



## Project Summary

# Conversion of Organic Wastes to Unleaded, High-Octane Gasoline

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The possibility of converting organic waste material into high-value liquids, such as gasoline, diesel fuel, fuel oils, and premium-quality lubricating oils, was the impetus for this project which demonstrated the compatibility of two technologies previously considered to be unrelated--the pyrolysis of organic wastes and the low-pressure polymerization of low-molecular-weight hydrocarbons to form polymer gasoline.

Specifically, this project developed a multistep chemical process to convert solid organic materials into a liquid hydrocarbon product--high-octane gasoline. Through selective pyrolysis, organic wastes were converted into gases rich in reactive hydrocarbons. The pyrolysis gases were compressed and purified, resulting in three gaseous streams: carbon dioxide; byproduct fuel gases (hydrogen, methane, and carbon monoxide); and reactive hydrocarbons. The latter stream was sent to the polymerization reactor where high-octane gasoline was formed. A bench-scale system demonstrated the selective pyrolysis, the gas purification, and the polymerization aspects of the process. The report projects that about 0.28 liters (0.074 gallons) per kilogram of organic material can be produced from municipal trash with this process.

*This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

In 1979, an economical process to convert organic waste material into gasoline was identified at the Naval Weapons Center (NWC), where a project was conducted to evaluate the feasibility of energy independence for remote military installations in the course of that project, utilization of the energy content of trash was evaluated. Two approaches were considered.

1. pyrolysis of wastes to form reactive hydrocarbons (e.g., ethylene), and their subsequent purification and conversion to a synthetic hydrocarbon gasoline which could then be substituted for gasoline derived from petroleum sources with no changes in storage facilities, engine design, toxicity, or performance; and
2. pyrolysis of wastes to form synthetic gas composed of carbon monoxide and hydrogen with subsequent catalytic conversion to methanol, which could then be used as a gasoline substitute after some distribution system and engine modifications.

Both of these processes appeared to have considerable merit as economical methods to dispose of waste materials while producing an energy product.

The critical technology that this program needed to demonstrate was in the area of selective pyrolysis of cellulosic organic waste materials into gases containing large amounts of olefins and

their subsequent processibility. If the selective pyrolysis could be verified and demonstrated, then the remainder of the process to make gasoline was seen as relatively straightforward, based, as it was, on industrial success with similar processes; i.e., the parallel process of an oil refinery. The most significant difference, of course, would be the use of cellulosic waste material rather than crude oil as feed stock.

### **Pyrolysis**

The handling of nonuniform waste solids is an order of magnitude more difficult than fluids. The capability of the pilot plant to operate on a wide variety of feedstocks will require a flexible system. Part of the design information required would be the characteristics of the potential feedstocks with regard to particle size, shape, moisture, etc. The design of the equipment to fluidize the solid feed would be critical to the success of the pilot plant, since many organic wastes tend to become fibrous when finely ground and are therefore difficult to fluidize. Once the feed is finely ground and fluidized in the grinder, it may be best to keep it flowing. Multi-training grinding equipment with its reserve capacity would be preferable to holding bins for the ground material.

The organic feedstock, finely ground and fluidized, would be pneumatically transported to the pyrolysis reactor which is envisioned as a number of long, red-hot stainless steel tubes heated to a temperature between 700°C to 800°C inside a furnace fired by char and byproduct gases. As is common in refinery practice, the tube diameter would be less than 10 centimeters. To obtain the desired throughput, a multitude of tubes are placed in parallel as in the petrochemical industry cracking crude oil to make ethylene. A key objective of the pilot-plant phase is determination of the fluidized solids stream's ability to divide into a multitude of smaller streams to feed into the individual pyrolysis tubes without plugging them.

Efficient recovery of the energy content of the pyrolysis stream leaving the reactor is dictated by the large amount of steam needed; such a recovery process is routinely practiced in ethylene plants. For the trash-to-gasoline process, a high-temperature heat exchanger would be required to reduce the pyrolysis stream temperature from about 760°C to about 200°C. The pyrolysis stream temperature cannot be lowered much below 200°C without risk of condensing tar vapors that

could foul the heat exchanger surfaces and cause the heat exchanger to plug up. The presence of the char and dirt in the pyrolysis stream would create the very high heat-transfer rates experienced with a fluidized bed, and also would prevent coke from fouling the heat transfer surfaces. The very fine char would be removed from the pyrolysis stream in parallel, small-diameter cyclones after the stream had passed through the heat exchanger. The diameter of the cyclones must be kept small to retain the fine char. The gas stream would be cooled rapidly by spraying "quench water" into it. This step causes the tar to condense into small droplets rather than to adhere to the heat-exchanger surfaces. Part of the hot quench water can be recycled through the heat exchanger as a supply of superheated dilution steam for pyrolysis. The steam will be further superheated in the pyrolysis furnace.

