CONRAD
INDUSTRIES, INC.

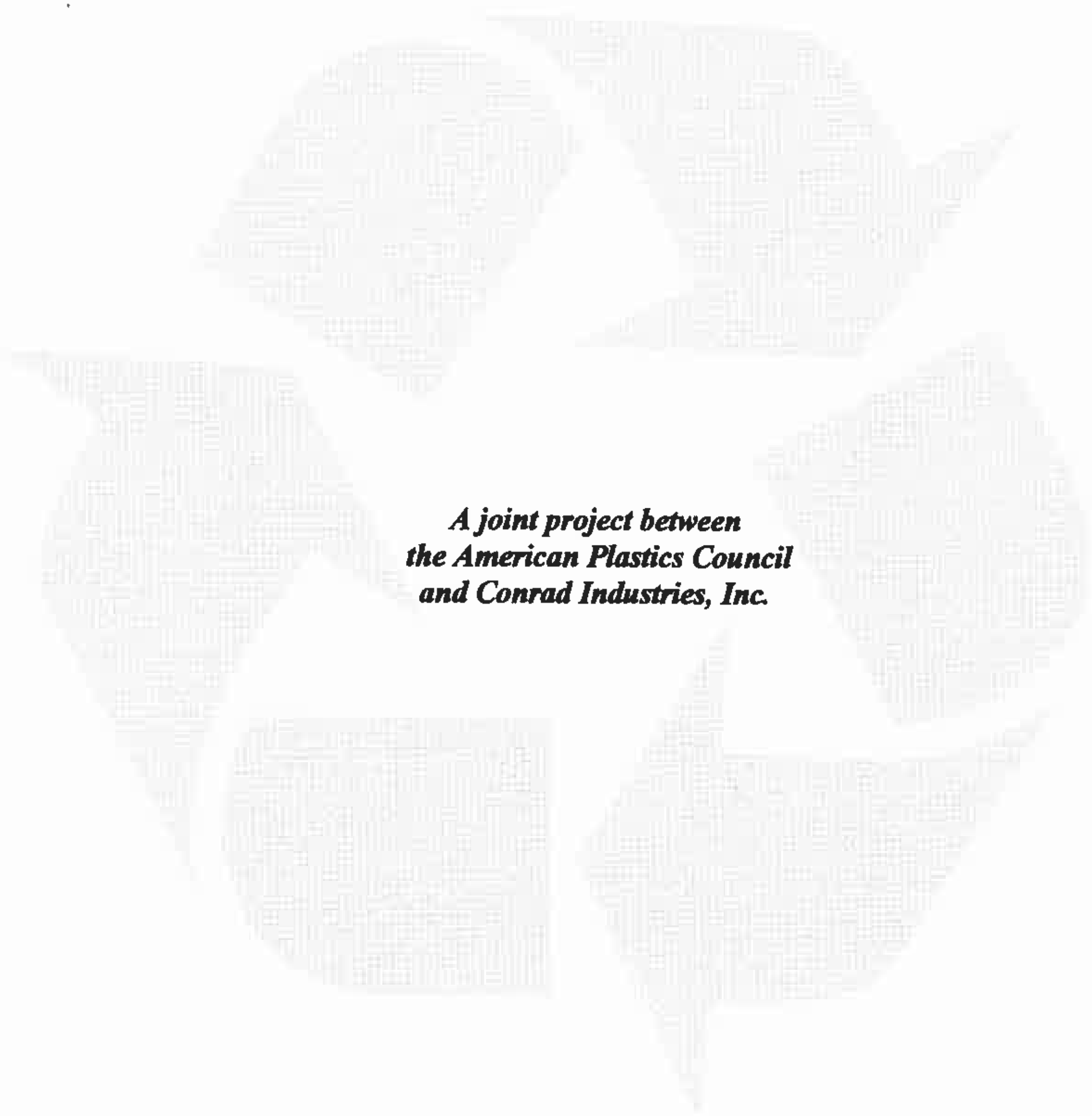
Advanced Recycling Of Plastics

A Parametric Study Of The Thermal Depolymerization Of Plastics

Final Report With The American Plastics Council

June 1995

ADVANCED RECYCLING OF PLASTICS
A Parametric Study of the Thermal Depolymerization of Plastics



A joint project between
the American Plastics Council
and Conrad Industries, Inc.

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June 1995

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TABLE OF ABBREVIATIONS

ABS	Acrylonitrile Butadiene Styrene
C2' + C3'	Ethylene + Propylene
CART	Commercial Advanced Recycling Unit
DART	Demonstration Advanced Recycling Unit
EER	Energy and Environmental Research Corporation, Irvine, CA
EERC	Energy and Environmental Research Center, University of North Dakota
FCC	Fluidized Cracking Catalyst
FID	Flame Ionization Detector
GC	Gas Chromatograph, Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
PCP-GW	Post-Consumer Plastic Goodwill
PCP-IN	Post-Consumer Plastic Indiana
PCP-NJ	Post-Consumer Plastic New Jersey
PCP-OR	Post-Consumer Plastic Oregon
PET	Polyethylene Terephthalate
PG	Pyrolysis Gas
PMCC	Pnesky-Martens Closed Cup
PP	Polypropylene
ppm	Parts Per Million
PS	Polystyrene
PU	Polyurethane
PVC	Polyvinylchloride
QH	Heavy Quench Oil From High Temperature Condensing Tower
QL	Light Quench Oil From Low Temperature Condensing Tower
TC	Thermocouple
TCD	Thermal Conductivity Detector
TL	Condensable Retort Oil From Retort Sampler
TPA	Terephthalic Acid
UHMWPE	Ultra High Molecular Weight Polyethylene
VOC	Volatile Organic Compounds

EXECUTIVE SUMMARY

The American Plastics Council (APC) worked with Conrad Industries to demonstrate that pyrolysis is a viable method for recycling post-use plastics into liquid petrochemical feedstocks. The project was conducted at Conrad Industries' Chehalis, Washington facility using a semiworks unit called the *Demonstration Advanced Recycling Technology* or DART unit. The DART unit was built by Kleenair Products (Clackamas, Oregon) and is an auger kiln reactor that applies heat to plastics in the absence of oxygen to produce a high yield of hydrocarbon product.

Seventy-six runs were conducted during the 20-month project. These runs were grouped according to the following designations: shakedown, parametric study, post-consumer plastic study and recycling of wax and chlorinated oils. Many of these runs were conducted with a "base" feedstock containing 60% high-density polyethylene, 20% polypropylene and 20% polystyrene. The liquid and noncondensable gas products were thoroughly analyzed at the site using gas chromatography and other analytical methods.

Initial shakedown runs were conducted for the purpose of confirming the operating reliability of the DART unit. During these runs, operating reliability was verified, system behavior was characterized and general operating conditions were established. Liquid yields for the early shakedown runs were less than 50%. Later shakedown runs focused on attaining high liquid yields and increasing capacity. During a portion of one of these runs, a liquid yield in excess of 80% was reached using base feedstock.

Following the shakedown runs, a parametric study was conducted to demonstrate the capability of recycling many different combinations of resin types using pyrolysis. A variety of resin types typically found in packaging and durable waste streams were recycled under a range of operating conditions. Analysis of product yield and composition led to a better understanding of the viability and economics of pyrolysis to recycle plastics. The most important pyrolysis process variable is temperature followed by retention time. At low retort temperatures, liquid oil yields of 65-75% are possible. Because of the design of the DART unit, the retention time was not easily altered.

The optimal process conditions to attain high liquid yields, good product quality, high feedstock throughput and ease of operation were determined during the parametric study. For base feedstock and plastic feedstocks containing low levels of polyethylene terephthalate (PET), polyvinylchloride (PVC) or intentionally added impurities, liquid yields of 65-75% were achieved with pyrolysis temperatures of 900-950 °F. Liquid produced from base feedstock at these temperatures contained about 55% aromatic compounds and 45% aliphatic compounds. Most of the aromatic compounds in the liquid product were monoaromatic species, such as benzene, toluene and styrene. Most of the aliphatic compounds were olefins and contained less than 20 carbon atoms. However, the concentration of heavier aliphatics was high enough to affect the viscosity of the liquid product. The noncondensable hydrocarbon gas that was produced at 900-950 °F from the above feedstocks contained primarily ethylene, propylene, C4 olefins and methane, with lower concentrations of ethane, propane, butanes and hydrogen. The combined yield of ethylene and propylene in the gas was highly predictive of the liquid yield.

During the parametric study, it was shown that pyrolysis of resin blends with elevated levels of polystyrene or low-density polyethylene exhibited behavior that was nearly identical to that of base resin. The presence of shredded paper at 4% did not appear to adversely affect the process in any way. Pyrolysis in the presence of a cracking catalyst did not have a significant effect on liquid yield or on the yields of individual hydrocarbons in the liquid or gas.

Processing resin blends with elevated levels of PET (20-40%) required substantially more heat than other plastic mixtures and resulted in liquid product containing a significant amount of solid terephthalic acid. It was shown that the presence of terephthalic acid in the liquid product could be eliminated at high pyrolysis temperatures.

The presence of PVC in the plastic feed at 1-3% resulted in product oil with total chloride levels of 5,000-10,000 ppm. It was demonstrated that at these same PVC levels, the total chloride concentration in the oil was reduced to less than 10 ppm with the addition of lime hydrate. The presence of low levels of PET (1-5%) in the feed in addition to PVC did not appear to have a detrimental effect on the resulting total chloride concentration in the oil. The primary factor governing the efficient and total removal of chloride from the system was the physical mixing ratio of plastic feed to lime hydrate. It was shown that efficient chloride removal could be achieved at a feed:lime hydrate physical mixing ratio of about 30:1 for a plastic blend containing 1% PVC and 3% PET.

Feeds containing 5% or more of polyurethane, acrylonitrile butadiene styrene or polyamide were recycled without difficulty. Hydrogen cyanide was not positively detected in the product oil or gas.

Pyrolysis of 100% polystyrene resulted in a 95% liquid yield and a styrene monomer yield of nearly 60%. Toluene and ethyl benzene concentrations were also high in the liquid product. The capacity of the DART unit for processing 100% polystyrene was almost double that for other resins.

100% polypropylene was processed at 850 °F with a liquid yield of 66%. The liquid product contained primarily olefins that resembled the molecular skeleton of polypropylene. The noncondensable gas contained elevated levels of propylene, isobutylene and *n*-pentane.

Four batches of post-consumer plastic from different regions of the country were successfully recycled. Although PVC, PET and various impurities were present in the post-consumer plastic, the addition of lime hydrate produced a liquid product that was very similar to liquid produced from base feedstock mixtures. Chloride levels in the liquid product were about 10 ppm for all post-consumer plastic batches.

There were no environmental problems associated with the process. Stack emissions were well within air quality limits. Fugitive emissions were monitored without any detection of leaks. Waste water that was generated during the process was treated at the Conrad Industries facility. The treated water was tested and was acceptable for disposal to the local water treatment facility.

The liquid product from the parametric study was thoroughly analyzed and was found to be acceptable as a refinery feedstock. A 5,000-gallon batch of oil was shipped to the Lyondell-Citgo Refinery in Houston, Texas for processing. The oil was mixed with Resid and used as a feed to the refinery's coker units. Most of the product was volatile and no processing difficulties were observed. It was determined that this type of feedstock is indistinguishable from many other petroleum feedstocks to a refinery.

Recycling plastics using pyrolysis is technically feasible. Many of the specific challenges which arose during the program were the result of the design of the DART unit, which was not optimized during this research project. The results of this project will enable a pyrolysis unit to be designed that will consistently produce marketable liquid products at yields in excess of 70% from post-consumer plastics containing mixed resins.

1. Introduction

Increasing the recycling rate for plastics will require innovative and cost effective recycling technologies. Recycling plastics back to their fundamental feedstocks has been one area of active research and shows promise in overcoming many of the problems that plague conventional recycling processes. These new technologies have been called 'Feedstock Recycling" or "Advanced Recycling Technologies" and include processes such as methanolysis of polyester and the thermal depolymerization of polyolefins. Advanced Recycling Technologies that recycle mixed plastics back to liquid petroleum feedstocks are being evaluated worldwide to better understand their technical feasibility, process economics and logistical viability.

1.1 Advanced Recycling Technologies

Conventional recycling processes that recycle paper, glass, metals and many plastics into similar or lower quality products are effective when there is a large, consistent, clean and cost effective waste stream available. Plastic soda bottles, milk jugs and automobile battery casings are just a few of the success stories in conventional plastics recycling. These plastic items represent products that are easily identified and collected, are used in large volumes, and have consistent resin properties and additives. Many other plastic products are not produced in large volumes, are not easily identified and cannot be separated from other plastic wastes without sophisticated analytical equipment or processes. This has led to the search for technologies that can recycle mixtures of plastic products into marketable products without costly sorting or cleaning.

Recycling plastics back to their fundamental petrochemical feedstocks may overcome some of the current difficulties and expensive steps encountered in plastics recycling. This concept of recovering feedstocks is referred to as *Feedstock Recycling* in Europe and Japan, and *Advanced Recycling Technology* in the United States. Many advanced recycling technologies are being developed throughout the world and several have been commercialized. Some advanced recycling technologies recover usable monomers, the actual building blocks for new plastics. The methanolysis of PET is an example of this type of recycling that is commercially practiced. Other advanced recycling technologies recover more basic petrochemical feedstocks such as naphtha. These petrochemical feedstocks are then used to make monomers for plastics or other petrochemical products.

Thermal depolymerization or pyrolysis is one method of advanced recycling that converts plastics back to petrochemical feedstocks. A robust thermal depolymerization process should be able to accept mixtures of many types of plastics and not require that the plastics be washed or sorted. Also, it should not require some of the grinding and extruding processes that are used in conventional recycling processes. Finally, the products from thermal depolymerization should have wide market applicability and be virtually indistinguishable from products made from virgin materials. Even though this recycling method showed great promise, no detailed studies had been performed to understand its technical and economic viability. Therefore in 1992, the American Plastics Council began a program to search out and evaluate existing process technologies that could be used to recycle plastics back to petrochemical feedstocks.

1.2 Conrad Industries, Inc.

This search led to Conrad Industries, Inc., Chehalis, Washington. Conrad Industries was originally formed in 1955 in western Washington State. The company operates systems and equipment for material handling, transportation and recycling. Most of the company's projects are local or regional in nature. In 1986, in order to further the recycling effort, Conrad Industries built a plant and system designed to thermally decompose 2,000 pounds per hour of rubber tire chips. Prior to this, during the lengthy research and development of the technology, Conrad Industries tested and developed a data bank of information covering a wide variety of feedstocks using this technology.

The Conrad recycling process uses an auger kiln reactor that applies indirect heat to the plastics in the absence of oxygen to produce liquid hydrocarbon products and minor amounts of carbon and light hydrocarbon gases. The process was designed by Kleenair Products Co., Inc. (Clackamas, Oregon) and Conrad Industries and was built by Kleenair Products.

The American Plastics Council (APC) approached Conrad Industries, Inc. early in 1992 suggesting that the two work together to demonstrate the viability of using pyrolysis to recycle plastics. Conrad Industries was chosen because their process technology was judged to be the most versatile, safe, and cost effective. They also had experience in recycling tires into carbon black, liquid petroleum and combustible gases and worked closely with the manufacturer of the equipment. Lastly, they owned a pyrolysis unit which was well suited for a detailed parametric study of the process. This unit was subsequently called the Demonstration Advanced Recycling Technology unit and is referred to as "the DART unit" throughout this report.

An APC project was started at Conrad Industries and was divided into three phases: the redesign and retrofit of the DART unit, an extensive parametric study on known plastic mixtures and the recycling of post-consumer plastic waste streams. The overall objectives of the APC/Conrad project were the following:

- Conduct a parametric study utilizing the DART unit and virgin resin blends
    - ➢ Determine the limitations of the technology regarding different resin types and critical impurities such as PVC and PET.
    - ➢ Determine the optimal process conditions for high liquid yield, good product quality, high feedstock throughput and ease of operation.

  - Investigate the process chemistry for different resin feedstocks and operating conditions.
  - Identify the operating and mechanical issues related to scale-up of the technology to the commercial level.
- Demonstrate the marketability of the product oil
- Study the economics of the process
- Determine the environmental impact of the process
- Successfully recycle post-consumer plastic
- Confirm the operating reliability of the DART unit
- Confirm the safety of the process

This comprehensive technical report discusses all aspects of the APC plastics recycling project at Conrad Industries. Section Two of the report describes the layout and operation of the plant, the configuration of the DART unit, an overview of the recycling process and the methods of chemical analysis. Section Three deals with the manner in which pyrolysis occurs in the DART unit. The results of the experimental recycling studies are discussed in Section Four. Sections Five and Six address environmental, health and safety issues related to the process. Finally, the Appendix includes additional summary data on the process, including various tables and other information related to the project.

2. Process Technology and Plant Operations

2.1 Description of Facilities

The layout of the Conrad Industries plant is shown in Figure 1.

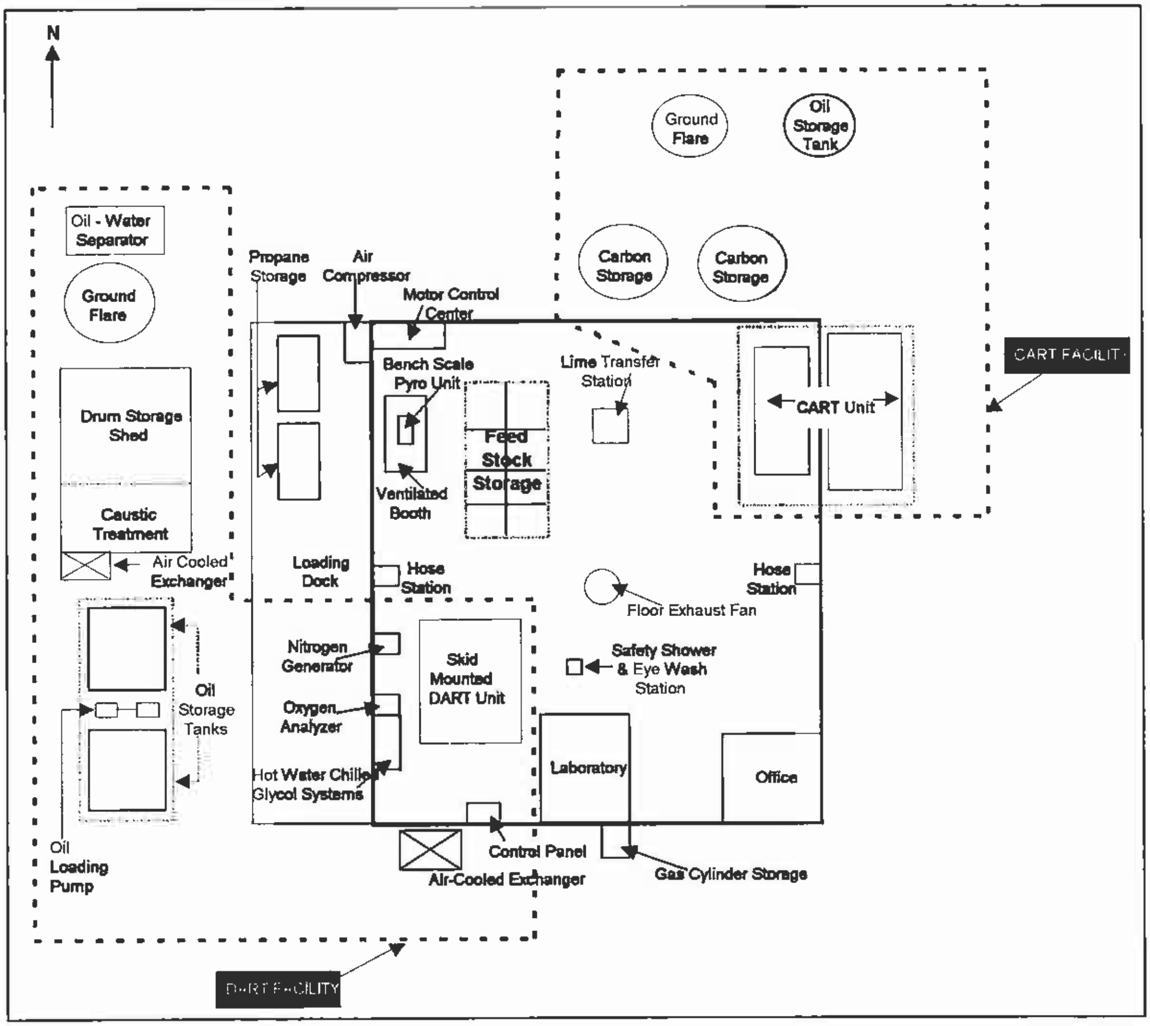

Figure 1 Conrad Industries, Inc. plant layout

The Conrad Industries plant is divided into three areas: the DART facility, the CART , (Commercial Advanced Recycling Technology unit) facility and an area common to both facilities. The plant consists of an unheated 10,000 sq. ft. building bordered externally on the south and west sides by a loading dock and a portion of the DART facility, on the north and east sides by a portion of the CART facility.

The DART unit is located in the southwest corner of the building. The DART unit is skid mounted and includes the plastic feed system, a lime hydrate feed system, pyrolysis unit, condensing system, acid gas scrubber, by-product solids collection system and product oil storage tanks. The stack on the retort furnace and the vents from the retort safety valves extend above the building roof. A ground flare is used for destruction of the by-product pyrolysis gas.

Adjacent to the DART unit is the operator control panel, oxygen analyzer, nitrogen generator and a system that provides circulating hot water and chilled ethylene glycol to the DART unit. A forced draft air-cooled heat exchanger for cooling the heavy oil is located outside of the building.

All products are stored outside of the main plant building. Product oil is stored in two triple-walled horizontal storage tanks fitted with internal electric heaters and a circulation pump. Off-specification product oils are stored in 55-gallon metal drums which are kept in a well ventilated storage shed next to the two product oil storage tanks. The storage shed also houses the system used for treatment of the acid gas scrubber liquid. The storage shed and the two storage tanks are curbed for spill containment, with rainwater passing through a dedicated oil-water separator.

The electricity and instrument air supplies are obtained from facilities that supply the entire plant. There is no emergency electrical power supply. The electrical classification within the building around the condenser is Class I, Div. 2, Group D. Propane gas for the retort burners and the ground flare is obtained from liquid storage containers located on the loading dock. A station for bulk handling and transfer of lime hydrate is located near the center of the building. Plastic feedstocks are received in cardboard containers (gaylords) in 1,000 lb. lots. These containers are stored inside the building adjacent to the DART unit.

A small laboratory is located in the building near the DART unit. The laboratory is outfitted with a 100 cfm ventilation hood and a small ceiling fan. The laboratory contains all of the instruments and equipment used for the chemical analyses described in section 2.7.

Building ventilation is achieved by a wall exhaust fan near the roof and a roof-mounted exhaust fan with air turn-over capacity of 1 cft/sqft located at the center of the building. The roof fan draws air through a 4' diameter duct from a position 2' above the ground. A 6" dedicated fire water line connects the Conrad facility to the Chehalis water main and can supply water at 80 psig to several hose stations within the building. A safety shower with eye wash is located in the building close to the laboratory and the DART unit. Product oil samples and flammable chemicals are stored in designated safety cabinets located external and adjacent to the laboratory within the plant.

2.2 Process Overview

For a more detailed description of the DART unit, refer to section 2.3.

Plastic feed mixtures are received in 1,000-pound gaylords and are introduced to the DART unit by the plastic feed system. Lime hydrate is introduced by the lime hydrate feed system. The DART unit contains a horizontally positioned cylindrical retort that is heated externally by the retort furnace. The retort contains the process auger, which mixes the material in the retort and conveys it toward the outlet end. Both lime hydrate and plastic enter at the top of the inlet end of the retort. After falling into the retort, the plastic mixes with the lime, melts and decomposes as the process auger conveys it toward the retort outlet.

The thermal decomposition products from plastics are solids and condensable and noncondensable gases. At the outlet end of the retort, the process auger transports the solids into the solids collection system. When the weight of the solids collection drum indicates that it has reached its capacity, it is disconnected, capped and replaced with an empty drum. The hot pyrolyzate gas exits from the outlet end of the retort to the two-stage condensing system. When the condensing tower sumps reach their capacity (as determined by observation of the Teflon gauge glasses on the tanks) the contents are pumped to one of the two 4,000-gallon storage tanks. If analytical testing determines that the oil is off-specification, the oil is pumped to temporary storage in 55-gallon drums. Off-specification oil is recycled by means of the oil/wax feed system. Noncondensable gas passes through the acid gas scrubber before being burned in the flare or in the retort burners.

2.3 Equipment Description and Configuration

A schematic representation of the entire DART unit as it currently exists is shown in Figure 2.

The following sections describe the general configuration of the unit. Precise technical information is confidential to Conrad Industries and Kleenair Products and has been omitted. Throughout the project, many modifications and additions were made to the DART unit, and these will be mentioned in their respective sections.

The DART unit has many features similar to the larger Conrad CART unit. However, the DART unit is a pilot plant which was retrofitted for the purpose of this research project. It was not designed nor optimized for commercial use but rather as a demonstration unit to better understand the feasibility of advanced recycling processes. Many of the difficulties are artifacts of this particular design, some of which led to design changes in future CART units.

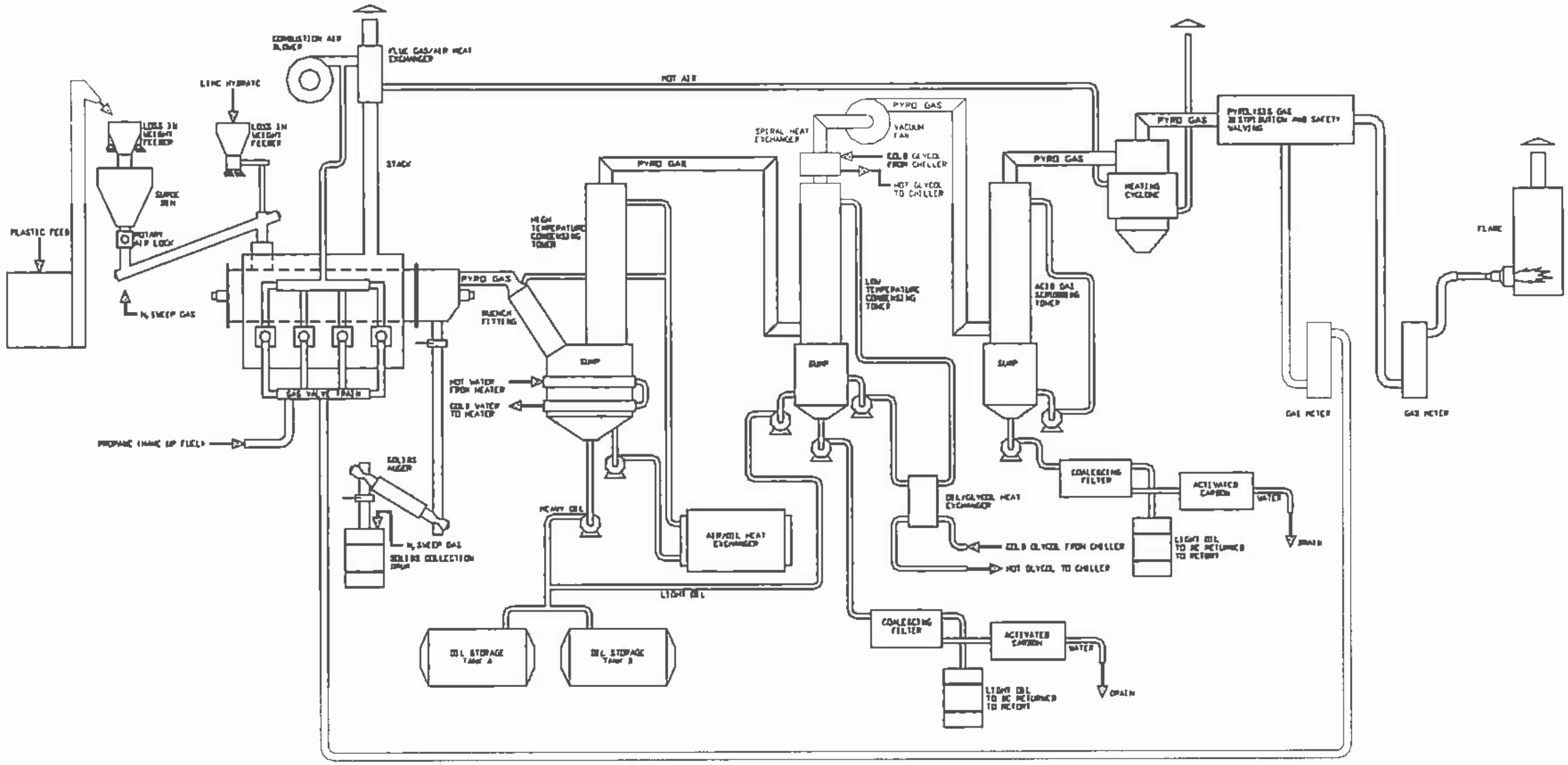

Figure 2 Schematic representation of the DART unit

2.3.1 Plastic Feed System

The configuration of the feed system for the DART unit is designed for plastic resin pellets or regrind. Feed systems to handle larger plastic pieces, such as crushed or chopped bottles are being evaluated. The configuration of the plastic feed system is shown in Figure 3 and includes a large, mobile feed hopper, vertical bucket elevator, loss-in-weight feeder, surge bin, rotary airlock/metering star valve and a feed auger leading to the retort.

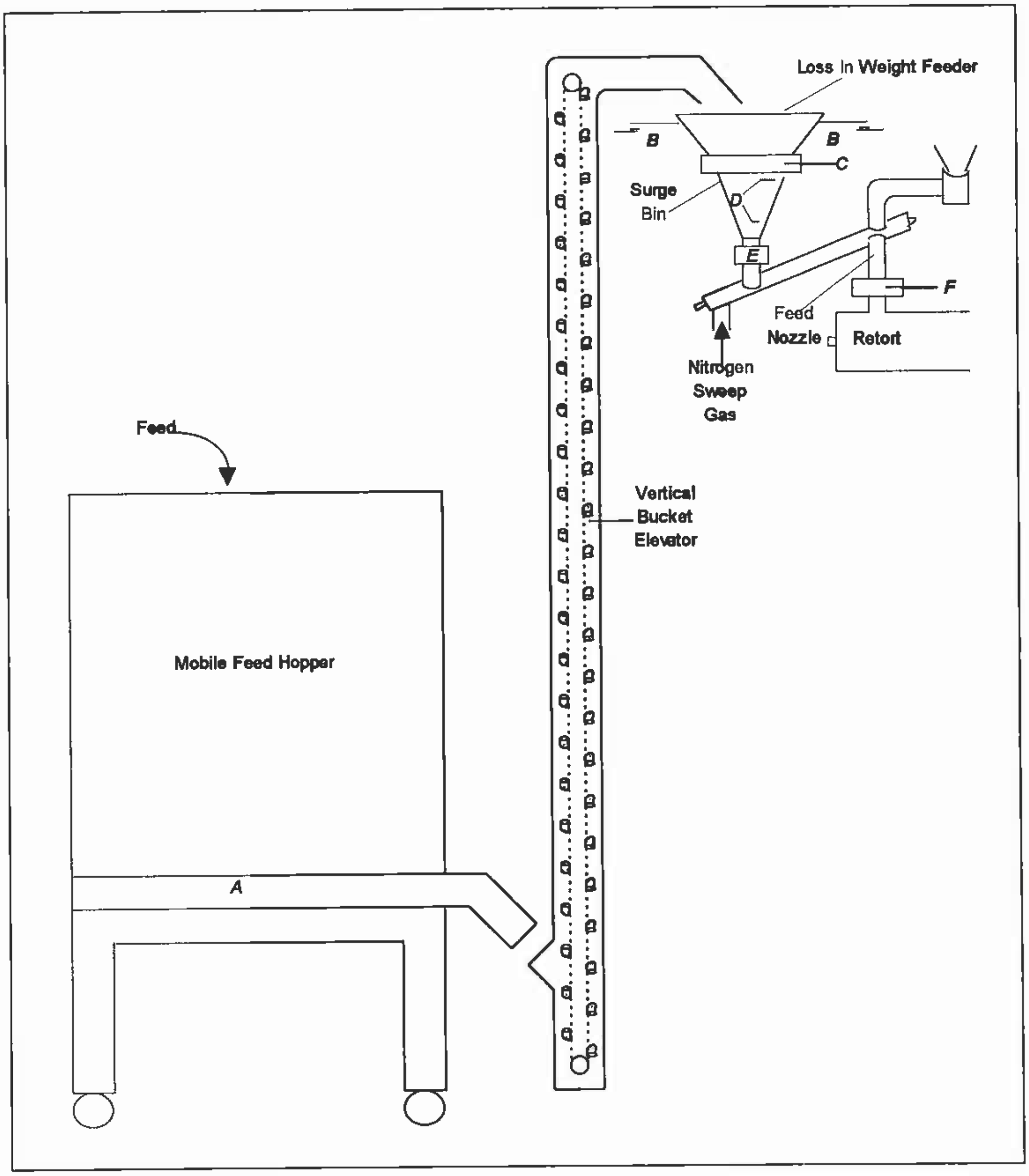

Figure 3 Configuration of plastic feed system

The flat bottom of the large feed hopper contains four augers that transfer material to one end of the hopper. There, a transverse auger (*A*) moves material to the bucket elevator which lifts the feed to the loss-in-weight feeder.

The load cells (***B***) on the loss-in-weight feeder are connected electronically to an operator feed control station (not shown). The control station allows 15 lbs. of material to accumulate in the loss-in-weight feeder before an automatic slide gate (***C***) dumps the material into the surge bin. The control station accurately records the cumulative weight of the material transferred to the surge bin and allows for determination of the plastic feed rate.

The surge bin is in the shape of an inverted cone with steep sloping sides. It is fitted with low and high level probes (***D***) that are interlocked through the main operator control center to activate operation of the large feed hopper and the bucket elevator.

The surge bin supplies material to the rotary airlock/metering star valve (***E***) which serves two purposes. First, it has a calibrated volume that is used to control flow by varying its speed. Second, the rotary airlock minimizes air leakage into the pyrolysis retort.

The plastic feedstock flows downward from the rotary air lock into an inclined feed auger. The feed auger is continuously purged with nitrogen to eliminate back flow of gases from the retort. The feed auger transports the material up to the vertical feed inlet nozzle which allows entry of feed directly into the top of the inlet end of the retort. For safety and control purposes, the inlet feed nozzle has a hydraulic air-tight knife gate valve (***F***) at its lower end. The knife gate valve is controlled and monitored by the main operator control center.

The following feed system configurations were used prior to adoption of the current system:

A. An alternate pneumatic vacuum transfer system was utilized to transfer pelletized plastic feed from bulk storage to the surge bin. The pellets were transferred through a vacuum hose from a large cardboard box on a floor-mounted scale to the intermediate bin. The scale was monitored visually to determine the plastic feed rate. This pneumatic system was only utilized for pelletized plastic and is still operational.

B. The loss-in-weight feeder was installed after Run 57. Before this time there was not an adequate method to measure the amount of non-pelletized feed introduced to the DART unit.

C. Before Run 74, a different surge bin was utilized. This bin was cylindrical with a gently sloping conical outlet. The bin was initially installed on load cells which allowed for monitoring of the surge bin weight at the main operator control center. The surge bin weight measurement was not reliable and was abandoned in favor of visually monitoring the floor-mounted scale.

D. Prior to installation of the vertical bucket elevator (Run 73), a vertical auger was utilized to transfer material from the large hopper to the loss-in-weight feeder.

2.3.2 Lime Hydrate Feed System

The configuration of the lime hydrate feed system is shown in Figure 4 and includes a bulk lime hydrate handling station, a pneumatic transfer mechanism and a lime hydrate receiver/feeder.

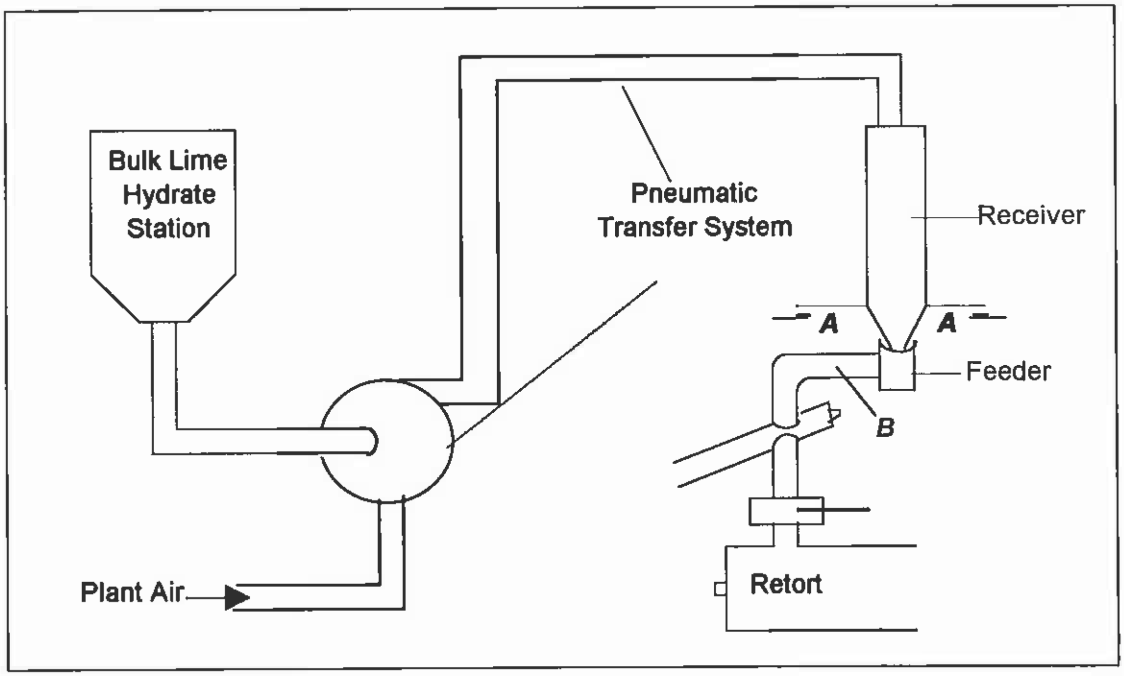

Figure 4 Lime hydrate feed system

The bulk lime hydrate handling station accepts reusable 500 lb. tote sacks of bulk lime hydrate. The pneumatic transfer system uses the air supply from the plant to convey the lime hydrate through the transfer piping to the receiver/feeder.

The lime hydrate receiver/feeder is fitted with high and low level probes that are interlocked to the pneumatic transfer system. The feed rate is controlled automatically or manually. A weighing mechanism (*A*) tracks weight loss due to the transfer of lime hydrate to the feeder. A single helix (*B*) moves the lime hydrate horizontally to the vertical feed nozzle, immediately above the entry point for the plastic feed. The lime hydrate and plastic feed mix as they enter the retort. A sufficient inventory of lime hydrate in the receiver/feeder efficiently minimizes air leakage into the retort.

The current lime hydrate system was installed as an entire integrated system after Run 69. Before that time, a less dependable system without a weighing mechanism was used. It consisted of a single, steeply sloping bin with a twin screw feeder and variable drive. Lime hydrate was introduced manually at the top of the bin from 50 lb. bags.

2.3.3 Oil/Wax Feed System

The oil/wax feed system is shown in Figure 5 and consists of a drum heater tank, an activated carbon vapor recovery system and an oil/wax feeder.

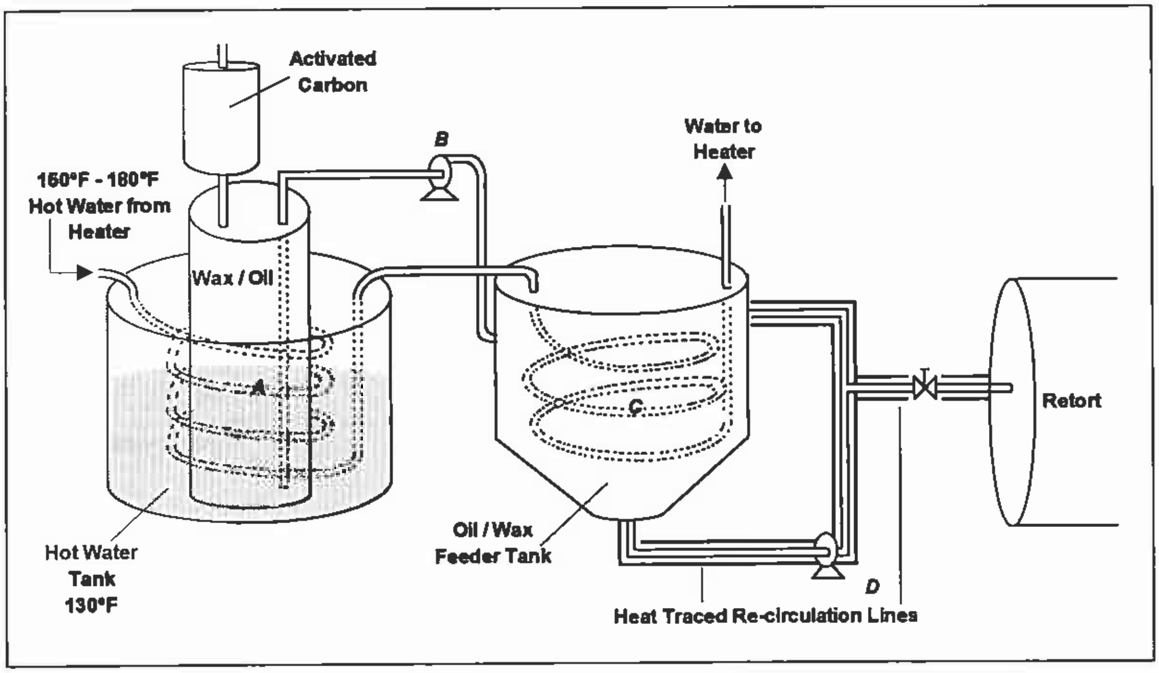

Figure 5 Oil/wax feed system

The drum heater is a 100-gallon open-top water tank with coils of 1-inch copper tubing around the inside walls (*A*). The tubing is connected to the hot water circulation system, which supplies water to the heater at 150-180 °F. The resulting water temperature in the tank is about 130 °F. 55-gallon drums of oil or light wax are placed in the tank and connected to a drum of activated carbon to eliminate fugitive emissions. When the drum contents are of sufficiently low viscosity, they are pumped to the oil wax feeder by means of an air operated diaphragm pump (*B*).

The tank in the oil wax feeder is surrounded by coils of copper hot water tubing (*C*) and insulation. The contents of the tank are maintained at about 130 °F and are continuously circulated through heated lines by means of a gear pump (*D*). Feed to the unit is accomplished through piping that is connected to the circulation lines.

2.3.4 Pyrolysis unit

The pyrolysis unit is shown in Figure 6 and includes the retort, process auger, outlet end bell and furnace chamber.

