yield a favorable return on investment of 12.53% and a net present worth of \$198 million. When the hydrogen is high, less MSW is processed over the lifetime of the project. However, in the last few years, over 90% of the MSW is disposed. For this scenario, a capital investment of \$2.4 billion is required, to yield a favorable return on investment of 17.61%, and a net present worth of \$1 billion dollars. The impact of the hydrogen demand and selling price therefore has a major impact, not affecting capital investment to a large degree, but improving greatly the return on investment and value of the project, as well as profits and cumulative cash flow.



Figure 71: Optimal waste in relation to the hydrogen selling price/demand.

D. Future Work

Presently, the model is set up to optimize the net present value of the in order to generate the largest profit. This follows the idea that the model is run to function as a private enterprise whose sole priority is to generate profit for its owners. The drawback to the city of New York is that a privately owned company will not process all of the city's solid waste. The mathematical model has been programmed to only accept trash from transfer stations and in quantities that output the maximum net present value and thus profitability. This leaves open the possibility that there exists large amounts of excess waste that the city must still pay to landfill.

However, it is not a foregone conclusion that the solution to the MSW problem is in the form of a private enterprise. If risk is too high or there exists no investors into a privately owned company, then the model possesses the capability to reverse course and determine the most cost efficient method to dispose of all the excess waste in the city. Essentially, it can minimize the financial loss to the city of New York by minimizing the waste disposal fees.

Or even perhaps, in light of aforementioned results, there exists the possibility of managing some combination where a fraction or all of the profitable aspects of the proposal is privately owned and the remainder is run by the city of New York. This could offset the large capital investment to the taxpayers of New York. For these reasons the potential market for this type of private enterprise in New York as well as possible forms of municipal investment and ownership must be further analyzed. There are several possible ramifications of private or public ownership such as tax deductions on the proposal, tax increases to the city, and the sale of bonds that all must be taken into consideration.

APPENDIX: SELEXOL

In the following calculations use the same units as the tabular values, with exceptions where noted with different units in parentheses. Costs are calculated in equations in thousands of dollars.

The first step in sizing the Selexol system is determining the solvent flow rate. The temperature, composition and flow rate of the shifted synthesis gas input to the system are the parameters used to specify the system. They are tabulated below, with the subscript '*i*' indicating the parameter value at inlet conditions. The solubility of carbon dioxide depends on the temperature and pressure of the solvent. Because of heat transfer from the gas to the solvent and because of the heat of solution, it is important to determine whether or not the temperature change in the stripper significantly affects the solubility and, consequently, the size and price of the system.

Fi	5206	lbmol/h
Pi	230	psia
Po	4	psia
Ti	77	°F
CO _i	74	lbmol/h
CO _{2, i}	1740	lbmol/h
H _{2, i}	3090	lbmol/h
CH _{4,i}	5	lbmol/h
H ₂ O _i	10	lbmol/h
N _{2,i}	37	lbmol/h
% CO ₂	99.99	mol%
removal		

Table 72: Selexol System Inlet Conditions

Approximately 1740 lbmol/h CO₂ must be removed from the vapor stream. Taking the solubility of Selexol at stripping conditions into account, this means that

$$\varpi = \frac{377 \cdot F_{CO_2}}{\chi_{30F}^{230\,psia}} = \frac{377 \frac{SCFCO_2}{lbmolCO_2} \cdot 1743 \frac{lbmolCO_2}{h}}{0.485 \frac{SCFCO_2}{galSel}} = 1,350,000 \frac{galSel}{h}$$

1.35 million gallons of Selexol per hour is required to take out 1743 lb moles per hour of CO_2 . This doesn't take into account the amount of carbon dioxide that carries over from the last flash.

At 4 psia, the amount of carbon dioxide carried over in the stream is

$$V_{CO_2,res} = \frac{\varpi \cdot \chi_{30F}^{4psia}}{377} = \frac{1,350,000 \frac{galSel}{h} \cdot 0.0668 \frac{SCFCO_2}{galSel}}{377 \frac{SCFCO_2}{lbmolCO_2}} = 240 \frac{lbmolCO_2}{h}$$

Reiterating until the solutions converge, the volumetric flow rate of Selexol that will remove 99.99% of the CO_2 in addition to holding the carbon dioxide carried over is 151,000 gallons per hour.

