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Conversion of Trash to Gasoline

by

James Diebold
and
Garyl Smith

Advanced Technology Division
Ordnance Systems Department

APRIL 1978

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Naval Weapons Center
CHINA LAKE, CALIFORNIA 93555

Naval Weapons Center
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FOREWORD

The concept of converting trash to gasoline was conceived and developed at the Naval Weapons Center during a study sponsored by the Department of Defense's Advanced Research Projects Agency. The demonstration of this concept in bench-scale hardware has been funded by the Environmental Protection Agency (IERL, Cinn) under EPA-IAG[redacted] through D7-0781. Demonstration of the concept is continuing and is expected to result in some modifications to the process as described herein.

The information documented herein was presented at the "Energy for the Future" seminar cosponsored by the Federal Laboratories Consortium for Technology Transfer and the San Diego Technology Action Center on 24 February 1978.

This report has been reviewed for technical accuracy by David P. Wirtz.

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28 April 1978

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(U) *Conversion of Trash to Gasoline*, by James Diebold and Garyl Smith. China Lake, California, Naval Weapons Center, April 1978, 22 pp. (NWC TP 6022, publication UNCLASSIFIED.)

~~(U)~~ This report describes a thermochemical process through which organic waste materials found in municipal trash are converted into a high grade gasoline product. The process involves three major steps: ~~(1)~~ selective pyrolysis to form gases relatively rich in olefins such as ethylene, propylene, and butylene; ~~(2)~~ compression and purification of the pyrolysis gases to concentrate the olefins; and ~~(3)~~ polymerization of the olefins to form polymer gasoline. Pyrolysis experimentation has resulted in about half of the energy in the organic feed being found in the gaseous olefin pyrolysis product. Polymerization of pure ethylene has produced a synthetic crude oil product containing about 90% gasoline having an unleaded motor octane of 90. Preliminary economic evaluation has shown the process to be suitable for relatively small plant sizes. The projected yield of gasoline and oils is about 0.19 ℓ/kg (46 gal/ton). The process is currently in the bench-scale development stage.

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The authors wish to acknowledge the contribution to the effort made by Dr. Charles B. Benham (currently with the Solar Energy Research Institute), particularly in the polymerization demonstration with pure ethylene and the early development of the economics and their presentation format.

INTRODUCTION

Converting cellulosic organic waste material into high value liquids, such as gasoline, diesel fuel, fuel oils, and premium quality lubricating oils, is more than an alchemist's dream. It is a necessity in today's world of gigantic land-fill dumps and rapidly increasing petroleum costs. This project has demonstrated the marriage of two technologies previously considered to be unrelated—the pyrolysis of organic wastes and the polymerization of low molecular weight hydrocarbons to form polymer gasoline.

To obtain an overview of organic waste, the literature was consulted for the composition of municipal solid waste (MSW). Some of the reported values averaged out as follows: about 13% by weight of the trash was inorganics, which included iron, aluminum, and bottles; about 27% was moisture; and 60% was organic material.[1] With regard to the value of the reclaimed materials, the inorganics have a potential value of $4.85/tonne of raw trash, compared to the organic material which had a reclaimed value of somewhere between zero and nearly $30/tonne. The economics of trash utilization clearly lies in converting the large organic fraction to a valuable product.

To obtain an idea as to the relative value of commonly used fuels, consider that in 1975 if the cost to a commercial user of interruptible natural gas for boiler fuel was $1.00 per unit of energy, then noninterruptible natural gas for homes was worth $1.42 per unit of energy, the relative value of viscous No, 6 fuel oil for boiler fuel was $3.08, and the value of gasoline was $5.48 per unit of energy. Recent relative increases in the value of natural gas have reduced the ratio of gasoline to natural gas prices temporarily. However, the widely predicted continuation of today's petroleum shortage will cause the value of gasoline to escalate at a rate much greater than boiler fuels. This is because, although coal can again become the primary boiler fuel for the nation, coal fueled automobiles having today's performance are not being actively developed.

The conversion of solid waste to automotive fuel was consequently investigated because of the high potential value of the product in a Department of Defense Advanced Research Projects Agency sponsored program.

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[1] Blum, S. L. "Tapping Resources in Municipal Solid Waste," Science, 191 (Feb. 1976), pp 669 - 675.

The synthesis of methanol from organic wastes was evaluated in detail with mass and energy balances developed about two different flow diagrams. This approach would have pyrolyzed the organic fraction to form synthesis gases which would then have been compressed, purified, and catalytically reacted to form methanol. During the course of this study, several references were found which indicated the possibility of using pyrolysis to form a significant amount of low molecular weight hydrocarbons rather than just carbon oxides, methane, and hydrogen. These gaseous hydrocarbons of interest were predominantly ethylene, propylene, and other olefins.[2]

In the 1930's the oil industry began to extensively pyrolyze ("crack") crude oil to increase the yield of gasoline. By-products of that process included large amounts of ethylene, propylene, and butylene. Extensive research was performed on the utilization of these by-product gases which led to the commercialization of their conversion to gasoline by both catalytic[3] and non-catalytic [4] processes. The gaseous hydrocarbons were compressed, purified, and then heated such that they reacted to link up with themselves to form the larger gasoline molecules by polymerization. This process produced a liquid which was over 75 percent gasoline. The proposed process substitutes solid organic wastes for the crude oil feedstock, but otherwise parallels the petroleum process used to make polymer gasoline. Due to the high ethylene content of the olefins formed during pyrolysis of cellulosic materials, the thermal or non-catalytic polymerization was chosen.

The overall process for converting organic wastes to gasoline consists of: first, the pyrolysis of the wastes to gases containing large amounts of olefins, i.e. ethylene, propylene, etc.; second, the compression and purification of the olefins; and third, the polymerization of the smaller olefins to form larger gasoline molecules. Overall this amounts to a process which removes the oxygen from the cellulosic trash to produce a gasoline consisting of hydrocarbons. Most of the rejected oxygen is in the form of carbon dioxide.

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[2] Benham, C. B. and J. P. Diebold. "Conversion of Solid Waste to Fuels," Naval Weapons Center, China Lake, CA, August 1975. (NWC TP 5791, publication UNCLASSIFIED.)

[3] Ipatieff, V. N., et al. "Polymerization, a New Source of Gasoline," Ind. Eng. Chem., 27, No. 9, pp. 1077-1081. (1935)

[4] Frolich, K. and P. J. Wiezevich. "Cracking and Polymerization of Low Molecular Weight Hydrocarbons," Ind. Eng. Chem, 27, No. 9, pp. 1055-1062. (1935)

The critical technology that this program needed to demonstrate was in the area of pyrolysis of cellulosic organic waste materials into gases containing large amounts of olefins and their subsequent processability. If the selective pyrolysis could be verified, and demonstrated, then the remainder of the process to make gasoline was thought to be relatively straight forward due to industrial experience with similar processes. In effect, the process parallels that of an oil refinery with the most significant difference being the use of todayś cellulosic waste material rather than eons-old organic matter (crude oil) as a feedstock.

Preliminary economic analyses looked very promising even for fairly small cities, so the Environmental Protection Agency (IERL, Cinn.) was contacted to generate interest in this economical approach to trash disposal. As a result of their interest in this process, an interagency agreement (EPA-IAG-D5-0781) was written for NWC to pursue the technical and economic feasibility of converting organic wastes to gasoline by evaluation in a bench-scale unit (5 kg/hr). This EPA effort was begun in June 1975 and has been continuing.