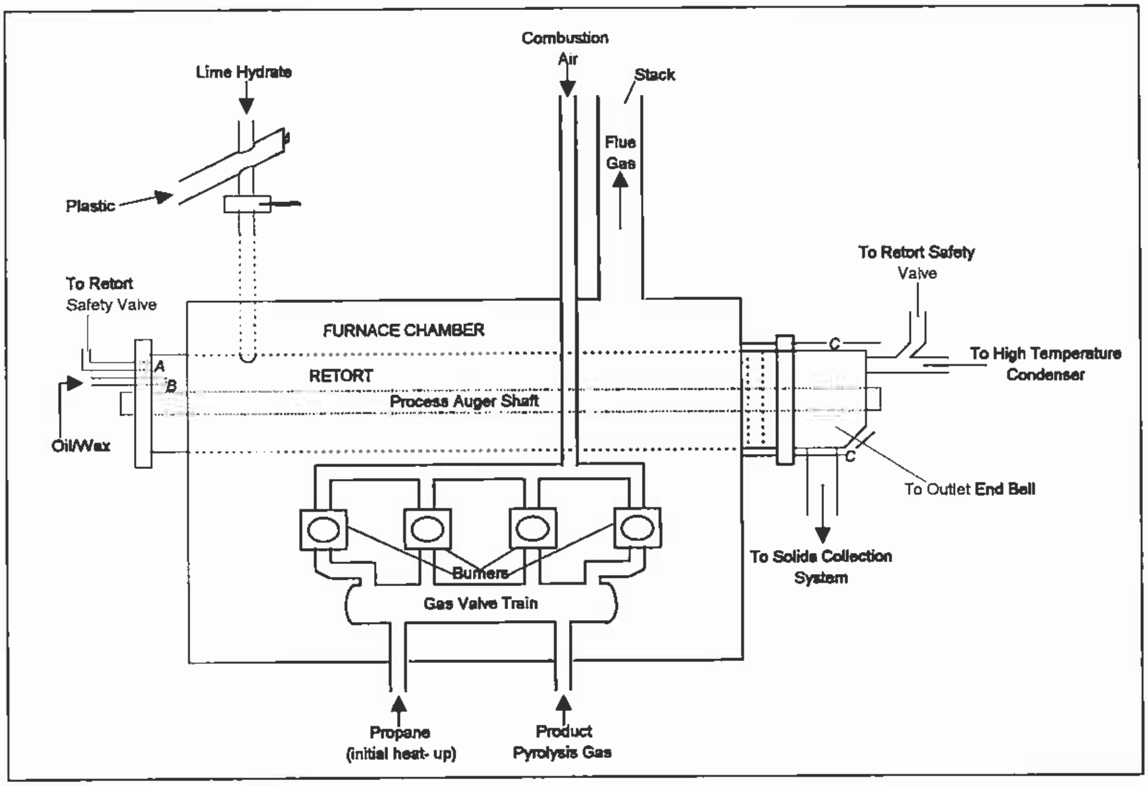

Figure 6 Pyrolysis unit

The retort is a horizontal, cylindrical vessel and serves as a combined reactor, heat exchanger and mixing device. The retort vessel extends completely through the furnace chamber with flanged connections terminating outside the chamber at each end. A steel cover on the inlet end of the retort allows access to the inside of the retort. One of the retort safety valves and the oil/wax feed inlet (B) is attached to this cover. The lime hydrate/plastic feed entry point is located on top of the retort very close to the inlet end but within the confines of the furnace chamber.

The hydraulically-driven process auger mixes the pyrolyzing material and moves it through the reaction vessel. It has a hollow shaft containing several thermocouples which are loose within the shaft, but maintain fixed positions along the shaft length. Figure 7 shows the positions of the thermocouples within the process auger shaft along with the positions of the burners and the furnace thermocouples.

The outlet end bell is located outside of the furnace chamber and houses shaft packing seals and shaft support bearings for the process auger. There are three openings in the outlet end bell. One opening connects the retort to the high temperature condenser, another to the solids collection system and the third to a retort safety valve.

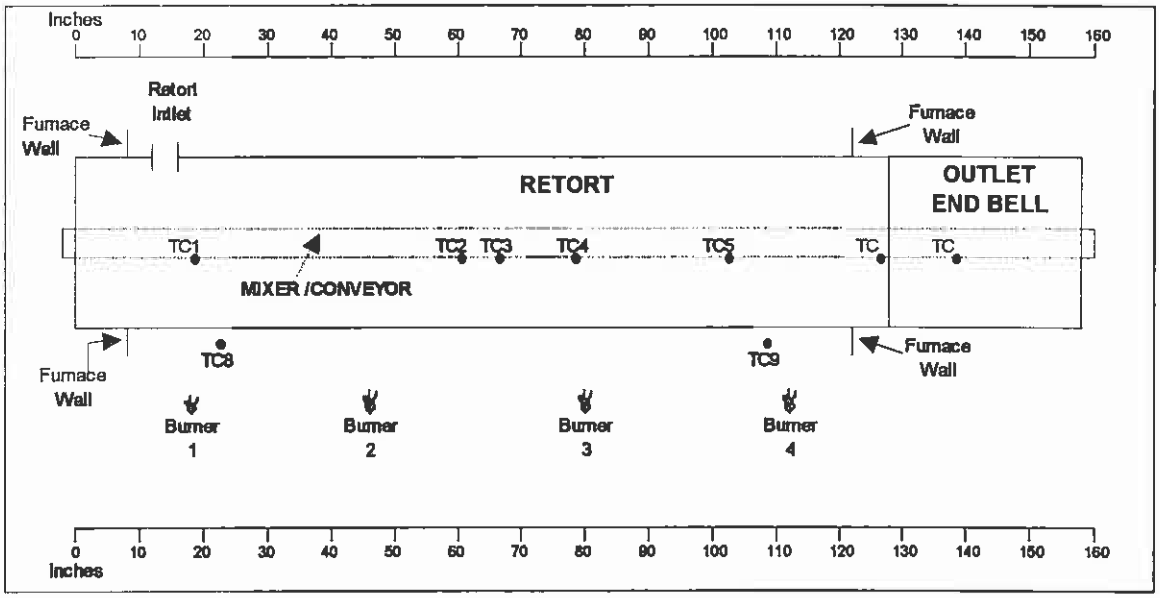

Figure 7 Thermocouple positions

An insulated furnace chamber surrounds the reaction vessel. Four gas burners along one side of the furnace fire box provide heat for the process. Flue gas products exit the fire box via a vertical stack. Propane gas is used to initially heat the furnace. Propane gas, combustion air and pyrolysis gas are controlled by an electronic central control system. When the furnace has reached the specified temperature, feeding of plastic is initiated. When adequate pyrolysis gas is generated to fuel the system, the flow of propane gas is shut off automatically.

Prior to Run 47, an inlet end bell also existed on the inlet end of the retort. During this time, the process auger extended into the inlet end bell. This end bell was permanently removed to reduce heat loss and solids formation at the inlet end of the retort.

Before Run 47, there was a horizontal inlet reamer that was used to dislodge solid material which had built up along the walls of the retort. The reamer was not used after Run 35 and was removed after Run 46.

2.3.5 Pressure Relief Valves

The retort pressure relief system consists of two safety valves that are located at the inlet and outlet ends of the retort. The relief valves consist of a horizontal weighted disk resting on a machined opening. The safety valve tail pipes terminate above the building roof. The pressure settings for the inlet and outlet safety valves are 10 in. H_2O and 5 in. H_2O, respectively. Before Run 34, the setting for both valves was 10 in. H_2O.

2.3.6 Solids Collection

The configuration of the solids collection system is shown in Figure 8 and consists of an outfeed auger and a drum for collection of solids.

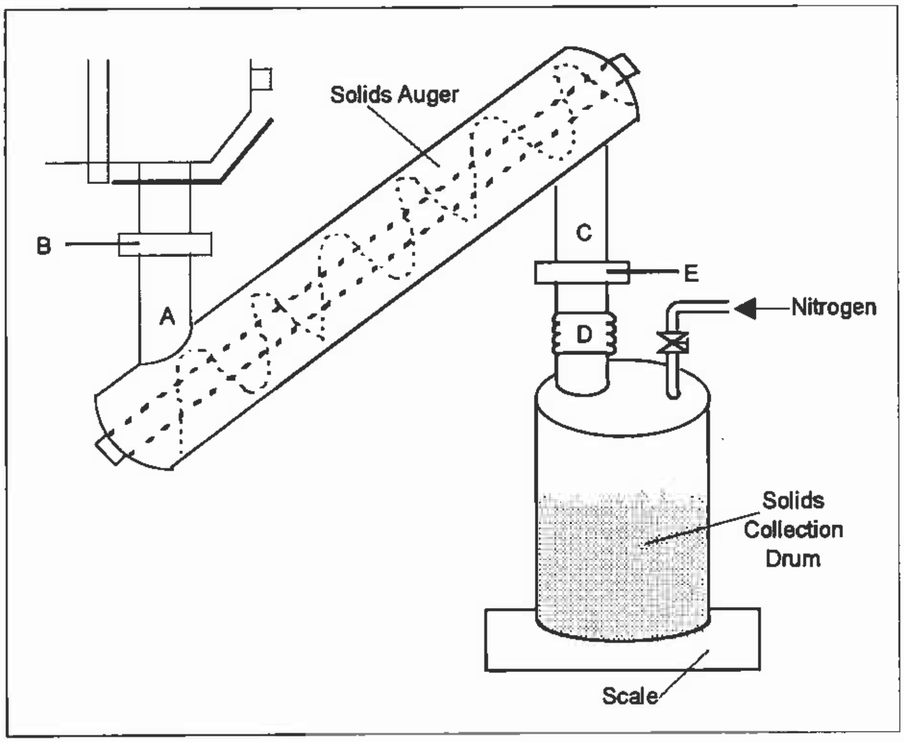

Figure 8 Solids collection system

A vertical transition (*A*) in the outlet end bell allows solids to fall from the retort end bell to the low point of the inclined solids auger. The transition contains a hydraulically-operated gate valve (*B*) which is utilized to isolate the collection drum when necessary as a safety precaution. The solids auger is also driven hydraulically and moves solid material to a point directly above the collection drum. The collection drum is attached to the solids auger by a transition (*C*) and a rubber boot (*D*). The transition contains a manually-operated gate valve (*E*). The drum is positioned on a utility scale.

To reduce the possibility of combustion occurring in the collection drum, nitrogen purge procedures were instituted after Run 13. Nitrogen gas is introduced at the top of the drum to minimize the introduction of air to the solids collection system. An optical sensor at the top of the solids auger was utilized to detect blockages. The sensor was removed after Run 13. The gate valve (***B***) in the vertical transition replaced a star valve after Run 12.

2.3.7 High Temperature Condensing Unit

The high temperature condensing unit is shown in Figure 9 and consists of a quench fitting, sump, condensing tower and forced-draft, air-cooled heat exchanger.

The hot pyrolyzate vapor exits the outlet end bell and passes through a quench fitting (*A*) before entering the condensing tower sump. The condensing tower consists of a Venturi scrubbing section (***B***) in the bottom of the tower and 2 valve trays with downcomers (welded construction) in the upper half. A mist pad is located at the top of the tower to minimize entrainment. Product oil is pumped at controlled rates into the quench fitting (*A*), the top of the tower (*C*) and the Venturi scrubber (***B***). The tower was operated over a range of temperatures, from 100 °F to 170 °F.

The sump is a rectangular vessel with a capacity of 165 gallons and is externally heated by hot water jackets. Product oil in the sump is cooled by circulating from a location near the low point of the sump through the forced-draft, air-cooled exchanger located on the external wall of the plant. The exchanger is housed in a removable enclosure and is outfitted with an optional water sprinkler system. Oil is pumped to storage from a different location near the low point of the sump. Sump level measurement is accomplished by a Teflon gauge glass.

2.3.8 Low Temperature Condensing Unit

Pyrolysis gas that does not condense in the high temperature condenser proceeds to the low temperature condensing unit. The low temperature condenser is shown in Figure 10 and consists of a plate exchanger, sump, condensing tower with a spiral heat exchanger and an oil/water separator.

The low temperature sump is a rectangular vessel with a capacity of 21 gallons. Sump level measurement is accomplished by a Teflon gauge glass.

Oil from the sump is pumped through the plate exchanger. Circulating ethylene glycol coolant at 32 °F cools the exchanger. After passage through the exchanger, cooled oil is returned to the top of the tower. Water that has collected in the bottom of the sump is periodically pumped to the water treatment system. The system consists of a coalescing filter, oil collection drum and activated carbon filter. The oil collected is then pumped to the bulk storage tank.

The condensing tower contains two valve trays and a spiral heat exchanger located at the vapor outlet. Circulating ethylene glycol coolant at 32 °F cools the spiral heat exchanger.

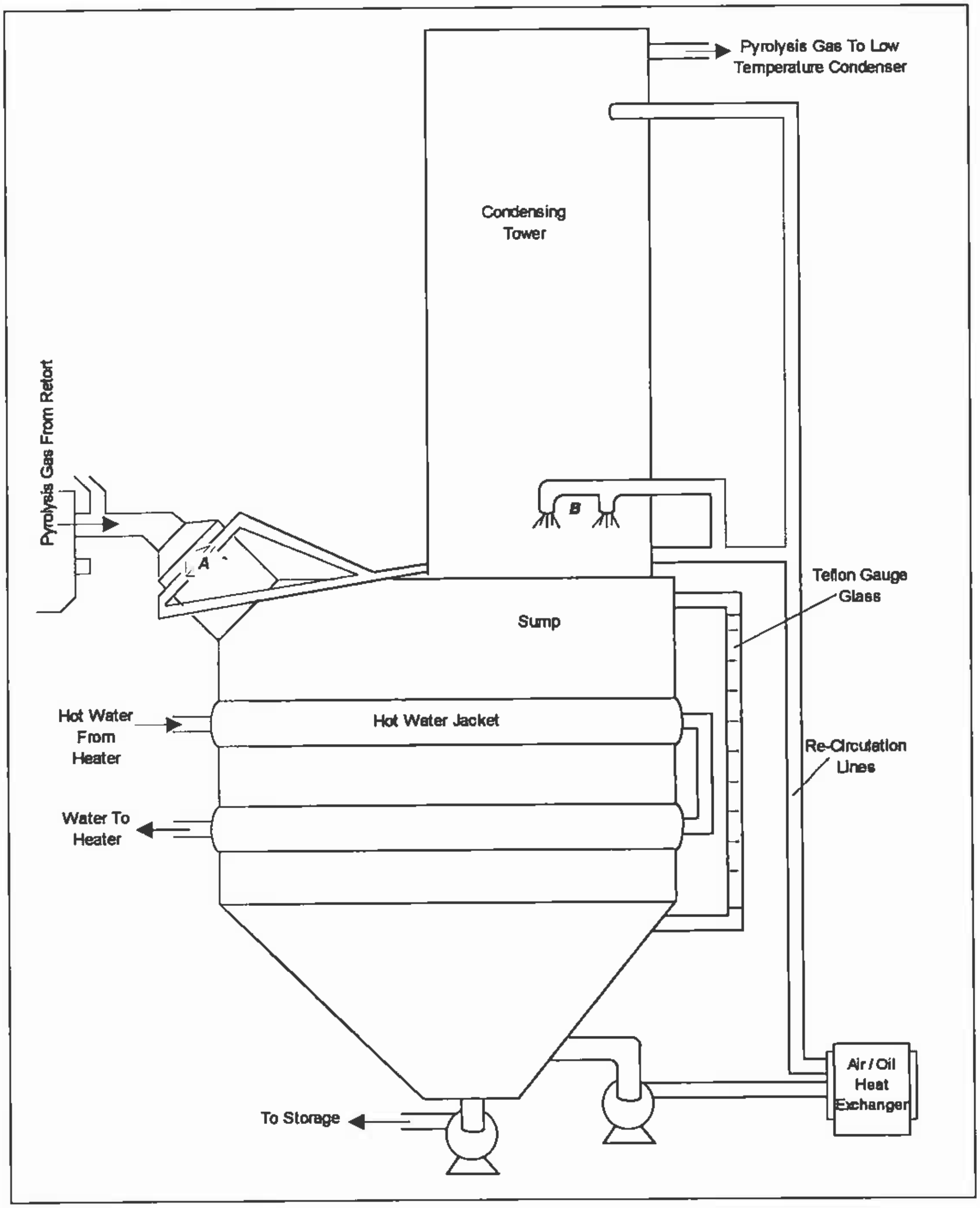

Figure 9 High temperature condensing unit

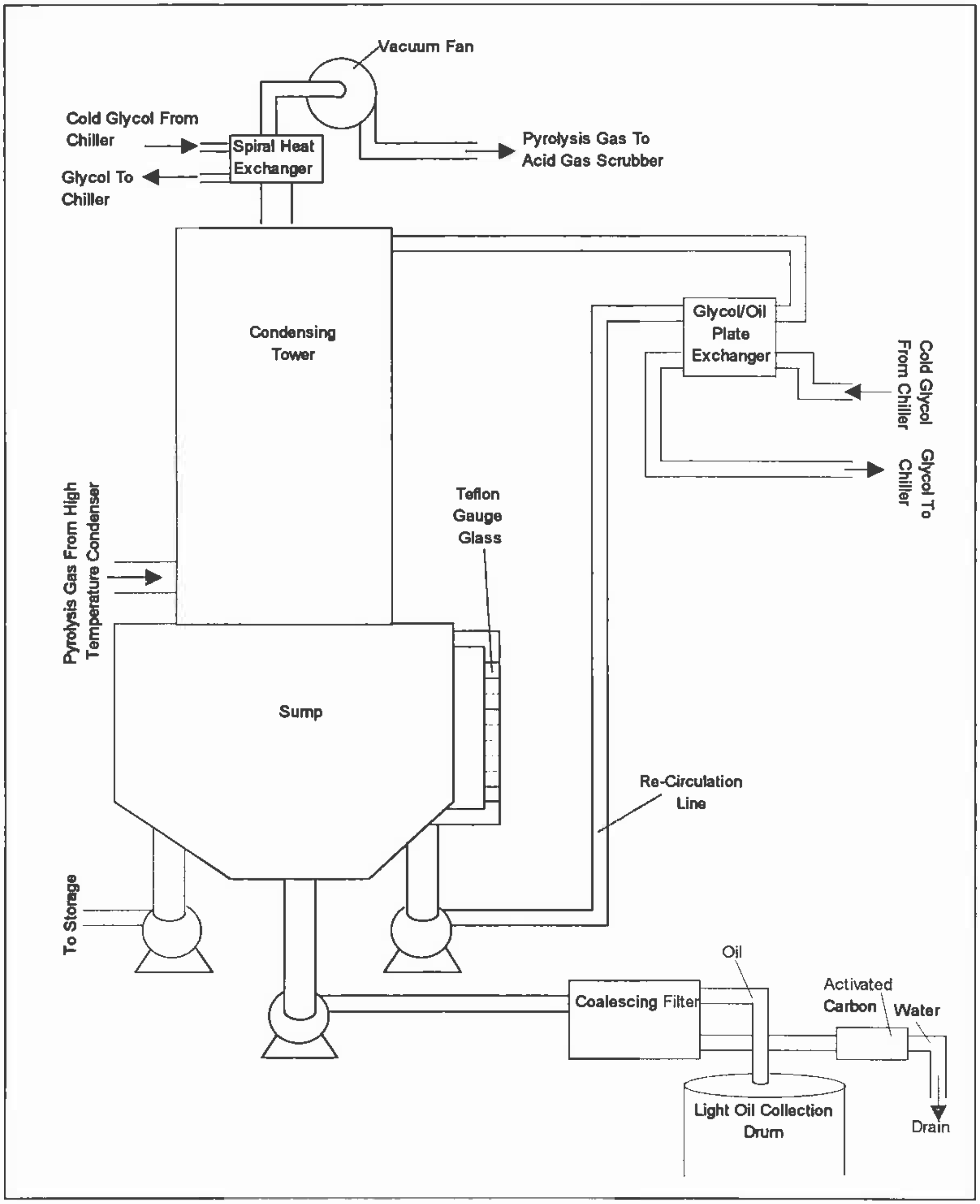

Figure 10 Low temperature condensing unit

2.3.9 Acid Gas Scrubber

The acid gas scrubber is located after the low temperature condenser and consists of a packed tower and sump. The scrubber is shown in Figure 11. The scrubber liquor contains sodium carbonate and sodium bicarbonate at a combined total of approximately 5% wt/wt. The sump has a capacity of 65 gallons.

Pyrolysis gas from the low temperature condenser enters at the bottom of the tower and passes through the tower packing before exiting to the heating cyclone. Scrubber liquor circulates through the packed tower via an electrically heated line to the top of the packing. The scrubber operates at a temperature of 10 °F higher than that of the low temperature condenser.

The scrubber liquor is occasionally replaced by a fresh solution. The used material is treated by passing it through a coalescing filter and an activated carbon filter. Light oil that is in the coalescing filter is collected in a drum for further processing in the DART unit. Water from the activated carbon filter is sampled for environmental analysis before being discharged.

Before Run 70, the acid gas scrubber was located in line between the high temperature and low temperature condenser towers. Before Run 41, the scrubber liquor contained sodium hydroxide at 1% wt/wt concentration. The sodium hydroxide scrubber liquor was pumped periodically to a neutralizing tank, where the pH was lowered to the 7-9 range with concentrated sulfuric acid.

2.3.10 Gas Handling

The gas handling system controls the flows and pressures of the noncondensable gas and consists of a vacuum fan, heating cyclone, gas flow meters and control valves. Parts of the system are shown in Figures 2, 6 and 10.

The vacuum fan is controlled by a SCR variable speed control located in the main operator control center. The fan speed is varied to maintain the retort operating pressure at negative 0.5 in. H_2O. To aid in control of pressure within the retort, a portion of the gas is circulated around the fan. Following the vacuum fan, the noncondensable gas passes through the acid gas scrubber before entering the heating cyclone. The heating cyclone operates at 150 °F to ensure that there is no condensation in the lines.

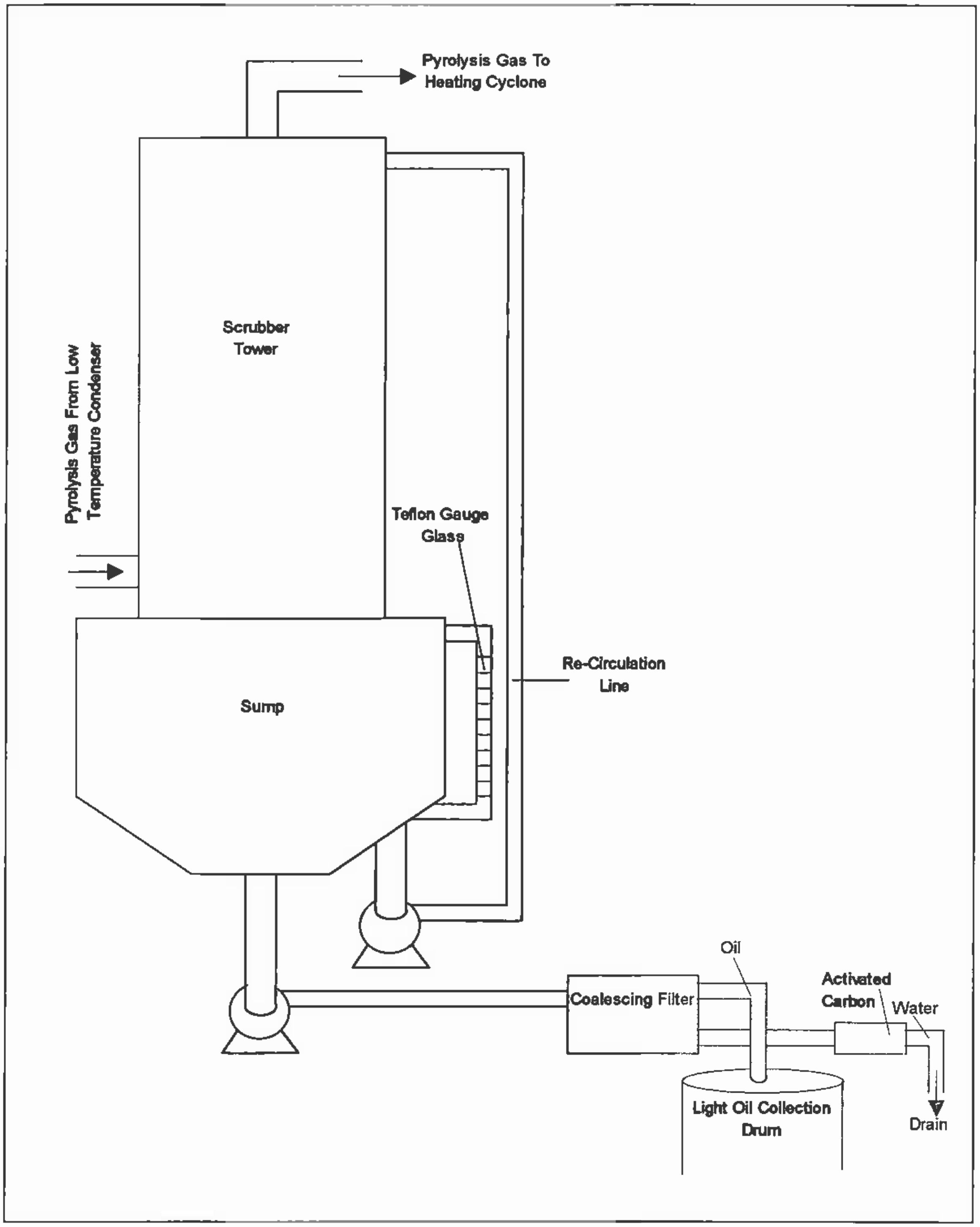

Figure 11 Acid gas scrubber

Control valves regulate the pressure and direct the gas from the cyclone to the furnace burners and to the flare. Flame arrestors are present to prevent flame propagation into the gas condensing system should a combustible mixture be present.

Rotameters with operating ranges of 0-1000 cfh measure the gas flow to the furnace burners and to the flare.

2.3.11 Flare

The flare (Figure 12) is located in a vertical refractory-lined chamber that discharges to the atmosphere through an elevated stack. Excess product gas enters the main nozzle mixing burner, which fires tangentially through the side wall near the bottom flare chamber. A flame temperature is maintained above 1400 °F. Cooling air enters the chamber through radial passages located above the plane of the burner. The cooling air is modulated to maintain the chamber temperature below 1900 °F.

2.3.12 Product Oil Storage

Product oil is stored in two horizontal steel tanks (Figure 13) that are lined internally for spill and corrosion protection. The capacity of each tank is 4000 gallons. Both tanks rest on strain gauges, which provide accurate measurement of the weight of each tank. Electrical immersion heaters are installed in each tank. The vents from each tank are connected to 55-gallon drums of activated carbon located at grade. Each 4,000-gallon tank is interconnected so that an air-operated diaphragm pump can circulate the tank contents, transfer material from one tank to the other or pump the oil to a waiting transportation truck. Both tanks are located on a spill pad which is drained to a spill retention 3-sided building housing the waste water treatment system and sample oil storage.

2.3.13 Process Control

A central distributive control system regulated process functions utilizing a Honeywell 9000. Individual control loops included the following:

- Feed rate
- Furnace
- Retort pressure control
- High temperature condensing unit temperature
- Flare temperature

The system also provided the following individual function controls:

- Retort auger speed control
- Pump down of the high temperature condensing tower sump
- Pump down of the low temperature condensing tower sump
- Pump down of the acid gas scrubber tower sump
- Inlet feed conduit and outlet gas conduit reamer actuation

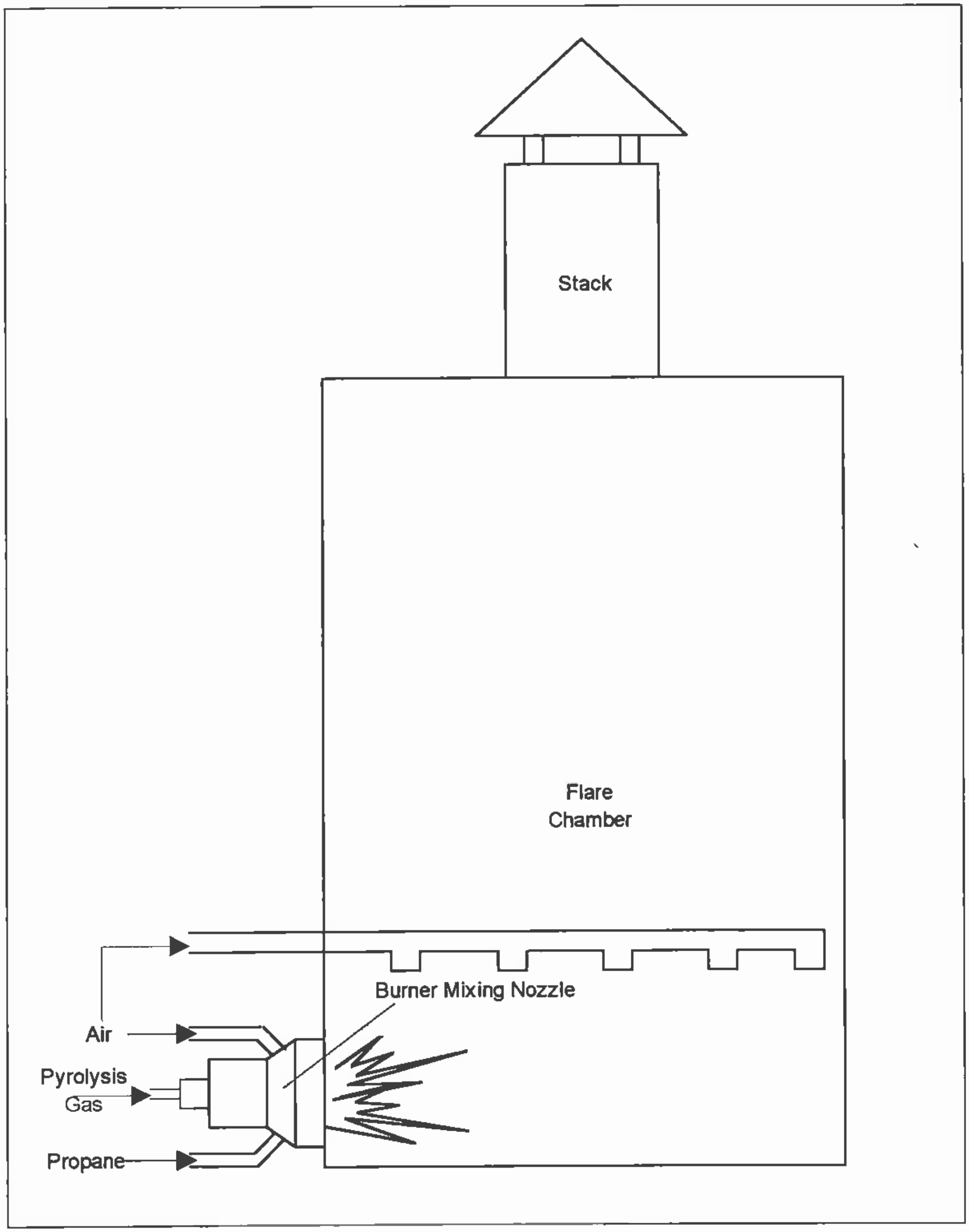

Figure 12 Flare

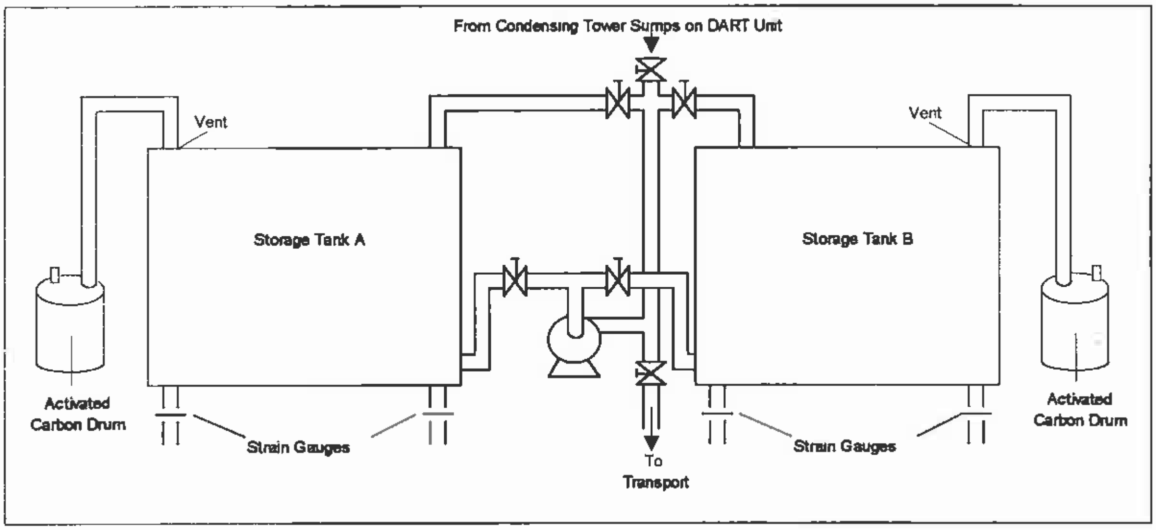

Figure 13 Product oil storage facility

Warning and interlock functions were controlled by the Honeywell 9000. The primary interlock strategy included the following actions:

- Shutting off of the feed
- Closing of the inlet slide gate valve
- Routing of excess pyrolysis gas to the flare

The following occurrences are some of the process deviations that initiated the interlock:

- High or low furnace temperatures
- High or low retort pressure
- Retort auger failure
- High differential pressures in the condensing system
- High or low temperatures in the condensing system
- High temperature in the flare

Operators were able to access the control functions and monitor operating parameters from a single control screen. Information was organized on a number of interactive menus. An alarm horn and alarm enunciator screen alerted operators to "out-of-limits" process functions or other system abnormalities.

The Honeywell 9000 unit also served as the platform for data acquisition. Data was communicated to computer storage for later analysis, while selected information was displayed and recorded on a panel-mounted, multi-channel chart recorder.

2.4 Plant Operations

The DART unit was operated on a 5 day per week basis, usually with only one test run during the period. Operators worked 12-hour shifts (7 a.m. - 7 p.m. and 7 p.m. - 7 a.m.) with two operators per shift. Two additional operators were available during the day shift for maintenance and facility upgrades. The normal operating schedule involved the following steps:

Monday:	Perform startup maintenance. Begin heating the furnace and retort to the target furnace temperature at a rate of 50-70 °F per hour.
Tuesday:	Commence DART operation with base resin at 40 lb/hr for one hour, 70 lb/hr for one hour and 100 lb/hr for four hours. After the system is stable, commence study with special feedstock or special DART operating conditions. Allow up to eight hours for DART system to reach stable operating conditions.
Wednesday:	Continue with DART operation.
Thursday:	Conclude study after 48-60 hours of total operating time. Conduct final purge of system by processing base resin for four to six hours. When gas generated from the retort has ceased, allow furnace and retort to cool down.
Friday:	When the retort has cooled down, end-of-run maintenance, inspections and repairs are performed.

During the portion of the run dedicated to the study, several related activities were ongoing. Product oil and gas were sampled and analyzed by gas chromatography (and other methods, if applicable) at regular intervals (every four to eight hours). Collected solids were sampled when the collection drum was changed. Acid gas scrubber liquor was sampled every eight hours and analyzed by titration to determine the remaining capacity for HCl capture. If necessary, the feedstock was sampled at regular intervals and analyzed for PET and PVC.

All aspects of the operation of the DART unit were continuously monitored by the operators and were manually recorded on operating log sheets. The Honeywell control center automatically recorded many process variables. The log sheets tracked operating variables (such as temperatures and pressures within the unit), feedstock and lime consumption, oil production and gas flow. At the conclusion of the run, all of this information was utilized to calculate a material balance for the study.

2.5 Utility Requirements

The main utility requirements for the DART unit include:

- Electricity
- Fuel Gas
- Nitrogen
- City Water
- Plant & Instrument Air

The DART unit was not outfitted with instruments for measuring utility usage.

Electricity

Capacity: 480V, 3 phase, 350 kva

Fuel Gas

Capacity: 1,000 gallons
Propane was used in most runs for firing the retort combustion chamber. In most instances the product gas was required at the flare to maintain the 1400 °F regulatory requirement.

Plant and Instrument Air

Capacity: 90 scfm @ 125 psig
16 scfm of air is required to generate maximum nitrogen flow.

Nitrogen

Capacity: Maximum nitrogen flow was 6 scfm.

Nitrogen was continuously injected into the lime hydrate and feed addition points. Nitrogen was injected intermittently to purge hydrocarbons from the carbon-lime collection drums prior to their removal from the retort system. Normal operation required 2 scfm of nitrogen.

City Water

Water was used to prepare the acid gas scrubber solution. Water was also available for the safety shower and fire hose station.

2.6 Process Sampling

During operation of the DART unit, samples of product oil, pyrolysis gas and solids were taken frequently. Samples of acid gas scrubber liquor were also obtained at regular intervals. The plastic feedstock was also sampled and analyzed in the laboratory periodically during the program.

Samples of oil that were representative of the immediate process conditions were obtained by removal of the hot pyrolyzate vapor from the outlet end bell using the retort sampler (Figure 14). These samples are identified as total condensable retort oil (TL) samples.

The samples were drawn by means of a peristaltic pump operating at 2000 mL/min. The hot pyrolyzate condensed as it passed through heated metal tubing from the outlet end bell to the 2L pyrex® collection flask. Final condensation occurred as the gas passed out of the flask through a vertically-mounted stainless steel condenser cooled with ethylene glycol at 32 °F. The noncondensable retort gas was pumped from the sampler to a location downstream of the gas delivery valve.

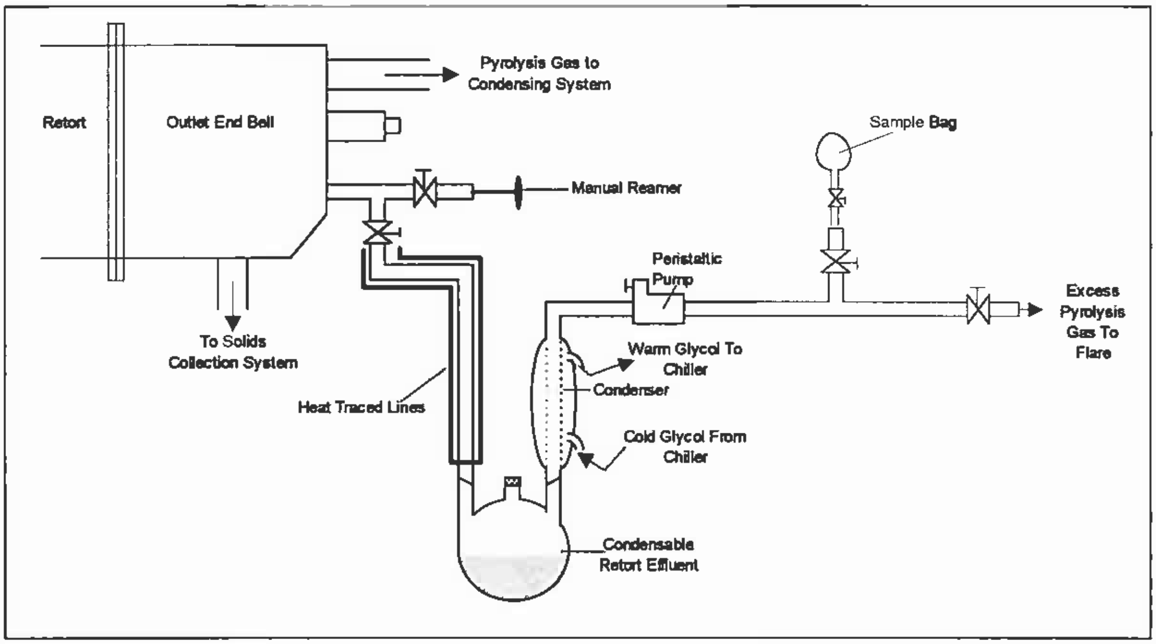

Figure 14 Retort effluent sampler

Heavy oil (QH) samples were drawn from an Isolok pneumatic sampling device. The sampler was positioned on the circulation line of the high temperature condensing unit.

Light oil (QL) samples were drawn from a spigot on the circulation line of the low temperature condensing unit. The spigot was flushed with fresh circulating light oil prior to collection of a sample.

Samples of noncondensable pyrolysis gas (PG) were collected at the exit from the heating cyclone at slightly above ambient pressure in a 2.25 L stainless steel vessel. The vessel was configured in such a way as to allow for continuous flushing through the vessel with pyrolysis gas.

Occasionally, the noncondensable pyrolysis gas was sampled at the exit from the peristaltic pump on the retort sampler. These gas samples had not passed through the acid gas scrubber. The gas samples were taken when it was necessary to know the concentration of acidic species or organochlorides in the gas. Evacuated gas sampling bags were utilized for these samples.

Samples of pyrolysis solids were taken manually from the solids collection drum. Operators wearing protective clothing purged the drum with nitrogen, isolated it from the DART unit and scooped the most recently deposited material from the top of the accumulated solids.

Samples of liquid from the acid gas scrubber were drawn from a spigot on the circulation line of the unit. The spigot was flushed with fresh circulating scrubber liquid prior to collection of a sample.

2.7 Methods Of On-Site Chemical Analysis

A variety of analytical methods were used for on-site chemical and physical analyses of oil, gas, solids and scrubber liquor produced in the DART unit. Analytical methods were also developed for the identification and quantitation of resin types in the plastic feedstock.

2.7.1 Oil

2.7.1.1 Gas Chromatography

Routine gas chromatography (GC) analyses of the liquid products were performed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a 15 m × 0.53 mm id HP-1 capillary column (0.88 μm film thickness) and a flame ionization detector. The temperature program consisted of a 10 °C/min ramp from 35 °C to 350 °C with a 10-min hold at 350 °C. Samples were prepared by a tenfold dilution into CS_2 and introduced with a Hewlett-Packard 7673 automatic sampler. Chromatograms were recorded on a Hewlett-Packard 3396 Series II integrator, which quantified the chromatographic peaks by integrated area percent. Identification of the chromatographic peaks was accomplished by duplicate GC/MS analysis at Montana State University using a Varian 3700 gas chromatograph with a 60 m × 0.25 mm id DB-1 capillary column (0.25 μm film thickness) interfaced to a VG 70E-HF dual sector (EB geometry) mass spectrometer operating in EI mode at a source temperature of 200 °C, (see appendix 8.5). The GC temperature program was identical to that described above. The integrator calibration file that resulted from the GC/MS analysis contained peak identification information for 172 peaks. Chromatographic signal files and report files were stored by the Hewlett-Packard Peak96 software on a Gateway 2000 486DX-33MHz PC that was interfaced to the integrator. Data abstraction and summarization were performed in Microsoft EXCEL. Simulated distillation analyses were performed on the integrator by re-analysis of the raw signal file on the GC using a Hewlett-Packard SIMDIS software package. Simulated distillation calibration was accomplished by analysis of a Hewlett-Packard C5-C40 aliphatic hydrocarbon standard.

2.7.1.2 Microcoulometry

Total halides in the oil were quantified using a Dohrmann DX-20B microcoulometer, which displayed the result as total nanograms of chlorine detected. Samples were introduced by a 1 µL syringe through the syringe port adapter. Usually, 3-5 determinations were made for each sample using a furnace temperature of 950°C and an analysis time of five minutes. Triplicate analyses of standard mixtures of chlorobenzene in isooctane were averaged to establish recovery. Recovery was defined as the mass ratio of chlorine injected to chlorine detected. Syringe injection delivery is determined for each oil sample by performing multiple 1 µL injections of the oil into glass wool within a GC sample vial. The vial is then weighed on an analytical balance to determine mass of delivery. Syringe injection delivery is roughly equivalent to sample density. The concentration in parts per million of total halides in the oil are calculated from the displayed value (as chlorine), recovery and syringe injection delivery.

2.7.1.3 Filtration

Occasionally, it was important to know the amount of xylene-insoluble filterable solids in the oil. This was accomplished by filtration over a 6 micron disk filter under aspirator suction. The deposited solids were then washed with near-boiling xylene, allowed to air dry and then weighed on the analytical balance.