The operating pressure of the system determines the efficiency of the solvent in removing the carbon dioxide. The solvent flow rate must be multiplied according to a proportional factor

$$\gamma = 1.55 - 0.0002 \, p_{stripper} = 1.55 - 0.0002 * 230 = 1.504$$

where the stripper pressure is in absolute pounds per square inch. So the total amount of Selexol required is

$$\gamma \varpi = 1.504 \cdot 151,000 \frac{galSel}{h} = 227,000 \frac{galSel}{h}$$

On a twelve minute loop (recirculating the solvent five times per hour), replacing a solvent system every five years and annualizing the cost of the solvent brings the Selexol cost to \$180,000/y.

The glycol solvent is designed to enter the absorber at 30 °F. The total change in temperature of the solvent in the absorber is given by

$$\Delta T = \Delta T_{xfer} + \Delta T_{rxn}$$

where ΔT_{xfer} is the temperature change due to heat transfer between fluids and ΔT_{rxn} is due to heat of solution. The change in temperature of the glycol solvent due to heat transfer from the gas, taking into account the specific gravity of Selexol, is

$$\Delta T_{xfer} = \frac{Q}{\omega \cdot MW_s \cdot C_{p,s}} = \frac{1,140,000 \frac{Btu}{h}}{\frac{151,000 \frac{gal}{h}}{7.85 \frac{lb}{gal} 1.03} \cdot 280 \frac{lb}{lbmol} \cdot 0.49 \frac{Btu}{lb^{\circ}F}} = 0.44^{\circ} F$$

where Q is the heat lost by the syngas in the stripper if the synthetic gas of inlet composition – minus 99.99% of the CO_2 and simulated in Pro/II – drops from 77 to 30 °F, $C_{p,s}$ is the specific heat of the Selexol, MW_s is the molecule weight of the Selexol and ω is the Selexol flow rate (lb-mol/h), calculated above. This is, apparently, not enough to affect the solubility of the Selexol.

The change in solvent temperature due to the heat of solution is

$$\Delta T_{rxn} = \frac{F_{CO_2} \cdot \Delta H_{soln}^{CO_2} \cdot MW_{CO_2}}{\omega \cdot MW_{Sel} \cdot C_p^{Sel}} = \frac{1743 \frac{lbmol}{h} \cdot 160 \frac{Btu}{lb} \cdot 44 \frac{lb}{lbmol}}{\frac{151,000 \frac{gal}{h}}{7.85 \frac{lb}{gal} 1.03} \cdot 280 \frac{lb}{lbmol} \cdot 0.49 \frac{Btu}{lb^{\circ}F}} = 4.8^{\circ} F$$

 $\Delta H_{soln}^{CO_2}$ is the heat of solution of CO₂ in Selexol, MW_i is the compound molecular weight, C_p^{Sel} is the specific heat of Selexol and ΔH_{Soln}^{CO2} is the heat of solution. The sum of these temperature changes reflects the maximum amount of heat of solution, but if the solvent flow rate were to approach a change an order of magnitude smaller, this would cause problems. As the system exists now, however, there are no problems with the current amount of solvent, so it is appropriate at this point to price the equipment.

The stripper column cost is \$1,640,000.

$$C_{Stripper} = -1380 + 16.5 \cdot p_i + 0.128 \cdot \left[\frac{F_{Sel} + F_i}{2}\right] = -1380 + 16.5 \cdot 230 + 0.128 \cdot \left[\frac{4,160 + 4,960}{2}\right]$$

The stripper operates by pressure differentials and gravitational forces. It does not require any energy to operate that is unaccounted in the remainder and its operating cost is nothing. The process heat exchanger operates similarly, with no hot or cold utilities. The flashes do not require any heat duty. The slump tank is simply a region of low turbulence and pressure drop to enhance recovery of hydrogen. It does not require any utilities. The CO_2 storage tank exists at ambient conditions. To summarize, there are no operating costs for the: stripper, slump tank, heat exchanger, flash tanks or storage tank.