EXPERIMENTAL

Figure 1 shows the currently evolved pyrolysis schematic. A finely ground organic fraction of municipal solid waste is continuously fed by a one-inch screw feeder. At the end of the screw feeder, the feed is fluidized and conveyed by a carrier gas stream (normally carbon dioxide) to the steam ejector. The mixture of solid waste, carrier gas, and steam then enter a long, red-hot 3/4 inch diameter tubular reactor. Reactor lengths of 2 and 6 meters resulted in pyrolysis times of about 50 to 150 milliseconds, respectively. The char is removed from the pyrolysis stream in a three inch diameter cyclone. The steam and tars are condensed out of the pyrolysis gas stream by the water quench system. The noncondensible gas stream volume is measured by an orifice flow meter and then either flared off or fed into a three stage compressor for storage at high pressure. This system pyrolyzes a nominal 5 kg of feed per hour.

The composition of the pyrolysis products has been found to be a function of the combination of temperature, residence time, and especially the dilution of the solid wastes in inert gases inside the reactor. As shown in Figure 2, the total hydrocarbon product (other than methane) can be varied by as much as 165% depending upon the

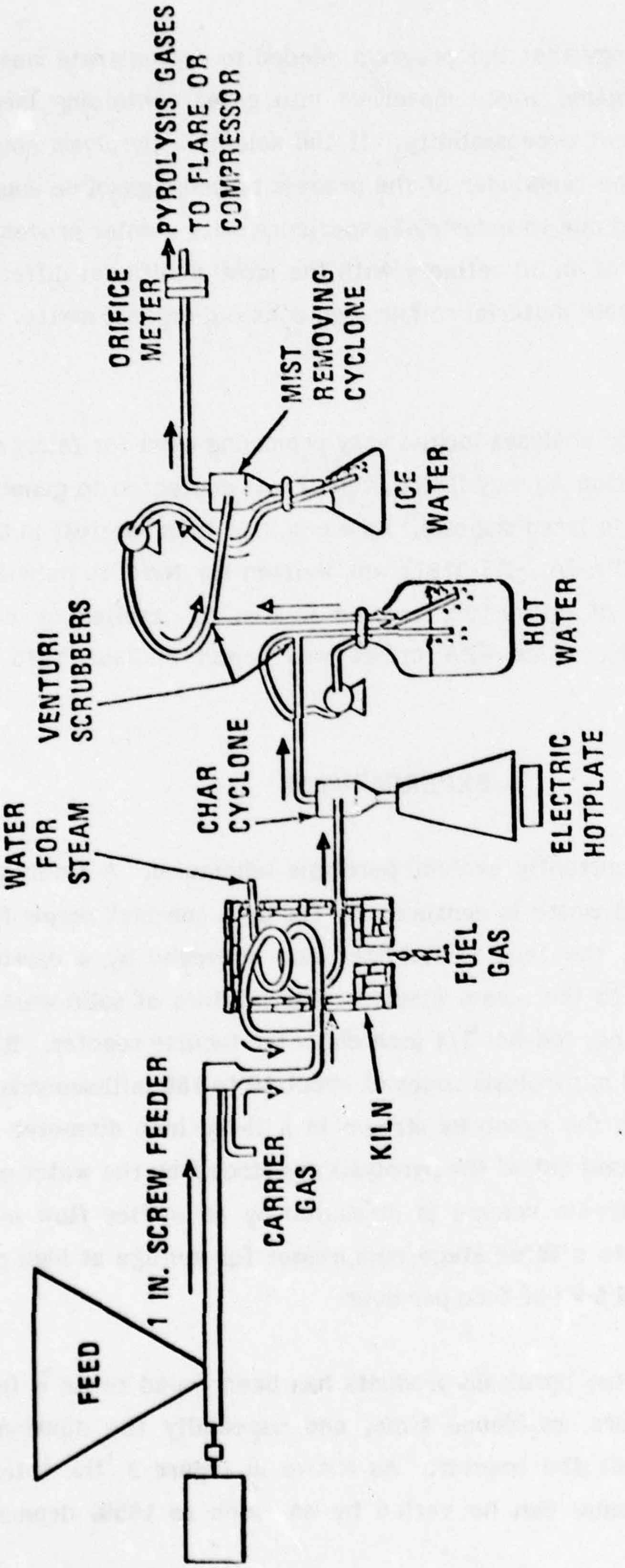

FIGURE 1. Pyrolysis Schematic (April 1977)

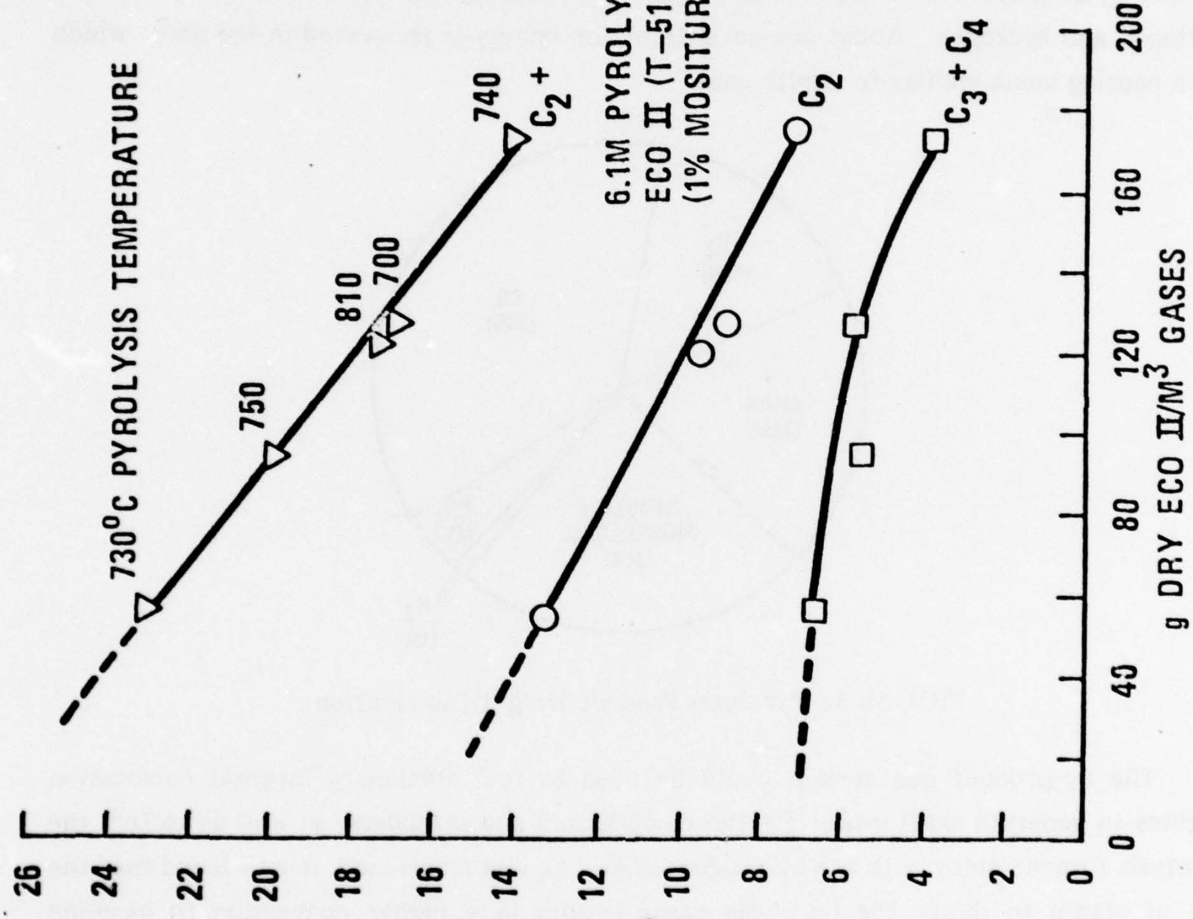

FIGURE 2. Products vs Concentration

relative dilution of the pyrolysis gases. Using the more favorable combination of these variables, a pyrolysis product distribution such as that represented in Figures 3 and 4 can be attained using organic material obtained from municipal solid wastes. This method of pyrolysis produces a product that is characterized by a relatively high weight fraction of gasoline precursors and carbon monoxide, relatively smaller amounts of char and carbon dioxide, and very little methane and hydrogen. Slightly more than half of the energy contained in the organic waste is recovered in the gasoline precursors. About one third of the energy is recovered in the "medium Btu" by-product gas stream of carbon monoxide, methane, and hydrogen. About one-seventh of the energy is recovered in the char, which has a heating value similar to lignite coal.