2.7.2 Gas

2.7.2.1 Gas Chromatography

Routine GC analyses of pyrolysis gas samples were performed on a second Hewlett-Packard 5890 Series II gas chromatograph that was specially configured for simultaneous, automated analyses of fixed gases and light hydrocarbons. A single pyrolysis gas sample was introduced simultaneously to two 0.25 mL gas sample loops from the pressurized stainless steel vessel. In addition to the sample loops, the GC was equipped with two thermal conductivity detectors (TCD) and four valves interfaced with the following five 1/8 in stainless steel packed columns:

1. 2 ft 20% Sebaconitrile on 80/100 Chromosorb PAW
2. 30 ft 20% Sebaconitrile on 80/100 Chromosorb PAW
3. 6 ft Porapak Q 80/100
4. 10 ft Molecular Sieve 13X 45/60
5. 4 ft Molecular Sieve 13X 45/60

The valves, columns and timing are configured so that chromatographic separation occurs in the manner described in the following paragraph.

Using the two separate sample loops, identical 0.25 mL injections of gas are made onto two different column configurations in the GC. In the first column configuration, H_2 is separated on column 5 and detected with TCD #1 using nitrogen carrier gas. TCD #1 is switched off, TCD #2 is switched on and column 5 is then backflushed. While the above analysis is taking place, the remainder of the gas constituents begin to be separated on the second column configuration. After 1,3-butadiene has passed from column 1 to column 2, column 1 is backflushed to TCD #2 using helium carrier gas (helium carrier gas is utilized for the remainder of the analysis). After O_2, N_2, CO and CH_4 have eluted from column 2, they are isolated on column 4. Column 3 is then introduced to the carrier gas flow path, where ethane and ethylene are isolated. CO_2, propane, propylene, all C4's and n-pentane elute from column 2 and are detected at TCD #2. When gas flow resumes on column 4, O_2, N_2, CO and CH_4 elute and are detected at TCD #2. When gas flow resumes on column 3, ethylene and ethane are detected.

Chromatographs were recorded on a Hewlett-Packard 3396 Series II integrator. The integrator quantified the chromatographic peaks by comparison with peak areas for a standard calibration gas mixture and converted the responses to gas volume (mole) percents. Chromatographic signal files and report files were stored by the Hewlett-Packard Peak96 software on the laboratory PC (mentioned previously) that was interfaced to the integrator. Data abstraction and summarization were performed in Microsoft EXCEL. From the volume percent data, EXCEL was utilized to calculate the specific gravity, average molecular weight and heating value of the pyrolysis gas, along with the weight percent of each gas component.

2.7.3 Solids

2.7.3.1 Gas Chromatography

Occasionally, the solids generated from the process contained significant concentrations of high molecular weight aliphatic hydrocarbons (waxes). These types of samples were analyzed by gas chromatography in the same way as the oil samples.

2.7.3.2 Chloride and Cyanide Ion Selective Electrode Measurement

When the solids appeared to be dry and free of hydrocarbons, they were occasionally analyzed for chloride and cyanide by ion selective electrodes. Samples were prepared in deionized water. The pH/ISE meter was calibrated with known standards in the expected concentration range of the sample. The concentration of chloride or cyanide in the solid sample was calculated from the displayed result and the mass ratio of solid material to deionized water.

2.7.4 Scrubber Liquor

2.7.4.1 Titration

During runs when the acid gas scrubber was utilized, regular titrations were performed to verify that the capacity of the scrubber had not been exceeded. The scrubber liquor contained both sodium carbonate and sodium bicarbonate. In order to determine the concentrations of both carbonate and bicarbonate in the sample, a two-stage titration was performed with standardized 1 M HCl. In the first stage, the titration was performed to a phenolphthalein end point to determine carbonate concentration. In the second stage, bicarbonate concentration was determined by continuing the titration to a methyl orange endpoint.

When the scrubber liquor contained sodium hydroxide, a single stage phenolphthalein titration was performed to determine alkalinity.

2.7.4.2 Chloride and Cyanide Ion Selective Electrode Measurement

Occasionally, scrubber liquor samples were analyzed for chloride and cyanide by ion selective electrodes. Samples were prepared by gravity paper filtration to remove oily residue. The concentration of chloride or cyanide was taken from the display of the calibrated pH/ISE meter.

2.7.5 Analysis of Plastic Feedstock

Analyses of the plastic feedstock were performed during some runs to roughly determine the nature of the resin types in a feed mixture. The plastic was immersed in a 10% solution of sodium chloride, where polyethylene, polypropylene and polystyrene float. The floating and sinking materials (PET and PVC) were separated, rinsed, dried and weighed to determine the concentration of low and high density plastics. If the plastic mixture was in pellet form, it was possible to visually separate the high density materials by resin type.

2.8 Off-Site Chemical Analyses

Many analyses of samples from the project were performed by contract laboratories or laboratories located off-site. All of these analyses are included with the supporting documents to this report.

The following sample analyses were performed:

Oil

- Gas chromatography/mass spectrometry analyses
- Physical properties characterizations
- Elemental analyses
- Fractional distillation

Solids

- Elemental analyses
- TCLP characterizations
- Particle size distribution

Scrubber liquor and other water samples

- Volatiles and semi-volatiles by GC/MS analyses
- Chemical and physical properties characterizations
- Elemental analyses

Plastic feedstock

- Analyses to determine resin type and concentration
- Elemental analyses

2.9 Methods Used For Yield Calculations

During the course of the project, yields were calculated by one of several related methods. Yield calculations changed primarily with the evolution of better methods for oil and gas measurement. As the project matured, the instrumental configuration of the unit evolved considerably and the reliability of oil and gas measurement devices increased substantially. Excellent yield data are available for nearly all runs that were conducted during the parametric study. Currently, the DART unit provides good measurement capabilities in the following five areas that are crucial to calculation of product yields: feed, heavy oil, light oil, gas and solids. The locations, and configurations of the actual measuring devices are described in section 2.3.

The operator feed control station records the weight of feed that was utilized during a run. Before Run 58, it was only possible to measure the weight of pelletized plastic that was processed. This measurement was accomplished by means of a floor mounted scale.

Heavy and light oil production were measured in one of three ways (listed in decreasing order of reliability and consistency): gauge glass measurement of sump oil level, strain gauge measurement of oil collected in the storage tanks and capacitance probe measurement of sump oil level. Currently, gauge glass measurements are utilized for both sumps. Specific gravities of the heavy and light oils were determined to be approximately 0.8 and 0.7, respectively at sump operating temperatures of 140 °F (heavy oil) and 50 °F (light oil). The geometric dimensions of the sumps were used to calculate the sump volumes at 0.5 in. increments. These estimated volumes and specific gravities were used to calculate the weight of oil produced over a given interval during a run. Verification of level measurements was performed by comparison of sump level calculations with the weight of oil collected in the storage tanks. Before installation of the gauge glasses after Run 26, oil production was based solely on the net weight of oils collected in the storage tanks. Capacitance probe measurements were primarily used for calculations during the shakedown runs. During runs in which oil with high levels of organochlorides (>100 ppm) were produced, the oil was pumped into 55-gallon drums. For these runs, only the gauge glass measurements were available for oil production measurements.

Gas flow rates were measured by rotameters. Total gas production volume was converted to weight after correcting for specific gravity and the volume of nitrogen which was added as a sweep gas in several parts of the unit.

Solids production was based on the weight of solids collected in a 55-gallon steel drum resting on a platform scale.

Before Run 26, heavy aliphatic hydrocarbons (waxes) condensed in the end bell and accumulated in the solids collection system. Analysis of the solid product by hot xylene washes revealed virtually no carbon residue. In these cases, the calculated oil yield is the cumulative total of liquid and wax production.

3. Pyrolysis Within The DART Unit

3.1 Pyrolysis

In true pyrolysis, organic materials are thermally decomposed within an oxygen-free, externally heated, temperature-controlled environment. Materials are fed at a controlled rate directly into the oxygen-free environment which is maintained at a controlled temperature of sufficient magnitude to ensure complete thermal degradation of the polymers.

For polymers such as thermoplastics, the pyrolysis process proceeds through the following steps:

- Melting of the polymer
- Heating of the liquid to incipient depolymerization temperature
- Thermal depolymerization (decomposition) of the polymer chain
- Volatilization of the low molecular weight products

As a result of pyrolysis, liquids, solids and noncondensable gases are produced. Polymers such as polypropylene, polyethylene and polystyrene are ideal feedstocks for pyrolysis because they consist entirely of carbon and hydrogen. Products from the pyrolysis of these types of materials therefore consist predominantly of light gases (such as hydrogen, methane and C2 - C4 gases), aromatic and aliphatic liquid hydrocarbons and minor amounts of coke.

In the DART unit, the pyrolysis process is thought to occur in the retort as shown in Figure 15.

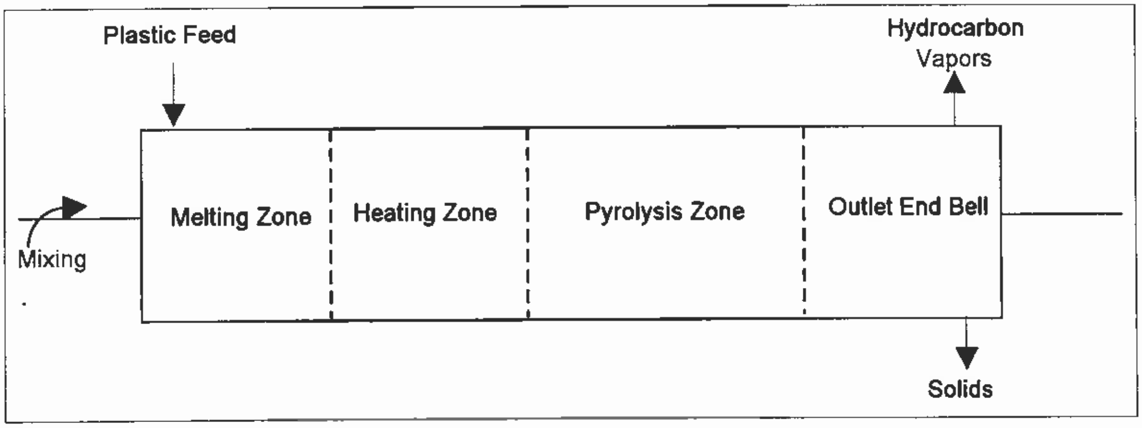

Figure 15 Pyrolysis within the DART unit

Plastic feedstock is introduced to the inlet end of the retort as a solid, where it melts. In the melting zone, the process auger gradually moves the semi-molten material away from the inlet while spreading the material over a wide area of the retort circumference. However, as the material melts and starts to depolymerize, its viscosity decreases and it accumulates as a liquid on the bottom of the retort.

In the melting and heating zone of the retort, the temperature of the lower retort surface increases in the direction of the outlet due to the large amount of heat required to melt the solid polymer material. As the semi-molten material moves through the heating zone, it continues to absorb heat from the lower retort surface until it reaches its depolymerization temperature. In the pyrolysis zone, the material depolymerizes and volatilizes. It is thought that melting, heating and decomposition of plastics do not occur as discrete processes within specific areas of the retort. Rather, it is likely that these processes occur simultaneously to some degree in all retort regions, since the process auger is operated in a cyclic forward-reverse rotation. There is thought to be even less separation of the various pyrolysis processes within the retort when the plastic feedstock contains different polymers, each with different melting and decomposition temperatures. However because of the temperature gradient within the retort most of the depolymerization and volatilization probably does not occur until the later half of the retort.

Hydrogen chloride (HCl) is produced by thermal decomposition of polyvinyl chloride (PVC) beginning at about 450 °F. When the plastic feedstock contains PVC, lime hydrate [$Ca(OH)_2$] is mixed with the plastic as it enters the inlet end of the retort. When the mixture of molten plastic and lime hydrate reaches 450 °F, liberated HCl is neutralized by reaction with the lime hydrate to form calcium chloride ($CaCl_2$) and water. Carbon dioxide (CO_2), hydrogen cyanide (HCN) or ammonia (NH_3) may be produced by thermal decomposition from polymers that contain oxygen or nitrogen as part of their molecular skeletons. It is thought that HCN and CO_2 are also neutralized by reaction with the lime hydrate.

3.2 Temperature Measurement

It is not possible to directly measure the pyrolysis reaction temperature in the DART unit. Because of this, it was necessary to establish an alternate means of measuring the retort temperature in order to approximate the actual pyrolysis temperature. Figure 7 shows the locations of the thermocouples within the shaft of the process auger. For all further discussions in this report, the *retort temperature* is defined as the temperature measured at thermocouple #3 (TC3). The *furnace temperature* is measured by thermocouples #8 and #9 (TC8 and TC9).

For a typical run (base feed at 100 lb/hr, furnace temperature at 1100 °F), the temperature near the inlet or feed entrance (TC1) is usually 200 °F lower than the mid-point of the retort (TC3) and 50 °F lower than TC5 near the outlet end of the retort.

3.3 Hydrocarbon Product Distribution

As stated previously, one of the primary goals of the project was to characterize the hydrocarbon product distribution from the pyrolysis of a variety of single polymers, polymer blends and waste plastic mixtures. In the DART unit, the hydrocarbon product distribution is dependent upon the following variables:

- Type of polymer(s)
- Pyrolysis severity

Hydrocarbon partial pressure is often an important variable in pyrolysis reactors because it determines how long the reactants are in the reactor and can greatly influence the product yields and compositions. Partial pressure does not play a major role in the DART unit for two reasons. First, the DART unit operates at slightly less than ambient pressure. Second, nitrogen gas that is added to the feed system partially lowers the hydrocarbon partial pressure within the retort. It is thought that the combined effect of the these factors may somewhat lower the propensity for coke formation in the DART unit. However, these factors are not thought to significantly affect the pyrolysis reactions in any other way.

In the DART unit, the pyrolysis product distribution was thoroughly investigated for a number of single and mixed polymers at several different levels of pyrolysis severity. These investigations are discussed generally below and in detail by polymer type in Section 4.2.

3.3.1 Type of Polymer

The type of polymer used as feedstock in the DART unit greatly affects the hydrocarbon product distribution. At low levels of pyrolysis severity (severity is discussed below), the carbon-carbon bond rupture is the dominant reaction process and results in products that resemble the molecular skeleton of the polymer. Polyolefins produce aliphatic hydrocarbons (primarily alpha olefins) and polystyrene produces high yields of styrene, with some styrene dimer and other alkyl aromatic compounds. Polymers like PET, PVC and polyurethane contain atoms other than carbon and hydrogen and decompose in a more complicated manner that is dependent upon severity and their molecular structure.

Results of the pyrolysis work at Conrad Industries confirmed related studies at the Energy and Environmental Research Center (EERC) in which a fluidized bed reactor was used. Both studies demonstrated that the different types of polymers depolymerize at different temperatures and that significant molecular rearrangements occur at elevated temperatures. Blends of various polymers also had a tendency to depolymerize at lower temperatures than the individual polymers in the blend. Similar results were found in this program using the DART unit.

Polystyrene and polypropylene depolymerize at lower temperatures because they have benzylic and tertiary carbons which can form more stable carbocations or radicals than carbon atoms found in polyethylene. The first step in depolymerization is either breaking a carbon-hydrogen or carbon-carbon bond. These bonds are easier to break if the resulting carbocation or radical can be stabilized by a larger carbon backbone. Aromatics and branched aliphatic backbones greatly increase this stability and lower the depolymerization temperatures.

The studies at Conrad Industries also confirmed EERC results, in which it was easy to depolymerize materials such as polypropylene and polystyrene and that these polymers can facilitate or catalyze the depolymerization of other polymers. For example, a 50:50 mixture of PP:HDPE completely depolymerized before ever reaching the depolymerization temperature for HDPE. The products also contained higher yields of liquid products than would PP if it were pyrolyzed alone at that temperature. These results are consistent with a mechanism where depolymerization begins in the polypropylene backbone. The resulting products are a mixture of PP, HDPE and joint PP-HDPE decomposition products and are more resistant to further depolymerization than PP decomposition products are alone. These results led to the use of a base mixture of HDPE:PP:PS for the DART program.

Substantial thermal rearrangements of the polymer chain occurred at elevated temperatures. For polyethylene and polypropylene, pyrolysis temperatures around 1300 °F produced elevated yields of aromatic products and noncondensable gases and decreased yields of aliphatics. At these temperatures two competing decomposition mechanisms must be occurring: a chain cleavage mechanism to produce lower molecular weight products in the C1-C5 range and a cyclization-dehydrogenation process to produce stable aromatic compounds. At higher DART retort temperatures, high yields of aromatics are seen.

3.3.2 Pyrolysis Severity

Results from several other pyrolysis research programs indicate that many factors determine the completeness of the pyrolysis process and the composition of products. For this study, the term 'þyrolysis severity" is used as a relative measure of the severity of the process conditions and the completeness of decomposition of the polymer feedstock. Pyrolysis severity greatly influences the hydrocarbon product distribution and severity is affected by the following variables:

- Temperature
- Polymer feed rate
- Residence time

For most of the studies, the feed rate was controlled at between 100 lb/hr and 120 lb/hr. Residence time is hardware-dependent and affected by the feed rate. It is discussed separately below. For a given polymer feedstock under these conditions, temperature is thought to be the predominant pyrolysis variable in most of the DART studies.

Under conditions of low severity in the DART unit, decomposition to relatively large molecular homologues of the polymer skeleton occurs. As a result, coke formation is low, overall gas production is low and the concentrations of hydrogen and methane are low.

At higher severity (i.e. high temperatures), more coke and larger amounts of gas with higher concentrations of hydrogen and methane are produced. As pyrolysis severity increases, oil production declines and the degree of unsaturation of the oil increases. Oil produced under conditions of high severity is highly aromatic (see section 3.3.1).

A commonly used indicator of operating severity is the temperature at the outlet of the retort, but because of mechanical conditions, it was not practical to install a thermocouple in the retort outlet. Some indication of temperatures reached within the retort was provided by temperatures measured by thermocouples installed at specific points within the hollow shaft of the process auger (see Figure 7).

3.3.3 Residence Time

Residence time is a measure of the time between the start of incipient cracking and the exit of pyrolyzate from the retort. Higher feed rates shorten the residence time because elevated gas production increases the velocity of the gas. At extremely high feed rates, molten liquid can accumulate in the solids collection system.

4. Results and Discussion

During the project, 76 runs were completed. The runs are classified into the following categories according to run objectives and results:

- Shakedown runs
- Parametric study
- Post-consumer plastic studies
- Recycling of wax and chlorinated oils

Appendix 8.7, Run Classifications, lists all of the runs, denoting dates, feedstock, objective and run results. Runs that are classified as aborted in Appendix 8.7 will not be further discussed unless the run produced significant valuable information.

A standard resin mixture was utilized for all of the shakedown runs and many of the runs in the parametric study. This mixture is denoted as the "base" blend for the project and was designed to be roughly representative of a typical post-consumer plastic waste stream. The resin types and concentrations in the base blend are listed below.

High-Density Polyethylene	60%
Polypropylene	20%
Polystyrene	20%

4.1 DART Shakedown Runs

All but two of the shakedown runs took place at the beginning of the project. The purpose of these runs was to check the operability of the DART unit, observe system behavior, determine operating conditions for maximum liquid yields and operate the unit at various feed rates. Prior to the start of these studies, a crumb rubber feedstock, prepared from tire tread, was fed to the DART unit at feed rates approaching 400 lb/hr with no indication of major difficulties.

4.1.1 Initial

The focus of the initial shakedown runs was to successfully operate the DART unit for an extended period of time without major mechanical or operating difficulties. In accordance with the original Test Plan (section 8.1), the first shakedown run was made at a furnace temperature of 1250 °F and base resin feed rate of 140 lb/hr. After four hours of operation, the run was aborted because incompletely pyrolyzed resin plugged the inclined auger in the solids collection system. Seven more short runs were performed during the first two weeks of operations. During this time, various mechanical and operational problems were debugged. During two of the trouble-free periods, AM-TEST Air Quality, Inc. performed extensive monitoring of emissions from the flare and retort furnace stacks.

In Runs 7,8 and 9, the operating reliability of the DART unit was established. Run 9 was the first long run that was not aborted due to mechanical or operating difficulties. Table I lists the results of Run 9.

Table I Operating and yield data from Run 9

Feed Rate	Furnace Temperature	Hours of Operation	Liquid Yield	Gas Yield
100 lb/hr	1450 °F	30	35%	65%

4.1.2 Process Optimization

With operability of the DART unit established, the focus of the remaining shakedown runs was to observe system behavior, determine operating conditions for maximum liquid yields and operate the unit over a range of feed rates.

Run 10 was conducted with a base resin feed rate of approximately 50 lb/hr. During the 96-hour run, the furnace temperature was lowered in four steps from 1300 °F to 1000 °F. As the furnace temperature was lowered, the liquid yield increased dramatically. A yield of approximately 80% was achieved at the end of Run 10, as shown in Figure 16. However, at the lowest furnace temperatures, a significant amount of moist material was collected in the solids collection drum. This material was identified by gas chromatography as a wax comprised of a mixture of C25-C50 aliphatic compounds.

The objective of Run 11 was to increase the feed rate in a controlled fashion to a value greater than 100 lb/hr. This run lasted 66 hours and was conducted over a range of furnace conditions. A feed rate of 120 lb/hr was achieved at the end of the run. In an attempt to reduce wax production, the furnace was controlled so that a temperature gradient was established within the furnace chamber. The maximum gradient resulted from temperatures of 1060 °F at the inlet end of the furnace chamber and 1220 °F at the outlet end. No reduction in wax production resulted from these furnace temperature gradient tests.

Runs 12-16 focused on reducing wax production by the use of various furnace temperature gradients. None of these efforts were successful, so the experiments were abandoned for the purpose of commencing with the parametric study. High wax yields were a result of design inefficiency in the end bell and were resolved when improvements were made in the end bell.

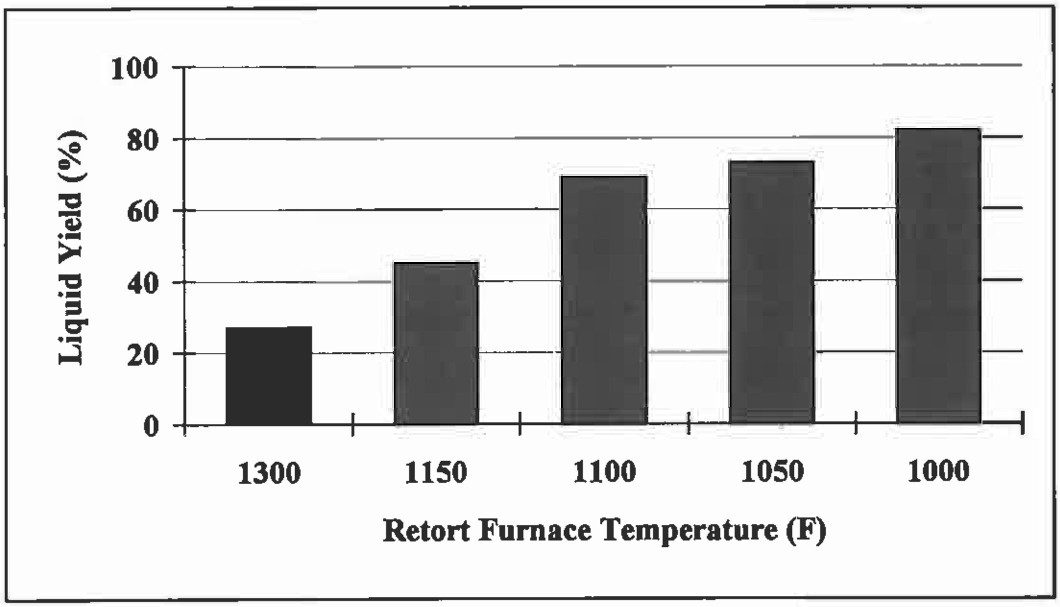

Figure 16 Liquid yield during Run 10

Several important mechanical additions and modifications to operating practices were made on the DART unit during the shakedown runs. After Run 9, the level capacitance probes in the high and low temperature condenser sumps were calibrated in weight units using diesel fuel. Use of these probes was later abandoned. During Run 10, thermocouples were installed at several points in the hollow shaft of the process auger. During Run 12, the practice of entering operating data on the computer was initiated. The retort sampler was commissioned during Run 12 and modified to its final configuration (see Figure 14) by Run 16. The rotary airlock that separated the outlet end bell from the solids collection system was also replaced by a simple gate valve during Run 12. A weigh scale was installed during Run 13 to measure the weight of material accumulating in the solids collection system. The safety practice of purging the solids auger with nitrogen was initiated in Run 14 to reduce the accumulation of pyrolysis gas in the solids collection system.

Gas flow measurements were suspected to be inaccurate throughout the shakedown runs. It was only after Run 24, when conventional rotameters were installed, that the gas flow measurements were considered to be reliable. Although hourly estimates of liquid production proved unreliable because of operating difficulties with the capacitance probes, the overall production of liquids was accurately measured by the strain gauges on the two 4,000-gallon oil storage tanks.

It should be pointed out that during the shakedown runs, the condition of the inside surface of the retort was unclear. It is now known that the interior surface of the retort becomes coated with hard amorphous carbon approximately ½" thick, which is the distance between the retort shell and the blades of the process auger. There is no indication of carbon spalling, so it must be assumed that this carbon coating is always present. The shakedown runs and yield calculations may have been affected by gradual carbon buildup from an initial clean surface condition.

The American Plastics Council/Conrad Industries, Inc. test program had targeted resin feed rates of 300 lb/hr but the maximum achieved during the shakedown period was less than 150 lb/hr. The reason for this is discussed in section 4.2.2.

4.2 Parametric Study

The general objective for the parametric study was to demonstrate the capability of pyrolysis for recycling many different combinations of resin types which might be encountered in post-consumer plastic packaging. To accomplish this objective, a variety of resin blends were studied under a range of different operating conditions using the DART unit. Initial studies used virgin resin in the form of "base blend". Later, several post-consumer plastic samples from a variety of sources were evaluated. The DART unit was used as a model for larger Conrad units and other pyrolysis designs. Excellent data and a better overall understanding of pyrolysis of waste plastics was achieved. However, the DART unit, because of its smaller size and older design provided limitations to achieving some of the initial goals (namely capacity). The initial goals of the parametric study were the following:

- Determine the limitations of pyrolysis for handling certain resin types and critical impurities.
- Evaluate conditions and techniques to maximize oil yield.
- Evaluate conditions and equipment design to increase capacity.
- Produce marketable oil with low levels of organochlorides.
- Develop an understanding of the gas, liquid and solid product compositions that result from variations in resin types and operating conditions.
- Develop an understanding of the process chemistry for different resin feedstocks and operating conditions.
- Compile data to be used for scale-up to a commercial recycling unit.

The parametric study is broken down into eleven major areas of emphasis according to type of feedstock. The discussion that follows focuses on product and compositional yields, process chemistry and process operation at a variety of operating conditions. A large number of runs were conducted using resin blends containing >95% base resin with low levels of PVC, PET or other material. Runs that utilized these slightly altered base resin blends provide valuable comparative information and are summarized in Section 4.2.12 in addition to sections dealing specifically with PVC, PET and other spiked feedstocks.

For most of the studies, a concerted effort was made to operate under similar conditions for all runs, so that valid comparisons could be made between the runs. Therefore, the target feed rate was 100-120 lb/hr for most runs. It is important to note that a large number of mechanical and operating improvements were made to the DART unit during the project. In some cases, these improvements may have significantly altered the pyrolysis process to a degree that may have impacted product and componential yields and process chemistry.

The following discussions refer frequently to retort temperature, which is defined in section 3.2.

4.2.1 Base Feed

Base resin (60:20:20 ratio of HDPE:PP:PS) was utilized for all of the shakedown runs and several of the runs in the parametric study. The first comprehensive study of base resin pyrolysis took place during Run 21. In this run, base resin was recycled at three different retort temperatures, 1100 °F, 980 °F and 890 °F. It can be seen from the yield data in Table II that oil production at 890 °F was more than twice that at 1100 °F. The gas yield dropped significantly over the same temperature range.

Table II Operating data and yields for Run 21

Run Number	21A	21B	21C
	Operating Conditions		
Feed Rate (lb/hr)	126	125	128
Furnace Temp. (°F)	1300	1200	1100
Retort Temp. (°F)	1100	980	890
	Normalized Yields (wt%)		
Oil Yield	35.0	63.0	79.0
Gas Yield	61.0	37.0	21.0
	Gas Component Yield (wt%)		
Hydrogen	0.12	0.04	0.02
Methane	4.6	2.0	0.7
Ethane	1.0	0.8	0.4
Ethylene	8.8	4.5	1.7
Propane	2.0	1.7	1.1
Propylene	14.6	8.1	3.7
Total C4's	16.7	11.2	5.9
Other	13.0	8.9	7.7

Table II Continued

Run Number	21A	21B	21C
Retort Oil Component Yield (wt%)			
Total Aliphatics	9.0	23.9	27.2
≤ C10	4.8	12.0	11.9
C11 - C20	2.9	6.6	7.4
> C20	1.3	5.3	7.9
Total Aromatics	22.2	29.0	36.9
Benzene	1.9	1.2	0.7
Toluene	5.3	5.5	6.9
Styrene	6.5	10.0	14.4
Unidentified	3.8	10.1	14.9

Table II shows that for Run 21, all of the gas componential yields decreased as the retort temperature decreased. The decrease in the yields of methane and hydrogen were more pronounced than for the other gas constituents.

Oil produced at a retort temperature of 1100 °F contained a higher aromatic/aliphatic ratio than oil produced at lower temperatures. The individual yields of the predominant aromatics in Run 21 show some interesting trends. Benzene concentrations increase at higher temperatures by a factor of three while toluene levels remain relatively unchanged. However the yield of styrene decreases as the temperature is increased. At high temperatures, it is not known whether styrene is lost through formation of dimers or through further breakdown to benzene and smaller hydrocarbons. Styrene is discussed further in section 4.2.3. Both high aromatic content and high benzene yield are expected at high pyrolysis severity because increased cyclization and dehydrogenation of aliphatic compounds are known to take place at elevated temperatures. The total yield of C21+ aliphatics was five times higher at a retort temperature of 890 °F than at 1100 °F, while the corresponding yields of C11-C20 and <C11 aliphatics were about two times higher. The high yields of heavy aliphatic compounds at lower temperatures help explain the presence of wax in the solids collection system. This topic is discussed later in this section.

Boiling range distributions of the retort oil produced during Run 21 under the three retort temperature conditions are shown in Figure 17 in graphical format.

As noted previously, accumulation of C25-C50 waxes in the solids collection system occurred during the shakedown runs and the first few parametric study runs. It is thought that the production of these compounds and their subsequent segregation in the solids collection system are due to three main factors. First, the low severity conditions that give rise to high oil yields are also responsible for less energetic decomposition of the polymer skeletons of PE and PP. This results in higher concentrations of aliphatic decomposition products in the C25-C50 range.

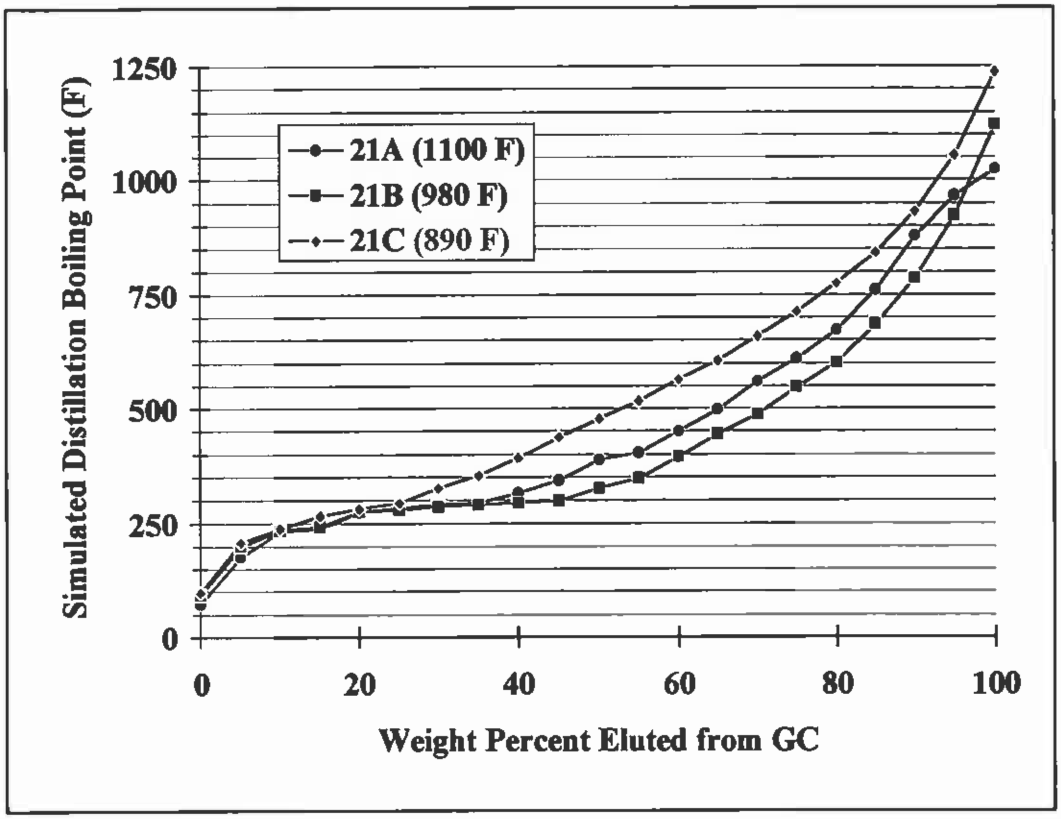

Figure 17 Boiling range distributions of retort oil from Run 21.

The retort temperature for each data series is indicated in parentheses.

Second, the inner surface of the outlet end bell is significantly cooler (~200-300 °F) than the hot pyrolyzate gas as it exits the retort. Molecular decomposition products with boiling points above the temperature of the inner end bell surface may therefore condense before reaching the first quench fitting in the high temperature condenser. Third, under conditions of low pyrolysis severity, the total molar gas production is also low, which results in a raising of the dew point of the retort gases. It is thought that low gas production exacerbates the problem of inner end bell condensation by allowing the hot pyrolyzate gas more time to pass through the cold end bell. The problem of wax accumulation in the solids collection system was solved after Run 26. The material collecting in the solids collection system consisted of dry carbon spalls (1/8" diameter flakes) which were probably formed by the process auger scraping against the retort walls (which are usually covered with a hard amorphous carbon deposit). The heavy aliphatic fractions were collected in the high temperature condensing system.

Gas chromatography/mass spectrometry (GC/MS) analysis of oil produced from base resin was performed by the Mass Spectrometry Facility at Montana State University in Bozeman, Montana. The oil was a composite sample of liquid product from the first 24 runs. The GC/MS analysis, a numerical analysis of the GC/MS data and accompanying explanatory information are listed in section 8.4 of the Appendix.

The physical and chemical properties of several oil samples produced from base resin were determined by Comsource American in Pasadena, Texas. The analytical results are shown in Table III and include information for two different samples. The sample identified as B06161445.PO was removed from the product storage tank on 6/16/93, after the first ten shakedown runs. The sample identified as B08161600.PO was removed from the product storage tank after the last shakedown run (Run 16), and is representative of an oil shipment sent to Lyondell Petrochemicals in Houston, Texas on 11/8/93.

Table III Physical and chemical properties of oil produced from base resin

Analysis	B06161445.PO	B08161600.PO
Specific Gravity	0.98	0.87
Flash Point, PMCC, °F	36	<20
Reid Vapor Pressure, psi	1.30	4.1
pH	4.7	5.8
Pour Point, °F	<30	20
Viscosity @ 75 °F, cst	2.65	3.50
Viscosity @ 122 °F, cst	1.73	1.50
Sulfur, ppm	391	649
Nitrogen, ppm	549	2081
Organic Halides, ppm	46.5	49.2
Inorganic Halides, ppm	69.5	67.8
Water, Karl Fischer, wt%	0.08	1.35

After Run 42, the inventory of base resin was insufficient for further testing, so additional base resin was ordered from Muehlstein. However, during initial tests with the new base blend during Run 43, serious operational difficulties developed that were related to incomplete pyrolysis of the resin mixture. Subsequent analysis by APC revealed that a significant portion of the new base blend was ultrahigh-molecular-weight high-density polyethylene (UHMWPE) rather than regular HDPE. Thermal depolymerization of UHMWPE is expected to require substantially higher temperature than regular HDPE due to the lack of branching and reactive centers. It is therefore strongly suspected that the difficulties experienced during Run 43 were a direct result of the presence of UHMWPE in the new base resin blend. This feedstock was not utilized for any further testing.

4.2.2 Capacity

The original APC/Conrad test plan assumed that resin feed rates of 300 lb/hr would be possible in the DART unit. However, beginning with the first shakedown run and continuing with several parametric study runs, it became apparent that this feed rate objective would be difficult to reach if high liquid yields were also to be attained. Attempts were made to determine the capacity (maximum feed rate possible) of the DART unit during Runs 22, 45 and 47. All of these runs were eventually suspended by the appearance of incompletely pyrolyzed resin in the solids collection system when the resin feed rates approached values near 200 lb/hr. The capacity of the DART unit was therefore defined as the maximum feed rate attained before the appearance of unpyrolyzed resin. A good approximation of the capacity of the DART unit for recycling base resin was attained during Run 45 (see Table IV), when a feed rate of 178 lb/hr was sustained for 14 hours without interruption or difficulty.

Table IV Operating and yield data from Run 45

Feed Rate	Furnace Temperature	Retort Temperature	Hours of Operation	Liquid Yield	Gas Yield
178 lb/hr	1450 °F	930 °F	14	68%	32%

The pyrolysis process consists of four endothermic steps: melting the plastic feedstock, heating the molten plastics to depolymerization temperature, depolymerization of the plastics and volatilization of the products. The critical factors which govern the capacity of the unit are feedstock type, temperature, heat transfer, and residence time. The DART unit is a single stage pyrolysis demonstration unit and has a relatively short retort, which results in a limited residence time.

At high feed rates, excessive amounts of waxy materials were produced and collected in the solids collection drum. This suggests that to increase the capacity of the DART unit, the residence time of the liquid polymer in the retort must be increased to allow it enough time to reach depolymerization temperature and complete the decomposition to volatile products.

The capacity of the DART unit for plastics was originally estimated at 300 lb/hr based on experience with the pyrolysis of crumb rubber from scrap tires at that feed rate. The discrepancy between the original tire-based feed rate objective and the results of DART capacity experiments derives from two major differences in the way that base resin and tires decompose in the unit. First, the thermal energy required to decompose tires to volatile products is less than that required for base resin. (Roughly 30% of the tire feedstock is carbon, which remains relatively unchanged by addition of heat.) Second, the efficiency of tire pyrolysis in the Conrad/Kleenair system is probably inherently greater than that for most plastics. It is believed that the tire feedstock is exposed to a large circumferential area of the inner retort surface by the interaction of the tire pieces with the process auger. Plastic is envisioned to rapidly melt and maintain contact as a liquid only with the lower retort surface. The combination of slightly higher efficiency with lower thermal energy requirement for decomposition results in a higher capacity of the unit for tires than for base resin.

The capacity of the DART unit for Polystyrene feedstocks is significantly greater than that for base resin. In Run 50 (discussed in detail in the next section), a feed rate of 250 lb/hr was achieved for 100% PS without any difficulty. It is estimated that for 100% PS, a feed rate substantially greater than 250 lb/hr would be attainable on the DART unit without further equipment modifications. The higher capacity of the unit for polystyrene is due to the ease at which polystyrene depolymerizes to a volatile product - styrene.

4.2.3 Polystyrene and Base Feed Spiked With Polystyrene

The pyrolysis of base resin spiked with 20% PS was studied during Run 18. The resin concentrations in the feed mixture are listed below.

High-density polyethylene	48%
Polystyrene	36%
Polypropylene	16%

During Run 18, the PS-spiked feed was recycled at three different retort temperatures, 1100 °F, 1000 °F and 910 °F. Table V lists the operating conditions, product yields and oil componential yields for the study. As with base resin, the yield of oil with a retort temperature of about 900 °F was roughly twice that for 1100 °F. Not surprisingly, the yield of aromatics was higher for PS-spiked feed than for base resin at all temperatures. When the retort oil yield of styrene is compared with the concentration of PS in the feed, the actual yield of styrene from PS can be calculated. These actual styrene yields are 22%, 36% and 47% for retort temperatures of 1100 °F, 1000 °F and 910 °F, respectively. It was expected that benzene would be a favorable decomposition product from resin blends high in PS, but the amount of benzene produced was surprisingly low.

Table V Operating data and yields for base feed and PS (Run 18)

Run Number	18A	18B	18C
	Operating Conditions		
Feed Rate (lb/hr)	110	113	110
Furnace Temp. (°F)	1300	1200	1100
Retort Temp. (°F)	1100	1000	910

Table V Continued

Run Number	18A	18B	18C
Normalized Yields (wt%)			
Oil Yield	36.0	52.0	77.0
Gas Yield	61.0	48.0	23.0
Retort Oil Selected Component Yield (wt%)			
Total Aliphatics	6.9	14.8	24.9
Total Aromatics	25.6	31.5	38.7
Benzene	2.1	1.1	0.9
Toluene	5.8	5.6	6.2
Styrene	7.6	12.8	16.9

100% PS was recycled during Runs 50 and 51. Run 50 used virgin PS pellets, while Run 51 used ground, densified post-consumer polystyrene supplied by Mobil. As shown in Table VI, the oil yields for both runs were extremely high, near 95%. Tables VII and VIII include process data and information from the raw GC analyses which provides insight into the PS depolymerization process. The designation of Styrene dimers in Tables VII and VIII refers to the total FID area percent for a group of prominent GC peaks that are suspected to comprise the various homologues of styrene-styrene dimers with GC retention times slightly longer than that for biphenyl.

Table VI Product yields from Runs 50 and 51

	Run 50	Run 51
Oil Yield (wt%)	95.6	94.0
Gas Yield (wt%)	3.5	6.0

In Run 50, PS was introduced to the DART unit at three different feed rates, 150, 195 and 250 lb/hr. At 250 lb/hr, PS pyrolysis was studied at retort furnace temperatures of 1250 °F and 1400 °F. It can be seen from Table VII that at high retort temperatures (GC Runs 733, 738 and 748) the concentrations of benzene and toluene are elevated with respect to methyl styrene and the styrene dimer peak group. At low temperatures (GC Runs 741, 742 and 743), the opposite is true. In addition, the concentration of methane in the pyrolysis gas was as high as 6.6% under high temperature conditions and as low as 2.9% at low severity. It appears from Table VII that there is a delicate relationship between styrene concentration and pyrolysis temperature. Unexpectedly, the concentration of styrene in the oil was highest at the intermediate/high severity level found in GC Run 748 and not at a low severity level such as for GC Run 743. The liquid yield for Run 50 was about 96%, which resulted in a 58% yield of styrene monomer.