The energy regained by the turbine is sent to the compressor. The outlet pressure of the turbine is given by

$$p_{a1} = 0.0402 \cdot p_i^{1.415} = 0.0402 \cdot 230^{1.415} = 88 \, psia$$

This outlet pressure is necessary to determine the power recovered by the turbine

$$P_T = H_s \cdot \frac{G}{1714} \cdot \eta = (230 - 88) \cdot \frac{17700}{1714} \cdot 0.78 = 1140 hp = 360 \text{ kW}$$

The turbine capital cost is estimated to be 312,000 dollars.

$$C_T(M\$) = 219 + 0.0809 \cdot P_T + 0.0201 p_{out} = 219 + 0.0809 \cdot 1140 + 0.0201 \cdot 5.99 = 312$$

The recycle compressor takes the vapor from the slump tank back to the stripper. Its capital cost is correlated to the power of the turbine and is \$1,070,000.

$$C_{\text{Recycle}}(M\$) = 4.46 \cdot P_T^{0.778} = 4.46 \cdot 1140^{0.778} = 1,070$$

Taking efficiencies of both the compressor (82%) and turbine (78%) into account, there is a net 490 kW in electric utility for which to account. This utility is listed as the operating cost of the compressor. The capital costs of the compressor and turbine, however, are based on the individual power requirements of each – 850 kW for the compressor and 360 kW for the turbine. The CO₂ storage compressors 2, 3 and 4 bring the flashed vapor up from 14.7 and 4 psia, respectively, to 25 psia. The power required by each compressor indicated to be

$$P_{Ci} = 0.0188 \cdot Q \cdot p_{in} \cdot \left[\left(\frac{p_{out}}{p_{in}} \right)^{0.283} - 1 \right] = 0.0188 \cdot Q \cdot p_{in} \cdot \left[\left(\frac{p_{out}}{p_{in}} \right)^{0.283} - 1 \right]$$

where Q is the volumetric flowrate of gases coming into the pump (ft^3/min), which is the total standard flow rate multiplied by the ratio of the pressure drop to the outlet pressure and standard pressure over the compressor outlet pressure. The cost of the two compressors are calculated with

$$C = 7.03 P_{Ci}^{0.677}$$

Compressor 2, with an inlet pressure of 1 atm, a volumetric flow rate of 1,220 ft³/min and a power requirement of 54.6 hp, costs \$105,500. Compressor 3 with an inlet pressure of 4 psia, a volumetric flow rate of 4,480 ft³/min and a power requirement of 229 hp, costs \$278,200.

If a compressor were used to raise the pressure of carbon dioxide to the pressures at which it will be stored, a more expensive final compressor to handle all of the carbon dioxide leaving the gas and take it from 25 psia to 1000 psia. The power required for this process is calculated to be 334,000 hp, or 249 MW.

$$P_{C4} = 0.0188 \cdot 1743 \cdot 377 \cdot \frac{14.7}{25} \frac{25}{14.7} \cdot \left[\left(\frac{1000}{25} \right)^{0.283} - 1 \right] = 334,000 hp$$

A system of compressors to bring the entire amount of CO_2 to 1000 psia will cost 44.9 million dollars. This could be taken into account in the model, but is not feasible at this time, so the carbon dioxide is assumed to leave the system at 25 psia with no sale price or cost for the transportation system.

$$C_{C4}(M\$) = 13.1 \cdot P_{C4}^{0.64} = 13.1 \cdot 334,000^{0.64} = 44,900$$

The slump tank that allows the turbulent vapor-liquid stripping mixture to settle and separate will cost 87,700 dollars.

$$C_{Slump}(M\$) = 2.00 \cdot F_{Sel}^{0.745}(\frac{kg}{s}) = 2 \cdot 160^{0.745} = 87.7$$

The power of the pump required to get the solvent back up to 230 psia is

$$P_{Pump} = H_s \cdot \frac{G}{1714\eta} = 226 psig \cdot \frac{3290 \frac{gal}{\min}}{1714 \cdot 0.78} = 556 hp$$

The cost of the pump is correlated to the power the pump requires. The pump costs \$114,000.

 $C_{Pump} = 1.23 \cdot 556^{0.716} = 114$

The temperature change of the fluid due to this pressure increase is

$$dT = 0.0082 \cdot \Delta p - 0.3093 = 0.0082 \cdot 226 - 0.3093 = 1.54^{\circ} F$$

This temperature increase brings the total temperature drop required by the refrigeration unit to 2.7 °F which, taking the specific heat of the solvent and the flow rate of the solvent into account makes the load 2.34 MM Btu/h. The power of the refrigerator, using HFC-134a with an evaporation temperature of 20 °C, is

$$P_{\text{Re frigerator}} = \frac{Load(Btu / h)}{1000(9 + \frac{T_{evap}}{10})} = \frac{2,340,000Btu / h}{1000(9 + \frac{20}{10})} = 213hp$$

The price of the refrigerator is \$504,000.

$$C_{\text{Re frigerator}} = 16.5 \cdot F_{\text{Sel}}^{0.362} \cdot \left(\Delta T_{\text{xfer}} + \Delta T_{\text{refrigeration}}\right)^{0.406} = 16.5 \cdot 4,160^{0.362} \cdot 2.7^{0.406} = 504$$