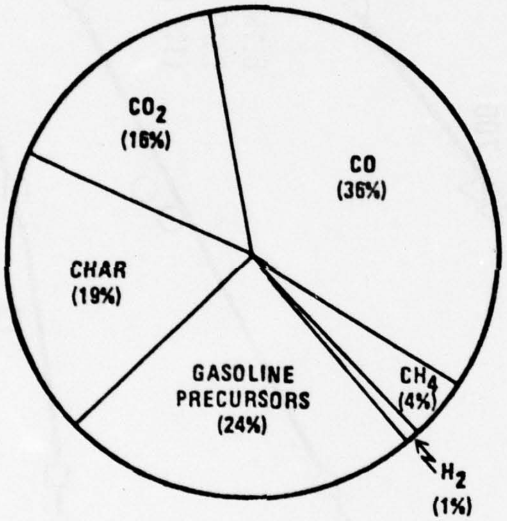

FIGURE 3. Pyrolysis Product Weight Distribution

The by-product gas stream could be used to fuel stationary internal combustion engines to generate shaft power for the compressors and shredders, as well as to fuel the pyrolysis furnace along with the by-product char. As was mentioned, it was found that the use of steam to dilute the pyrolysis gases results in a higher conversion to gasoline precursors by reducing secondary reactions. It now appears that the process will be optimized by making as much steam as possible by energy recovery from hot gas streams as well as by utilizing all of the char and the by-product fuel gases for process energy. This will result in only gasoline, "JP-5", and lubricating oils as the products from the organic fraction. These products will be readily marketable compared to char, pyrolytic oils, or "medium Btu" gas.

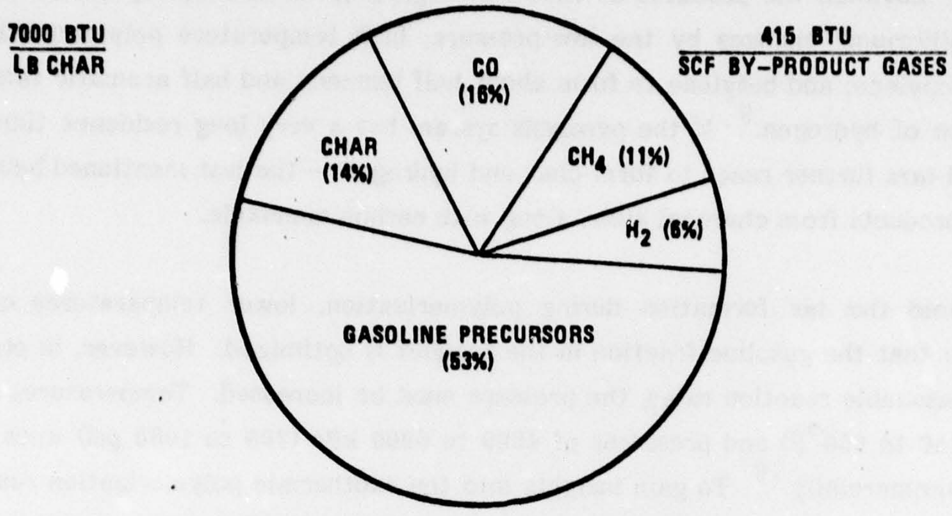

FIGURE 4. Pyrolysis Product Energy Distribution

It is interesting to note that the pyrolysis conditions found to be optimum for municipal solid wastes are coincidentally similar to those used by the petro-chemical industry to pyrolyze naphtha and crude oil to form ethylene: e.g. above 750°C (~1400°F), steam dilution, pyrolysis times of less than a second, and long tubular reactors having inside diameters of less than two inches.[5, 6, 7] It is even more interesting to note that if the carbon monoxide and carbon dioxide in the pyrolysis gas are ignored, and the remaining products are then normalized, that the relative weight percentages of the hydrocarbon products from naphtha,[6] solid wastes and oil shale[8] are very similar, as shown in Figure 6. It appears that the molecular fragments from the pyrolysis of both cellulosic and large hydrocarbon molecules are very similar and that they achieve a similar short-lived

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[5] Nelson, W. L., "Petroleum Refinery Engineering," McGraw-Hill, New York. 4th edition (1958) pp. 626-693.

[6] Prescott, J. H. "Pyrolysis Furnace Boosts Ethylene Yield by 10-20%," Chem. Eng., July 7, 1975, pp. 52-53.

[7] Zdonik, S. B., et al, "Function of Dilution Steam in Cracking," Oil Gas J, May 27, 1968, pp. 103-108.

[8] Sohns, H. W., et al. "Development and Operation of an Experimental Entrained-Solids Oil Shale Retort BUMINES RI5522. (1959)

"equilibrium" between the products as shown in Figure 5. If not rapidly quenched, this psuedo "equilibrium" changes by the low-pressure, high temperature polymerization of ethylene, propylene, and butylene to form about half benzene and half aromatic tars with the evolution of hydrogen.[9] If the pyrolysis system has a very long residence time, the benzene and tars further react to form char and hydrogen — the last mentioned being the traditional products from charcoal kilns, along with carbon monoxide.

To avoid the tar formation during polymerization, lower temperatures can be employed so that the gasoline fraction in the product is optimized. However, in order to maintain reasonable reaction rates, the pressure must be increased. Temperatures of 400 to 500°C (750 to 950°F) and pressures of 4800 to 6900 kPa (700 to 1000 psi) were often employed commercially.[10] To gain insights into the exothermic polymerization reaction, an experimental reactor was constructed as shown in Figure 6. This polymerization effort was conducted concurrently with the pyrolysis development, so no purified pyrolysis gases at elevated pressures were available for use. Since ethylene was the largest single constituent in the gasoline precursors found in the pyrolysis gases, bottled ethylene was purchased and used for this study. As shown in Figure 6, the ethylene was regulated into a one-half inch diameter stainless steel tube which had been coiled and placed in a constant temperature, fluidized sand bath. The sand bath served to initially heat the coiled reactor until the exothermic reaction was initiated, after which the bath served to remove the heat generated. The ethylene slowly moved down the length of the reactor for a few minutes while polymerizing. The polymerized gases were then cooled to condense out the gasoline and oils. Noncondensable gases were measured and then flared off. Conversions per pass were as high as 80 percent. The liquids formed had very low viscosities and when distilled produced about 90 percent gasoline. This distilled gasoline fraction was tested following the ASTM motor method and found to have a 90 octane rating in the unleaded condition (the research method would have resulted in a slightly higher octane number). The higher boiling liquids will yield a "JP-5" fraction and a lubricating oil fraction.

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[9] Cadman, W. H. "II Semi Industrial Production of Aromatic Hydrocarbons from Natural Gas in Persia," Ind. Eng. Chem, 26, No. 3, pp. 315-320.