Table VII Selected GC and process data from PS (Run 50)

GC Run No.	733	738	741	742	743	748
Sample I.D.	6/1 14:40	6/2 02:00	6/2 10:30	6/2 14:45	6/2 16:50	6/3 00:00
Feed Rate (lb/hr)	150	150	195	195	250	250
Furnace Temp. (°F)	1250	1250	1250	1250	1250	1400
Retort Temp. (°F)	1025	1002	915	898	837	981
Total Aliphatics	5.9	8.0	11.7	14.3	13.8	8.2
Total Aromatics	93.0	90.8	87.3	84.5	84.7	91.0
Benzene	0.8	0.4	0.3	0.3	0.2	0.6
Toluene	12.4	9.8	6.6	5.7	5.7	8.9
Ethyl Benzene	9.0	6.7	5.7	6.2	7.2	5.7
Styrene	59.3	61.1	62.1	59.1	56.9	64.9
Methyl Styrene	5.5	6.3	7.3	8.0	10.4	5.8
Styrene Dimers	2.9	4.9	8.4	10.4	10.5	5.4

During Run 51, it was impossible to measure the feed rate of the finely ground PS feedstock, so the yield values in Table VI were calculated from oil and gas production data. In this run, PS pyrolysis was studied at retort furnace temperatures of 1250 °F and 1100 °F. Table VIII shows that the pyrolysis results for Run 51 agree reasonably well with those for Run 50. However, the concentrations of benzene and toluene in GC Runs 753, 754 and 756 are much higher than for any portion of Run 50. In addition, the styrene concentration is markedly diminished in these runs. It is likely that the higher retort temperature recorded during the time when these samples were taken may have caused more extensive decomposition of the polystyrene. It is also possible that impurities in the waste polystyrene feed or degradation of the feedstock prior to the run may have contributed to the small differences between the data from Runs 50 and 51. The liquid yield for Run 51 was about 94%, which resulted in a 49% yield of styrene monomer.

Table VIII Selected GC and process data from PS (Run 51)

GC Run No.	753	754	756	763	766	767
Sample I.D.	6/8 10:30	6/8 14:00	6/9 02:00	6/9 17:15	6/9 23:00	6/10 01:00
Furnace Temp. (°F)	1250	1250	1250	1100	1100	1100
Retort Temp. (°F)	1054	1051	1070	922	874	884
Total Aliphatics	6.5	7.1	5.6	6.5	8.2	6.5
Total Aromatics	92.8	91.1	93.4	92.4	91.2	92.9
Benzene	1.3	1.4	1.7	0.5	0.4	0.5
Toluene	14.0	14.0	15.7	10.9	9.3	10.2
Ethyl Benzene	15.0	14.2	13.9	13.5	14.5	18.9
Styrene	49.1	48.1	48.6	54.0	56.0	52.0
Methyl Styrene	6.2	6.3	5.5	6.9	7.4	7.4
Styrene Dimers	2.2	2.5	1.9	3.4	4.8	3.3

The data from Runs 50 and 51 suggest that the DART unit is well suited for recycling polystyrene. High feed rates are easily attainable without mechanical difficulties, oil viscosity is relatively low and yields of styrene and other mono-aromatic species are very high. In future investigations, it may be possible to further fine-tune the DART unit specifically for polystyrene processing. Under optimal conditions, feed rates in excess of 300 lb/hr may be achievable on the DART unit with overall styrene yields of 60-65%.

4.2.4 Base Feed Spiked With Low-Density Polyethylene

The pyrolysis of base resin spiked with LDPE was studied during Run 19. The resulting resin concentrations in the feed mixture are listed below.

High-density polyethylene	44%
Polystyrene	15%
Polypropylene	14%
Low-density polyethylene	27%

As with the studies of base resin and base resin spiked with PS, the LDPE-spiked feed was processed at three different retort temperatures, 1100 °F, 1000 °F and 910 °F. Table IX lists the operating conditions, product yields and product componential yields for the study. The yield of oil at a retort temperature of 910 °F was twice that for 1100 °F. Comparison of the LDPE data in Table IX with the data for base resin in Table II reveals that the pyrolysis gas componential analyses for the LDPE-spiked feed are nearly identical to those for the base resin mixture at all three retort temperatures. As expected, the retort oil yield of C21+ aliphatic compounds was significantly less for the LDPE study than for base at retort temperatures of 1100 °F and 1000 °F. However, the C21+ yields are quite similar at 900 °F. The lower yields of C21+ aliphatic compounds can be explained by the extensive branching due to the co-monomer in LDPE. The material is acting more like PP than HDPE. In most other respects, the results of the LDPE study were very similar to those for base resin.

Table IX Operating data and yields for base feed and LDPE

Run Number	19A	19B	19C
Operating Conditions			
Feed Rate (lb/hr)	108	111	104
Furnace Temp. (°F)	1300	1200	1100
Retort Temp. (°F)	1100	1000	910
Normalized Yields (wt%)			
Oil Yield	41.0	52.0	82.0
Gas Yield	56.0	48.0	18.0

Table IX Continued

Run Number	19A	19B	19C
Gas Component Yield (wt%)			
Hydrogen	0.10	0.05	0.02
Methane	4.5	2.4	0.7
Ethane	3.0	2.9	0.9
Ethylene	8.4	5.3	1.5
Propane	1.8	1.9	1.0
Propylene	12.9	9.7	3.1
Total C4's	13.8	13.5	5.2
Other	11.6	12.4	5.6
Retort Oil Component Yield (wt%)			
Total Aliphatics	10.9	19.1	32.3
≤ C10	7.0	11.5	15.3
C11 - C20	3.0	6.0	8.6
> C20	0.9	1.6	8.4
Total Aromatics	25.8	27.0	35.4
Benzene	3.1	1.5	0.8
Toluene	6.4	5.8	6.4
Styrene	6.4	9.0	12.1
Unidentified	4.3	5.9	14.3

4.2.5 Polypropylene

Polypropylene, like polystyrene was easier to pyrolyze than the base resin blend (60% HDPE, 20% PP, 20% PS). During Run 76, pyrolysis of PP at a retort furnace temperature of 1200 °F resulted in a gas yield of 50%, while base resin required temperatures of 1300-1400 °F to reach the same gas yield. In addition, during one portion of Run 76, a retort temperature as low as 800 °F was attained before a relatively small amount of wax began to accumulate in the solids collection system.

Run 57 used a virgin PP feedstock, but only during a four-hour period. Although stable conditions were not reached due to the short duration of the run, valuable preliminary information was obtained. Runs 76A (retort temperature of 930 °F) and 76B (retort temperature of 840 °F) were made from post-consumer PP having an approximate purity of 95% (the balance consisted of polyethylene, cellulose and soil). Oil yields were about 50% for Runs 57 and 76A and 65% for Run 76B and are shown in Table X.

Table X Operating data and yields for PP (Runs 57 and 76)

Run Number	57	76A	76B
Operating Conditions			
Feed Rate (lb/hr)	112	94	94
Furnace Temp. (°F)	1150	1200	1050
Retort Temp. (°F)	905	930	840
Normalized Yields (wt%)			
Oil Yield	~50	48.1	65.7
Gas Yield	~50	49.7	30.9
Gas Component Yield (wt%)			
Hydrogen	0.06	0.05	0.03
Methane	1.2	1.7	0.9
Ethane	2.6	3.2	2.0
Ethylene	1.3	1.8	0.8
Propane	1.4	1.7	1.1
Propylene	12.6	12.3	7.6
Isobutylene	11.5	12.8	7.4
Other C4's	2.0	2.6	1.3
n-Pentane	6.3	5.9	3.6
>*n*-C5	8.8	6.4	5.1
Other	2.2	1.2	1.1
Retort Oil Component Yield (wt%)			
Total Aliphatics	35.4	28.9	44.7
≤ C10	23.7	21.0	28.7
C11 - C20	9.6	5.9	11.5
> C20	2.1	2.0	4.5
Total Aromatics	8.8	10.2	14.0
Benzene	0.6	1.0	0.9
Toluene	1.0	1.3	1.8
Styrene	0.5	1.4	1.7
Unidentified	5.8	9.0	6.9

The componential yield patterns for the gas and oil products from PP pyrolysis are unlike those for any other feedstock. At every temperature during the three runs, gas yields were high and three main components, propylene, isobutylene and n-pentane comprised more than 60% of the pyrolysis gas by weight. These compounds accounted for 31% and 19% of the total hydrocarbon yield at 930 °F and 840 °F, respectively. Another unique feature of the PP gas yields is that the ethane concentration is greater than that for ethylene. The yields of methane and ethylene were nearly equal to each other at both temperatures.

A distinguishing feature of PP pyrolysis is the predominance of a particular C9 olefin in the oil. In the raw oil analyses, the concentration of this single compound is as high as 25% and is five times greater than the concentration for any other species. The compound was identified as 2,4-dimethylhept-1-ene by GC/MS analysis at the Energy and Environmental Research Center (EERC) in Grand Forks, North Dakota. Also present at moderately high concentrations in the oil are a C5 olefin, C6 olefin, several C15 olefins and some C21 olefins.

A detailed discussion of the depolymerization mechanisms for PP is beyond the scope of this report, but the presence of tertiary carbon sites presumably allows facile rearrangements and chain cleavage. One mechanism that explains some of the observed compounds is the Rice-Kossiakoff cracking mechanism* shown in Figure 18.

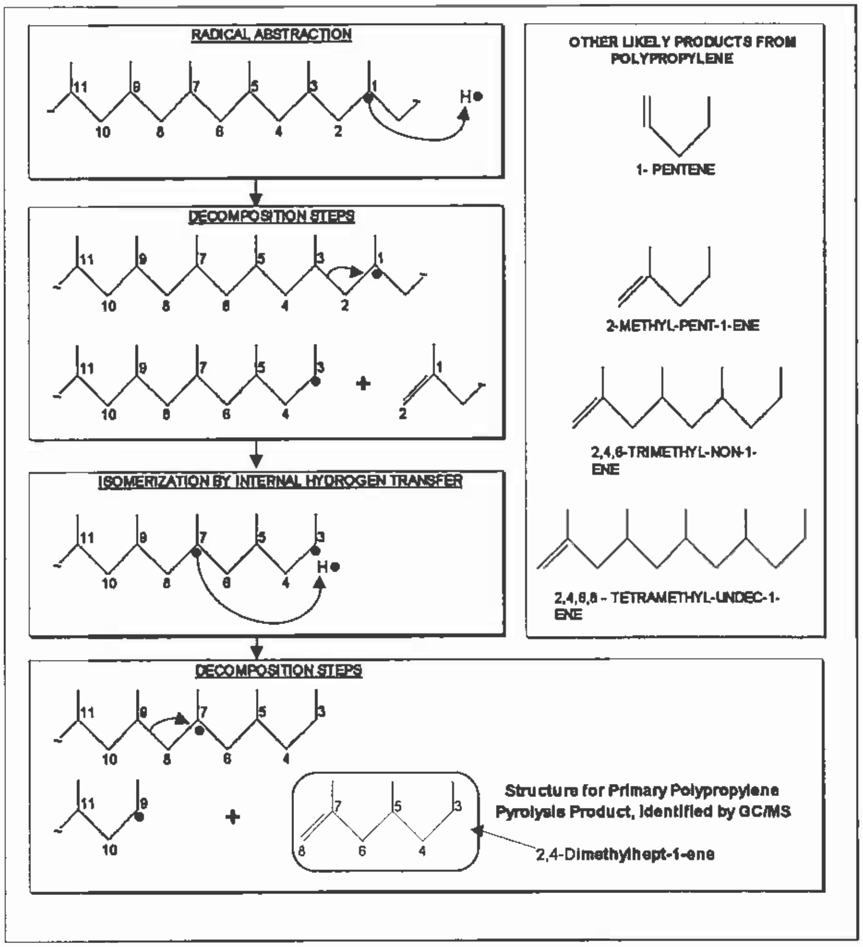

Figure 18 Rice-Kossiakoff cracking mechanism

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* Rebick, C. (1983) *In* "Pyrolysis: Theory and Industrial Practice" (L. F. Albright, B. L. Cymes and W. H. Corcoran, eds.), Academic Press, New York, pp. 69-87.

4.2.6 Base Feed Spiked With Polyethylene Terephthalate

Post-consumer plastics may contain significant levels of PET, and a series of studies were conducted using base resin spiked with PET in varying amounts to study its impact on pyrolysis. Table XI lists the results of these investigations.

Table XI Operating data and yields for base feed and PET (Runs 17 and 20)

Run Number	17A	17B	20
	Operating Conditions		
Feed Rate (lb/hr)	124	117	100
Furnace Temp. (°F)	1300	1200	1450
Retort Temp. (°F)	970	910	1200
	Normalized Yields (wt%)		
Oil Yield	62.0	80.0	32.0
Gas Yield	38.0	20.0	67.0
	Gas Component Yield (wt%)		
Hydrogen	0.04	0.02	0.30
Methane	2.1	0.8	8.5
Ethane	3.2	1.4	3.7
Ethylene	4.1	1.7	11.8
Propane	1.1	0.7	1.3
Propylene	6.3	2.8	12.3
Total C4's	7.9	4.0	8.8
Carbon Monoxide	1.7	1.4	2.9
Carbon Dioxide	1.7	1.7	4.4
≤ C5	9.9	5.5	13.0
	Retort Oil Component Yield (wt%)		
Total Aliphatics	29.2	36.9	5.8
≤ C10	16.4	12.4	1.8
C11 - C20	9.3	16.7	3.1
> C20	3.5	7.8	0.9
Total Aromatics	25.2	28.8	22.8
Benzene	1.9	0.9	5.5
Toluene	4.5	3.0	5.3
Styrene	5.5	6.4	4.1
Filterable Solids (TPA)	0.9	3.6	0
Unidentified	6.7	10.7	3.4

The first study of PET pyrolysis was conducted during Run 17 at furnace temperatures of 1200 °F and 1300 °F with feedstock containing the following resin concentrations:

High-density polyethylene	48%
Polystyrene	16%
Polypropylene	16%
Polyethylene terephthalate	20%

Comparison of Run 17 with the base resin studies in Run 21 show two major contrasts. First, at similar furnace temperatures and feed rates, dramatically different retort temperature profiles existed during the two runs. The auger shaft temperature at the retort inlet (measured by TC1 in Figure 7) was 200 °F cooler during Run 17 than during Run 21. Melting and the decomposition of PET-containing feeds apparently requires substantially more heat than the corresponding PET-free material. Second, in Run 17, extensive production of terephthalic acid (TPA) at low temperatures caused numerous operational difficulties. Since the TPA is a vapor above a temperature of 572 °F (its sublimation temperature), it was entrained in the gas exiting the retort, forming finely divided solids in the high temperature condensing sump where it was difficult to filter from the product oil. One of the two product oil tanks was isolated from the system because these solids had collected there. The solids were present at the same high levels in the retort oil samples and were easily filtered. Following laboratory vacuum filtration and hot xylene washing, off-site analysis revealed the solids to be 95% terephthalic acid (TPA).

The data from Runs 17A and B are listed in Table XI. Excessive production of TPA hindered attempts to operate the DART unit at retort furnace temperatures lower than 1200 °F. TPA yields were about 4 mol% at a retort temperature of 970 °F and 15 mol% at 910 °F. CO and CO_2 yields were nearly identical at both temperatures but were significantly higher during these runs than for any of the runs with base resin. TPA, CO and CO_2 are depolymerization products from PET and are explained later in this section. Benzene was thought to be a potentially important product, but was produced in relatively low yields. It is important to note that approximately 20% of the total peak area in the GC analyses was due to unidentified compounds.

During Run 20, the same feedstock was studied at a higher furnace temperature of 1200 °F with very different results. As shown in Table XI, liquid yields were much lower in Run 20 than in Run 17. CO, CO_2 and benzene yields were higher during Run 20 and the oil was more aromatic. More importantly, there was no sign of solid material in any of the oil samples. It is therefore assumed that TPA is not produced or is destroyed under high temperature conditions.

The depolymerization chemistry of PET is not known. However, some insight into the process can be gained by examination of Figure 19, which shows how some of the compounds that were produced during PET pyrolysis might have been generated. It is thought that TPA is produced under all conditions. If the severity is low, a substantial amount of the TPA does not undergo further decomposition and is collected as a solid in the product oil. (TPA is a solid that easily sublimes which explains its presence in the condensing unit.)

Under high severity conditions, little TPA is observed, and the elevated levels of benzene and carbon dioxide that are observed in the products are thought to result from the breakdown of TPA. Benzoic acid is also detected in the products. The high levels of carbon monoxide and methane may result from decomposition of a possible intermediate product, acetaldehyde. Ethylene is also a likely PET decomposition product.

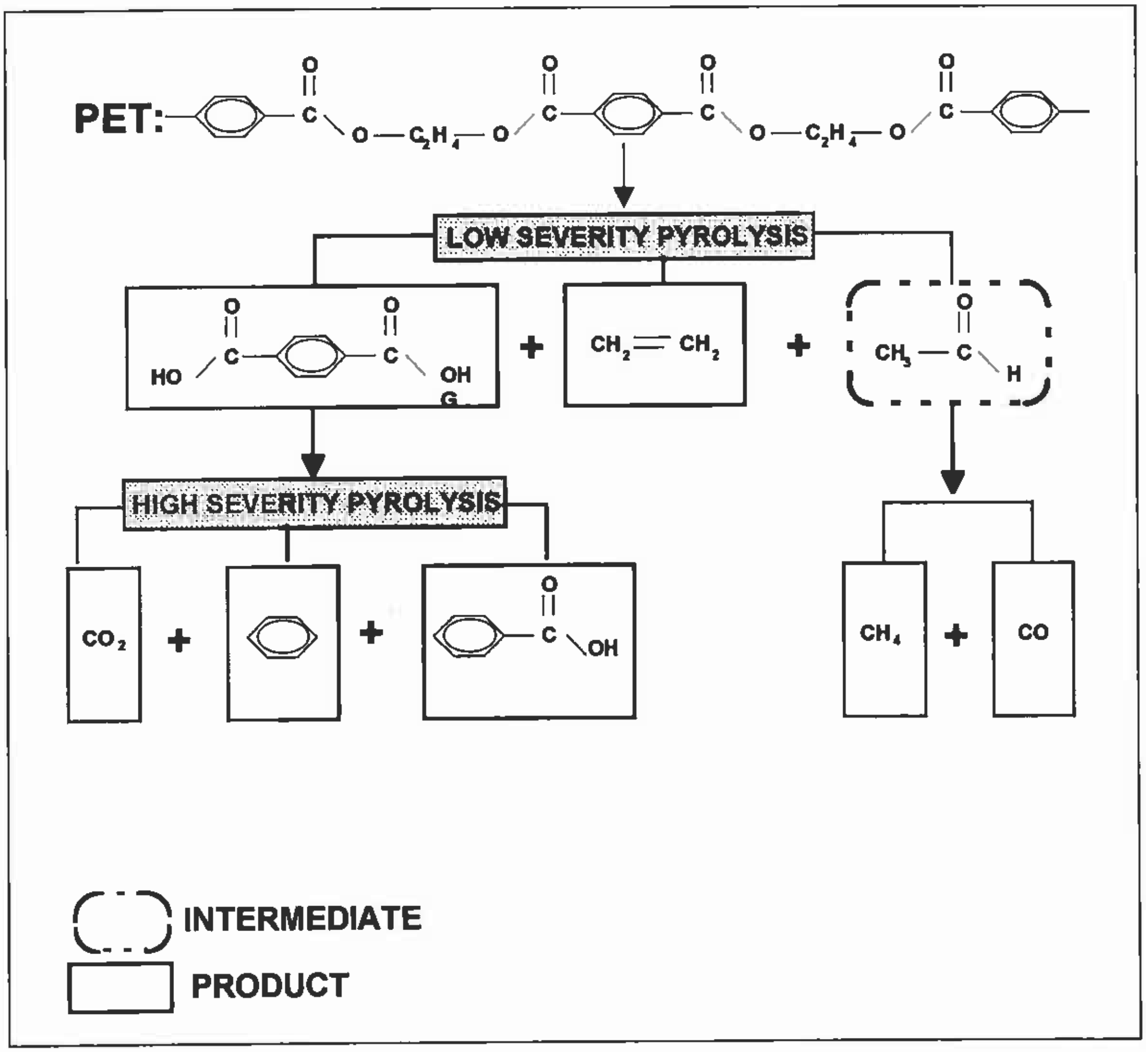

Figure 19 PET pyrolysis chemistry

The purpose of Run 40 was to determine the minimum weight ratio of lime hydrate to resin which would result in the complete removal of the carbon dioxide produced by decomposition of PET.

The following chemical reactions are thought to occur in the intimate mixture of pyrolyzing resin and lime hydrate and in the gas phase by suspended lime hydrate particles.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
$$Ca(OH)_2 \rightarrow CaO + H_2O$$
$$CaO + CO_2 \rightarrow CaCO_3$$

Although the reaction is not shown, it is also thought that $CaCO_3$ may be produced by the reaction of lime hydrate with any of the organic acids (like TPA or benzoic acid) that are present in the pyrolyzing mixture. Figure 20 shows the effect of the lime hydrate feed rate on the CO_2 removal and indicates that a ratio of ten pounds of lime hydrate for every one hundred pounds of resin feed is necessary for CO_2 removal.

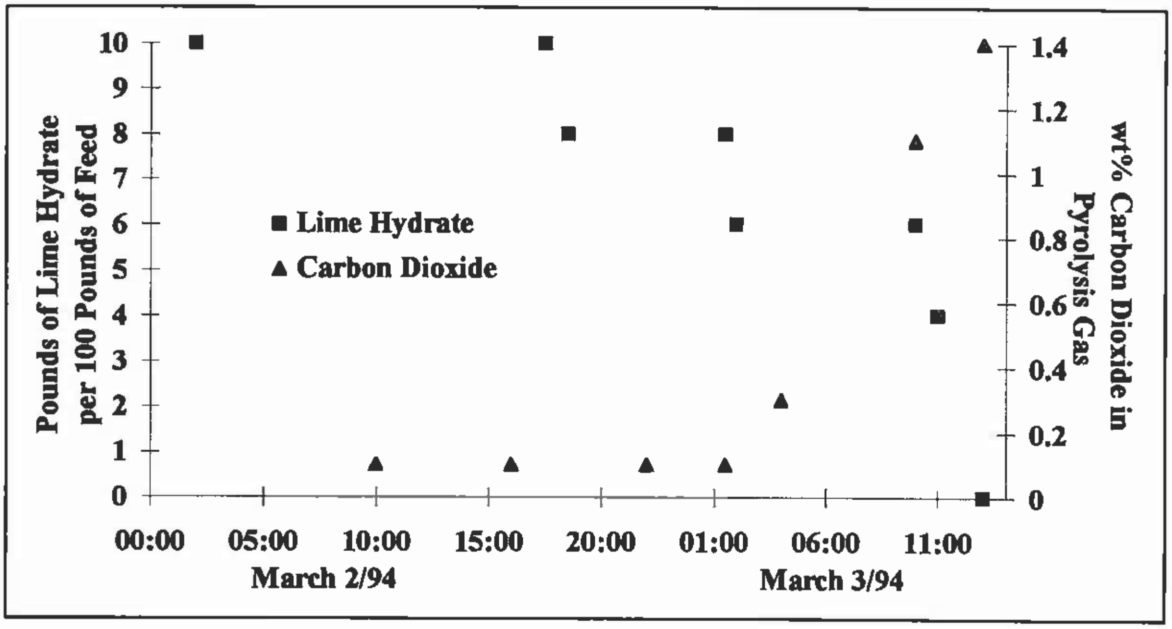

Figure 20 Effect of lime hydrate feed rate on CO_2 removal.

The purpose of Run 53 was to determine whether high temperature operation of the DART unit would eliminate TPA production at high loading levels of PET in the feed. For this run, the retort furnace temperature was 1400 °F and no lime hydrate was utilized. The run was initiated with 20% PET and concluded with 40% PET. For the 20% PET feed, the TPA concentration in the oil was approximately 0.4% compared with 4% TPA for the 40% PET feed. At this high severity, the liquid yield was only about 33%, which was well below the target yield of 70-80%.

4.2.7 Base Feed Spiked With Polyvinyl Chloride

In the initial stages of the parametric study, lime was considered to have great potential to capture HCl. It was determined that pilot scale testing could be conducted at less expense to verify this by using EERC and EER because they were already setup with pilot scale facilities.

APC-sponsored projects at the Energy and Environmental Research Center (EERC, University of North Dakota)[*] and the Energy and Environmental Research Corporation (EER, Irvine, CA)[‡], each studied the pyrolysis of PVC-containing feedstocks in support of the parametric studies at Conrad Industries. These laboratory scale studies indicated that the pyrolysis of plastic feeds containing 3% PVC produced oil with total chloride levels above 10,000 ppm. PVC will dehydrohalogenate at relatively low temperatures (300-350 °F) to produce HCl and a polyene backbone which then decomposes into aromatics and other unsaturated hydrocarbons. Further studies and review of the literature showed that the organochlorides are produced predominately in the condensation step and not during the pyrolysis or volatilization steps. In general, aliphatic organochlorides, which are the major products, contain relatively weak carbon-chlorine bonds that are probably labile at pyrolysis temperatures. The formation of organochlorides during condensation is also postulated for other pyrolysis and combustion processes containing carbonaceous materials and chlorine.

Studies at EER and EERC demonstrated that if the HCl is captured prior to the condensation step, total chloride yields in the product oil were significantly lowered to around 100 ppm. Two different chlorine capture processes were tested and found to be successful. Lime hydrate (calcium hydroxide) was added to the pyrolysis reactor (either a retort or fluidized bed) and chlorine was captured before it left the reactor. Hot calcium oxide beds were placed downstream of the retort and before the condensing system and were also effective in lowering the total chloride yields. However, if PET was present, the hot calcium oxide beds were quickly deactivated due to the excessive amounts of CO_2 and other acidic products produced from the PET decomposition. Because of these results, addition of lime hydrate with the plastic feedstock was chosen as the preferred chlorine capture method for the DART unit. The reaction for this chlorine capture is shown below.

$$Ca(OH)_2 + 2\,HCl \rightarrow CaCl_2 + 2\,H_2O$$

At EER, the pyrolysis reactor was a bench scale rotary screw device that was similar to the DART unit. EER results indicated that lime hydrate was effective in reducing total chloride levels to <100 ppm in the product oil at stoichiometric Ca:Cl ratios of approximately 4.

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[*] Sharp, L.L.; Ness, R.O. Aulich, T.R.; Randall, J.C. "Thermal Recycling of Plastics," final report to the American Plastics Council; EERC publication, March 1994.

[‡] Kryder, G.D.; Seeker, W.R.; "Research on Reduction of Organic Chlorides in Advanced Recycling Plastics Process," final report to the American Plastics Council; EER publication, June 1994.

After the initial tests at EER and EERC, a number of studies were performed on the DART unit with base resin blends containing various levels of PVC. Lime hydrate was utilized to capture the chlorine for all but the first PVC runs. As shown below, the DART unit operated at much greater efficiency for the capture of HCl than was demonstrated in the pilot scale studies by EERC and EER. The operating conditions, yields and Dohrmann total halide analytical results are included in Table XII.

Table XII Operating conditions, yields and total halide results for PVC studies

Run #	25	26	29	31	32	42
PVC Content	3%	3%	3%	0.5%	0.5%	3%
			Feed Rate (lb/hr)			
Resin	81	88	55	110	107	120
Lime Hydrate	0	i[1]	0	i	12	12
			Operating Temperatures (°F)			
Furnace Temperature	1350	1050	1250	1250	1250	1250
Retort Temperature	1225	870	956	842	947	920
			Normalized Yields (wt%)			
Oil Yield	58.6	61.1	65.6	67.6	61.4	NA[2]
Gas Yield	41.4	38.9	34.4	32.4	38.6	NA
			Retort Oil Total Chloride Levels (ppm)			
Mean	~4000	3890	6980	103	23	NA
Low	~1000	2770	4000	22	<10	65
High	~5000	5550	9360	177	75	1550

[1] i: inconsistent

[2] NA: not available

During Runs 25 and 29, lime hydrate was not utilized during pyrolysis studies of base resin spiked with 3% PVC. Levels of total chlorides were highest in the retort oil (TL) samples from the retort effluent sampler (see section 2.6), while total chlorides in the heavy and light oil were somewhat lower. Chloride levels in all oil samples climbed steadily during both runs, with the highest values (9,400 ppm) being recorded during Run 29. Since a 3% PVC mixture contains 1.7% chlorine by weight (which is equivalent to 17,000 ppm Cl), it appears that more than 50% of the available chlorine from PVC may be retained in the product oil during pyrolysis. The remainder is thought to exist as HCl, which is captured in the acid gas scrubber.

Lime hydrate addition was attempted during Run 26 with 3% PVC, but feeding inconsistencies with the new lime hydrate feeder plagued the run. Total chloride levels were high for all samples. It was discovered during Run 26 that there was significant carryover of lime hydrate to the high temperature condensing system due to entrainment of the small lime hydrate particles in the pyrolyzate gas exiting from the retort. The presence of this material in the heavy oil samples made it necessary to abandon routine Dohrmann analyses of the heavy oil. Total chloride analyses were carried out primarily on the retort oil samples after this time.

The PVC concentration in the feed was dropped to 0.5% for Run 31. With a lime hydrate feed rate of 5-10 lb/hr, total chlorides were reduced to values near 100 ppm. However, after termination of the run, it was discovered that all of the lime hydrate feed had been retained within the retort due to a blockage in the outlet to the solids collection system.

A consistent lime hydrate feed rate of 12 lb/hr was achieved for Run 32, in which a feedstock containing 0.5% PVC was processed. In this run, the concentration of total chlorides in the retort oil was reduced to values below 10 ppm. Since a feed mixture containing 0.5% PVC contains 2,840 ppm Cl, the HCl capturing efficiency of the lime hydrate during Run 32 was greater than 99.6%.

During one portion of Run 42, the effect of lime hydrate stoppage on organochloride generation was studied. To evaluate the effect, 3% PVC feedstock was processed at 120 lb/hr with 12 lb/hr of lime hydrate (stoichiometric $Ca:Cl_2$ ratio of 6). Samples of retort oil were collected prior to the stoppage and at various intervals thereafter. Figure 21 shows the results of the experiment. Initially, the concentration of total chlorides in the oil was 65 ppm. At 10 and 20 minutes, the chloride levels were 240 and 200 ppm, respectively. After 30 minutes, the levels had risen to 500 ppm, and at 35 minutes, the value was 640 ppm. After 42 minutes, the chloride concentration reached 1,550 ppm. Apparently, the inventory of lime hydrate in the retort was sufficiently high to prevent a sharp increase in total chloride concentration when the lime hydrate feed was interrupted. This conclusion is important because it implies that a sharp increase in organochloride products may not occur if a plug of PVC-rich feed enters the retort or if there is a temporary interruption of lime addition.

As mentioned previously, there was significant carryover of lime hydrate from the retort to the heavy oil condensing system. The resulting samples of heavy oil contained between 0.3% and 3% lime hydrate sediment. Although the presence of this material in the tower sump caused maintenance difficulties and some minor viscosity problems, it also provided an unforeseen benefit. With a small amount of unreacted lime hydrate continuously circulating in the high temperature tower, the heavy oil was maintained in an alkaline state. The alkalinity of the circulating heavy oil neutralized any HCl that had escaped from the retort during a process upset or lime hydrate feed lapse.

The initial investigations of the effectiveness of lime hydrate for scavenging hydrogen chloride liberated during PVC pyrolysis were based on a lime hydrate to chloride stoichiometric ratio of 4:1. For the EER work, which established this minimum requirement, base resin containing up to 10% PVC was used as the feedstock. The lime hydrate requirement to satisfy this 4:1 ratio was equivalent to one pound of lime hydrate for every ten pounds of feedstock.

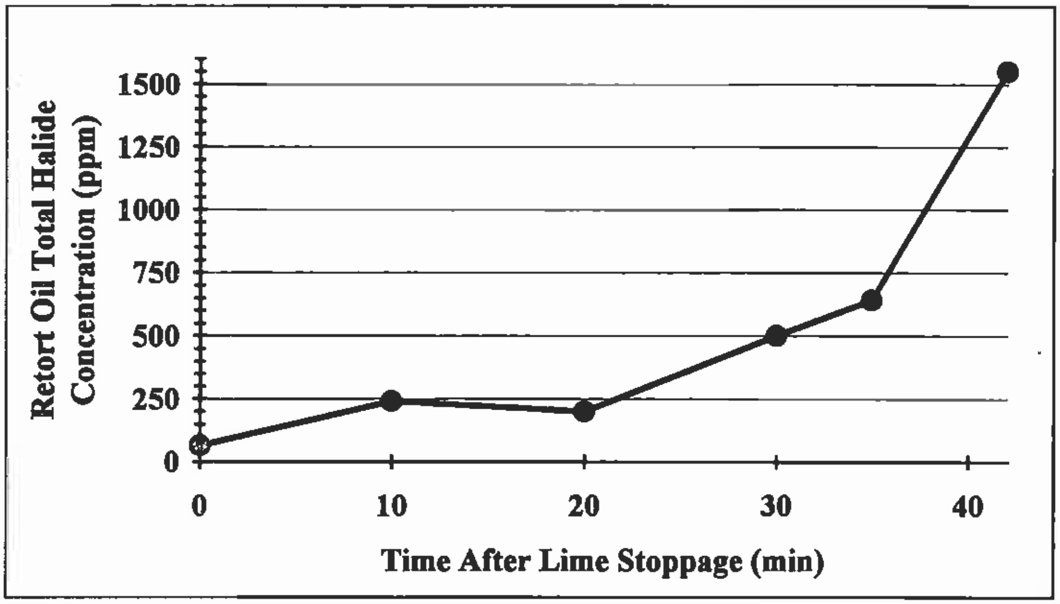

Figure 21 Effect of abrupt lime hydrate feed stoppage on retort oil total chloride levels

The lime hydrate feeding system on the DART unit was based on a resin feed rate of 300 lb/hr and a maximum PVC content of 7%. Two batches of PVC-containing feedstock had been prepared for the project, each containing 3% and 7% PVC, respectively. However, during the project, the maximum level of PVC was generally limited to 3% for feed rates of 100-120 lb/hr, which made the lime hydrate feed system oversized and difficult to control. (Ultimately smaller feed screws were installed.)

During several of the runs, the PVC content was lowered to 0.5%, which required only 0.5 lb/hr of lime hydrate per 100 lb/hr of resin feedstock. It was soon realized that such a low addition rate of lime hydrate would be too low to coat the individual resin feed pellets for effective HCl capture. Tumbling tests with different lime hydrate ratios indicated that a minimum 1:10 physical weight ratio of lime hydrate to resin feed might be necessary for adequate coating of the pellets. Most of the successful chlorine capture runs were therefore based not on a specific stoichiometric lime hydrate:chlorine ratio but on the 1:10 physical weight ratio. Finally for Run 70 when a reliable lime hydrate feed system was available, it was possible to produce an oil product with less than 30 ppm total chlorides with only 2.4 pounds of lime hydrate per 100 pounds of resin feed. Because the feed contained both PVC and PET, Run 70 is discussed in more detail in the next section. It is still somewhat unclear how the combined stoichiometric and physical mixing requirements determine the efficiency of HCl capture by lime hydrate.

Table XIII shows the boiling point distribution of organochlorides in oil produced from PVC-spiked feed. To generate this data, a sample of oil from 3% PVC feed was sent to Comsource American for fractional distillation. The various cuts were then analyzed on the Dohrmann microcoulometer for total chlorides. As shown in Table XIII, most of the organochlorides are in the 180-350 °F boiling range, which is in agreement with the data from EERC.

Table XIII Boiling point distribution of organochlorides in oil produced from PVC-spiked feed

Fraction (°F)	Oil Distribution (wt%)	Oil Organochloride Concentration (ppm)	Chlorine Distribution (wt%)
100-180	6.95	1328	17.1
180-350	38.90	1041	75.1
350-650	24.85	98	4.5
650+	27.85	64	3.3

4.2.8 Base Feed Spiked With Polyethylene Terephthalate and Polyvinyl Chloride

Pyrolysis of base feed mixtures containing 20% PET produced CO_2 and organic acids such as TPA (see section 4.2.6). During these runs, CO_2 yields were as high as 4.4% and TPA yields were as high as 3.6%. CO_2 and organic acids like TPA will react with lime hydrate in the retort and as a result, less lime hydrate will be available to neutralize the HCl produced from PVC. Because most post-consumer feedstocks will contain both PVC and PET and it is not known whether the presence of PET will affect the efficiency of chlorine capture by lime hydrate, a large number of runs were conducted with feedstocks containing various amounts of both PET and PVC. The results of these runs are summarized in Table XIV.

Table XIV Operating, yield and oil total chloride data from studies of feed containing PET and PVC

Run #	34	35	36	38	39	45	54	58	70
PVC Content (%)	0.5	0.5	1	0.5	0.5	1	5	1	1
PET Content (%)	2	5	10	2	2	3	5	3	3
Feed Rate (lb/hr)									
Resin	126	120	110	129	129	178	92	106	125
Lime Hydrate	9	15	12	17	12	14	18	12	4
Operating Temperatures (°F)									
Furnace Temperature	1300	1350	1300	1400	1400	1450	1350	1300	1350
Retort Temperature	933	975	980	1097	995	929	926	945	969

Table XIV Continued

Run #	34	35	36	38	39	45	54	58	70
	Normalized yields (wt%)								
Oil Yield	59.6	44.2	45.5	29.0	49.9	68.2	60.4	60.8	51.0
Gas Yield	40.4	55.8	54.5	71.0	50.1	31.8	39.6	39.2	49.0
	Retort Oil Total Chloride Levels (ppm)								
Mean	13	<10	18	16	18	10	109	28	481
Low	<10	<10	<10	<10	<10	<10	48	11	29
High	19	<10	63	31	29	11	271	45	2062

At nearly every PET and PVC concentration, the concentration of total chlorides in the retort oil samples was near the 10 ppm detection limit of the Dohrmann microcoulometer. Typically, there was at least a 6X molar excess of lime hydrate added to the retort. However, during Run 54, when the concentrations of PET and PVC were each 5% and the lime hydrate/plastic mixing ratio was 20%, the total chloride values never fell below about 50 ppm. Although the lime hydrate physical mixing ratio was high for this run, the resulting stoichiometric ratio was only a 4X molar excess. Inconsistencies in the operation of the lime feeder at such a low stoichiometric ratio probably account for the elevated total chloride levels in Run 54.

During Run 70, a study was conducted to determine whether it would be possible to process resin containing 1% PVC and 3% PET at the minimum lime hydrate feed rate of 4 lb/hr (4 lb/hr is the low limit of the lime hydrate feeder) and continue to produce oil with low levels of total chlorides. The stoichiometric requirement for $Ca(OH)_2$ is 2.2 lb/hr for 1% PVC and 3% PET at a resin feed rate of 125 lb/hr. (1 mole of $Ca(OH)_2$ can neutralize 1 mole of PET monomer or 2 moles of HCl.) Throughout the run the actual concentrations of PVC and PET in the feed were monitored by density separation (in salt water) followed by manual separation of the PVC and PET pellets. Frequent samples of retort oil were collected and analyzed on the Dohrmann microcoulometer for total chlorides. The actual concentrations of PVC and PET in the feed *did not remain constant at 1% and 3%, but varied significantly over the course of the run*. As a result, the chloride levels in the product oil varied over a very wide range and the run produced some unintentional but very interesting results. Figure 22 shows that in the early and late portions of the run, the concentrations of PET and PVC in the feed were close to the expected levels and the oil produced at these times contained low levels of chlorides. The successful 1.8 stoichiometric ratio for this portion of the run was an excellent result. During the middle portion of the run, the unintentionally high PVC and PET content caused production of oil with high chloride levels.

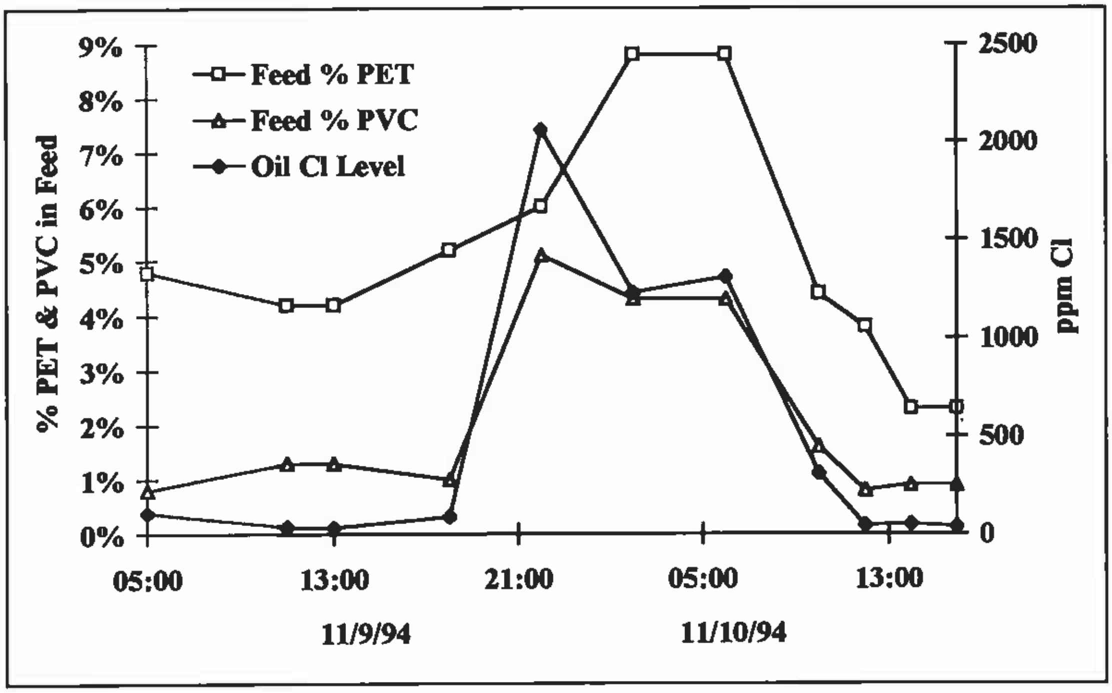

Figure 22 Effect of variation in feed content on retort oil total chloride levels during Run 70

4.2.9 Base Feed Spiked With Paper

Run 52 simulated the effects of pyrolyzing post-consumer plastic containing paper labels or other paper contamination. The feed contained 4% shredded paper and appeared to remain homogeneous during agitation in the surge bin. The run was conducted with and without lime hydrate addition to the retort. Carbon dioxide was present in the product gas at 0.1% (vol/vol) during addition of 5 lb/hr of lime hydrate and at 2.5% when lime hydrate was not used. During the portion of the run when lime hydrate was present, the contents of the solids collection drum appeared to contain a mixture of spent lime and ash. No operating difficulties occurred during the run, which indicated that the presence of paper will probably have no effect on the pyrolysis of plastics.

Table XV Operating and yield data from Run 52

Feed Rate	Furnace Temperature	Retort Temperature	Liquid Yield	Gas Yield
100 lb/hr	1250 °F	1029 °F	60.2%	39.8%

4.2.10 Base Feed Spiked With Nitrogen-Containing Polymers

The primary focus of these runs was to determine whether hydrogen cyanide (HCN) would be produced during pyrolysis of base resin feedstock spiked with low levels of nitrogen-containing polymers such as polyamides, polyurethane or acrylonitrile butadiene styrene. For all of these runs, special HCN safety procedures were instituted for plant operations.

Samples of the gas product that had not passed through the acid gas scrubber were obtained from the retort sampler. These gas samples were tested frequently for HCN using Sensidyne HCN sampling tubes. For some of the gas samples, analyses for ammonia were also performed. It is thought that the presence of ammonia in some of the samples may have interfered with the measurement of HCN. Because of this, samples of oil and by-product solids were analyzed for HCN at the site by washing the samples with concentrated sodium hydroxide solution and analyzing the wash by a cyanide-selective electrode. In addition, samples of oil, acid gas scrubber liquor and by-product solids from every run were sent to Comsource American for cyanide analysis. The oil from each run was also analyzed for total nitrogen.