The flash tank costs are depend on the solvent flow rate F (kg/s). Each costs \$21,100.

$$C_{Flash,i} = 0.983 \cdot F_{Sel}^{0.801} = 0.983 \cdot 46.2 \frac{kg}{s}^{0.801} = 21.1$$

The heat exchanger, which operates at 15.6 atm and exchanges 42.8 kW with a LMTD of 42.8°F, costs \$276,000.

$$\begin{split} C_{HX} &= 24.3 \cdot p^{0.280} \cdot \Delta T_{LM}^{-0.114} \cdot Q_{HX}^{0.388} = 24.3 \cdot 15.6^{0.280} \cdot 42.8^{-0.114} \cdot 217 Btu \, / \, h^{0.388} \\ &= 24.3 \cdot 2.16 \cdot 0.652 \cdot 8.06 = 276 \end{split}$$

- *a*. The total equipment power requirements and cost are tabulated below. The total equipment cost of the system is \$17,500,000. The power required by the system is 37.4 MW, or 3.02 E8 kWh/y.
- b. Appendix Model equations and variables
 - *i.* Algebraic Equations Used in the Model
 - ii. Major Constraints
- C. High Temperature incinerator case study

Energy Balance

Oxygen is separated from nitrogen in air via a cryogenic distillation facility and sent to both combustion chambers. The nitrogen is used as an inert blanket gas in other parts of

the plant. As it is fed to the chambers, the oxygen needs to be heated to vapor. One way to heat the oxygen and the rest of the material is to dissociate it with a plasma arc – large current dissociates oxygen gas into oxygen atoms – then send it to its respective chamber to provide heat for ignition. Temperatures in excess of 20,000 °C are achievable with these plasma torches, providing ample heat to destroy toxic organic materials, which will thermally dissociate into atoms around 2,000 °C.¹⁰⁵ Because of high current and resulting power demands, in addition to high melting point materials, plasma torches are expensive to own and operate, and so the processing of non-toxic materials does not warrant their use.¹⁰⁶ Concern for production of toxic organics coupled with the lack of heat energy available to achieve temperatures required for toxin destruction makes its utility justified in this application, however. A similar plant that used nitrogen as a heating medium in a non-transfer (heated gas, as opposed to direct electrical heating of a slag pool) plasma torch that processed 60 TPH of solid waste used plasma torches whose power consumption is about 23 MW.¹⁰⁷ To scale this process up to the required 1366 TPD fed to the reactor would require 23 MW, or 23000 kW * 365.25 d * 24 h = 200million kWh every year.

The amount of energy available in the feed, if it is extracted at 60% overall efficiency, is

$$.6 \cdot 10.9 \cdot 10^6 \frac{\text{Btu}}{\text{T}} \cdot 0.293 \frac{\text{MWh}}{10^6 \text{Btu}} \cdot 1500 \frac{\text{T}}{\text{day}} \cdot \frac{\text{day}}{24\text{h}} = 120M\text{W}$$

Realistic efficiencies approach 55%, leaving the revenue of 100 MW to recover the costs of capital, except that the operation of the oxygen separation facility – required to process a stoichiometric excess of 10 % - requires 1310 TPD O_2 .¹⁰⁸

$$\begin{split} m_{O_2} \approx 1015TPD \begin{bmatrix} (40wt\%_{water,out} - 25wt\%_{water,in})(\frac{Tmol_{H_2O}}{18TH_2O})(\frac{0.5Tmol_{O_2}}{Tmol_{H_2O}})(\frac{16TO_2}{Tmol_{O_2}})\\ + 24wt\%_{H_2,out}(\frac{TmolH_2}{2TH_2})(\frac{.5Tmol_{O_2}}{Tmol_{H_2}})(\frac{16TO_2}{Tmol_{O_2}})\\ + 40wt\%_{CO}(\frac{TmolCO}{44TCO})(\frac{Tmol_{O_2}}{Tmol_{CO_2}})(\frac{16TO_2}{Tmol_{O_2}}) \end{bmatrix} \cdot 1.1 = 1310TPD \end{split}$$

Models without the plasma torches could cut a significant portion of this operating cost, and it is suggested that a high-temperature alternative be investigated. However, a simple ignition source is not capable of preheating the cryogenic oxygen liquid to temperatures that will ensure thermal dissociation.