[10] Wagner, C. R. "Production of Gasoline by Polymerization of Olefins," Ind. Eng. Chem., 27, No. 8, pp. 933-936. (1935)

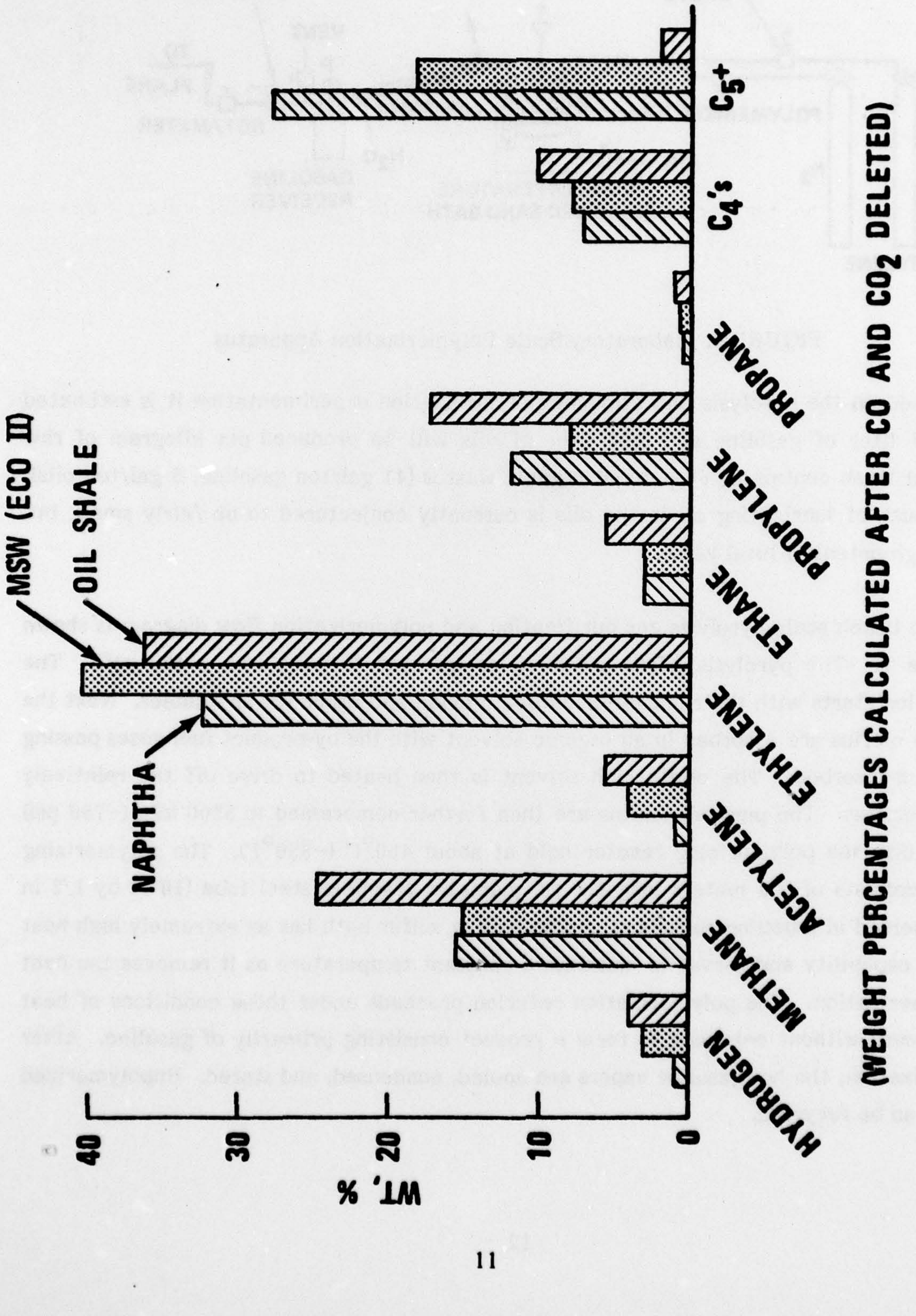

FIGURE 5. Pyrolysis Products Comparison Using Various Feedstocks

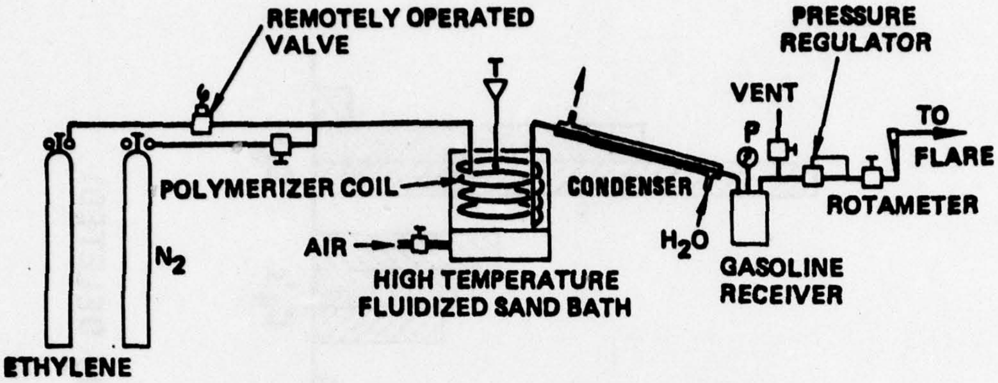

FIGURE 6. Laboratory Scale Polymerization Apparatus

Based on the pyrolysis and ethylene polymerization experimentation it is estimated that 0.17 liter of gasoline and 0.02 liter of oils will be produced per kilogram of raw municipal trash containing 60 percent organic wastes (41 gal/ton gasoline, 5 gal/ton oils). The amount of lubricating oil in the oils is currently conjectured to be fairly small, but with a high potential total value.

The bench scale pyrolysis gas purification and polymerization flow diagram is shown in Figure 7. The pyrolysis gases are first compressed to 3100 kPa (~450 psi). The purification starts with the removal of carbon dioxide and other water solubles. Next the desirable olefins are absorbed in an organic solvent with the by-product fuel gases passing through unabsorbed. The olefin rich solvent is then heated to drive off the relatively volatile olefins. The purified olefins are then further compressed to 5200 kPa (~750 psi) and fed into the polymerizing reactor held at about 450°C (~850°F). The polymerizing reactor consists of a 3 meters long 1.3 cm diameter stainless steel tube (10 ft by 1/2 in dia) immersed in a boiling sulfur bath. The boiling sulfur bath has an extremely high heat transfer capability and serves to maintain a constant temperature as it removes the heat of polymerization. The polymerization reaction proceeds under these conditions of heat and pressure without catalysts to form a product consisting primarily of gasoline. After polymerization, the hot gasoline vapors are cooled, condensed, and stored. Unpolymerized olefins can be recycled.