### **Low-Pressure Gas Cleanup**

After the pyrolysis gases are cooled, the small remaining tar mist must be removed prior to compression. This is a relatively persistent tar mist, which may require a scrubbing tower in conjunction with the quench system. To increase the degree of cleanup, the mist-laden pyrolysis gas stream may require electrostatic ionization prior to scrubbing. Bench-scale experience has indicated that although a second-stage scrubber followed by a demisting cyclone was helpful, the pyrolysis gas still needed to be filtered before entering the compressor. Unfiltered pyrolysis gases had a tendency to cause the compressor valves to gum up and stick. The cleanup of the pyrolysis stream to remove residual char and tar with well-designed scrubbers will be one of the important aspects of the pilot plant tests.

To compress the pyrolysis gases from about atmospheric pressure up to above 3100 kPa (450 psig) for storage, a three-stage reciprocating compressor was used. Pyrolysis-gas-storage pressures of up to 9300 kPa (1350 psi) were used. Normally, very little condensate was recovered from the intercoolers, although significant amounts of aqueous and organic condensates were recovered from the storage tank where the compressed gas was allowed to cool to ambient temperatures. The organic fraction is dark in color, but has a very low viscosity and may contain primarily low-molecular-weight aromatics; e.g., benzene, toluene, and xylenes. This organic phase is referred to as "pyrolysis

gasoline" in the ethylene industry and may be formed by the polymerization and dehydrogenation of olefins during the pyrolysis operation. This pyrolysis gasoline will be used both as the lean oil makeup for the hydrocarbon absorber, and as a high octane (100+) blending component for the final gasoline product. The pyrolysis gasoline will be sent to the lean-oil cleanup distillation column for purification. The aqueous phase of the compressor condensate may have use in the final stage of the gas scrubbing operation.

### **High Pressure Gas Purification**

The gas-purification section separates the pyrolysis gases into three separate streams: carbon dioxide; byproduct gases containing hydrogen, carbon monoxide, and methane; and product gases containing ethylene, propylene, and butylene. The hot-carbonate system was successfully piloted in the early 1950s. Although stainless steel reboiler, valves, and pumps are recommended, the remainder of the hot-carbonate system can be made of steel if a small amount of potassium dichromate is used to passivate the solution. To avoid the inadvantageous precipitation of abrasive potassium bicarbonate in the current bench-scale project, a solution of 25% potassium carbonate was selected. This concentration is nearly as effective as more concentrated solutions which easily precipitate to plug transfer lines if cooled slightly. To increase the efficiency of absorption and regeneration, modern installations add proprietary additives to the carbonate solutions. These proprietary additives may or may not be more effective than the small amount of contamination present in the pyrolysis gases since the bench-scale system worked so well.

### **Polymerization**

In the early 1930s, the petroleum industry began to commercially crack heavy feedstocks in order to make more gasoline. A major byproduct of this operation was the production of low-molecular-weight gases such as ethylene, propylene, and butylene. Research soon showed that the byproduct gases could be readily polymerized to form even more gasoline. This research was soon commercialized both with and without catalysts and was common until the petrochemical market for olefins developed in the 1950s.

The thermal or noncatalytic approach was selected for the organic-waste-to-

gasoline program because of the high ethylene content of the pyrolysis gases. The conditions required to polymerize ethylene with phosphoric or sulfuric acid catalysts are very severe relative to those used to polymerize propylene or butylene. A series of catalytic polymerization reactors with increasingly severe conditions might have to be employed to successfully polymerize the olefins. Also the acid catalyst is difficult to maintain in the active state at the temperature required to polymerize ethylene. In contrast, although requiring higher temperatures and pressures, the thermal polymerization preferentially polymerizes ethylene, which is the major component of the purified pyrolysis gases. Chosen early in the program, thermal polymerization still appears to be the best method. When an impure, randomly contaminated feedstock such as organic wastes is used, there is no concern about removing all of the possible catalyst poisons. The scale-up of the thermal polymerizing reactor is expected to present a very low risk, as it would be similar to previously commercialized reactors. The reactor probably would consist of a tube and shell heat exchanger followed by a soaker chamber.