Appendix: Wastewater Treatment Plant

BOD Material Balance

$$F_{in} - F_{out} = F_{T}$$

$$50,000 \frac{mg}{dm^{3}} - 200 \frac{mg}{dm^{3}} = 49,800 \frac{mg}{dm^{3}}$$

$$49,800 \frac{mg}{dm^{3}} \times 70 \frac{gal}{\min} \times 1 \frac{dm^{3}}{L} \times 3.78 \frac{L}{gal} \times .001 \frac{g}{mg} = 13177.1 \frac{g}{\min} BOD$$

Water Material Balance

$$F_{in} = F_{out}$$

$$(1,000\frac{g}{L} - 50,000\frac{mg}{L} \times .001\frac{g}{mg}) \times 70\frac{gal}{\min} \times 3.78\frac{L}{gal} = 251,370\frac{g}{\min}H_2O$$

Oxygen Material Balance

$$F_{in} = F_{Out}$$

$$40\frac{tons}{d} \times 2200\frac{lbs}{tons} \times 453.6\frac{grams}{lb} \times .042\frac{d}{hr} \times .0167\frac{hr}{min} = 27,998\frac{g}{min}O_2$$

These values are needed in the later discussion of the total capital investment for the wastewater plant.

Appendix: Steam Reformation and Water Gas Shift

All equipment costs were found in "Plant Design and Economics for Chemical Engineers" Fifth Edition. Peters And Timmerhaus. McGraw-Hill Higher Education 2003.

Steam Reformation

A steam reformation algorithm was used from "Case Study 111" p133 of "Chemical Reactor Design for Process Plants," by Rase, Howard R. Copyright 1979, John Wiley & Sons. New York.

The Microsoft Excel Worksheet file entitled "Waste to Hydrogen Processing Plant" sets up and solves the algorithm.

Water-Gas Shift

Kinetic data for the water-gas shift was obtained from "Case Study 105" p44 of "Chemical Reactor Design for Process Plants," by Rase, Howard R. Copyright 1979, John Wiley & Sons. New York.

The Microsoft Excel Worksheet file entitled "Waste to Hydrogen Processing Plant" details all subsequent calculations that were obtained from the chemical engineering software, PROII.

Each PROII file and the Excel file can be found in the folder "Hydrogen Plant Simulations, Capital & Operating Costs".

Appendix: The Mathematical Model

For the data section, first the sets are defined. The New York City MSW mathematical model contains four sets. They are as follows:

i = *MSW* Transfer Stations in New York City (The *i*'s were represented by *i*1 through *i*13. See "Transfer Stations".)

j = *plant locations* (*The j's were represented by j1 through j13. See "Site Locations".*)

 $k = consumer \ locations$ (The k's varied according to what product was being considered in the model. See "Consumer Locations".)

 $t = time \ period \ in \ years$ (The time period for the project was 2005 through 2025.)

These sets are used as basic building blocks for the mathematical model. From these sets, other data can be inserted into the model in the form of tabulated data and defined parameters.

i. Tabulated Data

- 1) The amounts of waste available at each transfer station (according to contracts and capacities)
- 2) The distances from each transfer station to each possible plant location
- *3) The distances from each possible plant location to each possible consumer location.*

ii. Additional Parameters

- *1) Recovered materials as revenue (scrap metals)*
- 2) Transportation costs (MSW to processing plant, products to consumers, left over residue to disposal)
- 3) Land cost (\$/acre) for each plant location
- 4) Fixed costs for each plant area (front end, purox, production plant i.e. for hydrogen, methanol, synthetic fuel, etc.)*
- 5) Site improvement costs
- 6) Operating costs (labor, insurance, utilities, etc.)
- 7) Maximum capacities for each plant area
- 8) Taxes

*Marshall & Swift equipment indices were added to accurately represent equipment costs and capital investments. These were used in the equations section.

iii. Model Equations and Variables
The center of the mathematical model lies within this section made up of equations and variables. As discussed earlier, the main objective of the mathematical model is to maximize/minimize a particular entity or variable. The objective function for the New York City MSW model is to maximize the net present worth of the project, which is an equation dependent on other calculated equations, parameters, and variables. The variables are changed by the model to achieve the objective function. Below are the main algebraic equations, important constraints, and variables used in the model.

iv. Algebraic Equations used in model

1) <u>Net Present Worth, NPW (i = return on investment = 12%)</u> $NPW = \sum_{i=1}^{n} \frac{CF_k}{(1+i)^i} + \frac{CF_n + V_s + I_w}{(1+i)^n} - TCI$