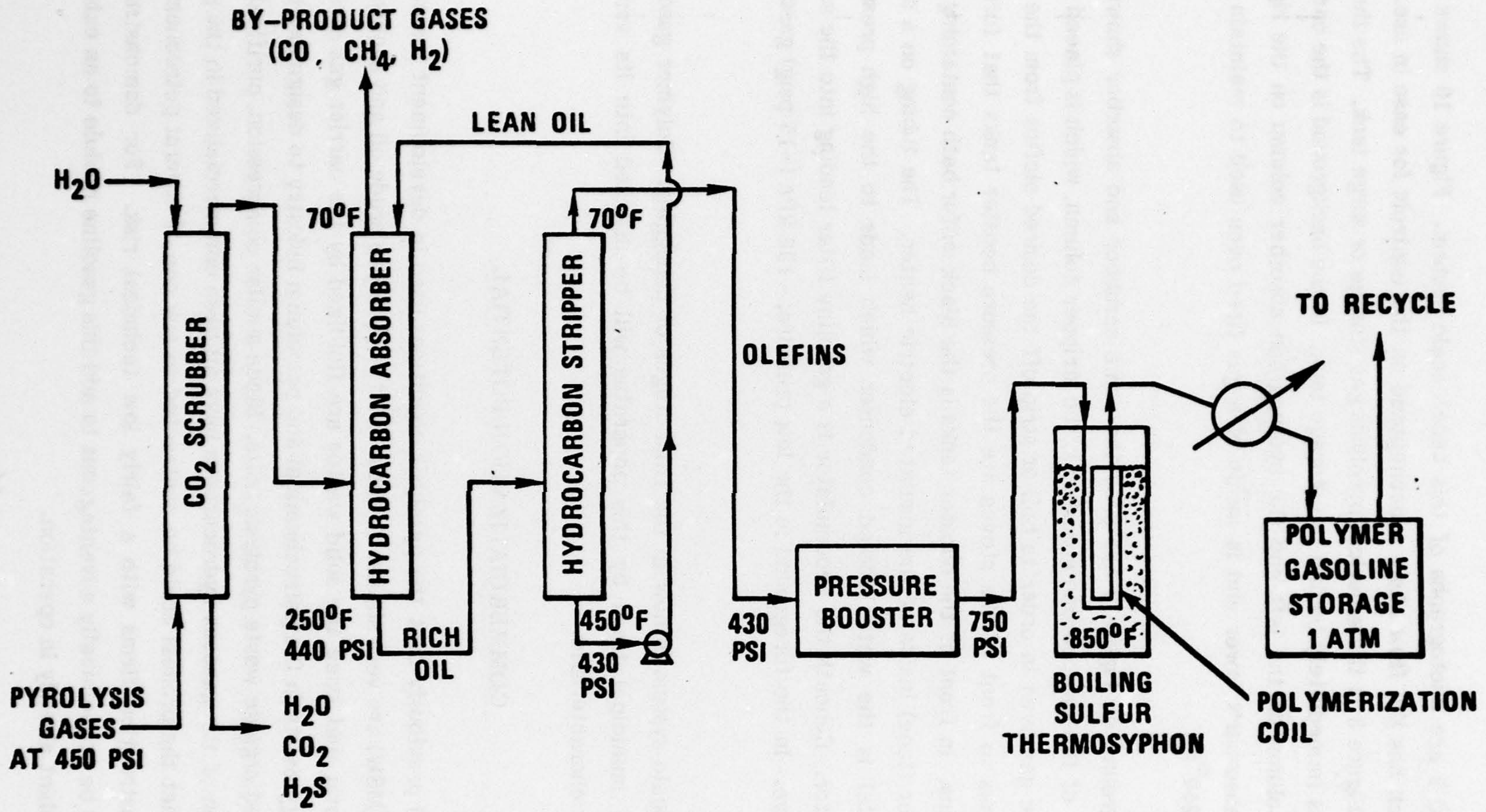

FIGURE 7. Pyrolysis Gas Purification and Polymerization to Gasoline

Figures 8 and 9 are photographs of this bench scale system. Figure 10 shows the control panel, which has the flow chart superimposed on the controls for ease in use. In the foreground of Figure 8 is the spherical pyrolysis gas storage or surge tank. The three-stage compressor is immediately behind the storage tank. In the background is the carbon dioxide scrubber column on the left and the hydrocarbon absorber column on the right. The hydrocarbon absorber's lower end is inside of a gas fired oven used to maintain the rich oil at 120°C (250°F).

In the background of Figure 9 are seen the same scrubber and absorber shown in Figure 8. In front of the hydrocarbon absorber is the stripper column, which is placed in a higher temperature gas oven in order to boil or strip off the desired olefins from the oil. The two short tanks in front of the stoves are the pressure booster tanks that further compress the olefins. In front of the booster tanks is the black sulfur bath containing the polymerizer reactor (tube) inside of the insulated electric heater. The tubing on a slant from the horizontal is the water cooled condenser which leads to the high pressure gasoline accumulator. Beneath the accumulator is a gasoline filter leading into the small solenoid dump valve. In the foreground is the low pressure, ~100 kPa (~15 psig) gasoline storage tank.

This bench scale system is now in the final stages of debugging. Polymer gasoline crude made from municipal trash by this apparatus will be distilled into its various fractions and fully characterized.

COMMERCIALIZATION POTENTIAL

It was noted previously that the pyrolysis conditions used in development for municipal solid waste (MSW) are very similar to those used to pyrolyze crude oil and naphtha to ethylene. It follows that once the solid wastes are fluidized by the carrier gas stream, that the technology exists in the petrochemical and petroleum industry to design and build commercially-sized organic waste pyrolysis units. Since similar compression, purification, and polymerization of the gaseous hydrocarbons have all been commercialized in the past, it would appear that the process could be contracted to any one of several petrochemical or petroleum construction firms with a fairly low technical risk. For demonstration purposes, it would be economically advantageous to add this gasoline module to an existing trash processing plant already in operation.

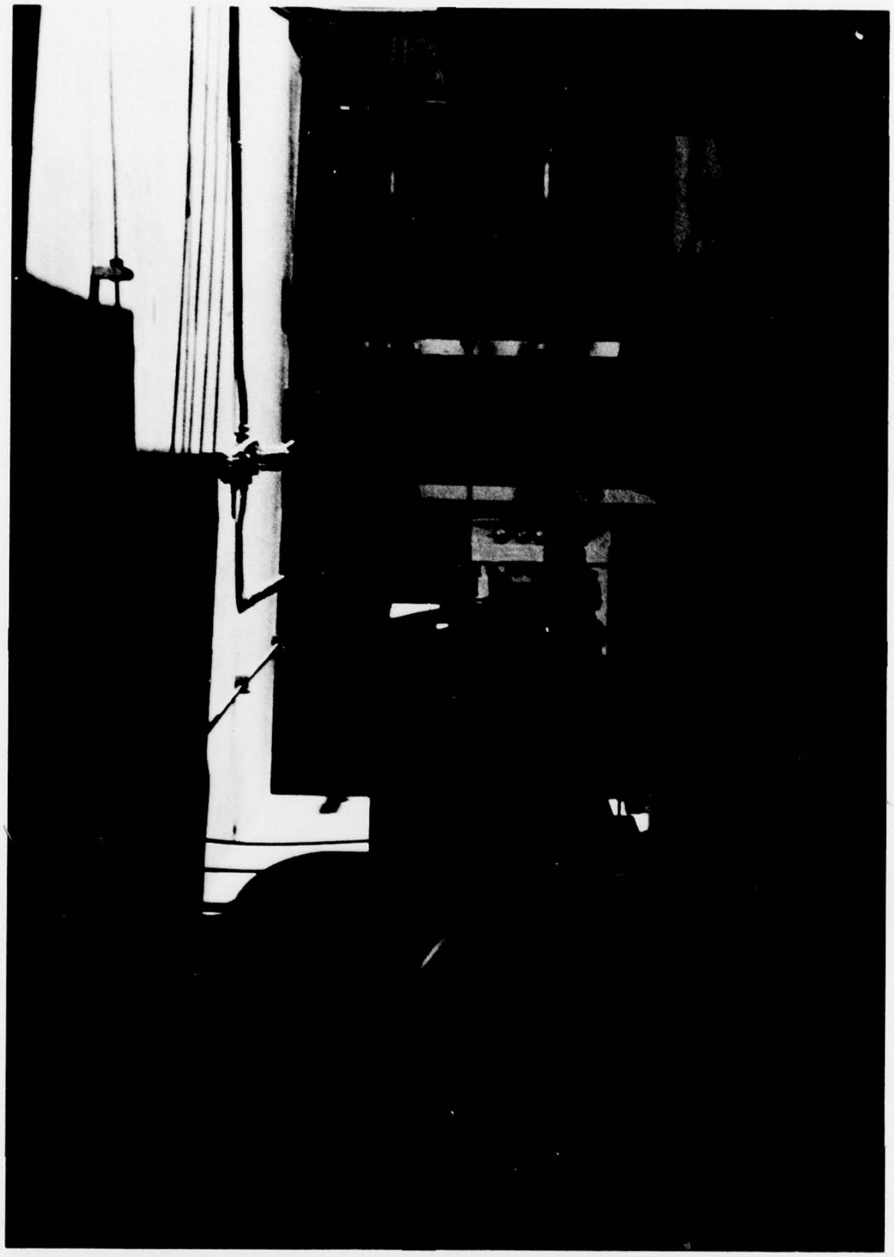

FIGURE 8. Pyrolysis Gas Compression, Storage, and Purification Equipment.