### **Product**

The present project's laboratory work confirmed the ease of thermal polymerization with pure ethylene. The 1935-era octane values are 10 to 15 units lower than today's values--this project's polymer gasoline had an unleaded motor octane of 90 compared with the 75 to 80 range of the 1935 era. After a single distillation, it appears that the polymer gasoline product probably will have an unleaded octane rating and distillation characteristics suitable for the United States market. At present United States' gasoline consumption rates, the market impact of the gasoline produced from organic wastes will be relatively small, posing no immediate danger of market depression.

Thermal polymerization of ethylene and other olefins also produces synthetic oils having excellent viscosity characteristics. For example, the lubricating oils formed by thermal polymerization of ethylene, propylene, 1-butene, 2-pentene, or 1-hexene all had pour points less than  $-32^{\circ}\text{C}$  ( $-25^{\circ}\text{F}$ ). When cracked paraffin wax, consisting primarily of alpha olefins, was used as the feedstock, the pour point was  $-34^{\circ}\text{C}$  ( $-30^{\circ}\text{F}$ ) and the

viscosity index was 137. Temperatures up to  $450^{\circ}\text{C}$  ( $850^{\circ}\text{F}$ ) and pressures up to about 17,000 kPa (about 2500 psi) required very short residence to avoid product degradation. Attempts to further thermally polymerize a previously thermally polymerized gasoline fraction resulted in a very low oil yield, indicating that extended residence time in the original polymerization to form gasoline will not significantly affect the oil yields at the moderate temperature of  $320^{\circ}\text{C}$  and extended reaction time of 9.5 hours.

The market for byproduct lubricating oil may be considerably more difficult to exploit than the gasoline market due to public consciousness of the brand names of lubricating oils. Extensive testing will be needed before the byproduct oil can be compared with the leading synthetic oils made from chemically pure feedstocks, although fairly simple laboratory tests can easily verify its general suitability as a lubricant.

### **Economic Scale-Up Considerations Municipal Waste Feedstock**

To determine the economic feasibility of the process to convert municipal trash into gasoline required a long list of assumptions. For the use of municipal trash as feedstock, it was assumed that the trash contained 60% dry organic material, 13% inorganics (iron, aluminum, and glass), and the balance moisture. A credit of \$4.85 per tonne (\$4.40 per ton) of trash processed was assumed for the value of the reclaimed metals and glass. A yield of 45 gallons of hydrocarbon liquids per ton of raw trash processed was assumed and referred to simply as "gasoline." The relative economics of the process were taken to be a function of capital cost, plant size, gasoline (hydrocarbon) value, and the dump fee per ton of trash credited to the process. The plant size can be expressed in terms of the population served by the process, by assuming a daily per capita trash generation rate of 2.25 kg/day (2.5 tons daily per 1000 people).

An in-house preliminary economic evaluation was made by identifying the major equipment items and estimating the installed cost and operating cost. This study indicated that a 91-tonne/day (100-ton/day) plant would involve a capital cost of \$6.32 million and an annual operating cost of \$815,000 in early 1978 dollars. To verify this analysis, the sponsor (EPA) let a contract to DOW Chemical Company, Freeport, TX, to

conduct an independent process evaluation. Dow's preliminary cost estimate for a 91-tonne/day (100-ton/day) plant was \$7.6 million capital costs and \$873,000 annual operating costs in early 1978 dollars. Most of the 17% extra capital cost identified by Dow was related to process changes that had occurred since the original in-house study had been completed. To obtain extrapolations of the Dow cost estimates, the capital costs were scaled using 0.65 as the exponential scaling factor, whereas 0.20 was used as the labor scaling factor. It is interesting to keep in mind that petroleum prices are widely predicted to inflate at annual rates of 3 to 7% faster than the overall economy, due to the projected increase in deeper wells and offshore rigs needed to maintain oil production rates. At 3% compounded for 10 years, gasoline value would increase by 34%, whereas at 7% annual increase it would double in 10 years. The gasoline value to be considered is the local wholesale value, not the much lower value often quoted at a world-scale refinery located in some large seaport or oilfield. By extrapolation it can be shown that the larger the plant size, the more economical the gasoline to produce.

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*The complete report, entitled "Conversion of Organic Wastes to Unleaded, High-Octane Gasoline," (Order No. PB 84-148 865; Cost: \$14.50, subject to change) will be available only from:*

*National Technical Information Service*

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