Overall, the studies with nitrogen-containing plastics were quite successful. For the most part, HCN was not present at a measurable level in the product samples. When it was detected, HCN was present at very low levels. There were no reported operating or safety problems throughout the runs.

4.2.10.1 Polyurethane

Base resin feedstock containing polyurethane (PU) was processed during Run 71. Two types of PU were processed, TDI-PU and MDI-PU. 50/50 mixtures of the two polymer types were blended with base resin to give total PU levels of 1%, 3% and 5%. The polymer mixtures were first introduced to the DART unit at the 1% and 3% levels to determine whether processing was possible without formation of HCN. After successfully feeding PU at these concentrations without HCN production, three extended runs of 10 hours were maintained using the 5% 50/50 TDI/MDI resin mixture, a 5% MDI-only mixture and a 5% TDI-only mixture. At the conclusion of the run, the PU levels in the feed were increased stepwise to 100% PU over a 4-hour period. The run was very smooth for all PU feedstock blends, and nothing unusual was observed at any time in the operation. The Table XVI contains results from a 10 hour portion of the run where a 5% mixture of 50:50 MDI:TDI PU was used as feedstock. The componential yields were very similar to runs with base resin.

Table XVI Operating and yield data from Run 71

Resin Feed Rate	Lime Hydrate Feed Rate	Furnace Temperature	Retort Temperature	Oil Yield	Gas Yield
103 lb/hr	4 lb/hr	1250 °F	964 °F	64.5%	35.5%

As shown in Table XV, cyanide levels were low in the oil, scrubber water and by-product solids. The cyanide analyses from gaseous samples were unclear, due to the difficulties in perceiving color changes in the HCN measurement tubes. The tubes registered occasional possible positive responses of <50 ppm during the course of the run. However, experiments were also conducted in which a measured volume of the product gas was bubbled through a sodium hydroxide solution, which was analyzed by a cyanide-selective electrode. In these analyses, cyanide was not detected in the product gas. On-site analyses of the oil and by-product solids indicated that if present, the level of HCN was very low, <5 ppm, at all PU levels. In the Comsource analyses, cyanide was not detected in the oil or scrubber water. Cyanide was only detected at low levels in the by-product solids.

Table XVII Results of cyanide, nitrogen and ammonia analyses from Run 71

Sample Type	Cyanide (ppm)	Kjeldahl Nitrogen (%)	Ammonia (%)
Oil from 5% TDI/MDI PU	<0.1	0.18	
Scrubber water from 5% TDI/MDI PU	<0.1		
Solids from 5% TDI/MDI PU	40.0		
Gas from 5% TDI/MDI PU	0-50		0.02
Oil from 100% TDI PU	<0.1	4.25	
Solids from 100% TDI PU	3.4		
Gas from 100% TDI PU	0-20		6.0

At no time during the run did any of the personal HCN monitors, stationary monitors or cumulative detection tubes register the presence of HCN in the plant or laboratory.

Although the chemistry is not understood, analyses of the gas produced from 100% TDI-PU indicated that ammonia was present at 6%. The oil contained 0.18% total nitrogen when the feedstock contained 5% PU and 4.25% total nitrogen when 100% PU was utilized.

4.2.10.2 Acrylonitrile Butadiene Styrene

Base resin feedstock containing acrylonitrile butadiene styrene (ABS) was processed during Run 72. As with Run 71, the experiments were initiated by conducting short runs with 1% ABS and 3% ABS. After successfully feeding ABS at these concentrations, an extended run of 10 hours was maintained with a feed mixture containing 5% ABS. The yields and operating conditions from Table XVIII were very similar to those for base resin and for 5% polyurethane.

Table XVIII Operating and yield data from Run 72

Resin Feed Rate	Lime Hydrate Feed Rate	Furnace Temperature	Retort Temperature	Oil Yield	Gas Yield
127 lb/hr	4 lb/hr	1300 °F	990 °F	64.4%	35.6%

Table XIX shows the results of cyanide, nitrogen and ammonia analyses. The gas cyanide analyses were unambiguous and indicated that HCN was not present in the gas. In the Comsource analyses, cyanide was undetected in the oil, by-product solids and scrubber water. Ammonia was again detected in the gas at values of 1.0-1.5% when the feedstock contained 5% ABS. The oil produced from 5% ABS contained 0.14% total nitrogen.

Table XIX Results of cyanide, nitrogen and ammonia analyses from Run 72

Sample Type	Cyanide (ppm)	Kjeldahl Nitrogen (%)	Ammonia (%)
Oil from 5% ABS	<0.2	0.14	
Scrubber water from 5% ABS	<0.1		
Solids from 5% ABS	<20.0		
Gas from 5% ABS	<1		1.0-1.5

At no time during the run did any of the personal HCN monitors, stationary monitors or cumulative detection tubes register the presence of HCN in the plant or laboratory.

4.2.10.3 Polyamide

Base resin feedstock containing polyamide was processed during Run 73. The polyamide was a commercial grade of nylon 66. The run plan was identical to that for Run 72 in that successful short runs of 1% and 3% polyamide preceded a long run with a base feed mixture containing 5% polyamide. As Table XX shows, the yields and operating conditions were again very similar to those for base resin and for Runs 71 and 72.

Table XX Operating and yield data from Run 73

Resin Feed Rate	Lime Hydrate Feed Rate	Furnace Temperature	Retort Temperature	Oil Yield	Gas Yield
114 lb/hr	4 lb/hr	1300 °F	1050 °F	62.9%	37.1%

As shown in Table XXI, no cyanide was detected in any of the gas, oil, by-product solids or scrubber water samples. Cyanide was also not detected in the plant or laboratory. The oil produced from 5% polyamide contained 0.21% nitrogen.

Table XXI Results of cyanide and nitrogen analyses from Run 73

Sample Type	Cyanide (ppm)	Kjeldahl Nitrogen (%)
Oil from 5% polyamide	<0.2	0.14
Scrubber water from 5% polyamide	<0.1	
Solids from 5% polyamide	<20.0	
Gas from 5% polyamide	<1	

4.2.11 Pyrolysis With Catalyst

The use of cracking catalysts is common in many petrochemical pyrolysis processes. It was postulated that the presence of cracking catalyst in the DART unit might promote depolymerization and increase liquid yields at lower temperatures. Run 65 focused on processing the base resin blend in the presence of a silica-alumina-based fluid catalytic cracking (FCC) catalyst supplied by Amoco. With a retort furnace temperature of 1150 °F and a resin feed rate of 100 lb/hr, the catalyst was introduced via the lime feeder at a nominal feed rate of 20 lb/hr. Due to the proprietary nature of the catalyst, not much is known about the specific makeup, age or intended uses for the catalyst.

Table XXII compares the partial analyses (not yields) of oil and gas samples taken before and after the addition of FCC catalyst during Run 65.

Table XXII Yield data from FCC catalyst run

Component	Before Addition of FCC Catalyst (wt%)	After Addition of FCC Catalyst (wt%)
	Yields	
Oil	59.0	60.5
Gas	41.0	39.5
	Pyrolysis Gas	
Hydrogen[1]	2.5 (0.12)	4.4 (0.20)
Methane	4.1	4.3
Ethylene	8.2	6.7
Propylene	19.9	17.9
Total *n*-Butenes	11.2	14.5
	Retort Oil	
Total Aromatics	63.9	58.8
Benzene	2.2	2.3
Toluene	11.0	7.9
Styrene	23.4	19.2

Table XXII Continued

Component	Before Addition of FCC Catalyst (wt%)	After Addition of FCC Catalyst (wt%)
	Retort Oil	
Total Aliphatics	31.8	36.4
<C11	15.8	21.0
C11 - C20	12.1	11.6
>C20	3.5	3.2
Total Paraffins	7.4	8.9
Total Olefins	15.0	17.4
Total Di-olefins	6.3	7.5

[1] The hydrogen concentration is expressed in volume percent, with weight percent in parentheses.

Subtle changes occurred in yields of specific components, but overall, the presence of FCC catalyst did not have an overwhelming effect on the oil and gas component concentrations. In the gas, the concentrations of both ethylene and propylene dropped after addition of catalyst, while the concentrations of hydrogen and unbranched butenes increased. Methane remained relatively unchanged. The concentration of aromatics dropped slightly with catalyst present, although the benzene levels were similar. The concentrations of C5 - C10 aliphatic compounds in the oil increased dramatically with catalyst present, while the concentrations of the larger aliphatics were relatively unchanged. The presence of catalyst did not appear to specifically enhance the production of paraffins over olefins or vice versa.

4.2.12 Comparative Summary of Runs

Examination of run data where base resin was mixed with minor amounts of PVC, PET, polyamide, ABS, polyurethane or paper suggest that they can be included with the base resin results for correlation purposes. These data, listed in descending order of pyrolysis liquid yields, are shown in Table XXIII. There is a fairly good correlation between the combined ethylene and propylene yields (C2'+C3'), liquid yield and retort temperature for most of these runs in which base resin comprised >95% of the feedstock, as shown in Figures 23, 24 and 25. The linear least squares fit of the data points in Figure 24 is especially good and shows that C2'+C3' is highly predictive of liquid yield. Figure 23 shows that retort temperature is somewhat predictive of the liquid yield. Figure 25 shows that C2'+C3' is directly proportional to temperature. This information may be useful in the design and operation of a commercial recycling unit in which high oil yield is an important objective. Based on the good correlations of pyrolysis oil yield with the combined yields for ethylene and propylene, it can be concluded that the presence of lime hydrate generally does not have a large effect on the pyrolysis of the base resin mixture. Figures 26 - 31 show the following:

Figure 26	The yield of total C4's shows a slight linear decrease with increasing pyrolysis liquid yield.
Figure 27	The yields of total aromatics and aliphatics in the liquid appear to converge at higher liquid yields.
Figure 28	The yield of >C20 aliphatics (waxes) shows an apparently nonlinear increase with increasing oil yield.
Figure 29	The benzene yield decreases in a roughly linear relationship with liquid yield.
Figure 30	The toluene yield shows slight positive change at higher liquid yields, with most values near 5-6 wt%.
Figure 31	The styrene yield shows an apparent linear increase with increasing liquid yield.

Table XXIII Selected data from runs that utilized predominately base resin

	Feed Additives (%)					Gas and Retort Oil Component Yields (wt%)							
Run Number	PVC	PET	Other	Liquid Yield (%)	Retort Temp. (°F)	Ethlene + Propylen	C4's	Total Aliphatics	>C20 Aliphatics	Total Aromatics	Benzene	Toluene	Styrene
21C				77	830	5.9	6.5	27.2	7.5	36	0.7	6.7	14
41	3			70	923	9.9	9.7	27.3	2.5	35.6	1.2	4.6	18.1
21B				68.5	980	10.7	9.5	23.9	5.6	31.5	1.3	6	10.9
45	1	3		68.2	929	11	9.1	28.5	4.5	33	2.5	5.4	13
31	0.5			67.6	842	9.7	11	34.3	3.4	28.4	1.5	5.3	8.8
29	3			65.6	956	9.3	10.3	23.6	3.5	33.7	1.4	5.4	13.3
71			5[1]	64.5	956	11.8	10.4	24.8	3.2	41	1.4	6.2	17.5
72			5[2]	64.4	990	11.1	10.2	20	2.6	40.3	1.5	6.3	15.7
73			5[3]	62.9	1050	12	10.9	18.1	2.9	40.3	2.1	7.8	15

Table XXIII Continued

	Feed Additives (%)					Gas and Retort Oil Component Yields (wt%)							
Run Number	PVC	PET	Other	Liquid Yield (%)	Retort Temp. (°F)	Ethlene + Propylen	C4's	Total Aliphatics	>C20 Aliphatics	Total Aromatics	Benzene	Toluene	Styrene
32	0.5			61.4	947	12.2	12.2	26.4	3.7	29.4	1.3	4.9	11.4
26	3			61.1	870	14.2	10.8	20.7	4.3	32.6	1.3	5.1	11.6
58	1	3		60.8	945	11.5	10.9	24.3	0.5	34.4	1.8	5.7	15.7
52			4[4]	60.2	1029	13.6	11.5	19.1	2	36.2	1	5.9	14.7
34	0.5	2		59.6	933	12.2	11.7	31.8	5.6	25.9	1.5	4.9	10
47	1	3		58.6	1002	14	11.2	16.8	2.4	31.7	3.2	5.7	11.1
22				51.4	990	17.6	14.1	17.3	2.8	28.6	1.8	6.2	9.7
70	1	3		51	969	14.4	13	18.6	2.5	26.9	1.9	4.4	10.2
39	0.5	2		49.9	995	18.2	14.3	15.1	1.6	31	3.7	6.1	10.4
40		2		43	1117	22	12.6	11.2	0.9	29.2	3.1	5.5	10.3
21A				39	1100	23.4	16.7	9	1.4	36	2.1	6	7.3
38	0.5	2		28.2	1097	27.1	15.8	6.3	0.6	21.5	3.9	3.4	2.3

[1] Polyurethane

[2] Acrylonitrile butadiene styrene

[3] Polyamide

[4] Paper

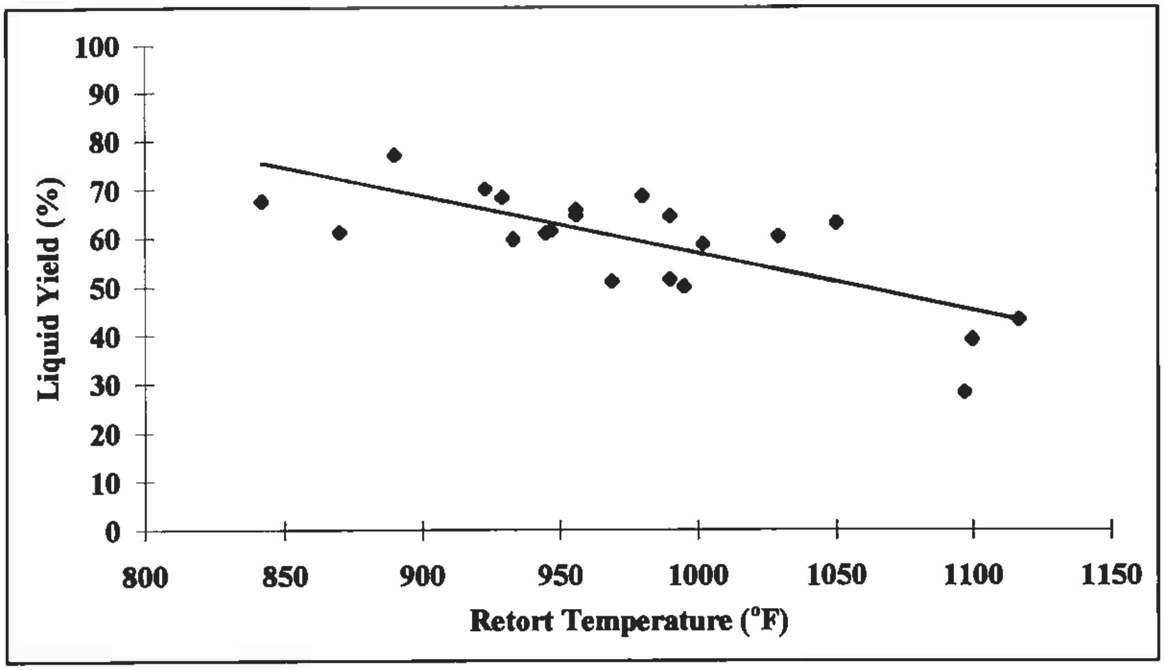

Figure 23 Variation in liquid yield with retort temperature for parametric study

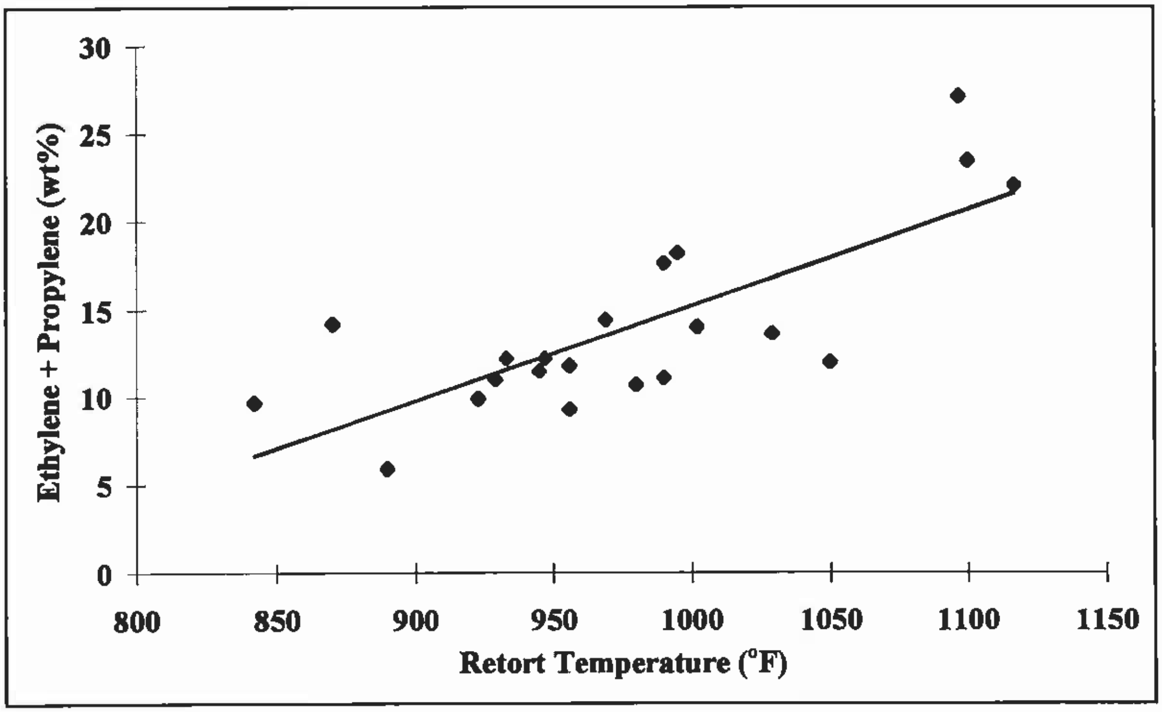

Figure 24 Variation in combined ethylene and propylene yields with retort temperature for parametric study

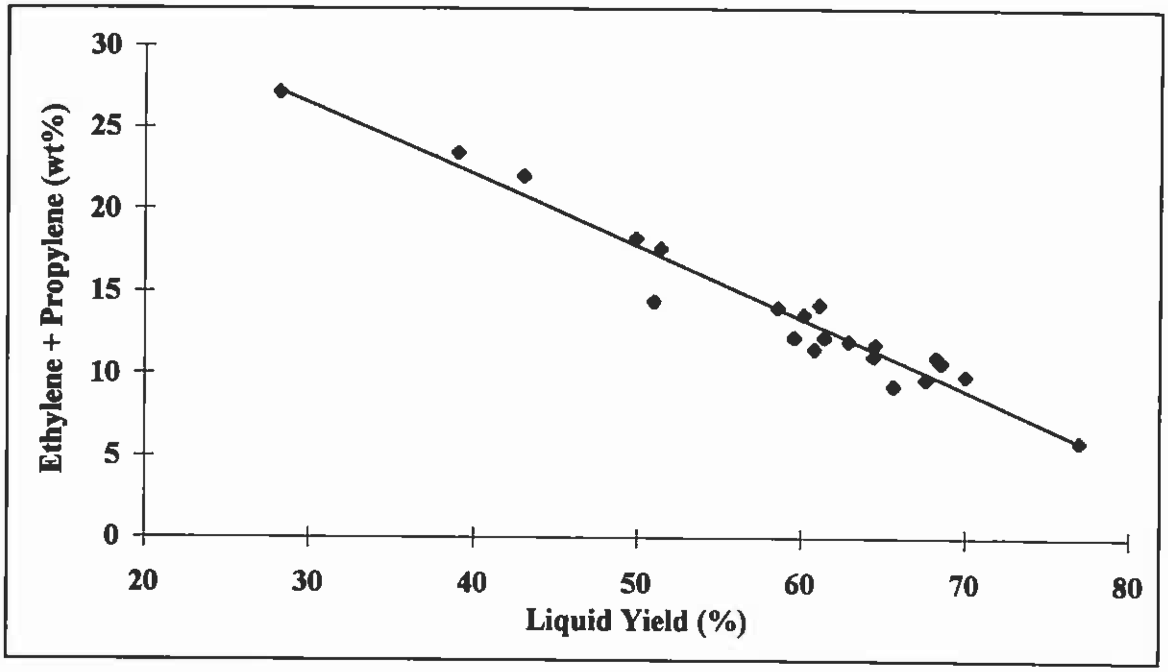

Figure 25 Variation in combined ethylene and propylene yields with liquid yield for parametric study

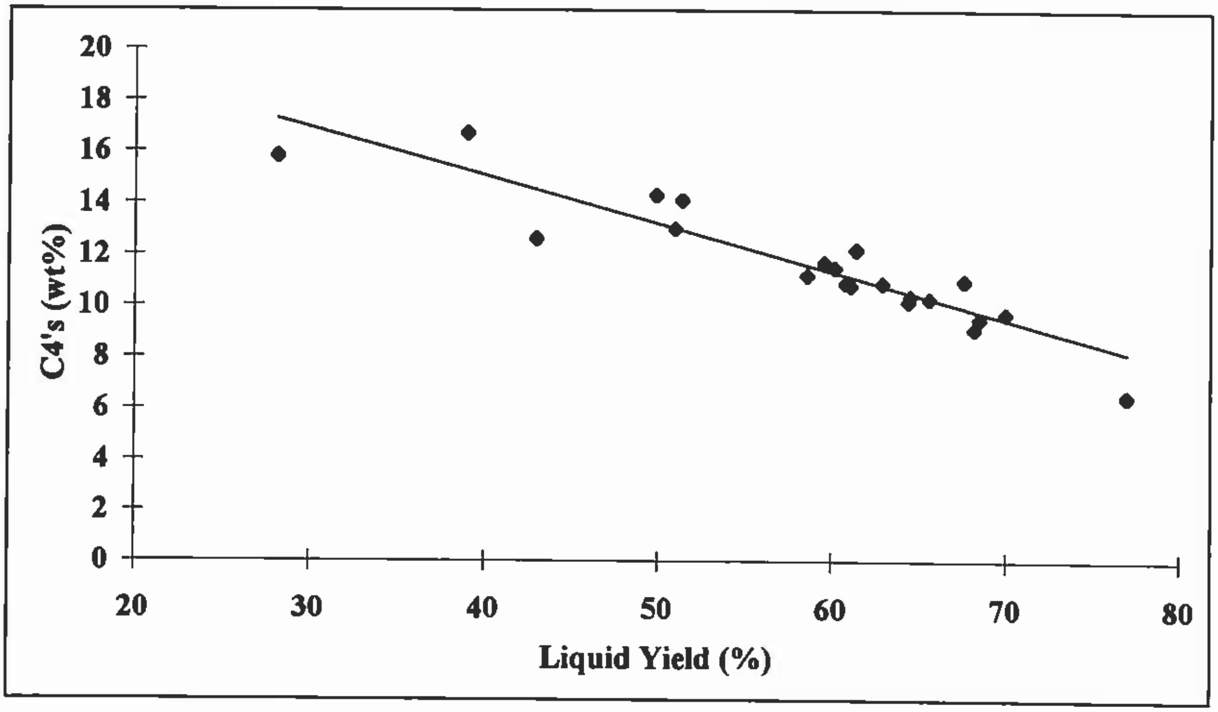

Figure 26 Variation in yield of C4's with liquid yield for parametric study

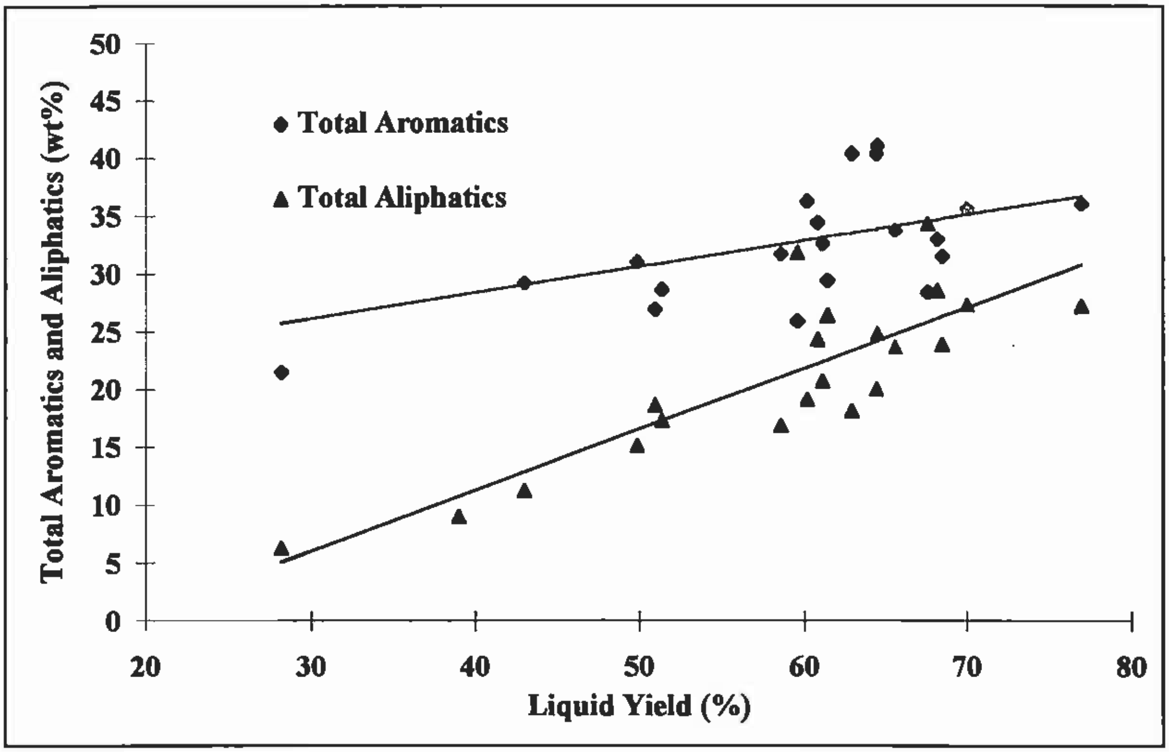

Figure 27 Variation in aromatics and aliphatics yields with liquid yield for parametric study

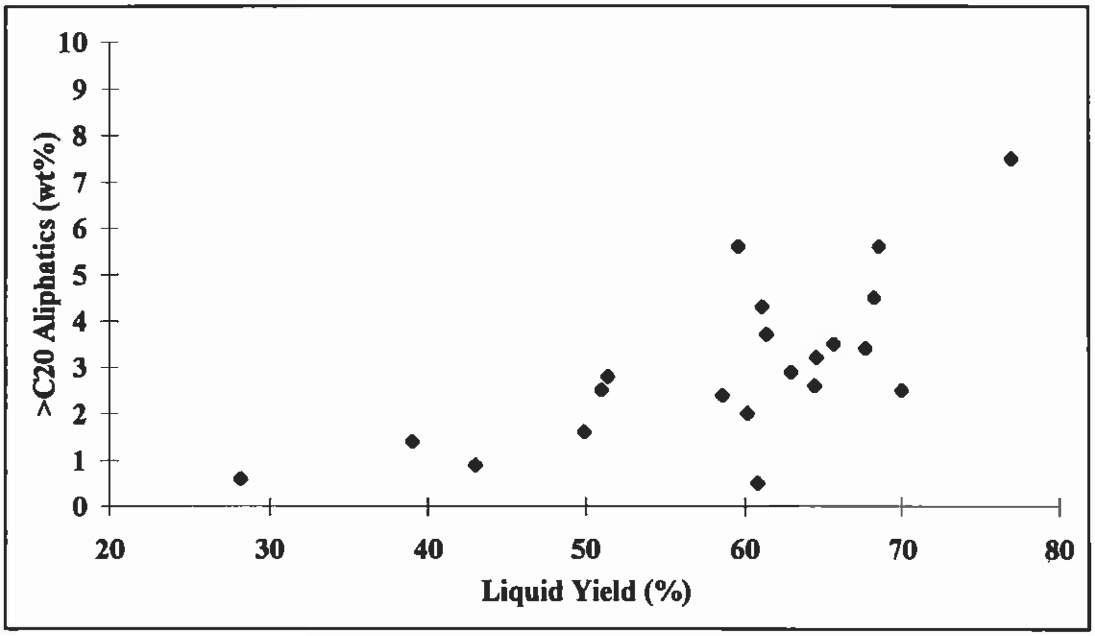

Figure 28 Variation in yield of >C20 aliphatics with liquid yield for parametric study

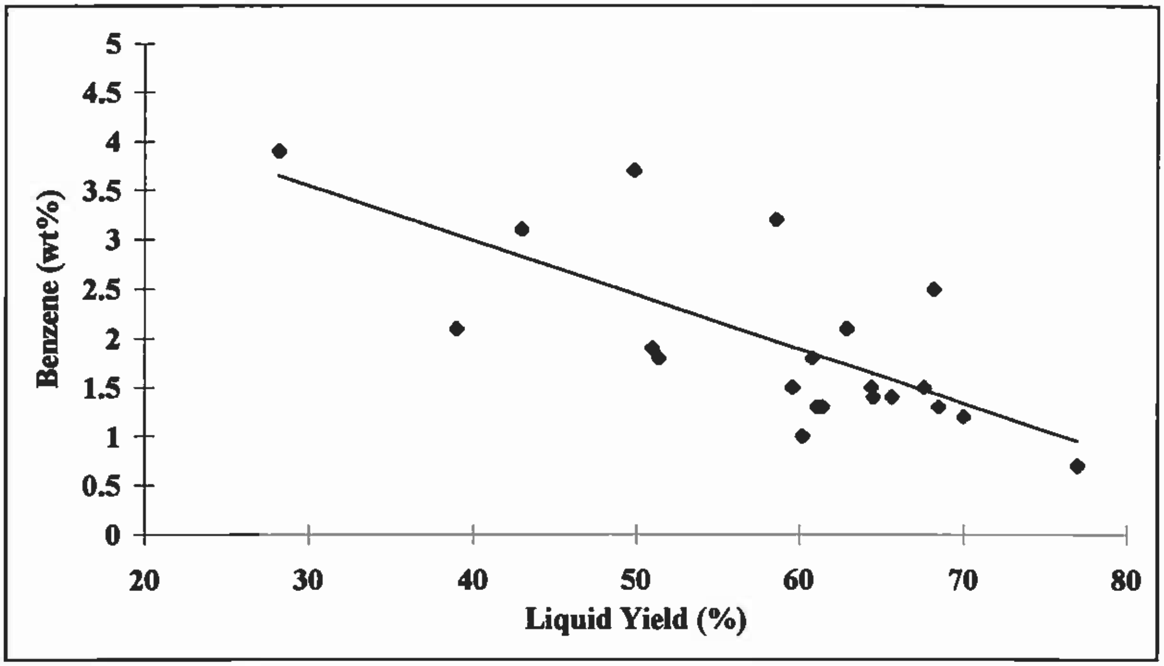

Figure 29 Variation in benzene yield with liquid yield for parametric study

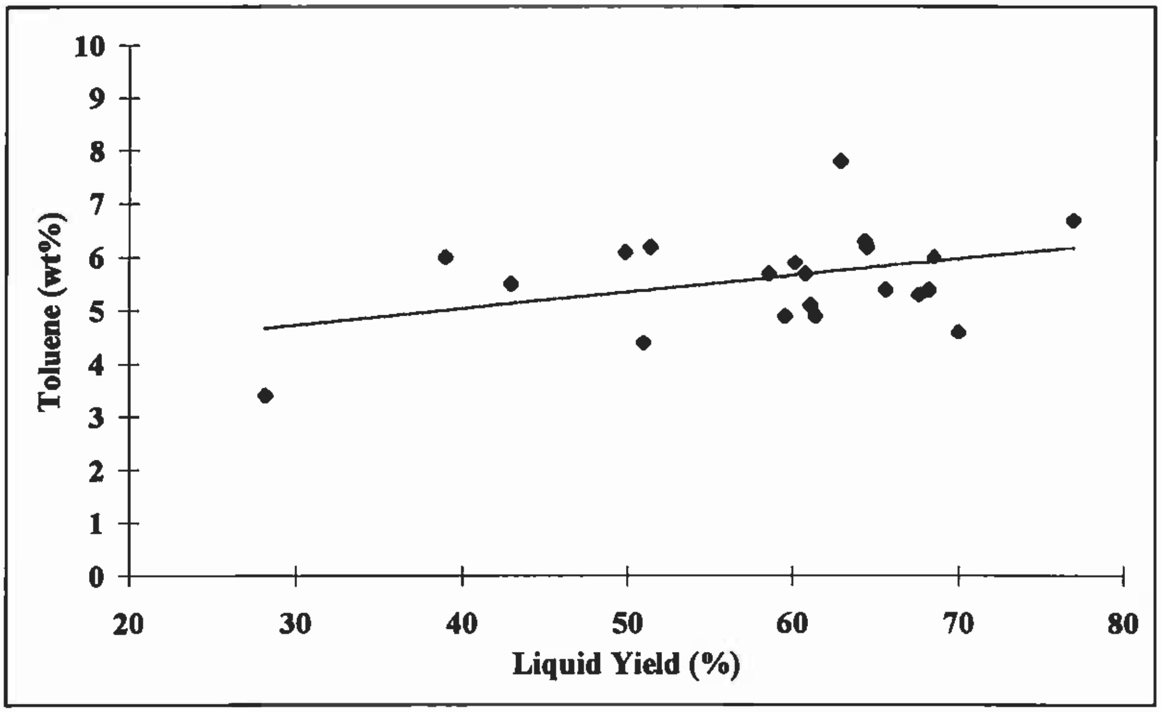

Figure 30 Variation in toluene yield with liquid yield for parametric study

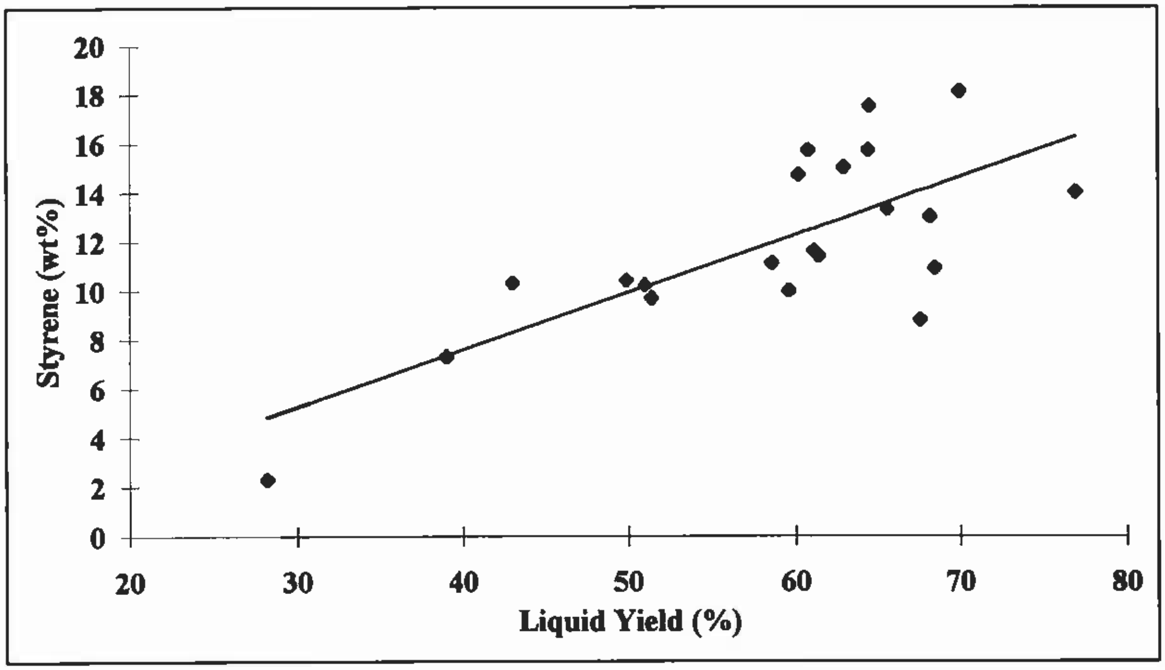

Figure 31 Variation in styrene yield with liquid yield for parametric study

4.3 Post-Consumer Plastic Study

Four different batches of post-consumer plastic (PCP) were received from different regions of the United States. PCP-OR was from a recycling operation in Portland, Oregon. PCP-NJ was from a PET/HDPE/PVC recycling operation in New Jersey. PCP-IN originated from a PET bottle recycling operation in Richmond, Indiana. PCP-GW was supplied by the Goodwill plastic bottle recycling effort in Oregon and was unsorted. Table XXIV compares the resin levels in the PCP feedstocks with the makeup of the base resin blend. PCP-NJ and PCP-IN are relatively similar. PCP-GW differs substantially in that PET comprises a large percentage of the total. PVC concentrations in all of the batches appeared to be very low. Mixed post-consumer plastics are expected to contain PVC at relatively low levels. However, clear PET (primarily from 2-liter beverage bottles) and HDPE natural (primarily from 1-gallon milk containers) may represent more than 50% of the stream composition. If these plastics are removed from the stream for conventional mechanical recycling, PVC concentrations may approach 5% or more. Polyamide was detected at extremely low levels in PCP-GW. Because of this, caution was exercised during all of the studies in the event that pyrolysis in the DART unit would liberate HCN. Analyses of the pyrolysis gas and ambient air analyses did not detect measurable quantities of HCN.

Table XXIV Resin levels in post-consumer plastic feedstocks

	Normalized Weight Percent Of Each Feedstock Constituent						
Feedstock	LDPE	HDPE	PP	PS	PET	PVC	Other
Base Resin	0.0	60.0	20.0	20.0	0.0	0.0	
PCP-OR	1.6	75.4	5.6	8.6	8.3	0.5	
PCP-NJ[1]	4.0	78.9	14.0	0.4	0.2	1.5	1.0[2]
PCP-IN	3.6	70.6	22.2	ND[3]	0.9	ND	2.7[4]
PCP-GW	3.6	43.4	13.0	3.1	33.7	0.6	2.6[5]

[1] Since the totes were not uniform in appearance, a composite sample from all of the PCP-NJ totes was analyzed.

[2] Dirt and paper

[3] ND: Not detected

[4] 2.1% EVA and 0.6% dirt and paper

[5] 0.4% polyamide, 0.4% polycarbonate and 1.8% dirt and paper

Table XXV shows the operating data, product yields and componential yields for the six runs in which PCP was utilized as a feedstock.

Table XXV Operating data, product and componential yields for post-consumer plastic studies

Run Number	49	59	60	61	63	75
Feedstock	PCP-OR	PCP-NJ	PCP-NJ	PCP-IN	PCP-GW	PCP-GW
Feed Rate (lb/hr)	56&100	105	121	108	74	119
Furnace Temp. (°F)	1250	1300	1300	1300	1350	1400
Retort Temp. (°F)	1000	950	942	970	1095	1054
	Normalized Yields (wt%)					
Oil Yield	43.4	57.9	60.2	55.2	30.8	32.0
Gas Yield	56.6	42.1	39.8	44.8	69.2	68.0
	Gas Component Yield (wt%)					
Hydrogen	0.2	0.1	0.1	0.1	0.6	0.4
Methane	3.2	1.9	1.8	1.9	5.6	5.2
Ethane	3.7	2.9	2.7	2.7	4.1	4.3
Ethylene	6.2	4.2	4.4	4.0	7.5	7.2
Propane	1.7	1.8	1.5	1.4	1.5	1.8
Propylene	11.2	7.9	7.3	8.2	10.9	11.6
Total C4's	15.3	11.8	11.2	12.2	12.9	14.3
Other	15.1	11.5	10.8	14.3	26.1	23.2

Table XXV Continued

	Retort Oil Component Yield (wt%)					
Total Aliphatics	14.4	37.8	41.6	31.6	5.8	11.0
≤ C10	7.2	16.0	13.8	15.3	2.4	5.6
C11 - C20	5.6	15.4	17.9	11.5	2.8	4.0
>C20	1.6	6.4	9.9	4.8	0.6	1.4
Total Aromatics	26.4	12.7	12.1	14.4	23.1	17.3
Benzene	2.2	1.0	0.7	1.1	3.8	5.2
Toluene	4.5	1.8	1.3	2.2	3.3	2.4
Styrene	7.4	0.7	0.7	4.1	4.6	2.1
Unidentified	2.6	7.4	6.5	9.2	1.9	3.7

Table XXVI lists the total chloride analyses for the product oil.

Table XXVI Retort oil total chloride analyses from post-consumer plastic studies

		Feed Rate (lb/hr)		Retort Oil Total Chloride Levels (ppm)		
Run #	Feed	Resin	Lime Hydrate	Mean	Low	High
49	PCP-OR	100	10	18	14	22
59	PCP-NJ	105	8	25	13	39
60A	PCP-NJ	121	20	28	28	28
60B	PCP-GW	121	10	32	25	39
61	PCP-IN	108	7	26	14	60
63	PCP-GW	74	10	22	21	22
75	PCP-GW	119	20-30	17	10	24

Figure 32 graphs retort temperature vs. liquid yield for the PCP studies. Also included in Figure 32 is the least squares fit of the corresponding data from the parametric study (taken from Figure 23). In general, retort temperatures were higher for the PCP runs than for many of the base feed runs.

Compared with the parametric study runs, the PCP runs exhibited a slightly depressed liquid yield for a given retort temperature. Runs 63 and 75 diverge significantly from the parametric study model. It is thought that high PET levels reduce the accuracy of retort temperature for prediction of liquid yield. Figure 33 shows the relationship between C2'+C3' and liquid yield for the PCP studies. As before, Runs 49, 59, 60 and 61 lie close to the parametric study model, while Runs 63 and 75 diverge.