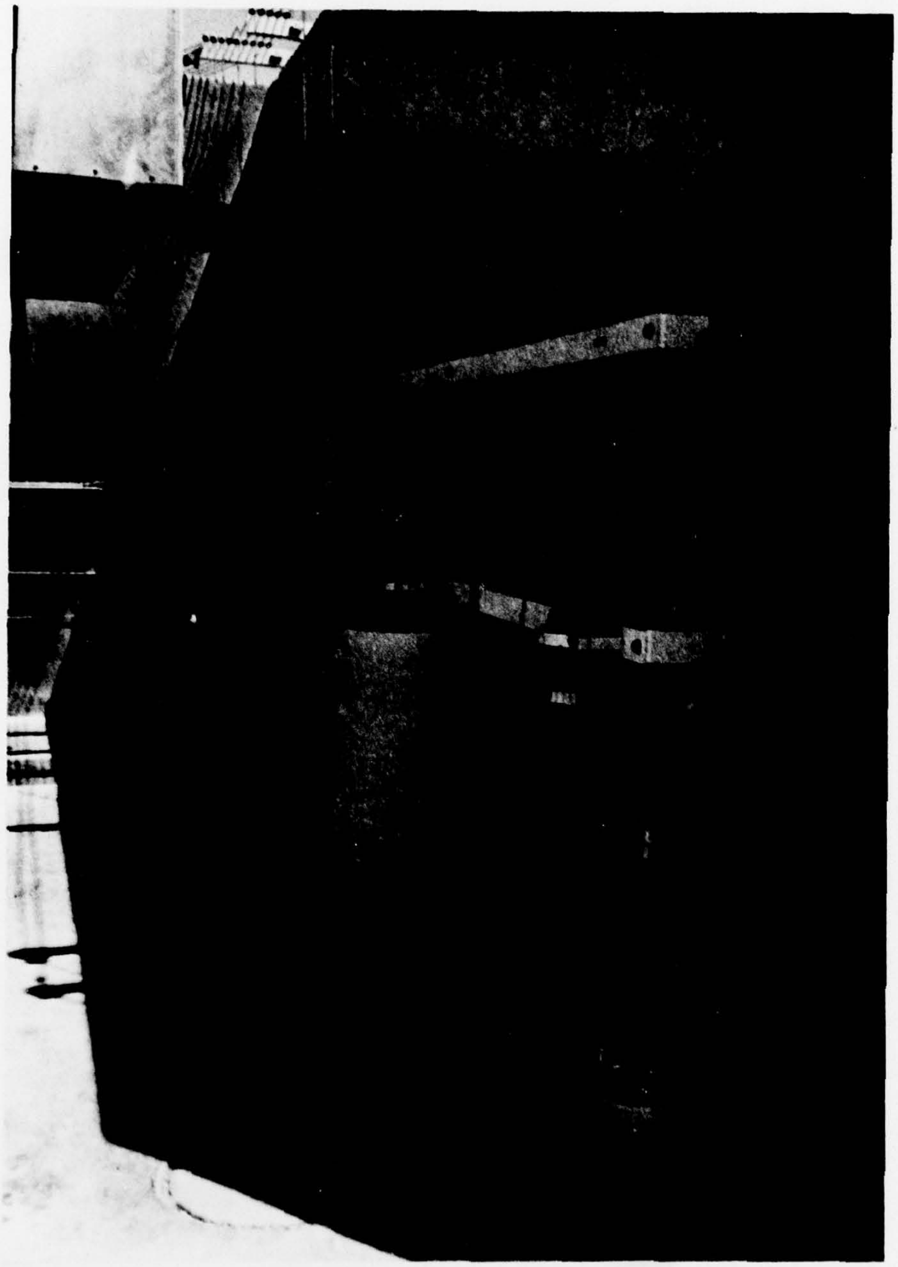

FIGURE 9. Pyrolysis Gas Purification, Pressure Boosting, Polymerization, and Gasoline Storage Equipment.

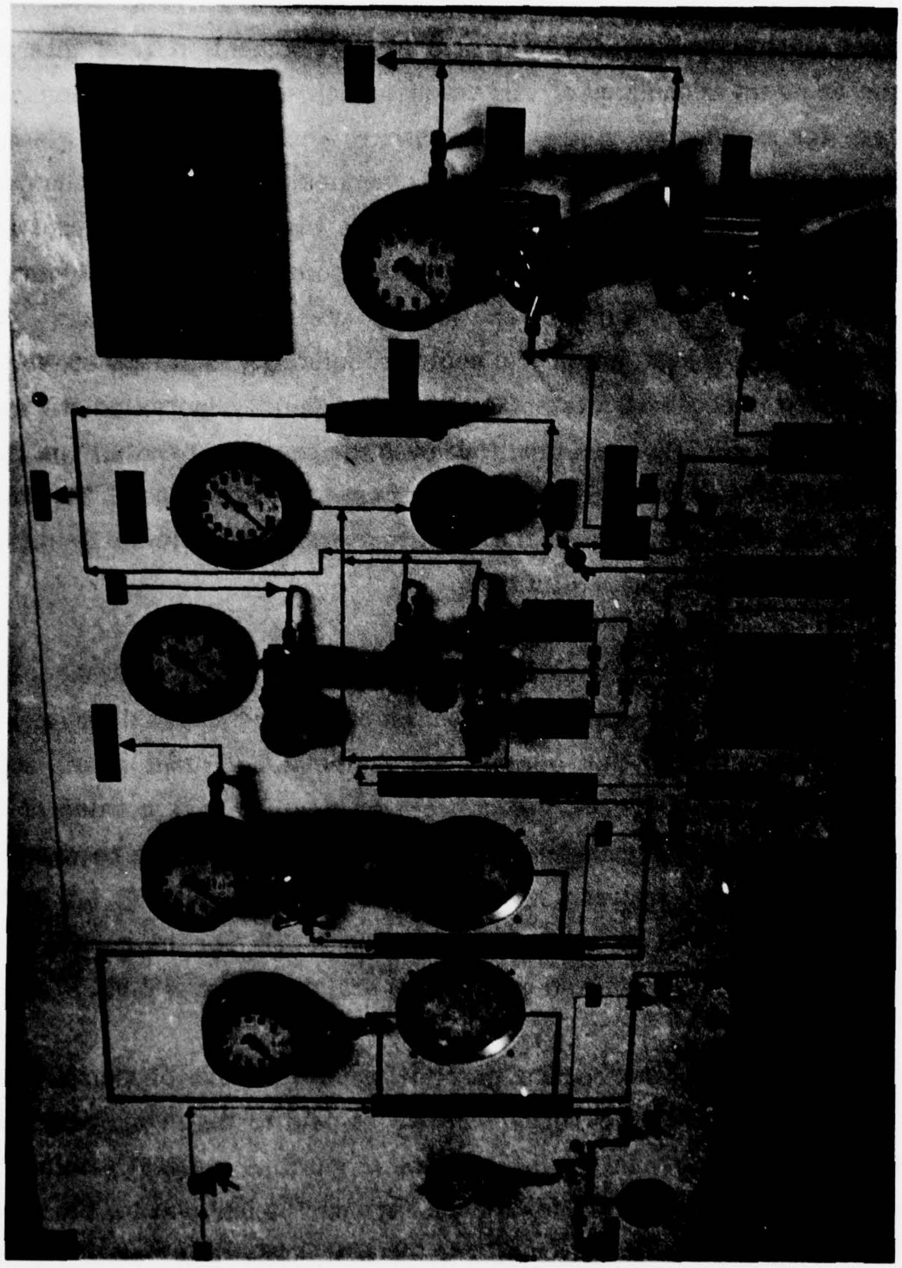

FIGURE 10. Control Panel for Pyrolysis Gas Conversion to Gasoline.