 $V_s = salvage \ value$ $I_w = working \ capital$

2) Cash flow, CF (year t) $CF_t = P_t - T_t + D_t$

 D_t = depreciation year t

3) <u>Total Capital Investment, TCI (year t, location j)*</u>

$$TCI = K_{purox} + K_{front end} + K_{wo} + K_{product plant} + K_{land}$$

K =capital investment for purox, front end, water treatment plant, production plant, and land *TCI found for each year at each location

4) Gross profit, P (year t) $P_t = S_t - OC_t - D_t$ 5) <u>Taxes, T (year t)</u> $T_t = P_t$ *fixed income tax rate

6) Income from sales, S (year t, location j1-j13)

$$S_{t,j} = \sum_{j=1}^{j=13} \left(w_{t,j} * \left[dp + f_{je} p_{fe} + f_{al} p_{al} + f_{product} p_{product} \right] \right)$$

 $w_{t,j}$ = amount of waste sent from transfer station j to processing plant at year t (tons/yr)

dp = disposal surcharge(\$/ton) $f_{fe}, f_{al}, f_{product} = fraction per ton of waste recovered for ferrous scrap, aluminum scrap, and fraction of finished product produced per ton of waste$ p_{fe} , p_{al} , $p_{product}$ = selling price of recovered ferrous scrap, aluminum scrap, and finished product per ton waste

7) <u>Total Operating Cost, OC (year t)</u>

$$OC_t = OC_{purox} + OC_{front\ end} + OC_{product\ plant} + OC_{transportation} + OC_{dispose}$$

 OC_{purox} , $OC_{front end}$, $OC_{product plant}$ =operating costs of purox, front ends, and production plants

8) **Operating cost purox units, OC**_{purox} (year t)

$$OC_{purox} = \left(\left(\left(C_{elect} * P_{purox} \right) + \left(C_{fuel} \left(F_{steamheat} + F_{mobile} \right) \right) + \left(C_{water} * W \right) \right) * \sum_{j=1}^{j=13} w_{j,t} \right) \right) + \left(C_{mobile} * \sum_{j=1}^{j=13} w_{j,t} * \left(\frac{MS_{indexyeart}}{MS_{year75}} \right) \right) + (labor)$$

 $C_{elect} = cost of electricity (\$/kW)$ $P_{model} = Power consumption (kW/waste ton)$ $C_{fuel} = cost of fuel (\$/gal)$ F = fuel required for steam and mobile equipment (gal/waste ton) $C_{water} = cost of water (\$/gal)$ W = water required (gal/waste ton) $C_{mobile} = cost to operate mobile equipment (\$/waste ton)$

NOTE: Operating cost for front end very similar

9) **Operating cost of production plant**

 $OC_{product \ plant} = Variable \ oper. \ costs \ (\$/waste \ ton)^* \sum_{j=1}^{j=13} w_{j,t} + fixed \ oper. \ Costs$

10) Cost to dispose residue from production plant, OC_{dispose} (year t)

$$OC_{dispose} = C_d (\$/ton)) * \sum_{j=1}^{j=13} w_{j,t}$$

 C_d = surcharge to dispose waste per ton

11) <u>Transportation Cost, OC_{transportation} (year t)</u>

$$OC_{transportation} = C_{transport MSW} * \sum_{i=1}^{i=13} \sum_{j=1}^{j=13} w_{i,j} * d_{i,j}$$
$$+ C_{productTransport} * \sum_{j=1}^{j=13} \sum_{i=1}^{i=13} w_{i,j} * f_{product} * d_{j,k}$$

 $C_{transport MSW} = cost (\$/ton-mile)$ to transfer MSW

 $C_{productTransport} = cost$ (\$/ton-mile) to transfer finished product $d_{i,j}$ =distance from transfer station i to plant location j $d_{j,k}$ = distance from plant location j to consumer location k

ii. Major Constraints

- 1) Amount of waste taken from transfer station must be less than the amount available (for private).
- 2) Amount of waste taken from transfer station must be less than the number of puroxes times their capacities.
- 3) Maximum number of purox units added per location per year is 5 units
- *4) Expansion of front end, purox units, and production plants must be less than the maximum capacities for each plant unit*

iii. Variables

- 1) Amount of waste sent from transfer station to processing plant
- 2) Capital investment
- 3) Operating costs
- 4) Transportation cost
- 5) Number of puroxes
- *6) Net profit*

Cash flow

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