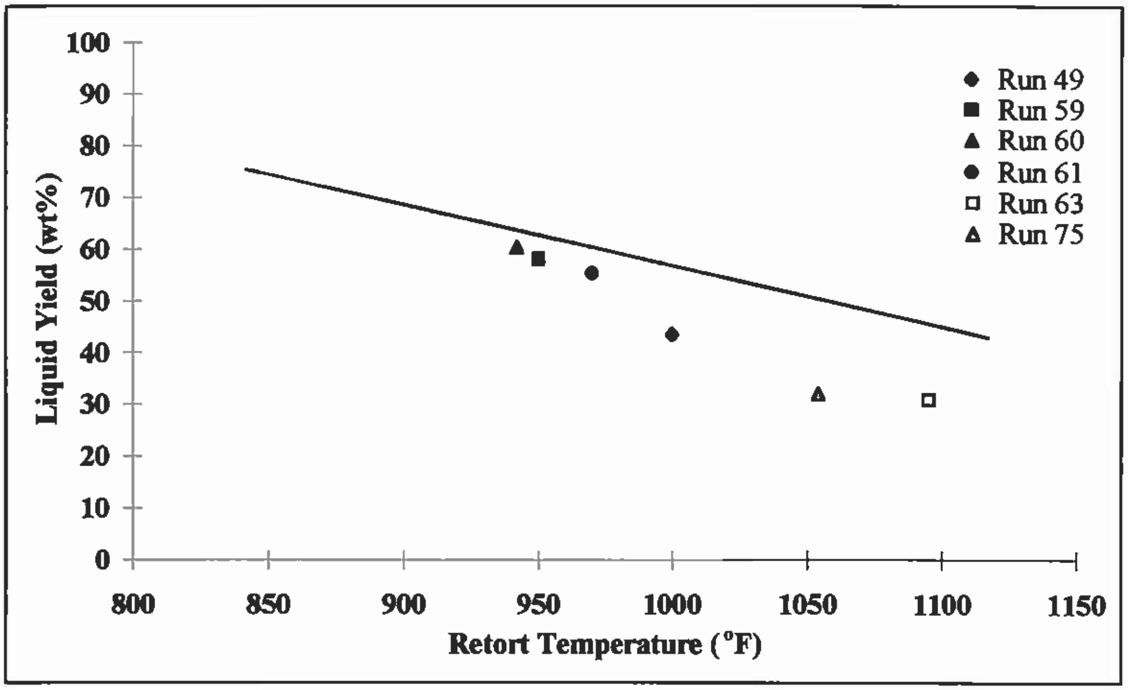

Figure 32 Variation in liquid yield with retort temperature for post-consumer plastic studies

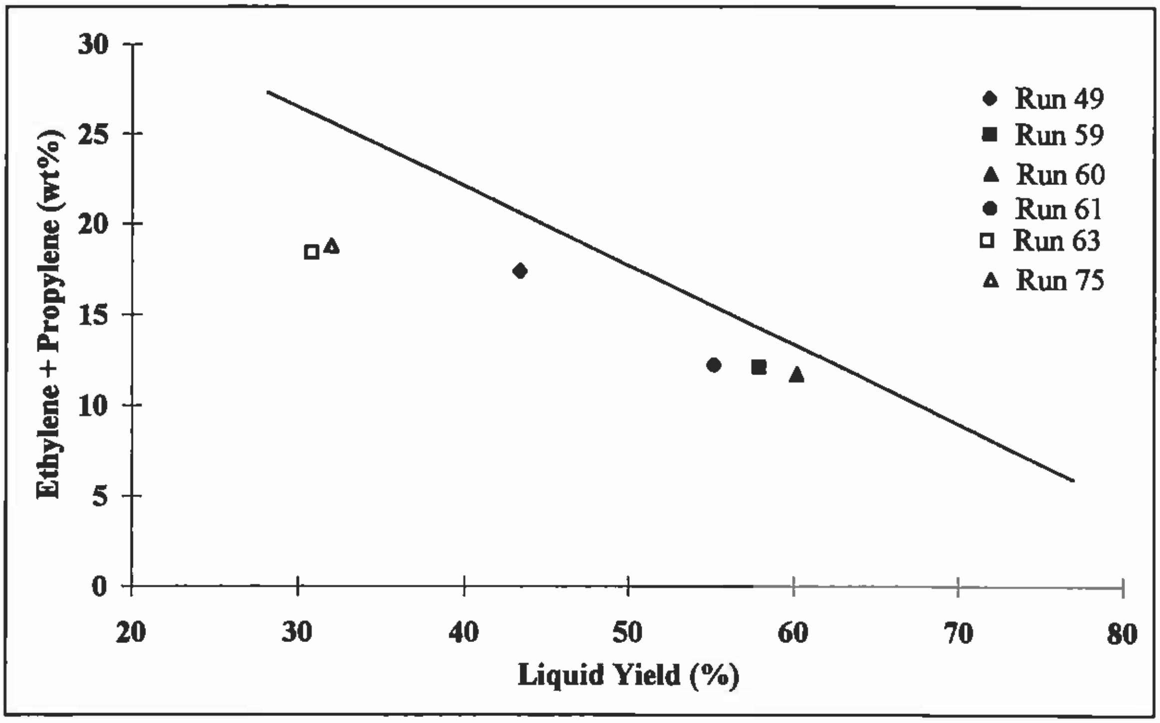

Figure 33 Variation in combined yields of ethylene and propylene with liquid yield for post-consumer plastic studies

A GC/MS analysis of oil produced from post-consumer plastic was performed at Southwest Research Institute. The oil was a retort sample from Run 49 when PCP-OR was processed in the DART unit. The GC/MS analysis is listed in section 8.4 of the Appendix.

4.3.1 Oregon

PCP-OR contained high levels of HDPE (75%), moderate levels of PP, PS and PET (5-9%) and low levels of PVC (0.5%). The PCP-OR feedstock was recycled during Run 49 at a retort temperature of 1000 °F and with lime hydrate addition at 10 lb/hr. The run began with a feed rate of 56 lb/hr and concluded at 100 lb/hr. The goal of the run was to successfully recycle post-consumer plastic for the first time. A secondary goal was to determine whether any mechanical modifications to the DART unit might be necessary for processing chopped post-consumer bottles.

Oil produced from PCP-OR was moderately low in viscosity, with no evidence of TPA. The overall oil yield was low (43%) for the run due to the moderately high retort temperature of 1000 °F. With a few minor differences, the gas and oil component yields are very similar to those from Run 36, which utilized base resin with 1% PVC and 10% PET. The concentration of total chlorides in the oil was very low, ranging in value from 14-22 ppm.

The run progressed without any major mechanical difficulties. Because of the inability of the vacuum feed transfer system to transfer chopped post-consumer bottle plastic, a new feed hopper was utilized for introducing the chopped post-consumer bottle plastic to the surge bin.

4.3.2 New Jersey

PCP-NJ contained primarily polyolefins (97%), PVC (1.5%) and low levels of PET and PS. During Run 59 and a portion of Run 60, PCP-NJ was recycled with lime hydrate at a retort temperature of 940-950 °F. Polyolefins (primarily HDPE) comprised 97% of the plastic mixture. The oil analyses (see Table XXIV) indicated the presence of high levels of heavy aliphatics, which contributed to the high viscosity of the oil. Identifiable aromatic compounds were present at extremely low levels in the product oil, a result that probably derives from the extremely low levels of PET and PS in the feed. The total oil yields of 58% and 60% were somewhat lower than had been attained with base resin mixtures. Part of the reason for this lower yield is thought to be the near absence of polystyrene and polypropylene from the feed and the relatively low retort temperature. Polypropylene and polystyrene are thought to depolymerize relatively early and help catalyze polyethylene depolymerization. Unidentified compounds comprised 11-13 wt% of the oil.

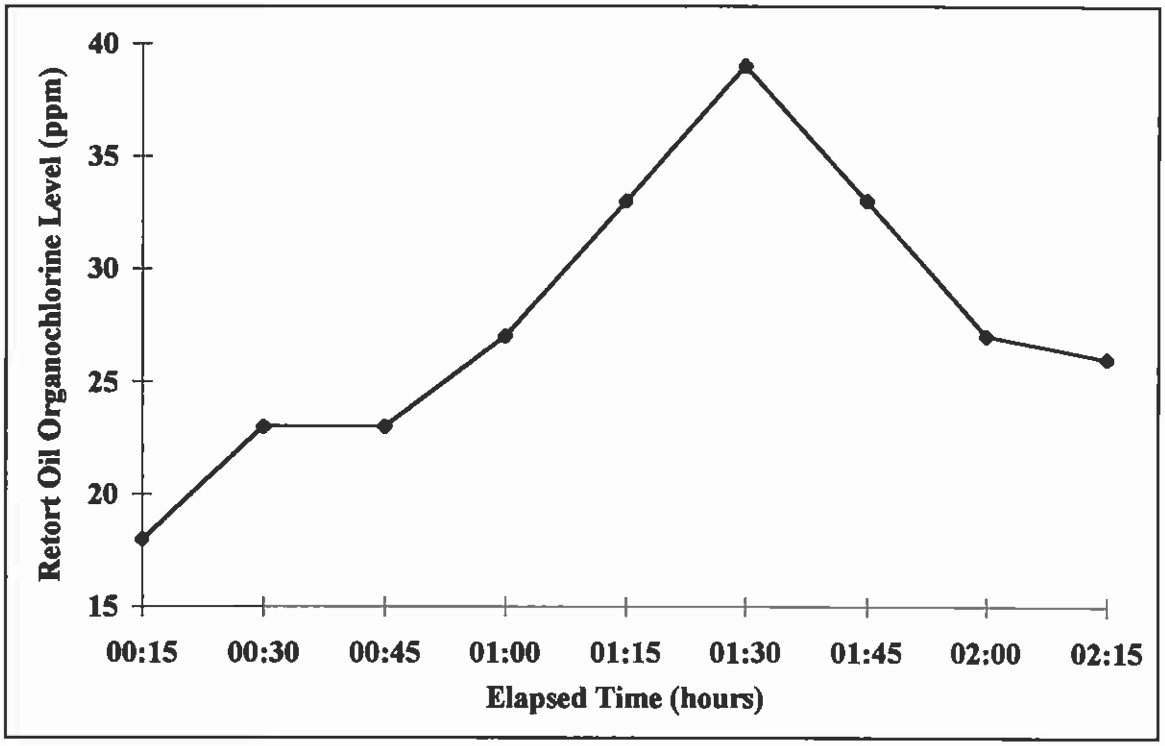

Figure 34 Retort oil total chloride analyses following the addition of high-PVC PCP during Run 59

Run 59 was the only study in which post-consumer plastic with moderately high levels of PVC (1.5%) was processed. Early in the run, it was noted that there was extreme non-uniformity of appearance between each tote (see the footnote at the bottom of Table XXV). In addition, many of the totes contained layers of chopped plastic that were not uniform in appearance. Throughout the run, the concentrations of dense materials in the PCP feedstock (potentially including PET, PVC, glass, metal and rocks) were monitored by separation in salt water followed by manual separation of the dense plastic from the other material. During these tests, one of the samples contained ~8% dense plastic material by weight. Each of the remaining 14 tote samples contained <0.2% dense material. The 8% dense material was analyzed on the Dohrmann microcoulometer and was identified as a chlorine-containing polymer. A subsequent off-site analysis verified that the material was a copolymer of PVC with polyvinylacetate. For a 2.5 hour period during Run 59, the PCP containing 8% PVC was processed in the DART unit with 8 lb/hr lime hydrate while performing retort oil total chloride analyses every 15 minutes. None of the analyses indicated chloride levels >40 ppm. Figure 34 shows the total chloride analyses over time following the addition of the PVC-containing post-consumer plastic.

4.3.3 Indiana

PCP-IN was recycled during Run 61. This plastic mixture was very similar to PCP-NJ except that PVC was not detected. Polyolefins (primarily HDPE) again comprised 97% of the plastic mixture. Although no PVC was detected in the feed, lime hydrate was added as a precaution at 7 lb/hr. The retort temperature was 970 °F and the feed rate was 108 lb/hr. Liquid yields were lower due to the lack of easily depolymerized resins (PP or PS) in the feed.

As with Runs 59 and 60A, aliphatic compounds made up a major portion of the oil. Unidentified compounds accounted for nearly 19 wt% of the oil. The gas analyses were nearly identical to those from PCP-NJ. Nearly all of the Dohrmann analyses indicated low total chloride levels, although one retort sample appeared to have a slightly elevated concentration (60 ppm).

4.3.4 Goodwill

Nearly all post-consumer plastic that was available to the project contained low concentrations of PET. However, PCP-GW contained 34% PET because the plastic was intentionally not sorted to remove bottles made from high-value PET and HDPE-natural resins. Even though post-consumer plastic was not expected to contain high levels of PET, it was of interest to determine whether pyrolysis was viable for this type of feedstock. Run 60B and 63 were short "shakedown" studies and were conducted with a retort temperature of 1050 °F - 1100 °F, which was sufficiently high to eliminate TPA problems. Lime hydrate was added at 10 lb/hr. Several oil and gas samples were obtained, along with information about the operating reliability of the DART unit. From the short runs, it was determined that the high PET concentration did not adversely affect the capture of HCl from the 0.6% PVC that was present. The levels of total chlorides in the oil samples ranged from 21 - 39 ppm. The gas analyses showed high levels of carbon oxides, which were also seen in the studies with PET-spiked feedstocks. Liquid yields were very low (30%) because of the elevated retort temperatures and the extremely high levels of PET present in the feed.

The objective of Run 75 was to investigate the relationship, at low pyrolysis severity, between lime hydrate addition rate and terephthalic acid production for the PCP-GW plastic mixture. The run was conducted over a retort temperature range of 950-1000 °F, which was far below the temperatures used previously to process high-PET feedstocks without formation of TPA. It was thought that the presence of a large amount of lime hydrate might reduce the tendency for TPA production, which had been observed at low retort temperatures like those used in Run 75.

Before reaching stable operating conditions on the DART unit, it was apparent that elevated feed rates of lime hydrate did not inhibit the production of TPA. Lime hydrate was initially introduced at 20 lb/hr, and TPA was observed in the retort oil samples. After eight hours of operation, the lime hydrate feed rate was raised to 30 lb/hr. After an additional eight hours, it became clear that TPA production was not diminished, and the study was concluded. Retort oil samples contained about 4.5% TPA by weight. It was concluded that higher retort temperature is the only effective method to avoid TPA problems.

Although the retort temperature was relatively low throughout the run, the oil yield was lower than expected, about 32%. As was the case during Runs 60B and 63, the oil samples contained low levels of total chlorides.

4.4 Recycling of Wax and Chlorinated Oils

Five runs were dedicated to the recycling of wax and chlorinated oils. The focus of these runs was twofold: to investigate the utility of the DART system for recycling light hydrocarbon waxes and chlorinated oil wastes, and to demonstrate that on-site remediation of wastes from the project was possible. Information about the process technology that was used to recycle wax and chlorinated oils is not listed. The chlorinated pyrolysis oil feedstocks for these runs were generated during Runs 25, 26 and 29 and contained total chlorides at various concentrations from 1000 - 5000 ppm. The melting range of the wax was 100-130 °F and was produced at various times throughout the project.

The intent of Runs 37, 43 and 44 was to discover whether it would be possible to feed chlorinated pyrolysis oil with base resin and generate product oil with acceptable total chloride levels. As shown in Table XXVII, the range of total chloride concentrations in the product oil during these three runs ranged from <10 to 82 ppm. It is thought that during portions of Run 43, the lime hydrate feeder operated inconsistently, which may explain some of the higher levels of total chlorides. Product oil from Runs 67 and 68 contained a maximum of 24 ppm total chlorides.

Table XXVII Retort oil total chloride levels from oil recycling studies

		Feed Rate (lb/hr)			Retort Oil Total Chloride Levels (ppm)		
Run #	Feed Type	Base Resin	Oil	Lime Hydrate	Mean	Low	High
37	Cl-oil + resin	117	53	10	23	11	48
43	Cl-oil + resin	72	69	10	19	<10	82
44	Cl-oil + resin	71	42	10	11	<10	17
67	Cl-oil	0	97	10	20	15	24
68	Cl-oil	0	130	5	16	12	20

Table XXVIII compares the hydrocarbon analysis of the chlorinated oil feedstock with the yields (not concentrations) of the hydrocarbon components in the oil produced during Run 67. Also shown is the conversion factor, which facilitates comparisons of individual component yield losses. Overall, only about 30% of the oil was converted to gas during the dechlorination process. With the exception of benzene, all of the main oil components were converted to smaller hydrocarbons. From the data it appears that a large amount of styrene was converted, possibly to toluene and benzene (along with methane and ethylene). The heavy aliphatic hydrocarbons were lost in higher proportion than the other aliphatics.

Table XXVIII **Feedstock analysis and product component yields for Run 67**

Component	Feedstock Component Concentrations (wt%)	Product Yields (wt%)	Conversion Factor (%)
Total Liquid Yield		69.2	–30.8
Total Aromatics	53.8	41.6	–23
Benzene	2.4	2.8	+17
Toluene	8.6	8.0	–7
Styrene	21.1	9.8	–54
Total Aliphatics	33.2	19.8	–40
<C11	15.5	9.0	–42
C11 - C20	12.5	8.7	–30
>C20	5.2	2.1	–60
Unidentified	13.0	7.8	

During a portion of Run 68, low melting point waxes that were produced earlier in the project were processed. Although no analytical results are available for the products, it is known that a substantial amount of gas was produced along with a quantity of relatively low viscosity oil.

It is assumed that the majority of organochloride compounds in the pyrolysis oil feedstocks are monochlorinated species. It is not known whether the efficiency of chlorine capture would be reduced if polychlorinated species such as methylene chloride, 1,1,1-trichloroethane or other chlorinated solvents were present in the oil. However, the combined successful results from processing a polychlorinated resin (PVC) and recycling chlorinated pyrolysis oil imply that the DART unit may be useful as a future means of recycling chlorinated oil wastes.

4.5 Characterization of By-products

For most of the studies in which PVC-spiked plastic or post-consumer plastic were processed, lime hydrate was added to the retort to capture hydrogen chloride. After passing through the retort, the utilized and excess lime along with some carbon was collected as part of the solid residue. The solid residue also contains impurities present in the lime hydrate along with inorganic constituents present in the original plastic, including fillers, residual catalyst and mold release agents. The following reactions involving lime hydrate are thought to occur in the retort.

$$Ca(OH)_2 \rightarrow CaO + H_2O$$
$$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$$
$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Solid residue samples from Run 49 (PCP-OR) and Run 59 (PCP-NJ) were characterized at EERC. Based on the results of elemental and bulk inorganic analyses, Table XXIX summarizes the overall constituent concentrations in the solid residue samples. As expected, the samples are composed primarily of calcium carbonate, lime and carbon. Smaller amounts of sand and calcium chloride are present along with a variety of other constituents. The chloride level in the sample from Run 59 was fairly high, which is consistent with the relatively high level of PVC present in the plastic feedstock (1.5%). Plastic feedstock from Run 49 contained 0.5% PVC.

Table XXIX Characterization of by-product solids

Constituent	Run 49 (%)	Run 59 (%)
$CaCO_3$	53.7	41.2
CaO	22.6	26.5
Organic Carbon	9.0	12.0
SiO_2	1.45	5.30
$CaCl_2$	0.76	2.14
Hydrogen	0.72	0.47
TiO_2	0.68	1.50
Al_2O_3	0.62	1.21
MgO	0.38	0.65
Na_2O	0.30	0.71
$Fe_2O_3 + Fe_3O_4$	0.16	0.29
Sulfur	0.08	0.18
Total	90.45	92.15

Graphs showing the particle size distribution for each sample are shown in Figures 35 and 36. Both samples show a bimodal size distribution with nearly all particles less than 100 μ.

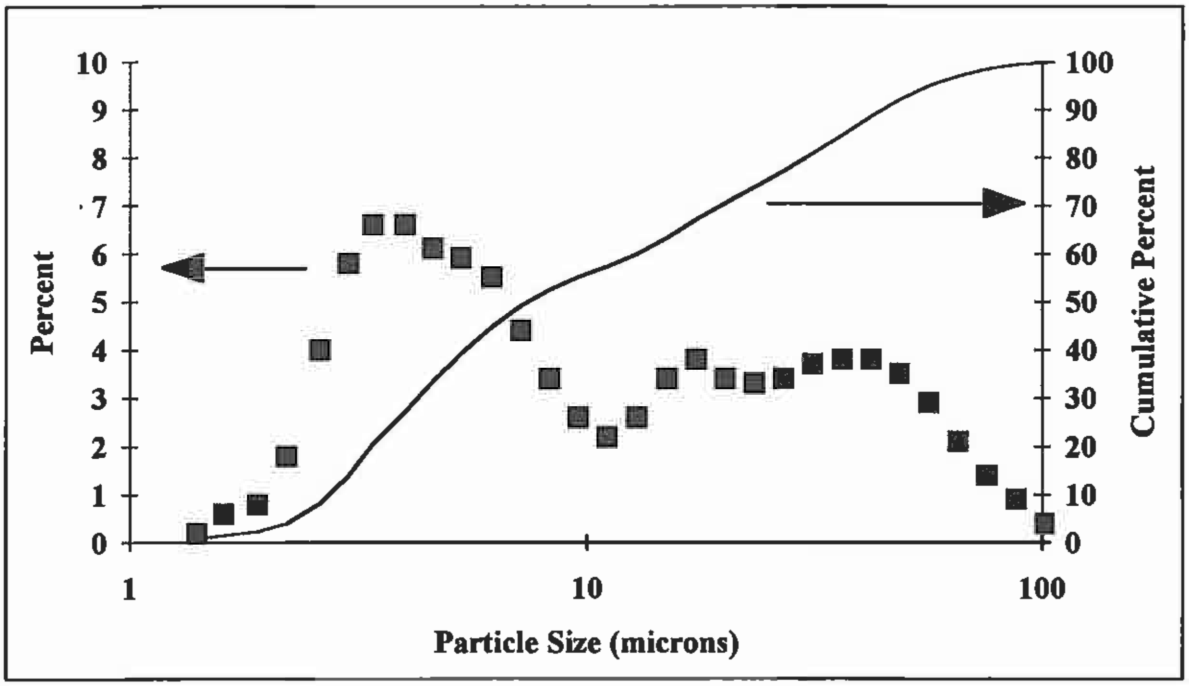

Figure 35 Particle size distribution of by-product solids from Run 49

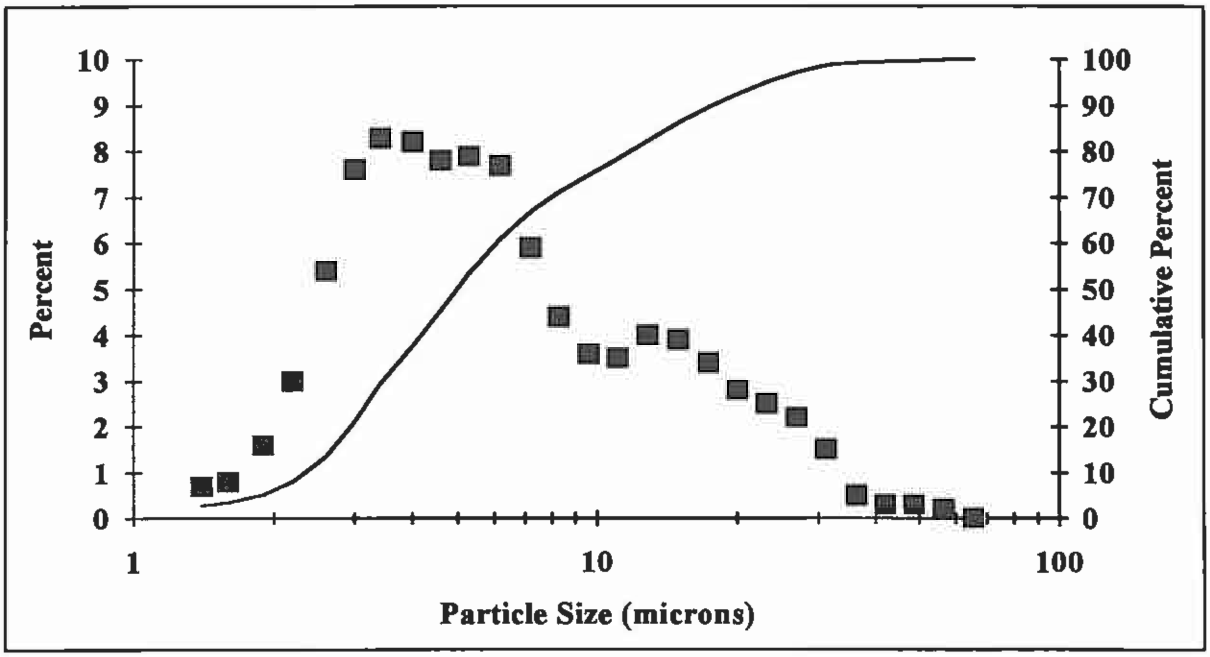

Figure 36 Particle size distribution of by-product solids from Run 59

4.6 Product Market Potential

4.6.1 Product Liquid

A primary objective of the recycling project was to produce a marketable liquid product with good value. For this reason, extensive refinery trials were conducted at two different refineries. During these trials, the liquid product was successfully processed into hydrocarbon streams from which basic petrochemical building blocks of gasoline, heating oil and other petroleum-based products are made.

A total of 37,500 pounds of liquid product was shipped to Lyondell Petrochemicals in Houston, Texas on 11/8/93. The liquid was mixed at a low level (<5%) with Resid and processed in the Lyondell-Citgo Delayed Coker unit. From the feedstock mix, 110,000 pounds of petroleum coke were produced along with coker naphtha, light gas oil and heavy gas oil. The liquid samples were analyzed by Comsource American in Pasadena, Texas. The petroleum coke samples were tested by Commercial Testing and Engineering Company in Deer Park, Texas. Although minor variations in the data were noticed, no significant differences were observed. In the opinion of the professional staff at Lyondell, the use of this type of feedstock would be indistinguishable from other feedstocks processed in the delayed coking unit of a refinery. It was also believed that most of the liquid product from plastics was volatilized and left the coker as naphtha, light gas oil and light gases.

A total of 68,500 pounds of liquid product was shipped to the Book Cliffs Energy Corporation Refinery in Green River, Utah on 4/1/94 and 9/7/94. The liquid was mixed with an equal amount of used industrial oil and injected into the vacuum column. The gas oils were then drawn off and the light ends were taken out. The gas oils were processed in the catalytic cracker to produce a 50/50 yield of high octane gasoline and diesel fuel. Based on the successful trial and the high level of octanes in the DART liquid product, the Book Cliffs personnel have proposed a dedicated run with the liquid product from the APC/Conrad project.

4.6.2 By-product Solids

Although not a primary goal of the project, some studies have been conducted to investigate the marketability of the by-product solids from the project. Samples of the solids were processed at Tide Corporation in Albuquerque, New Mexico. The solids were compressed into dense bricks for potential use as building material. TCLP tests of the bricks indicated that the product was environmentally safe. For more information, see sections 4.5 and 5.3.

4.6.3 Wax

Accumulation of C25-C50 waxes in the solids collection system occurred during some of the shakedown runs and early parametric study runs. Chevron Research and Technology Company in Richmond, California has conducted preliminary bench-scale cracking trials with the wax. Although the trials were viewed positively by the Chevron personnel, the trial results were proprietary and were not released by Chevron.

5. Environmental

5.1 Air Permitting

5.1.1 Stack Emissions

The purpose of air emission testing was to quantify emissions of particulate matter, SO_2, NO_x, CO, metals, base/neutral/acid semi-volatile organic compounds (BNA's) and speciated volatile organic compounds (VOC's) as well as HCl and polychlorinated dibenzodioxins and dibenzofurans. The tests were performed by an independent air emissions testing firm. Many runs were conducted with PVC plastics and it was essential to quantify the impact on organochlorides in the air stream and to capture the HCl before release to the atmosphere.

Table XXX lists the results of the first air emission test, conducted in May 1993. The test occurred during Run 7, in which base resin was processed.

Table XXX Results of May, 1993 air emission test

ANALYTE	AVERAGE CONCENTRATION IN RETORT EXHAUST	AVERAGE CONCENTRATION IN FLARE EXHAUST
Particulate	0.020 lb/hr	0.012 lb/hr
CO	0.33 ppm	0.167 ppm
SO_2	1.4 ppm	0.8 ppm
NO_x	273 ppm	146.5 ppm
BNA's	Nearly all compounds were undetected. Trace amounts of chlorinated organic compounds were detected at values that were so close to their detection limit, they were thought to be false positives.	
VOC's	For the most part, these compounds were not detected. The only compounds that were present at levels above their detection limit were acetone, methylene chloride (CH_2 - Cl_2) and trichloroethylene. These were not considered significant because they are common laboratory contaminants.	
Metals	The average concentrations were below detection limits or were not considered to be significant.	

The purpose of the next air test was to evaluate the emissions of the flare exhaust while the DART unit was operating with a feedstock that contained 3% PVC without lime hydrate addition. The test occurred during Run 25 and is summarized in Table XXXI. The Southwest Air Pollution Control Authority (SWAPCA) desired that the level of the HCl be less than 12 ppm. The measured value of 4.5 ppm was substantially below this limit. No benzene limit was set. However, the 0.271 mg/min was considered to be acceptable by SWAPCA.

Table XXXI Results of October, 1993 air emission test

ANALYTE	AVERAGE CONCENTRATION IN FLARE EXHAUST
CO	1.0 ppm
HCl	4.50 ppm
NO_x	57.5 ppm
Benzene	0.271 mg/min

The final air emission test occurred during Run 39, February of 1994. During this run, feedstock containing 2% PET and 0.5% PVC was processed without the acid gas scrubber and with a plastic/lime hydrate physical weight ratio of 10/1. The results of the test are shown in Table XXXII.

Table XXXII Results of February, 1994 air emission test

ANALYTE	AVERAGE CONCENTRATION IN RETORT EXHAUST	AVERAGE CONCENTRATION IN FLARE EXHAUST
Particulate	0.001 gr/dscf	0.002 gr/dscf
CO	1.0 ppm	0 ppm
NO_x	53.5 ppm	53.5 ppm
Benzene	2.2 ug/m^3	ND
Total Tetra-Octa Polychlorinated Dibenzofurans (PCDF)	0.180 ng/m^3 † 0.950 ng/m^3 ✠	0.248 ng/m^3 † 2.72 ng/m^3 ✠
Total Tetra-Octa Polychlorinated Dibenzodioxins (PCDD)	0.259 ng/m^3 † 1.34 ng/m^3 ✠	0.551 ng/m^3 † 6.09 ng/m^3 ✠
Total PCDF & PCDD Tetra-Octa	0.438 ng/m^3 † 2.29 ng/m^3 ✠	0.798 ng/m^3 † 8.81 ng/m^3 ✠
Polynuclear aromatic hydrocarbons were not detected in the retort stack nor in the flare.		

† uncorrected

✠ corrected @ 7% O_2

On March 2, 1995, SWAPCA issued a Notice of Construction to Conrad Industries, Inc. to operate the Advanced Recycling Technology Systems for processing post-consumer plastic. The Notice of Construction was given on the condition that air emission testing be conducted to quantify emissions to atmosphere using the best available control technology.

A ninety-nine percent Destruction Removal Efficiency of hydrocarbons for the retort exhaust and thermal oxidizer (flare exhaust) was specifically required to meet California South Coast Air Quality Management District "BACT" Guidelines & Regulations. These regulations are considered among the most stringent in the country.

SWAPCA required the following additional emission limits for the project:

• SO_2	1.0 ton/yr
• NO_x	2.0 ton/yr
• CO	0.5 ton/yr
• Opacity	0
• Particulate	0.005 gr/dscf
• HCl	99.9% removal

With the exception of NO_x, these conditions were met based on the excellent overall results. SWAPCA granted a variance on the NO_x emission limit because the DART unit still achieved greater than 99% destruction removal efficiency.

The following summarizes the air emission results:

CO	The average concentration was less than 5 ppm uncorrected or corrected for both the retort and the flare, which is well below typical emission standards.
NO_x	The DART unit averaged 60 ppm on the final two emission tests, which is well within the required ranges and standards.
SO_2	The average concentration was zero.
PCDD/PCDF	The average emission concentration for total PCDD and PCDF was 0.438 and 0.798 ng/m^3 (uncorrected) and 0.609 and 1.40 ng/m^3 @ 7% O_2 for the retort and flare respectively. This is far below EPA subpart emission standards.
PAH	Results were generally below the detection limit.
Benzene	The typical benzene standard is 500 ppbv listed by the National Emission Standard for Hazardous Air Pollutants. Emissions from the DART unit ranged from 0.2 to 1.4 ppbv, which is well below this standard.

5.1.2 Fugitive Emissions

EPA regulations mandate that VOC fugitive emissions be controlled under the New Source Performance Standards (NSPS).

An emissions control service was retained to monitor the DART unit. The emissions control service began by identifying, logging and tagging the required components and generating a component list. Monitoring began with all components being scheduled for monitoring either monthly or quarterly. EPA NSPS regulations state that after five consecutive quarters, with leak detection at less than 2%, annual monitoring only is required. To date 238 components have been monitored on the DART unit for four consecutive months without detection of any leaks. Continued on-line maintenance will result in a substantial reduction in emission monitoring costs.

5.2 Water

Waste water was generated during the parametric study and originated from two sources: water that collected in the light oil condensing sump and spent acid scrubber water.

The contaminants in both types of waste water were similar, so a common on-site treatment process made the water acceptable for disposal to the local water treatment facility.

Before treatment, the waste water was considered to be a potentially hazardous waste due to the presence of benzene at 120 ppm. After treatment the benzene level was 1 ppb, which was well below the 15 ppb effluent limit in the state water discharge permit for the Conrad facility.

The acid gas scrubber was used whenever resin feed containing PVC was tested. Initially, the scrubbing medium was a circulating solution containing less than 1% NaOH. The total dissolved salt concentration was maintained between 6 and 12 wt%. With adequate lime hydrate addition to the retort, there were no indications of any breakthrough of hydrogen chloride (HCl) into the scrubber. However, carbon dioxide was present in the non condensable gases, which resulted in a waste stream of aqueous sodium carbonate and sodium bicarbonate. The solution was periodically drained to a neutralization system, where addition of 93% sulfuric acid lowered the pH to 8-9.

Relocation of the scrubber to downstream of the light oil condensing tower coupled with the use of sodium carbonate solution in the scrubber eliminated the need for two hazardous substances, sodium hydroxide and sulfuric acid. Since sodium carbonate solution was ultimately converted to sodium bicarbonate in the scrubber by the continuous influx of CO_2, the waste stream did not require acid addition to meet acceptable pH limits.

Waste water treatment involved first passing the water through a 3-5 micron coalescer filter to remove turbidity and any suspended oils. The water was then passed through two activated carbon drums in series.

One surprising result was a slightly elevated concentration of arsenic in the waste water, nearly 0.5 ppm. A search revealed that the arsenic source was lime hydrate, where a typical arsenic concentration is 7-15 wt. ppm.

As shown in Table XXXIII, the concentrations of hydrocarbon contaminants were greatly reduced by the treatment process.

Table XXXIII Levels of hydrocarbon contaminants in waste water

CONTAMINANT	MEASURED CONCENTRATION IN UNTREATED WATER (mg/l)[1]	MEASURED CONCENTRATION IN TREATED WATER (mg/l)[2]	REGULATED CONCENTRATION (mg/l)[3]
Acetone	330	ND[4]	NA
Benzene	120	.001	0.015
2-Butanone[5]	50	ND	200[6]
Ethylbenzene	8.8	0.0073	0.030
Methylene Chloride	4.5	ND	NA
Styrene	45	0.017	NA
Toluene	67	0.015	0.040
Total Xylenes	ND	0.039	NA

[1] Based on a sample of untreated interface water collected by Conrad Industries on March 3, 1994

[2] Based on a sample of treated interface water collected by Conrad Industries on July 5, 1994

[3] Quarterly average effluent limitations from State Waste Discharge Permit

[4] Not detected

[5] Methyl ethyl ketone

[6] As defined by the Toxicity Characteristics List, WAC 173-303-090 (8)

5.3 Solids

5.3.1 By-product Solids

During the runs in which lime hydrate was added to the retort, a significant quantity of by-product solids were generated. These solids were studied by EERC[*] and are characterized in section 4.5 of this report. A portion of the EERC work centered on the leaching characteristics of the by-product solids that resulted from Run 49 (PCP-OR) and Run 59 (PCP-OR).

Initially, TCLP tests that were performed by MVTL Laboratories, Inc. indicated that the samples were environmentally nonhazardous. The subsequent leaching study by EERC confirmed the nonhazardous characterization of these samples. Table XXXIV lists the results of the leaching study.

Table XXXIV Leaching results for by-product solids

	Run 49 (μg/L)		Run 59 (μg/L)		Reg. Limits (μg/L)	
	18-hr	7-day	18-hr	7-day	PDWS[1]	RCRA[2]
Ag	<1.5	<1.5	<1.5	<1.5	50	5,000
As	<4	<4	<4	<4	50	5,000
Ba	3,060	4,520	2,680	2,900	10,000	100,000
Cd	<0.1	<0.1	<0.1	<0.1	10	1,000
Cr	<50	<50	<50	<50	50	5,000
Hg	<0.1	<0.1	<0.1	<0.1	2	200
Pb	771	638	23.4	38.8	50	5,000
Se	3.8	3.7	6.7	5.6	10	1,000

[1] Primary drinking water standard

[2] Resource Conservation and Recovery Act

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[*] Pflughoeft-Hasset, Debra F.; Dockter, Bruce A., Eylands, Kurt E., Hasset, David J. "Characteristics of Residues from Thermal Recycling of Plastics" final report to the American Plastics Council; EERC publication, June, 1995

6. Health and Safety

The health and safety of the plant personnel is under continuous evaluation. Before any of the initial shakedown runs were performed, an exhaustive safety review of the DART unit was conducted by Conrad Industries and Kleenair Products personnel in conjunction with engineers from APC member companies. In addition, the plant operators were thoroughly educated about the hazards of working in a refinery-type environment before any actual studies were conducted. As the studies began and previously unforeseen health and safety issues became important, additional training of the operators was undertaken. Finally, when the nature of the specific industrial hygiene issues became apparent during the course of the project, a comprehensive industrial hygiene plan was developed by an outside contractor in conjunction with Conrad personnel.

6.1 Industrial Hygiene

The purpose of the Industrial Hygiene (IH) Plan is to provide and maintain a safe and healthful work place for all plant personnel. Industrial Hygiene monitoring is required to characterize work place exposure to airborne contaminants. The IH sampling plan applies to all hazardous contaminants to which there is a potential for airborne exposure on a routine or non-routine basis.

IH monitoring is conducted only by trained employees. Employee training is conducted by a Certified Industrial Hygienist.

IH sampling is conducted to adequately characterize exposure to the following contaminants:

- Benzene
- Hydrogen sulfide
- Carbon monoxide
- Metals (lead, cadmium, arsenic)
- Hydrogen cyanide
- Other potential airborne contaminants produced in the recycling process under feedstock conditions not previously evaluated

Each of the above contaminants is monitored at a specific frequency. Employees are notified within a specific time period of the results of IH sampling analyses. Detailed records are kept which include specific sampling conditions, sampling procedures, monitored employee information and environmental variables. Sampling and monitoring equipment is calibrated prior to and after each use.

Specific procedures for hydrogen cyanide safety and monitoring are found in a separate plan entitled Hydrogen Cyanide Safety Guidelines and Emergency Response.

During processing, sludge tank cleaning or leaks, spills, ruptures or breakdowns, there exists the potential for the release of significant levels of contaminants to which exposure has not been characterized. If this type of situation occurs, exposure monitoring is conducted in accordance with applicable standards using NIOSH- or OSHA-approved sampling protocols and analytical methods.

Sampling results are interpreted in accordance with applicable exposure limits (WISHA Action Levels, PEL's, STEL's and Ceiling Limits) and recommended exposure guidelines (ACGIH TLV's).

6.2 Safety Review

Prior to construction of the DART unit, a series of safety review meetings were held. The intent of the project was to utilize an existing machine and make changes only where necessary. Therefore, the safety meetings focused on examination of the existing machine on a section-by-section basis. The meetings also aided development of an acid gas liquid scrubber system which was necessary for the planned testing.

The safety review meetings were chaired by industry safety personnel. During the safety review, a DART process or function was described and hazardous scenarios were constructed by industry representatives which addressed potential safety issues associated with each process or function. These safety issues were resolved by ascertaining the resulting process effects, judging what, if any, safety implications were likely, deciding whether the current protection strategy or equipment was adequate, and if needed, recommending changes that would enhance safety.

The safety review also scrutinized related items pertaining to feed verification and storage, analytical sampling, product storage and shipping, and general plant safety.

6.3 Operator Training

Operator training encompasses all facets of facility operation. American Plastics Council members, along with an environmental consultant, identified state and federal requirements. They also defined specific training areas known to be needed prior to beginning DART parametric studies. Training was prioritized based on DART equipment progress and personnel exposure potential. Training began with operational issues such as general health and safety, first aid, emergency response, and forklift handling. Operator training progressed to hazardous material handling, hazardous communications, environmental awareness and advanced environmental training.

Employee training is essential to facility operations. Training topics therefore included good housekeeping and material management practices, as well as spill prevention and response. At least annually, facility operators also receive training regarding pollution control laws and regulations, as well as reviewing the facility Dangerous Waste

Procedures manual, Stormwater Pollution Prevention Plan, and the Oil Spill Prevention Control and Countermeasure Plan. Training focusing on the specific features of the facility was provided to aid in the prevention of releases of oil, petroleum products and hazardous substances and to prevent pollution of soil, surface water, and groundwater. Personnel training was typically provided during employee safety meetings.

The training curricula is perpetually developed to encompass changes required in personal protective equipment (PPE), safety procedures (which change as the equipment is added or modified), and personal exposure areas are encountered.

The addition of the acid gas scrubber necessitated training in the handling of the entire pH range. Operator involvement in the lab opened another avenue of safety procedures and the studies on PVC and nitrogen-containing compounds required creation of specific operating rules.

Extensive training was required in the operation of the DART unit. Procedures for safe process start-up, operation and shutdown, as well as troubleshooting and alarm response were created and are included in the DART procedures manual.

7. Conclusion

During the project, the American Plastics Council and Conrad Industries demonstrated that pyrolysis is a viable method for recycling post-consumer plastics into liquid petrochemical feedstocks. Seventy-six runs were conducted on the DART unit at the Conrad Industries facility during the 20-month project. The liquid and noncondensable gas products were thoroughly analyzed at the site using gas chromatography and other analytical methods.

Initial shakedown runs were conducted for the purpose of confirming the operating reliability of the DART unit. Following the shakedown runs, a parametric study was conducted to demonstrate the capability of recycling many different combinations of resin types using pyrolysis. A variety of resin types typically found in packaging and durable waste streams were recycled under a range of operating conditions. Analysis of product yield and composition has led to a better understanding of the viability and economics of pyrolysis to recycle plastics. The most important pyrolysis process variable is temperature followed by retention time. At low retort temperatures, liquid oil yields of 65-95% are possible.

The optimal process conditions to attain high liquid yields, good product quality, high feedstock throughput and ease of operation were determined during the parametric study. For base feedstock and plastic feedstocks containing low levels of polyethylene terephthalate (PET), polyvinylchloride (PVC) or intentionally added impurities, liquid yields of 65-75% were achieved with pyrolysis temperatures of 900-950 °F. Liquid produced from base feedstock at these temperatures contained about 55% aromatic compounds and 45% aliphatic compounds. Most of the aromatic compounds in the liquid product were monoaromatic species, such as benzene, toluene and styrene. Most of the aliphatic compounds were olefins and contained less than 20 carbon atoms. However, the concentration of heavier aliphatics was high enough to affect the viscosity of the liquid product. The noncondensable hydrocarbon gas that was produced at 900-950 °F from the above feedstocks contained primarily ethylene, propylene, C4 olefins and methane, with lower concentrations of ethane, propane, butanes and hydrogen. The combined yield of ethylene and propylene in the gas was highly predictive of the liquid yield.

During the parametric study, it was shown that pyrolysis of resin blends with elevated levels of polystyrene or low-density polyethylene exhibited behavior that was nearly identical to that of base resin. The presence of shredded paper at 4% did not appear to adversely affect the process in any way. Pyrolysis in the presence of a cracking catalyst did not have a significant effect on liquid yield or on the yields of individual hydrocarbons in the liquid or gas.

Processing resin blends with elevated levels of PET (20-40%) required substantially more heat than other plastic mixtures and resulted in liquid product containing a significant amount of solid terephthalic acid. It was shown that the presence of terephthalic acid in the liquid product could be eliminated at high pyrolysis temperatures.

The presence of PVC in the plastic feed at 1-3% resulted in product oil with total chloride levels of 5,000-10,000 ppm. It was demonstrated that at these same PVC levels, the total chloride concentration in the oil was reduced to less than 10 ppm with the addition of lime hydrate. The presence of low levels of PET (1-5%) in the feed in addition to PVC did not appear to have a detrimental effect on the resulting total chloride concentration in the oil. The primary factor governing the efficient and total removal of chloride from the system was the physical mixing ratio of plastic feed to lime hydrate. It was shown that efficient chloride removal could be achieved at a feed:lime hydrate physical mixing ratio of about 30:1 for a plastic blend containing 1% PVC and 3% PET.