ECONOMIC EVALUATION

Although the trash-to-gasoline process is still in development, it is of interest to briefly examine the apparent economics of this process when scaled to an economic size. The overall process for converting as-received trash to reclaimed metals, glass, and gasoline was economically evaluated using classical chemical engineering techniques.[11] This method of preliminary cost estimation involved the identification and costing of major equipment items such as compressors, heat exchangers, distillation columns, etc. The equipment costs were then multiplied by the sums of several Chilton factors[12] which took into account the costs of piping, automatic controls, buildings, facilities, engineering, etc. Taking into account the overall cost of building the facility increased the capital cost by an overall factor of slightly more than four over the equipment costs. The capital costs were used along with the size of the plant to estimate operating costs. The method of financing plays a very important role in the operating costs and is radically different for municipalities and private enterprise situations.

Municipal financing was assumed to be amortized over 25 years at 6.5 percent annual interest. The trash feed was assumed to contain 60.2 percent organic material, 27 percent moisture, 5.5 percent iron, 0.5 percent aluminum, 6.6 percent glass, and 0.2 percent other metals. The reclaimed inorganics were assumed to have a value of $4.85 per tonne of raw trash. It was assumed that 0.19 liter of liquids would be recovered per kg of trash and that the per capita trash production was 2.5 kg per day (5 1/2 lbs/day). Only one plant size was costed out in detail (72 1/2 tonnes/day), and the capital cost of other plant sizes were extrapolated using an exponential scaling factor of 0.65.

Figure 11 shows the cost to produce gasoline as a function of dump fee and population (plant size) where positive dump fees are those paid to the municipally funded plant. Due to the gross uncertainty in the future price of gasoline, several gasoline price parameter lines are shown. For example, for a plant serving 100,000 people, the gasoline

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[11] Peters, M. S. and K. D. Timmerhaus. "Plant Design and Economics for Chemical Engineers," 2nd Ed., McGraw-Hill, N. Y. (1968)

[12] Holland, F. A., et al. "How to Estimate Capital Costs," Chem. Eng., April 1, 1974, pp. 71-76.

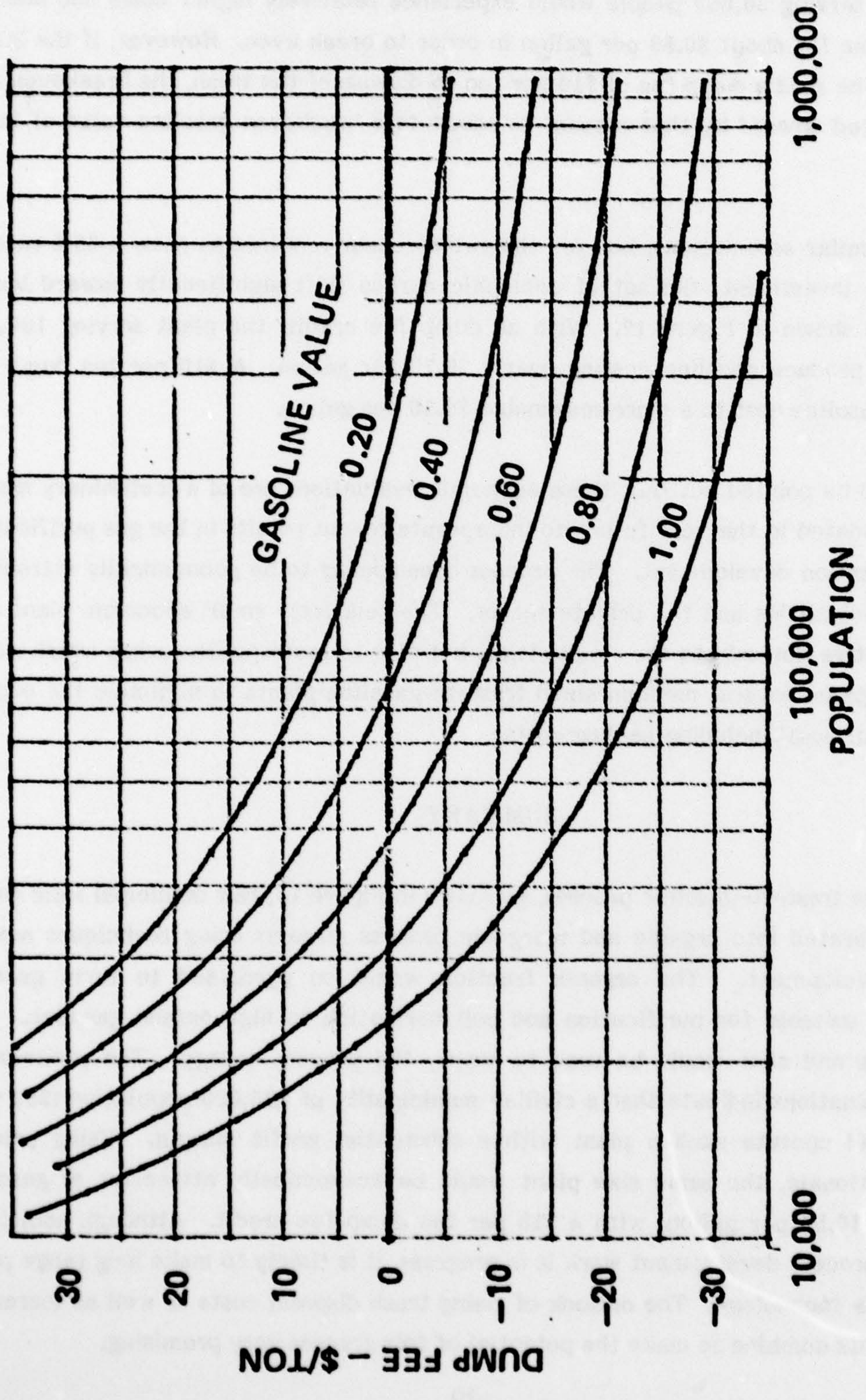

FIGURE 11. Necessary Dump Fee for Economic Operation of Solid Waste Facility Assuming Municipal Operation at 6.5% Amortization.

product would have to wholesale for at least $0.35 per gallon with a zero dump fee. A smaller plant serving 50,000 people would experience relatively higher costs and need to sell the gasoline for about $0.58 per gallon in order to break even. However, if the latter plant were to be paid a dump fee of $10 per ton to dispose of the trash, the breakeven line would be shifted upward by that amount to result in a breakeven gasoline value of $0.26 per gallon.