Feeds containing 5% or more of polyurethane, acrylonitrile butadiene styrene or polyamide were recycled without difficulty. Hydrogen cyanide was not positively detected in the product oil or gas.

Pyrolysis of 100% polystyrene resulted in a 95% liquid yield and a styrene monomer yield of nearly 60%. With further study, it may be possible to achieve styrene monomer yields of 65-70%. Toluene and ethyl benzene concentrations were also high in the liquid product. The capacity of the DART unit for processing 100% polystyrene was almost double that for other resins.

100% polypropylene was processed at 850 °F with a liquid yield of 66%. The liquid product contained primarily olefins that resembled the molecular skeleton of polypropylene. The noncondensable gas contained elevated levels of propylene, isobutylene and *n*-pentane.

Four batches of post-consumer plastic from different regions of the country were successfully recycled. Although PVC, PET and various impurities were present in the post-consumer plastic, the addition of lime hydrate produced a liquid product that was very similar to liquid produced from base feedstock mixtures. Chloride levels in the liquid product were about 10 ppm for all post-consumer plastic batches.

There were no environmental problems associated with the process. Stack emissions were well within air quality limits. Fugitive emissions were monitored without any detection of leaks. Waste water that was generated during the process was treated at the Conrad Industries facility. The treated water was tested and was acceptable for disposal to the local water treatment facility. The by-product solids from the process were thoroughly analyzed and found to contain primarily calcium oxide, calcium carbonate and carbon. The solids were not considered to be environmentally hazardous.

The liquid product from the parametric study was thoroughly analyzed and was found to be acceptable as a refinery feedstock. A 6,000-gallon batch of oil was shipped to the

Lyondell-Citgo Refinery in Houston, Texas for processing. The oil was mixed with Resid and used as a feed to their coker units. Most of the product was volatile and no processing difficulties were observed. It was determined that this type of feedstock is indistinguishable from other petroleum feedstocks to a refinery.

Recycling plastics using pyrolysis is technically feasible. Many of the difficulties which arose during the program were the result of the design of the DART unit, which was not optimized during this research project. The results of this project will enable a pyrolysis unit to be designed that will consistently produce marketable liquid products at yields in excess of 70% from post-consumer plastics containing mixed resins.

8. Appendices

8.1 Original APC/Conrad Industries Test Plan

Table XXXV, on page 138 outlines the original test plan for the Conrad DART unit.

8.2 Lime Hydrate: Physical and Chemical Properties

8.2.1 Properties of Lime Hydrate

The following discussion on the properties of lime hydrate was based, in part, on information from "Chemical Technology of Lime and Limestone", 2nd Edition, by Robert Boynton (John Wiley & Sons Inc.-Publishers).

8.2.1.1 Typical Surface Area

Lime (CaO)	0.8 m^2/g	(by BET method)
Lime Hydrate [$Ca(OH)_2$]	10.0 m^2/g	(by BET method)

This surface area difference may explain why studies by EER and EERC discovered that lime hydrate was more effective than lime in their evaluation of HCl scavenging agents when pyrolyzing PVC.

Also the particle size distribution of the lime hydrate may also contribute to its effectiveness.

8.2.1.2 Particle Size Distribution

Cumulative Percentage by Weight (typical range)	
On 10 microns	5 - 30%
On 5 microns	20 - 60%
Through 2 microns	20 - 30%

Particles below 5 microns are difficult to collect by centrifugal force (cyclones) either in a gaseous or liquid medium. As a consequence a significant proportion of the lime hydrate fed to the retort is swept over into the heavy oil condensation tower where it settles out in the sump. There is no simple device which can be installed in the gas outlet to the pyrolysis retort to diminish this carryover.

In addition to reaction of the lime hydrate with HCl in the retort, there will be reaction of lime hydrate and possibly some lime with some of the carbon dioxide formed by oxidation of hydrocarbons in the retort:

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$
$Ca(OH)_2 \rightarrow CaO + H_2O$ (at 1004 °F)
$CaO + CO_2 \rightarrow CaCO_2$ (starts at 750 °F, rapid at 1100 °F)

Based on the temperature requirements, much of the un-reacted lime in the solids collection drum should be there as lime (CaO) and possibly some calcium carbonate ($CaCO_3$) while the lime in the heavy oil condensation tower sump should be in hydrated form [$Ca(OH)_2$] because of the water formed in the retort by reaction of oxygen (introduced with the resin feed) with pyrolysis products.

8.2.1.3 Lime hydrate reaction with HCl

Very rapid at room temperature.
With lime (CaO) the reaction is fast at temperatures above 175 °F
$Ca(OH)_2 + 2\ HCl_v \rightarrow CaCl_2 + 2H_2Ov$
(water soluble)

8.2.1.4 Lime hydrate reaction with HCN

$Ca(OH)_2 + 2\ HCN \qquad Ca(CN)_2 + 2H_2O$

Calcium cyanide in solid form slowly hydrolyzes to HCN in the presence of water (liquid or vapor). Any calcium cyanide collecting in the carbon-lime drum can slowly hydrolyze to yield HCN when exposed to the environment.

Any calcium cyanide collecting in the heavy oil sump would slowly hydrolyze to HCN as the water vapor in the retort product vapors are condensed. HCN vapors would then pass over into the light oil condensation tower.

8.3 Bench Scale Pyrolysis Reactor

Throughout the studies, a bench scale pyrolysis reactor (Figure 16) was used for preliminary studies of special feedstocks. The bench scale unit is housed within a small ventilated enclosure. The unit consists of an electrically heated oven with a maximum temperature limit of 1500 °F. The pyrolysis chamber rests within the furnace cavity and houses a trough for the pyrolysis feedstock. Hot pyrolyzate vapors exit the chamber to a water-cooled condenser. Oil condensate collects in a 2-liter flask, while non-condensable gas is routed to a Bunsen burner through a water bubbler/flame arrestor.

Although it was very useful for crude tests, several important differences existed between the bench scale unit and the DART unit. First, the bench scale unit operated as a batch processor, while the DART unit operated with continuous feeding. Second, unlike the DART unit, the bench unit had no means of agitation or mixing of the material in the pyrolysis chamber. Third, because it operated as a batch processing unit, the volume of the chamber was filled with air at start-up.

8.4 GC/MS Analysis of Oil Produced From Base Resin

8.5 GC/MS Analysis of Oil Produced From Post-Consumer Plastic

8.6 Material Balance and Yield Data

Table XXXVI on the following pages provides production data, calculated yields and normalized yields for Run 11 through Run 76B.

8.7 Run Classifications

Table XXXVII on the following pages provides a classification for each run as well as that run's objective and result.

8.8 Run Data Summary

Table XXXVIII on the following pages provides a summary of the feedstock, operating conditions, and yields for Run 17A through Run 76B.

MONTANA
STATE
UNIVERSITY
1893•CENTENNIAL•1993

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January 9, 1994

A Report Prepared For

Dr. Kyle Strode
Conrad Industries, Inc.
121 Melhart Road
Chehalis, WA 98532

The Analysis of Sample B11171500.PO

by

Gas Chromatography / Mass Spectrometry

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January 9, 1994

Dr. Kyle Strode
Conrad Industries, Inc.
121 Melhart Road
Chehalis, WA 98532

Dear Dr. Strode;

The analysis of the sample (B11171500.PO) you submitted to our facility on November 21, 1993, has been completed. The report of the findings, the chromatograms, mass spectra, and library comparisons are included herein. A brief description of the information contained in the data listings and graphs will also be presented.

The gas chromatograph and mass spectrometer parameters for the data acquisition can be found on their respective cover pages. The only information missing from these pages are the helium flow velocity through the column (30 cm/sec, adjusted at 250°C) and the sample injection volume (0.5ul, split 100:1). Also, the injection port temperature of the gas chromatograph was 280°C and the GC/MS Interface temperature was 320°C. The gas chromatograph used for the analysis was a Varian 3700 equipped with a 60 meter DB-1, 0.25 mm i.d. capillary column with a 0.25 micron film thickness. The mass spectrometer was a VG 70E-HF dual sector (EB geometry) operating at a source temperature of 200°C. The data was collected and processed on a VG 11-250 data system based on the DEC PDP 11/73 computer system. Peak areas of each component were measured manually; the measurement was valley-to-valley rather than baseline-to-baseline. Mass spectral identification of each component was performed by a combination of library searches and manual interpretation. Peak areas, chromatogram scan numbers, and compound identification information was entered into a Quatropro spread sheet for further data reduction. A disc containing this spreadsheet has been included with the data packet. To simplify the data reduction process, the assumption was made that all the compounds have an equal electron ionization cross-section - or an equal molar response.

A listing of the processed data contained in this report is as follows:

1. Several chromatograms, printed in various formats. One chromatogram has been greatly expanded to allow annotation of the peaks with the compound identification.

2. A peak area summary page listing total hydrocarbon peak areas, total aliphatic hydrocarbon peak areas, and total aromatic hydrocarbon peak areas. Also included in the summary page is the measured total ion current peak area. This measurement was conducted by two methods, a) baseline-to-baseline from scan 1-7200 of the chromatogram, and b) valley-to-valley from scan 1-7200 of the chromatogram. The summed TIC is presented for each method of measurement, followed by the percent of the of the total ion current which was compound identified and peak area measured.

3. A listing of all the identified and peak area measured components in the chromatogram. This listing comprises a total of 9 pages. The first 5 pages contains only the aliphatic hydrocarbons. The first column provides two pieces of information - the carbon number and the number of sites of unsaturation (i.e., "4.1" signifies a four carbon compound with one site of unsaturation). The second column is the scan number where the compound can be found in the chromatogram. The third column is the peak area of the compound. The forth column contains the percent contribution of the compound with respect to the aliphatic hydrocarbons. The fifth column contains the percent contribution of the compound with respect to the total hydrocarbons in the chromatogram.

> - Note: The percent contribution of each compound is based on a summation of the individually measured peak areas, not the measured total ion current. -

The next two pages is a listing of the aromatic hydrocarbons with the same general representation as found previously with the aliphatic hydrocarbons. The major difference in the representation is the first column. This column contains in the proposed elemental composition and mass of the compound. The final two pages contains a listing of the aromatic compounds and also includes the sub-structure identification of the compound. In some instances, the compound has been specifically identified; in others, the compound shows the base functionality with the degree of substitution and the number of sites of unsaturation. Some name-identifications begin with a question mark. These are a 'best-guess' approximation of its identity. Please keep in mind that many isomers may exist for many of the elemental formulas. Standards would be required for specific identification of most of the compounds.

4. The last seven pages of the report consist of graphs which visually represent the distribution of the components of the sample. The data contained in each graph is as follows:

> a) Total Hydrocarbon Distribution: This graph represents the percentage distribution of hydrocarbons based on carbon number. Each carbon number is the summation of peak areas of the aliphatic and aromatic hydrocarbons containing that particular number of carbon atoms.

b) Aliphatic Hydrocarbon Distribution (1): This graph represents the percentage distribution of the aliphatic hydrocarbons, by carbon number, with respect to the total aliphatic hydrocarbon peak area.

c) Aliphatic Hydrocarbon Distribution (2): This graph represents the percentage distribution of the aliphatic hydrocarbons, by carbon number, with respect to the total measured hydrocarbons in the sample.

d) Saturated vs Olefinic Hydrocarbons (1): This graph represents the percentage distribution of the saturated vs unsaturated aliphatic hydrocarbons, by carbon number, with respect to the total aliphatic hydrocarbon peak area. At each carbon's number, the right hand bar represents the intensity of the saturated hydrocarbon.

e) Saturated vs Olefinic Hydrocarbons (2): This graph represents the percentage distribution of the saturated vs unsaturated aliphatic hydrocarbons, by carbon number, with respect to the total measured hydrocarbon peak area. At each carbon number, the right hand bar represents the intensity of the saturated hydrocarbon.

f) Aromatic Hydrocarbon Distribution (1): This graph represents the percentage distribution of the aromatic hydrocarbons, by carbon number, with respect to the total aromatic hydrocarbon peak area.

g) Aromatic Hydrocarbon Distribution (2): This graph represents the percentage distribution of the aromatic hydrocarbons, by carbon number, with respect to the total measured hydrocarbon peak area.

When reviewing the data, please keep in mind that all compound identification was carried out with the assumption that the pyrolysis process was conducted in an oxygen free environment. That is, the assumption was made that there is no oxygen in any of the compounds. Also, inspection of the mass spectrum of each compound did not indicate the presence of any chlorine containing species.

If you have any questions concerning the enclosed data, please do not hesitate to contact me. Also, we thank you for choosing the Montana State University Mass Spectrometry Facility for conducting this analysis. If we can be of further assistance to you in the future, please feel free to call upon us.

Best Regards,

Joe Sears

Dr. Joe Sears
ecl

DATA SUMMARY

Total Aliphatic Hydrocarbon Peak Area	9.68E+10
Total Aromatic Hydrocarbon Peak Area	6.65E+10
Total Hydrocarbons Peak Area	1.63E+11

(All Peak Areas Measured Valley-to-Valley)

Measured Total Ion Current Area

	Method 1 (to baseline)	Method 2 (Valley-Valley)
	2.61E+11	1.15E+11 (scan 1-2000)
		4.76E+10 (scan 2000-4000)
		2.04E+10 (scan 4000-6000)
		2.03E+09 (scan 6000-7200)
Total Ion Current	2.61E+11	1.85E+11
Percent Peak Area Accounted For		
	62.48	88.14

Gas Chromatography / Mass Spectrometry Analysis
Sample Origination: Conrad Industries Inc. / Dr. Kyle Strode
Sample Received: November 21, 1993
Sample Analyzed: November 22, 1993 / Dr. Joe Sears
Data Reduction Completed: January 5, 1994

ALIPHATIC HYDROCARBONS

Carbon No.	Scan No.	Peak Area	% Aliphatics	% of Total
4.1	144	9.05E+08	0.93	0.55
4.1	148	1.40E+08	0.14	0.09
4.1	150	6.17E+07	0.06	0.04
5.1	156	1.31E+08	0.14	0.08
5.1	158	4.35E+07	0.04	0.03
5.2	163	5.85E+07	0.06	0.04
5.2	165	4.31E+07	0.04	0.03
5.1	168	4.95E+08	0.51	0.30
5.1	170	5.62E+08	0.58	0.34
5.0	172	6.37E+08	0.66	0.39
5.0	174	7.11E+08	0.73	0.44
5.1	176	5.34E+08	0.55	0.33
5.1	178	3.71E+08	0.38	0.23
5.1	183	5.87E+08	0.61	0.36
5.2	186	2.40E+08	0.25	0.15
5.1	190	3.38E+08	0.35	0.21
5.2	193	3.90E+08	0.40	0.24
5.2	203	2.63E+08	0.27	0.16
5.2	205	3.38E+08	0.35	0.21
5.1	210	2.35E+07	0.02	0.01
6.0	216	1.91E+08	0.20	0.12
6.1	220	1.45E+08	0.15	0.09
6.2	223	1.80E+07	0.02	0.01
6.1	236	1.81E+09	1.87	1.11
6.1	238	1.27E+09	1.31	0.78
6.2	243	3.35E+07	0.03	0.02
6.0	247	3.29E+08	0.34	0.20
6.0	250	2.16E+08	0.22	0.13
6.1	253	2.35E+08	0.24	0.14
6.2	257	4.98E+08	0.51	0.30
6.1	264	1.65E+08	0.17	0.10
6.2	273	1.06E+08	0.11	0.06
6.1	279	2.13E+08	0.22	0.13
6.1	282	1.15E+08	0.12	0.07
6.2	288	1.96E+08	0.20	0.12
6.3	291	4.77E+08	0.49	0.29
6.2	293	4.63E+08	0.48	0.28
6.3	296	4.55E+08	0.47	0.28
7.1	310	1.77E+08	0.18	0.11
7.2	323	1.27E+08	0.13	0.08
7.2	325	6.99E+07	0.07	0.04
7.1	329	6.49E+07	0.07	0.04
6.3	333	1.17E+08	0.12	0.07
6.3	336	3.62E+08	0.37	0.22
6.3	338	3.13E+08	0.32	0.19
7.1	345	6.84E+06	0.01	0.00
7.1	348	9.07E+06	0.01	0.01
6.2	354	1.44E+07	0.01	0.01
6.2	358	5.15E+08	0.53	0.32

ALIPHATIC HYDROCARBONS

Carbon No.	Scan No.	Peak Area	% Aliphatics	% of Total
6.2	360	3.93E+08	0.41	0.24
7.2	364	6.45E+07	0.07	0.04
7.1	374	1.10E+07	0.01	0.01
7.1	385	1.73E+08	0.18	0.11
7.1	395	2.43E+09	2.51	1.49
7.2	402	2.80E+07	0.03	0.02
7.2	412	8.56E+07	0.09	0.05
7.2	415	3.36E+08	0.35	0.21
7.0	418	8.49E+08	0.88	0.52
7.0	421	4.79E+08	0.49	0.29
7.2	427	1.22E+08	0.13	0.07
7.1	430	7.79E+07	0.08	0.05
7.2	436	7.27E+07	0.08	0.04
7.2	446	2.27E+08	0.23	0.14
7.2	448	1.49E+08	0.15	0.09
7.1	455	3.18E+08	0.33	0.19
7.1	457	2.49E+08	0.26	0.15
7.1	484	3.58E+07	0.04	0.02
7.2	490	2.99E+08	0.31	0.18
7.3	495	4.31E+08	0.45	0.26
8.1	564	4.80E+08	0.50	0.29
7.2	571	2.41E+07	0.02	0.01
7.2	575	4.79E+08	0.49	0.29
7.3	579	1.43E+08	0.15	0.09
7.3	588	5.41E+08	0.56	0.33
8.0	590	7.13E+08	0.74	0.44
6.2	593	2.45E+08	0.25	0.15
8.1	603	5.71E+07	0.06	0.03
8.2	606	4.50E+07	0.05	0.03
8.2	612	1.02E+08	0.10	0.06
8.1	633	5.09E+07	0.05	0.03
8.1	651	2.33E+09	2.41	1.43
8.1	656	3.13E+07	0.03	0.02
8.2	660	2.05E+08	0.21	0.13
8.2	664	7.31E+07	0.08	0.04
8.1	674	1.39E+08	0.14	0.09
8.0	683	1.07E+09	1.10	0.65
8.1	692	1.92E+08	0.20	0.12
9.1	699	2.23E+08	0.23	0.14
8.2	715	1.31E+08	0.14	0.08
8.2	724	1.60E+08	0.16	0.10
8.2	732	5.72E+07	0.06	0.04
8.2	740	1.06E+08	0.11	0.06
8.3	751	7.36E+07	0.08	0.05
9.1	762	3.92E+08	0.40	0.24
9.1	814	6.03E+09	6.23	3.69
9.1	845	3.65E+08	0.38	0.22
7.2	872	1.68E+08	0.17	0.10
9.1	952	1.06E+08	0.11	0.06
9.1	974	2.31E+09	2.39	1.41
10.1	983	4.18E+08	0.43	0.26
9.0	1006	1.02E+09	1.05	0.62
9.1	1015	1.87E+07	0.02	0.01
9.2	1039	1.78E+08	0.18	0.11
9.3	1043	4.47E+07	0.05	0.03

ALIPHATIC HYDROCARBONS

Carbon No.	Scan No.	Peak Area	% Aliphatics	% of Total
9.2	1057	6.64E+07	0.07	0.04
9.2	1063	3.79E+07	0.04	0.02
9.1	1079	7.05E+07	0.07	0.04
9.2	1135	7.18E+07	0.07	0.04
9.2	1166	7.99E+07	0.08	0.05
10.1	1187	1.45E+07	0.01	0.01
10.1	1235	1.53E+08	0.16	0.09
10.1	1272	1.23E+08	0.13	0.08
10.1	1303	2.92E+09	3.01	1.78
11.1	1315	2.84E+08	0.29	0.17
10.0	1339	1.07E+09	1.10	0.65
10.1	1344	9.01E+07	0.09	0.06
11.0	1372	3.21E+08	0.33	0.20
11.0	1385	3.02E+08	0.31	0.19
11.1	1434	3.62E+07	0.04	0.02
11.1	1506	5.29E+07	0.05	0.03
12.1	1592	5.20E+08	0.54	0.32
12.1	1605	3.86E+08	0.40	0.24
11.1	1620	7.85E+08	0.81	0.48
11.1	1629	2.07E+09	2.14	1.27
11.0	1663	1.23E+09	1.27	0.75
11.1	1666	1.70E+08	0.18	0.10
11.2	1716	9.00E+07	0.09	0.06
13.2	1818	1.09E+08	0.11	0.07
12.2	1884	1.88E+08	0.19	0.11
14.2	1892	9.86E+07	0.10	0.06
12.1	1902	3.05E+08	0.32	0.19
12.1	1916	1.15E+08	0.12	0.07
12.1	1943	2.17E+09	2.24	1.33
12.1	1949	4.71E+07	0.05	0.03
12.0	1975	1.33E+09	1.37	0.81
13.2	2195	9.18E+07	0.09	0.06
14.1	2203	2.87E+08	0.30	0.18
13.1	2241	1.87E+09	1.93	1.14
13.0	2272	1.11E+09	1.14	0.68
???????	2291	9.34E+08	0.96	0.57
15.1	2312	1.99E+08	0.21	0.12
15.1	2338	3.78E+08	0.39	0.23
16.1	2418	1.15E+08	0.12	0.07
???????	2452	2.35E+08	0.24	0.14
14.2	2488	3.35E+08	0.35	0.21
14.1	2523	2.09E+09	2.15	1.28
14.0	2551	8.00E+08	0.83	0.49
???????	2651	1.70E+08	0.18	0.10
15.2	2754	2.70E+08	0.28	0.17
15.1	2766	7.06E+07	0.07	0.04
15.1	2788	1.31E+09	1.35	0.80
15.0	2815	1.07E+09	1.10	0.65
18.1	2878	1.25E+08	0.13	0.08
18.1	2903	1.34E+08	0.14	0.08
18.1	2947	1.39E+08	0.14	0.09
16.2	3007	2.02E+08	0.21	0.12
16.1	3017	5.10E+07	0.05	0.03
16.1	3040	1.50E+09	1.55	0.92

ALIPHATIC HYDROCARBONS

Carbon No.	Scan No.	Peak Area	% Aliphatics	% of Total
16.0	3065	9.79E+08	1.01	0.60
16.1	3089	2.80E+07	0.03	0.02
17.2	3249	2.54E+08	0.26	0.16
17.1	3277	1.21E+09	1.25	0.74
17.0	3300	9.11E+08	0.94	0.56
17.0	3317	1.34E+08	0.14	0.08
17.1	3325	4.86E+07	0.05	0.03
21.1	3394	1.99E+08	0.21	0.12
21.1	3459	1.32E+08	0.14	0.08
18.2	3476	2.26E+08	0.23	0.14
18.1	3502	1.30E+09	1.34	0.79
18.0	3524	9.67E+08	1.00	0.59
21.1	3535	6.08E+07	0.06	0.04
18.0	3549	8.47E+07	0.09	0.05
19.2	3692	1.96E+08	0.20	0.12
19.1	3717	1.18E+09	1.22	0.72
19.0	3737	8.07E+08	0.83	0.49
24.1	3857	1.03E+08	0.11	0.06
20.2	3898	1.27E+08	0.13	0.08
20.1	3921	8.90E+08	0.92	0.54
20.0	3940	8.86E+08	0.92	0.54
???????	3949	4.50E+07	0.05	0.03
25.2	4001	8.13E+07	0.08	0.05
21.2	4096	1.87E+08	0.19	0.11
21.1	4118	9.17E+08	0.95	0.56
21.0	4135	8.74E+08	0.90	0.54
???????	4266	4.01E+07	0.04	0.02
???????	4275	9.27E+07	0.10	0.06
21.2	4284	2.33E+08	0.24	0.14
22.1	4303	8.73E+08	0.90	0.53
22.0	4321	8.32E+08	0.86	0.51
28.2	4410	8.50E+07	0.09	0.05
23.2	4466	1.19E+08	0.12	0.07
23.1	4485	7.56E+08	0.78	0.46
23.0	4501	6.76E+08	0.70	0.41
24.2	4640	9.28E+07	0.10	0.06
24.1	4657	7.54E+08	0.78	0.46
24.0	4672	6.86E+08	0.71	0.42
24.1	4697	7.09E+07	0.07	0.04
???????	4782	5.20E+07	0.05	0.03
25.2	4807	9.65E+07	0.10	0.06
25.1	4823	6.05E+08	0.62	0.37
25.0	4837	6.12E+08	0.63	0.37
25.1	4863	2.42E+07	0.03	0.01
26.2	4967	5.93E+07	0.06	0.04
26.1	4983	5.09E+08	0.53	0.31
26.0	4996	6.13E+08	0.63	0.37
26.2	5008	4.73E+07	0.05	0.03
27.2	5122	9.32E+07	0.10	0.06
27.1	5136	4.51E+08	0.47	0.28
27.0	5149	5.00E+08	0.52	0.31
			0.00	0.00
28.2	5271	8.73E+07	0.09	0.05
28.1	5285	3.56E+08	0.37	0.22

ALIPHATIC HYDROCARBONS

Carbon No.	Scan No.	Peak Area	% Aliphatics	% of Total
28.0	5297	4.67E+08	0.48	0.29
28.1	5331	3.79E+07	0.04	0.02
29.2	5415	4.06E+07	0.04	0.02
29.1	5427	3.04E+08	0.31	0.19
29.0	5439	4.82E+08	0.50	0.29
30.2	5555	3.38E+07	0.03	0.02
30.1	5566	2.27E+08	0.23	0.14
30.0	5577	3.56E+08	0.37	0.22
31.2	5690	1.39E+07	0.01	0.01
31.1	5700	1.83E+08	0.19	0.11
31.0	5710	3.08E+08	0.32	0.19
32.2	5821	1.71E+07	0.02	0.01
32.1	5830	1.75E+08	0.18	0.11
32.0	5840	2.83E+08	0.29	0.17
33.1	5957	1.40E+08	0.14	0.09
33.0	5966	3.03E+08	0.31	0.19
34.1	6080	1.35E+08	0.14	0.08
34.0	6088	2.86E+08	0.30	0.18
35.1	6204	1.18E+08	0.12	0.07
35.0	6213	2.44E+08	0.25	0.15
36.1	6340	8.34E+07	0.09	0.05
36.0	6349	1.71E+08	0.18	0.10
37.1	6490	4.50E+07	0.05	0.03
37.0	6501	6.91E+07	0.07	0.04
38.1	6663	2.70E+07	0.03	0.02
38.0	6674	5.87E+07	0.06	0.04
39.0	6875	4.82E+07	0.05	0.03
40.0	7107	3.24E+07	0.03	0.02
Total Aliphatic Hydrocarbon Peak Area		9.68E+10	100.00	59.28

AROMATIC HYDROCARBONS

Formula - Mass	Scan No.	Peak Area	% Aromatics	% of Total
C6H6 - Benzene	318	3.47E+09	5.21	2.12
C7H8 - Toluene	560	9.51E+09	14.30	5.82
C8H10 - 106	836	6.03E+09	9.06	3.69
C8H10 - 106	856	1.81E+09	2.72	1.11
C8H8 - 104	940	1.60E+10	24.04	9.79
C8H10 - 106	943	5.40E+08	0.81	0.33
C9H12 - 120	1033	8.31E+08	1.25	0.51
C8H10 - 106	1083	1.11E+08	0.17	0.07
C9H10 - 118	1093	6.19E+08	0.93	0.38
C9H12 - 120	1127	8.40E+08	1.26	0.51
C9H12 - 120	1152	2.79E+08	0.42	0.17
C9H12 - 120	1156	1.66E+08	0.25	0.10
C9H12 - 120	1176	1.72E+08	0.26	0.11
C9H10 - 118	1220	3.93E+08	0.59	0.24
C9H10 - 118	1243	2.95E+08	0.44	0.18
C9H10 - 118	1253	3.35E+08	0.50	0.21
C9H12 - 120	1255	7.80E+08	1.17	0.48
C9H10 - 118	1262	2.08E+08	0.31	0.13
C10H14 - 134	1310	1.05E+08	0.16	0.06
C10H14 - 134	1319	1.96E+08	0.30	0.12
C10H14 - 134	1349	1.38E+08	0.21	0.08
C10H12 - 132	1358	8.04E+08	1.21	0.49
C10H14 - 134	1365	8.16E+07	0.12	0.05
C9H10 - 118	1379	1.73E+08	0.26	0.11
C9H8 - 116	1402	1.19E+09	1.79	0.73
C10H12 - 132	1413	1.65E+08	0.25	0.10
C10H12 - 132	1420	5.37E+07	0.08	0.03
C9H12 - 120	1430	5.46E+07	0.08	0.03
C10H14 - 134	1442	4.33E+07	0.07	0.03
C10H14 - 134	1448	7.62E+07	0.11	0.05
C10H12 - 132	1462	5.04E+08	0.76	0.31
C10H14 - 134	1466	3.71E+08	0.56	0.23
C10H14 - 134	1472	5.08E+07	0.08	0.03
C10H12 - 132	1494	1.72E+08	0.26	0.11
C10H12 - 132	1513	3.19E+07	0.05	0.02
C10H10 - 130	1523	1.50E+08	0.22	0.09
C10H14 - 134	1530	2.66E+08	0.40	0.16
C10H14 - 134	1535	1.92E+08	0.29	0.12
C10H12 - 132	1545	2.46E+08	0.37	0.15
C10H14 - 134	1554	6.34E+07	0.10	0.04
C11H16 - 148	1563	1.35E+08	0.20	0.08
C11H14 - 146	1571	1.09E+08	0.16	0.07
C11H14 - 146	1577	8.12E+06	0.01	0.00
C11H14 - 146	1586	3.09E+08	0.47	0.19
C10H12 - 132	1588	1.35E+08	0.20	0.08
C10H12 - 132	1647	9.31E+07	0.14	0.06
C10H12 - 132	1675	2.22E+08	0.33	0.14
C10H12 - 132	1681	4.10E+07	0.06	0.03
C10H12 - 132	1692	7.96E+07	0.12	0.05
C11H14 - 146	1728	8.79E+07	0.13	0.05
C10H10 - 130	1741	6.54E+08	0.98	0.40
C10H8 - 128	1750	4.03E+07	0.06	0.02
C10H10 - 130	1756	5.45E+08	0.82	0.33
C10H10 - 130	1759	2.61E+08	0.39	0.16
C10H10 - 130	1770	1.53E+08	0.23	0.09

AROMATIC HYDROCARBONS

Formula - Mass	Scan No.	Peak Area	% Aromatics	% of Total
C10H14 - 134	1779	5.36E+08	0.81	0.33
C11H14 - 146	1792	1.49E+08	0.22	0.09
C10H8 - 128	1842	2.64E+09	3.98	1.62
C11H14 - 146	1860	6.82E+07	0.10	0.04
C11H12 - 144	1870	1.08E+08	0.16	0.07
C11H14 - 146	1984	5.97E+07	0.09	0.04
C11H10 - 142	2174	7.11E+08	1.07	0.44
C11H12 - 144	2191	1.04E+08	0.16	0.06
C11H10 - 142	2218	1.23E+09	1.85	0.75
C13H20 - 176	2286	3.36E+08	0.50	0.21
C12H10 - 154	2409	7.52E+08	1.13	0.46
C12H12 - 156	2454	2.40E+09	3.61	1.47
C12H12 - 156	2458	1.58E+08	0.24	0.10
C13H12 - 168	2469	1.30E+08	0.20	0.08
C12H12 - 156	2484	2.81E+08	0.42	0.17
C12H12 - 156	2533	2.62E+08	0.39	0.16
C12H12 - 156	2541	1.93E+08	0.29	0.12
C13H12 - 168	2547	5.83E+08	0.88	0.36
C12H12 - 156	2577	3.74E+07	0.06	0.02
C12H10 - 154	2584	1.89E+08	0.28	0.12
C13H12 - 168	2693	1.55E+08	0.23	0.10
C13H12 - 168	2714	1.39E+08	0.21	0.09
C14H14 - 182	2781	4.88E+08	0.73	0.30
C13H10 - 166	2932	1.81E+08	0.27	0.11
C14H12 - 180	2986	6.94E+07	0.10	0.04
C15H16 - 196	3116	8.21E+08	1.23	0.50
C15H14 - 194	3144	3.98E+07	0.06	0.02
C14H12 - 180	3214	5.20E+07	0.08	0.03
C14H12 - 180	3227	7.32E+07	0.11	0.04
C14H12 - 180	3234	1.25E+08	0.19	0.08
C15H12 - 192	3288	8.31E+07	0.12	0.05
C15H12 - 192	3363	4.09E+07	0.06	0.03
C14H10 - 178	3387	3.88E+08	0.58	0.24
C14H10 - 178	3408	5.20E+07	0.08	0.03
C16H12 - 204	3554	3.28E+08	0.49	0.20
C15H12 - 192	3573	1.25E+08	0.19	0.08
C15H12 - 192	3641	1.12E+08	0.17	0.07
C15H12 - 192	3651	1.40E+08	0.21	0.09
C15H12 - 192	3688	9.12E+07	0.14	0.06
C16H12 - 204	3794	4.26E+08	0.64	0.26
C16H10 - 202	3967	1.19E+08	0.18	0.07
C17H14 - 218	4051	1.13E+08	0.17	0.07
C16H10 - 202	4065	2.16E+08	0.33	0.13
C17H14 - 218	4104	5.77E+07	0.09	0.04
C14H14 - 182	4139	1.01E+08	0.15	0.06
C14H14 - 182	4208	3.52E+07	0.05	0.02
C14H12 - 180	4254	8.10E+07	0.12	0.05
C23H26 ?? - 302	4472	4.21E+07	0.06	0.03
C18H12 - 228	4666	2.08E+08		
C18H12 - 228	4681	3.98E+07	0.06	0.02
C24H24 ?? - 312	5093	3.19E+07	0.05	0.02
C24H18 ?? - 306	5403	2.05E+08	0.31	0.13
???? - 414	5734	2.22E+07	0.03	0.01
Total Aromatic Hydrocarbon Peak Area		6.65E+10	100.00	40.59

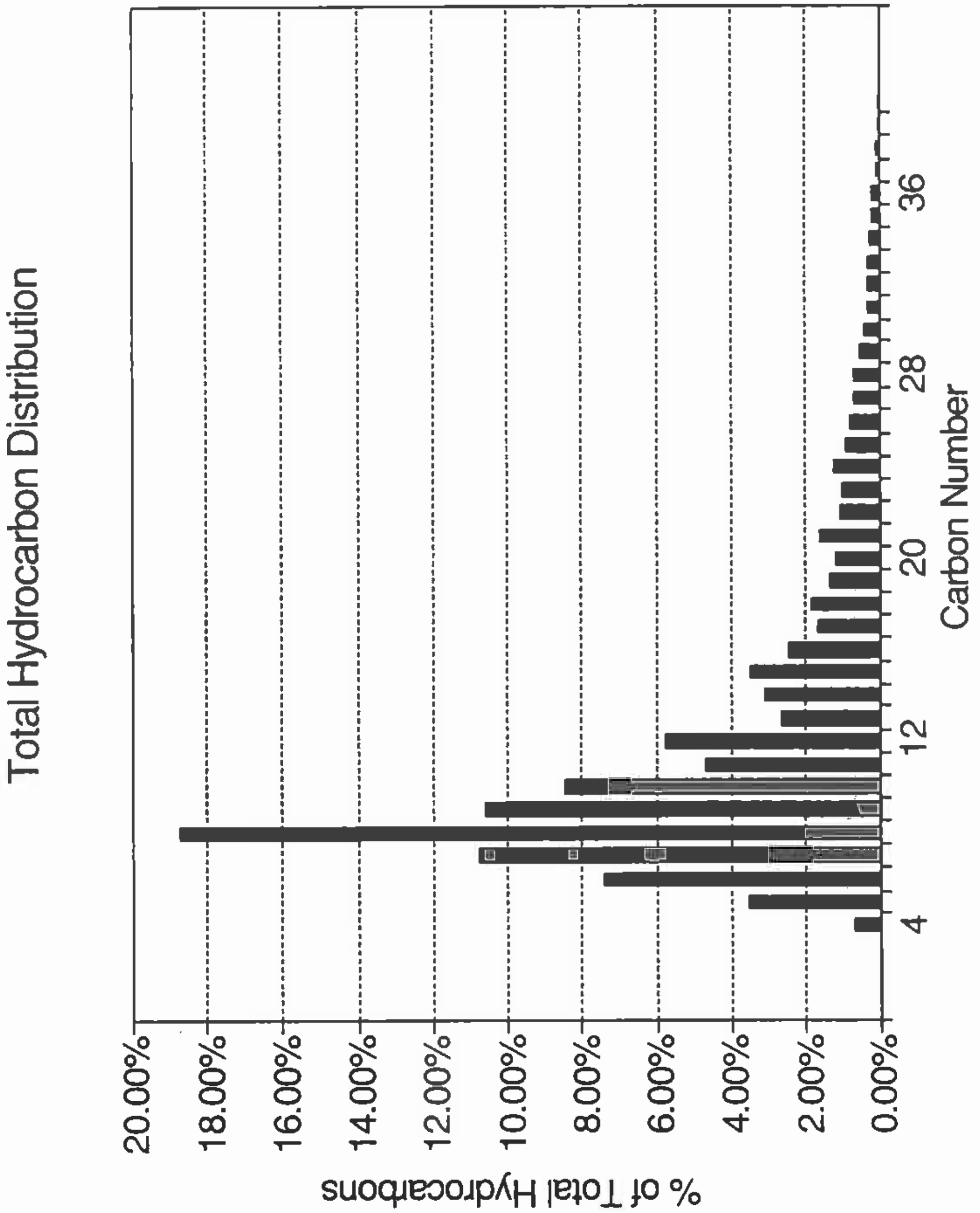
AROMATIC HYDROCARBONS

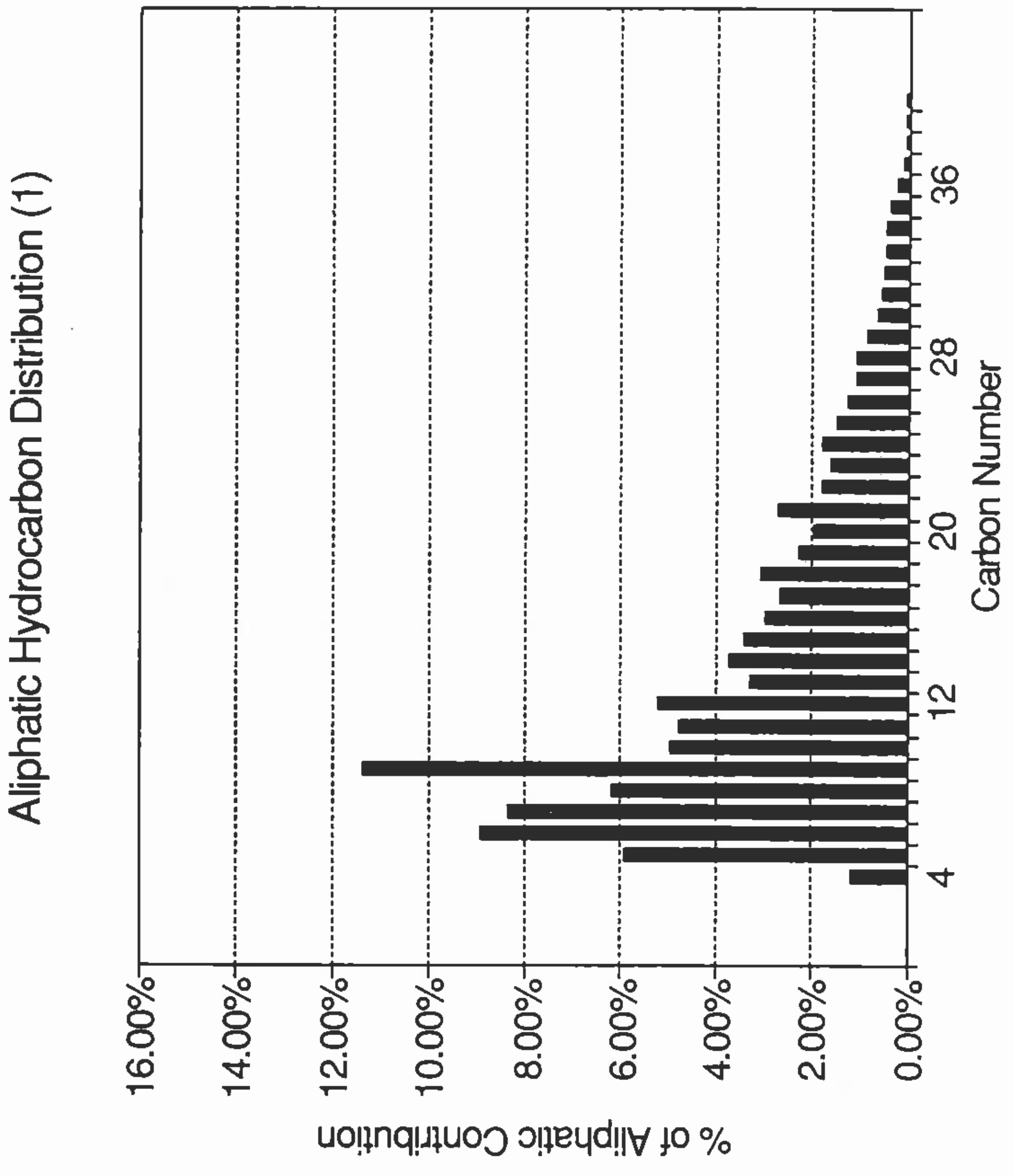
Formula - Mass	Scan No.	% of Total	Sub-Structure Identification
C6H6 - Benzene	318	2.12	Benzene
C7H8 - Toluene	560	5.82	Toluene
C8H10 - 106	836	3.69	Benzene, Ethyl-
C8H10 - 106	856	1.11	Xylene, m,p-
C8H8 - 104	940	9.79	Styrene
C8H10 - 106	943	0.33	Xylene, o-
C9H12 - 120	1033	0.51	Benzene, C3.0 substituted
C8H10 - 106	1083	0.07	?? Cyclopentadiene, C3 substituted
C9H10 - 118	1093	0.38	Benzene, C3.1 substituted
C9H12 - 120	1127	0.51	Benzene, C3.0 substituted
C9H12 - 120	1152	0.17	Benzene, C3.0 substituted
C9H12 - 120	1156	0.10	Benzene, C3.0 substituted
C9H12 - 120	1176	0.11	Benzene, C3.0 substituted
C9H10 - 118	1220	0.24	Benzene, C3.1 substituted
C9H10 - 118	1243	0.18	Benzene, C3.1 substituted
C9H10 - 118	1253	0.21	Benzene, C3.1 substituted
C9H12 - 120	1255	0.48	Benzene, C3.0 substituted
C9H10 - 118	1262	0.13	Benzene, C3.1 substituted
C10H14 - 134	1310	0.06	Benzene, C4.0 substituted
C10H14 - 134	1319	0.12	Benzene, C4.0 substituted
C10H14 - 134	1349	0.08	Benzene, C4.0 substituted
C10H12 - 132	1358	0.49	Benzene, C4.1 substituted
C10H14 - 134	1365	0.05	Benzene, C4.0 substituted
C9H10 - 118	1379	0.11	Benzene, C3.1 substituted
C9H8 - 116	1402	0.73	Indene, 1H- or Benzene, 1-Propynyl-
C10H12 - 132	1413	0.10	Benzene, C4.1 substituted
C10H12 - 132	1420	0.03	Benzene, C4.1 substituted
C9H12 - 120	1430	0.03	Benzene, C3.0 substituted
C10H14 - 134	1442	0.03	Benzene, C4.0 substituted
C10H14 - 134	1448	0.05	Benzene, C4.0 substituted
C10H12 - 132	1462	0.31	Benzene, C4.1 substituted
C10H14 - 134	1466	0.23	Benzene, C4.0 substituted
C10H14 - 134	1472	0.03	Benzene, C4.0 substituted
C10H12 - 132	1494	0.11	Benzene, C4.1 substituted
C10H12 - 132	1513	0.02	Benzene, C4.1 substituted
C10H10 - 130	1523	0.09	? Indene, 1H-Methyl-
C10H14 - 134	1530	0.16	Benzene, C4.0 substituted
C10H14 - 134	1535	0.12	Benzene, C4.0 substituted
C10H12 - 132	1545	0.15	Benzene, C4.1 substituted
C10H14 - 134	1554	0.04	Benzene, C4.0 substituted
C11H16 - 148	1563	0.08	
C11H14 - 146	1571	0.07	
C11H14 - 146	1577	0.00	
C11H14 - 146	1586	0.19	
C10H12 - 132	1588	0.08	Benzene, C4.1 substituted
C10H12 - 132	1647	0.06	Benzene, C4.1 substituted
C10H12 - 132	1675	0.14	Benzene, C4.1 substituted
C10H12 - 132	1681	0.03	Benzene, C4.1 substituted
C10H12 - 132	1692	0.05	Benzene, C4.1 substituted
C11H14 - 146	1728	0.05	
C10H10 - 130	1741	0.40	? Indene, 1H-Methyl-
C10H8 - 128	1750	0.02	Azulene
C10H10 - 130	1756	0.33	? Indene, 1H-Methyl-
C10H10 - 130	1759	0.16	? Indene, 1H-Methyl-
C10H10 - 130	1770	0.09	? Indene, 1H-Methyl-