Using similar assumptions, but for the entrepreneur required to show a 20% rate of return on the investment, the set of economic curves shift significantly toward larger plant sizes as shown in Figure 12. With no dump fee credit, the plant serving 100,000 people would produce gasoline costing nearly $0.75 per gallon. A $10 per ton dump fee reduces the gasoline cost to a more reasonable $0.50 per gallon.

It should be pointed out that these economic evaluations are of a preliminary nature and will be updated in the near future to incorporate recent results in the gas purification and polymerization development. The process does appear to be economically attractive for both municipalities and the private sector. The relatively small economic plant size will be attractive not only to the small cities, but also to metropolitan areas which would strategically place several medium sized trash-to-gasoline plants to minimize the overall cost of trash disposal including hauling costs.

SUMMARY

With this trash-to-gasoline process, as shown in Figure 13, raw municipal solid waste would be separated into organic and inorganic process streams using techniques now in full-scale development. The organic fraction would be pyrolyzed to form gaseous hydrocarbons suitable for purification and polymerization to high octane gasoline. By-product gases and char would be used to supply the process energy. The preliminary economic evaluations indicate that a civilian municipality of 100,000 population (250 tons per day) could operate such a plant with a substantial profit margin. Using private enterprise rationale, the same size plant would be economically attractive at gasoline prices above $0.50 per gallon, with a $10 per ton dump-fee credit. Although additional bench-scale process development work is in progress, it is timely to make long range plans to exploit this technology. The outlook of rising trash disposal costs as well as increased petroleum costs combine to make the potential of this process very promising.

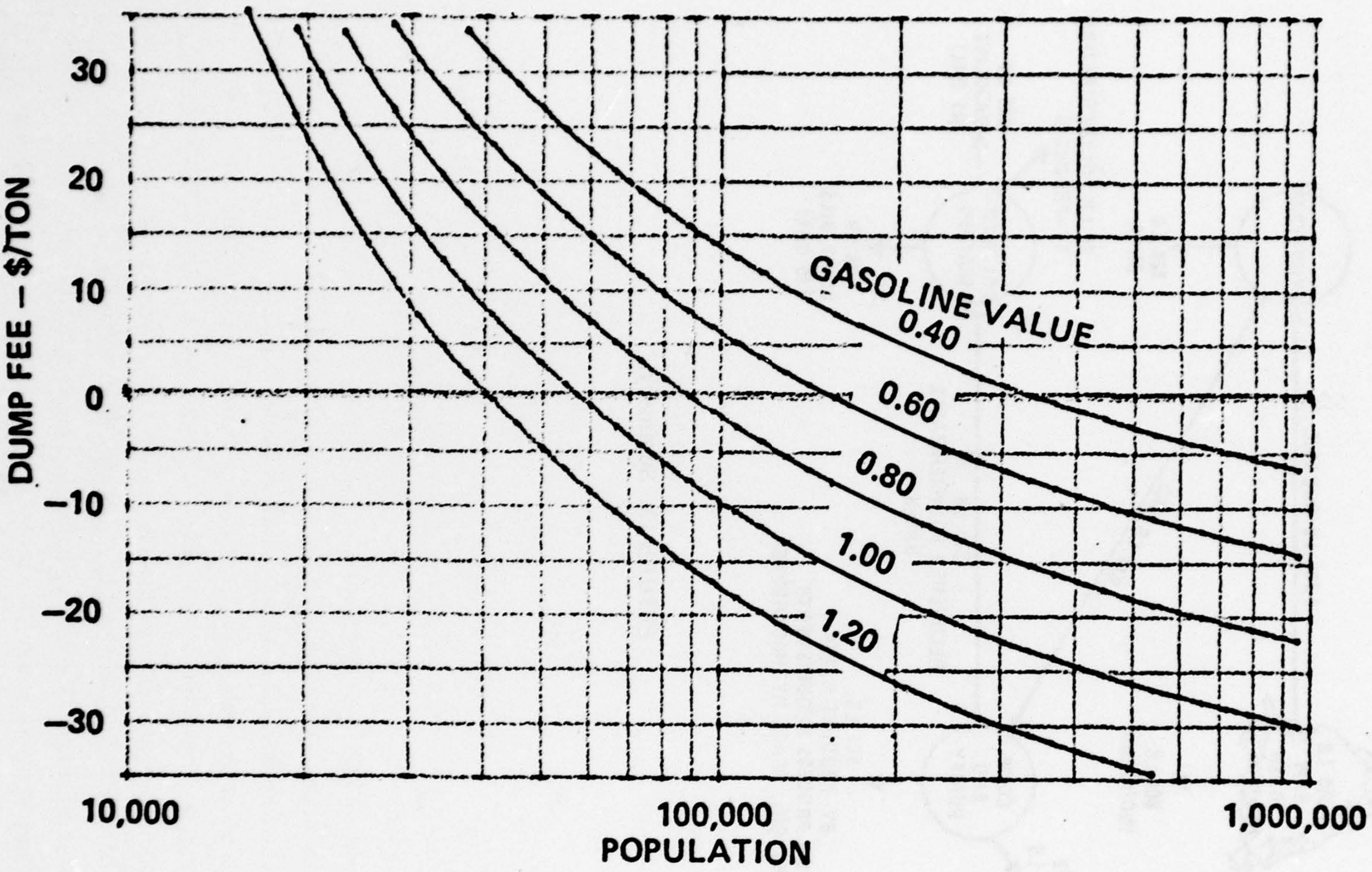

FIGURE 12. Necessary Dump Fee for Economic Operation of MSW Plant Assuming Commercial Investment at 20% Rate of Return.

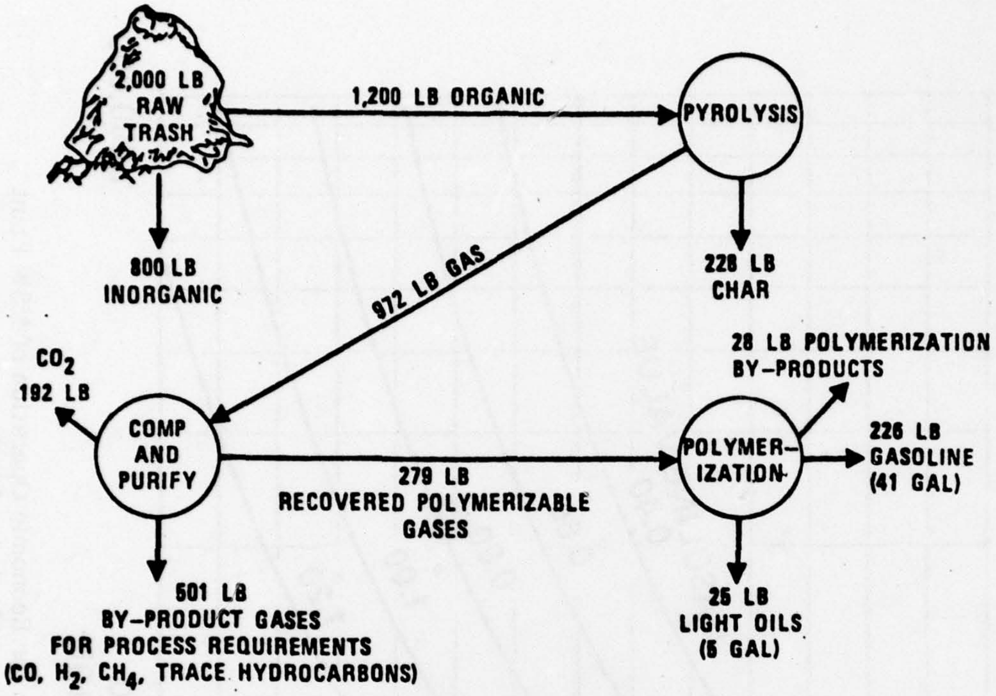

FIGURE 13. Summary.