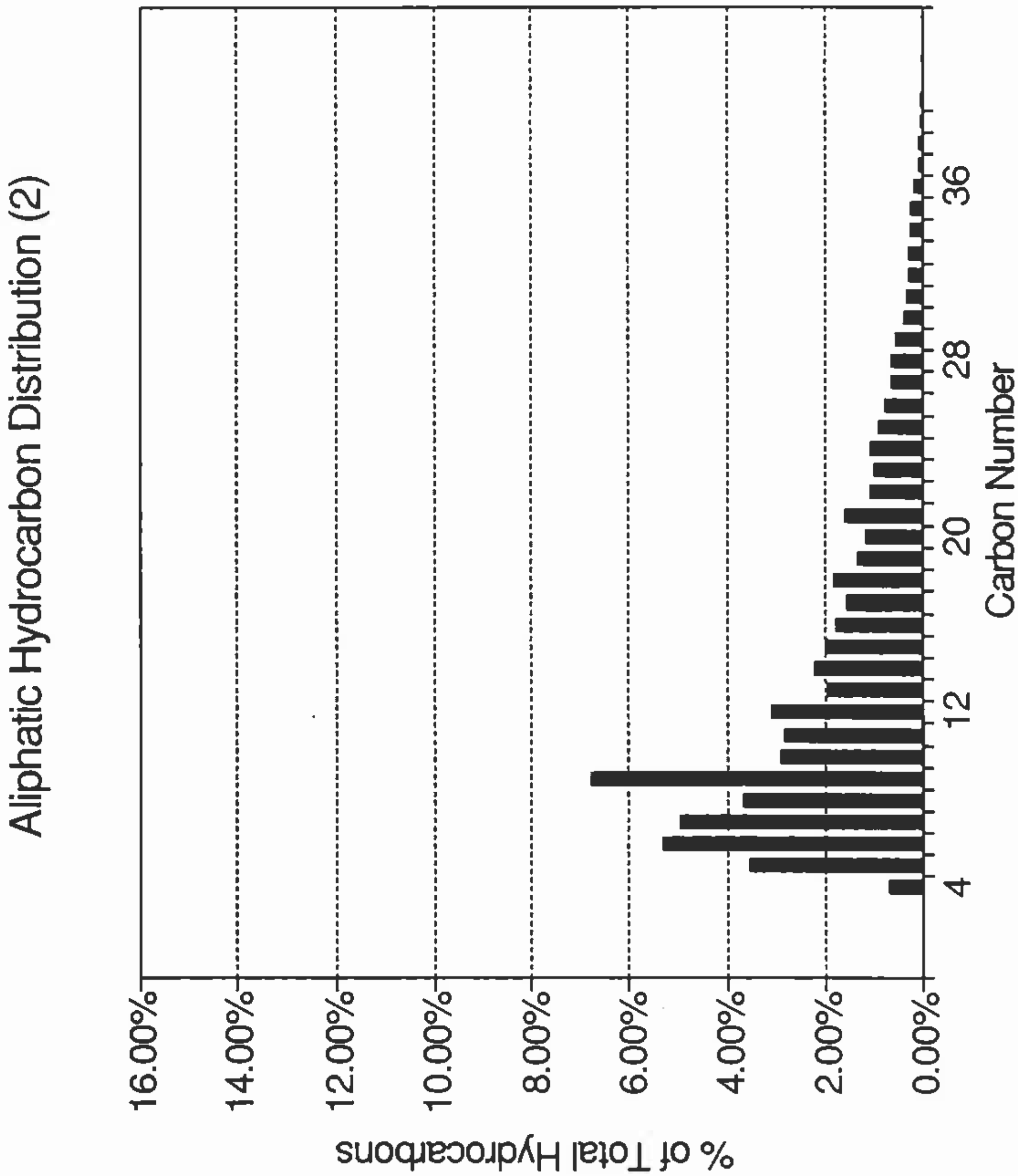
AROMATIC HYDROCARBONS

Formula - Mass	Scan No.	% of Total	
C10H14 - 134	1779	0.33	
C11H14 - 146	1792	0.09	
C10H8 - 128	1842	1.62	Naphthalene
C11H14 - 146	1860	0.04	
C11H12 - 144	1870	0.07	
C11H14 - 146	1984	0.04	
C11H10 - 142	2174	0.44	Naphthalene, Methyl-
C11H12 - 144	2191	0.06	
C11H10 - 142	2218	0.75	Naphthalene, Methyl-
C13H20 - 176	2286	0.21	Hexyl-Toluene
C12H10 - 154	2409	0.46	Biphenyl, 1,1'
C12H12 - 156	2454	1.47	Naphthalene, C2.0 substituted
C12H12 - 156	2458	0.10	Naphthalene, C2.0 substituted
C13H12 - 168	2469	0.08	? Biphenyl, Methyl-
C12H12 - 156	2484	0.17	Naphthalene, C2.0 substituted
C12H12 - 156	2533	0.16	Naphthalene, C2.0 substituted
C12H12 - 156	2541	0.12	Naphthalene, C2.0 substituted
C13H12 - 168	2547	0.36	Biphenyl, Methyl-
C12H12 - 156	2577	0.02	Naphthalene, C2.0 substituted
C12H10 - 154	2584	0.12	Acenaphthylene
C13H12 - 168	2693	0.10	Biphenyl, Methyl-
C13H12 - 168	2714	0.09	Biphenyl, Methyl-
C14H14 - 182	2781	0.30	Biphenyl, C2.0 substituted
C13H10 - 166	2932	0.11	Fluorene, 9H-
C14H12 - 180	2986	0.04	? Phenanthrene, Dihydro-
C15H16 - 196	3116	0.50	? Benzene, 1,1'-(1,3-Propanediyl)Bis-
C15H14 - 194	3144	0.02	
C14H12 - 180	3214	0.03	? Phenanthrene, Dihydro-
C14H12 - 180	3227	0.04	? Phenanthrene, Dihydro-
C14H12 - 180	3234	0.08	? Phenanthrene, Dihydro-
C15H12 - 192	3288	0.05	
C15H12 - 192	3363	0.03	
C14H10 - 178	3387	0.24	Phenanthrene
C14H10 - 178	3408	0.03	Anthracene
C16H12 - 204	3554	0.20	? Naphthalene, Phenyl-
C15H12 - 192	3573	0.08	
C15H12 - 192	3641	0.07	
C15H12 - 192	3651	0.09	
C15H12 - 192	3688	0.06	
C16H12 - 204	3794	0.26	? Naphthalene, Phenyl-
C16H10 - 202	3967	0.07	
C17H14 - 218	4051	0.07	
C16H10 - 202	4065	0.13	
C17H14 - 218	4104	0.04	
C14H14 - 182	4139	0.06	
C14H14 - 182	4208	0.02	
C14H12 - 180	4254	0.05	
C23H26 ?? - 302	4472	0.03	
C18H12 - 228	4666		? Naphthacene
C18H12 - 228	4681	0.02	? Chrysene
C24H24 ?? - 312	5093	0.02	
C24H18 ?? - 306	5403	0.13	
???? - 414	5734	0.01	

Total Aromatic Hydrocarbon Peak Area 40.59

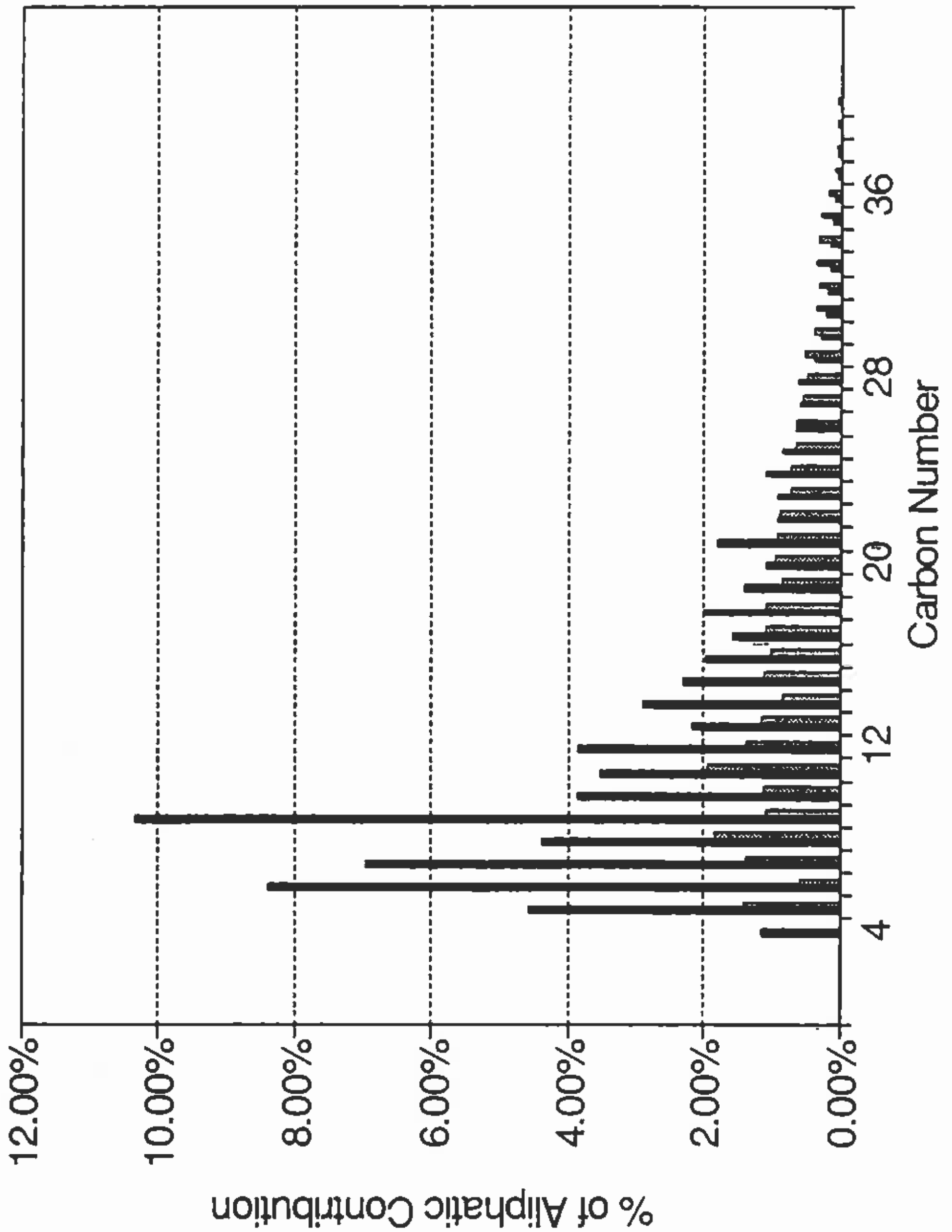

Total Hydrocarbon Distribution
% of Total Hydrocarbons
20.00%
18.00%
16.00%
14.00%
12.00%
10.00%
8.00%
6.00%
4.00%
2.00%
0.00%
Carbon Number
4
12
20
28
36

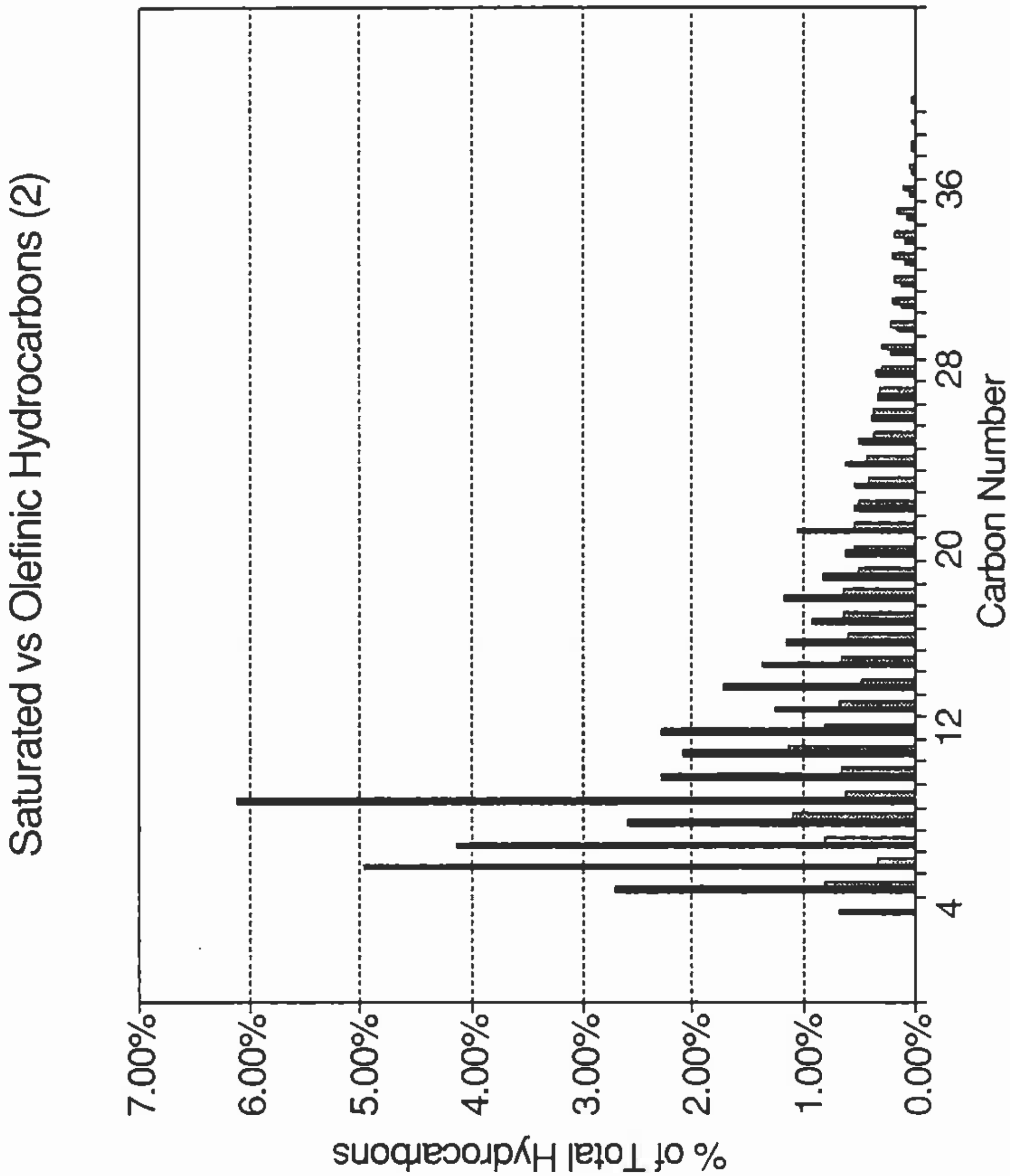

Aliphatic Hydrocarbon Distribution (1)
% of Aliphatic Contribution
16.00%
14.00%
12.00%
10.00%
8.00%
6.00%
4.00%
2.00%
0.00%
4
12
20
28
36
Carbon Number

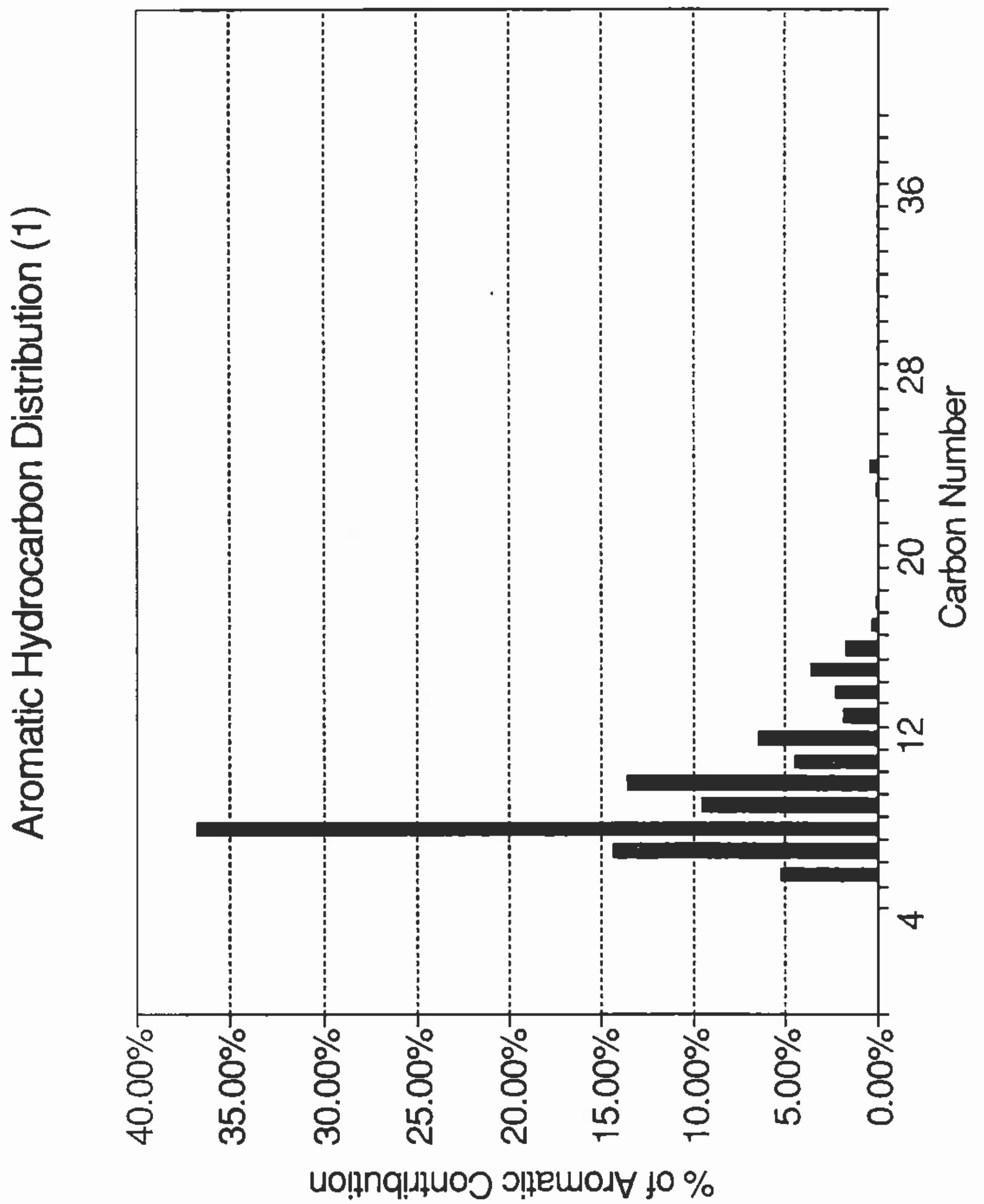


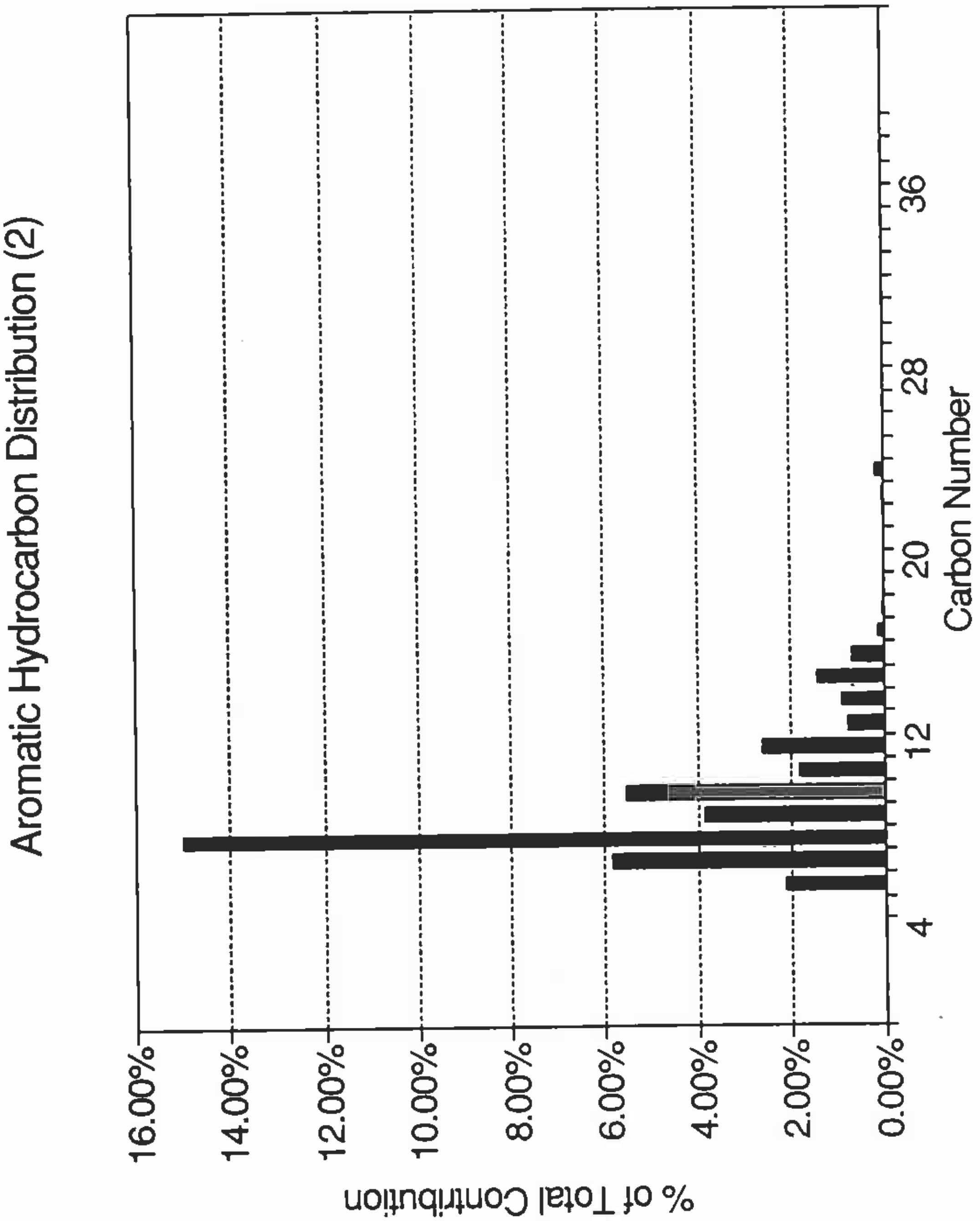
Aliphatic Hydrocarbon Distribution (2)

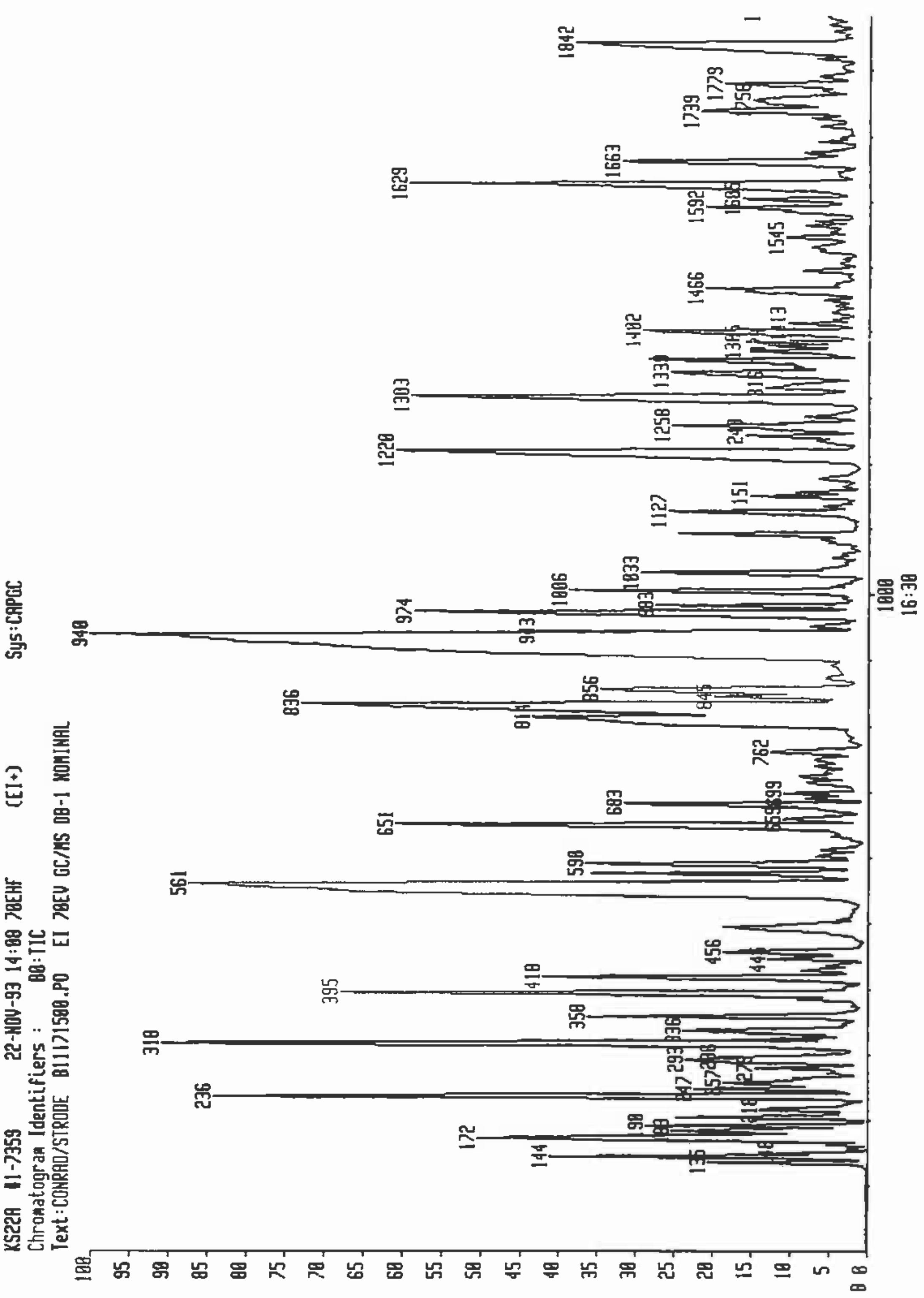
Saturated vs Olefinic Hydrocarbons (1)




Saturated vs Olefinic Hydrocarbons (2)


Aromatic Hydrocarbon Distribution (1)
% of Aromatic Contribution
40.00%
35.00%
30.00%
25.00%
20.00%
15.00%
10.00%
5.00%
0.00%
4
12
20
28
36
Carbon Number


Aromatic Hydrocarbon Distribution (2)
% of Total Contribution
16.00%
14.00%
12.00%
10.00%
8.00%
6.00%
4.00%
2.00%
0.00%
4
12
20
28
36
Carbon Number


KS22A #1-7359 22-NOV-93 14:08 70EHF (EI+) Sys:CAPGC
Chromatogram Identifiers : 00:TIC
Text:CONRAD/STRODE B11171500.PO EI 70EV GC/MS DB-1 NOMINAL
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0 0
1000
16:30
144
172
135
236
310
395
418
456
561
598
651
683
762
836
814
856
940
974
913
1006
1033
1127
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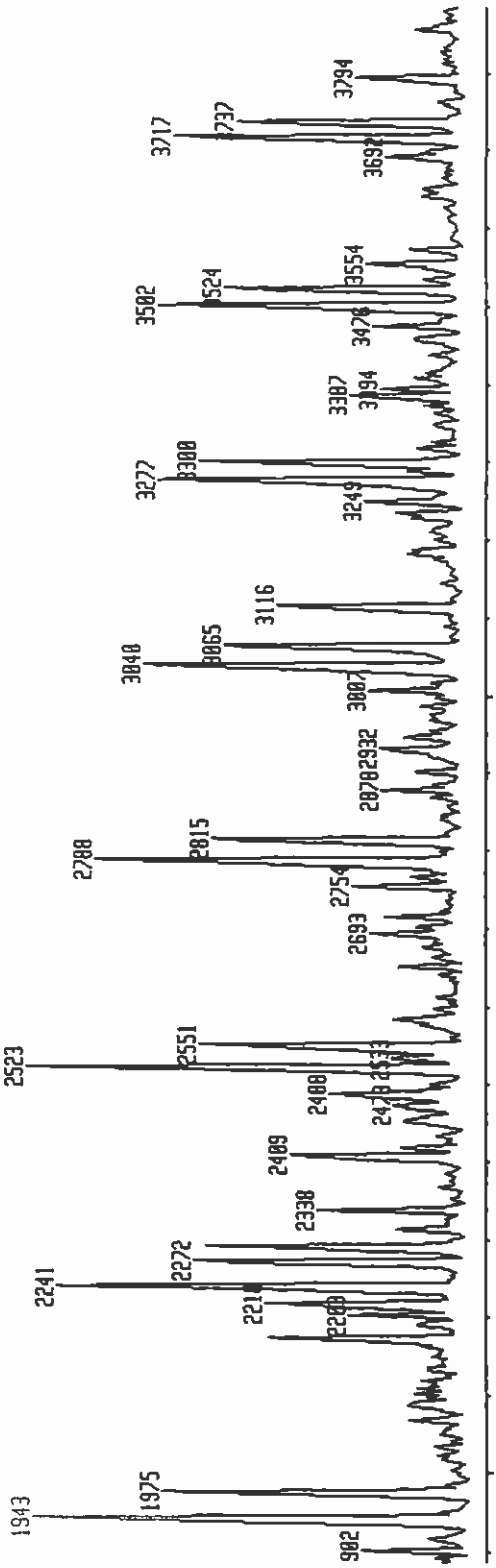
1402
1466
1545
1592
1629
1663
1739
1779
1842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1975
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2000
32:49
2241
2272
2214
2200
2338
2409
2523
2551
2400
2478
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2693
2754
2788
2815
2878
2932
3000
49:00
3040
3065
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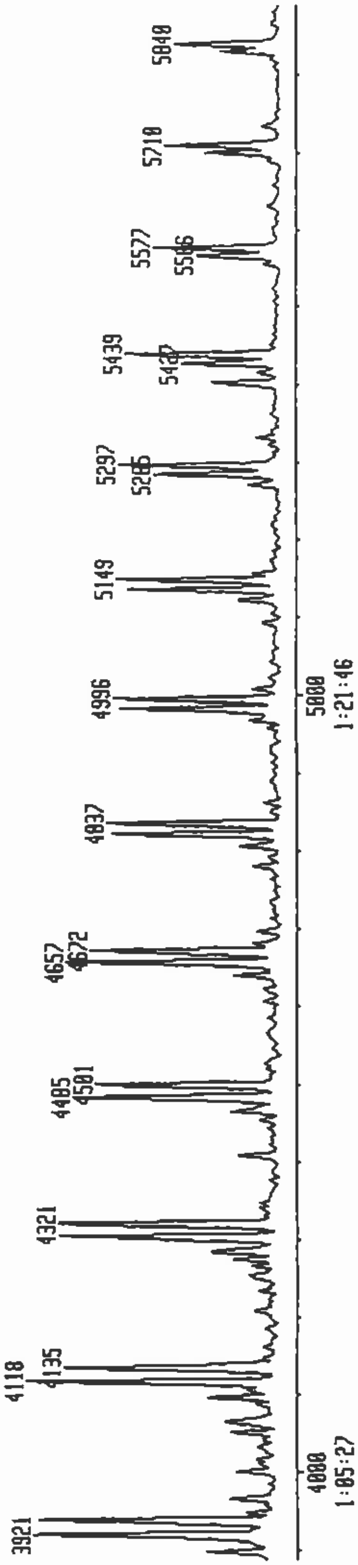
3554
3717
3737
3692
3794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4000
1:05:27
4118
4135
4321
4485
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4672
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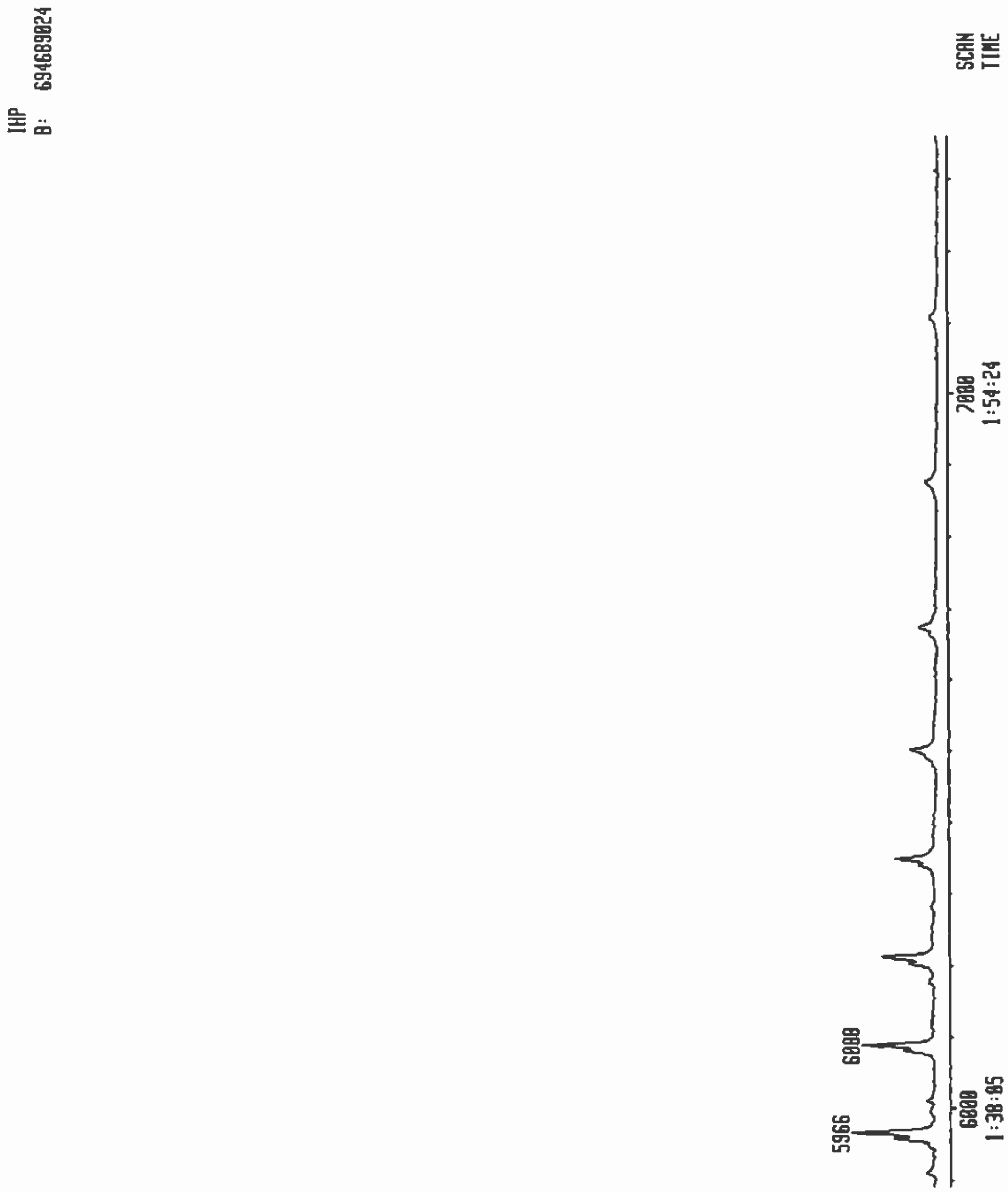
4996
5000
1:21:46
5149
5285
5297
5427
5439
5566
5577
5710
5840


IHP
B: 694689024
SCAN
TIME
5966
6000
6000
1:38:05
7000
1:54:24

SOUTHWEST RESEARCH INSTITUTE

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Chemistry and Chemical Engineering Division
Department of Environmental Engineering

June 17, 1994

Conrad Industries
Analytical Laboratory
121 Melhart Road
Chehalis, WA 98532

Attention: Dr. Kyle Strode

Subject: GC/MS Analysis Results for Post Consumer
Oil Sample C05260600.TL
SwRI Project 01-5969-013

Dear Dr. Strode:

This letter provides the GC/MS analysis results for the subject sample. The sample was diluted (11.1 mg/2 ml) with methylene chloride and analyzed on a J&W DB-5MS 30M x.25 mm ID (.25 µ film) capillary column. The identifications are provided on the accompanying table and are labeled as tentative because of lack of comparison to authentic materials under similar conditions. Also provided for your review is a copy of the chromatogram.

There is a series of peaks which appear repeatedly to the end of the chromatographic analysis. This series consists of a small peak representing a mono unsaturated alkene followed by a larger alkene peak of the same molecular weight and followed by the corresponding saturated alkane of the same carbon number. This series predominates the latter part of the chromatogram and continues to approximately C_{35}. These compounds, due to the repetitive nature, from C_{16} to C_{35} are not listed on the table.

SwRI and myself appreciate the opportunity to be of continued service to you, Conrad Industries and the APC. Should you have questions concerning the analysis, please call me at 210/522-2119.

Sincerely,

H.G. Wheeler, Jr.
Senior Research Scientist

HGW/lp
Attachments

SAN ANTONIO, TEXAS
HOUSTON, TEXAS • DETROIT, MICHIGAN • WASHINGTON, DC

TENTATIVELY IDENTIFIED COMPOUNDS
SAMPLE CO5260600.TI.

Scan #	Tentative ID			Area	Area %
79	butene	C_4H_8	MW=56	100616	0.84
98	pentene	C_5H_{10}	MW=70 or dimethyl cyclopropane isomer	254156	2.11
135	hexene	C_6H_{12}	MW=84	191680	1.59
205	methyl cyclopentene	C_6H_{10}	MW=82 or isomer	241392	2.01
214	benzene			183968	1.53
221	methyl cyclopentadiene	C_6H_8	MW=80 or hexatriene isomer	32976	0.27
230	cyclohexene	C_6H_{10}	MW=82 or hexadiene isomer	39760	0.33
242	heptene	C_7H_{14}	MW=98 or a cycloheptane isomer	148672	1.24
250	unknown		MW=100	23472	0.20
337	toluene			938912	7.80
340	methyl cyclohexene	C_7H_{12}	MW=96 or isomer	120032	1.00
356	cycloheptadiene	C_7H_{10}	MW=94 or methyl hexatriene or isomer	28856	0.24
374	octene	C_8H_{16}	MW=112 or cyclooctane	182816	1.52
388	branched alkane	C_8H_{18}	MW=114	52656	0.44
453	branched alkene	C_9H_{18}	MW=126	102665	0.85
487	ethyl benzene			905984	7.53
492	dimethyl benzene			173840	1.44
501	dimethyl benzene			120832	1.00
543	ethenyl benzene	C_8H_8	MW=104 or cyclic isomer	3643950	30.30
557	branched alkane	C_9H_{20}	MW=128	53934	0.45
595	methyl ethyl benzene	C_9H_{12}	MW=120	88312	0.73
634	C_3 alkenyl benzene	C_9H_{10}	MW=118	44576	0.37
648	C_3 alkyl benzene	$C_{29}H_{12}$	MW=120	63932	0.53
662	methyl ethyl benzene	C_9H_{12}	MW=120	76627	0.64
677	C_3 alkyl benzene	C_9H_{12}	MW=120	16328	0.14

TENTATIVELY IDENTIFIED COMPOUNDS
SAMPLE CO5260600.TL

Scan #	Tentative ID			Area	Area %
691	C_3 alkyl benzene	C_9H_{12}	MW=120	16112	0.13
699	methylethenyl benzene	C_9H_{10}	MW=118 or isomer	364472	3.03
719	decene	$C_{10}H_{20}$	MW=140	411554	3.42
733	decane	$C_{10}H_{22}$	MW=142	46144	0.38
746	C_4 alkyl benzene	$C_{10}H_{14}$	MW=134	38268	0.32
778	methyl ethenyl benzene	C_9H_{10}	MW=118 or isomer	77046	0.64
790	methyl ethenyl benzene	C_9H_{10}	MW=118 or isomer	34496	0.29
806	methyl ethynyl benzene	C_9H_8	MW=116 or isomer	113180	0.94
829	butyl benzene	$C_{10}H_{14}$	MW=134 coeluting with butenyl benzene $C_{10}H_{12}$ MW=132 or isomers	64090	0.53
844	alkyl benzene	$C_{10}H_{14}$	MW=134	36908	0.31
876	unsaturated coeluting with a C_4 alkyl benzene and a C_4 alkenyl benzene			52010	0.43
887	undecene	$C_{11}H_{22}$	MW=154 or isomer	81763	0.68
891	undecene	$C_{11}H_{22}$	MW=154	252270	2.10
904	undecane	$C_{12}H_{24}$	MW=156	63028	0.52
944	methyl propenyl benzene	$C_{10}H_{10}$	MW=132 or isomer	20098	0.17
982	butynyl benzene	$C_{10}H_{10}$	MW=130 or isomer	69404	0.58
994	butynyl benzene	$C_{10}H_{10}$	MW=130 or isomer	37933	0.32
1009	butynyl benzene	$C_{10}H_{10}$	MW=130 or isomer coeluting with 1-propanone,2-methyl-1-phenyl $C_{10}H_{12}O$ or isomer	22832	0.19
1039	naphthalene	$C_{10}H_8$	MW=128 or isomer coeluting with $C_{12}H_{24}$ MW=168 unsaturated	60464	0.50
1043	naphthalene	$C_{10}H_8$	MW=128	90800	0.75
1049	Dodecene	$C_{12}H_{24}$	MW=168 or isomer	56586	0.47
1053	Dodecene	$C_{12}H_{24}$	MW=168	154490	1.28

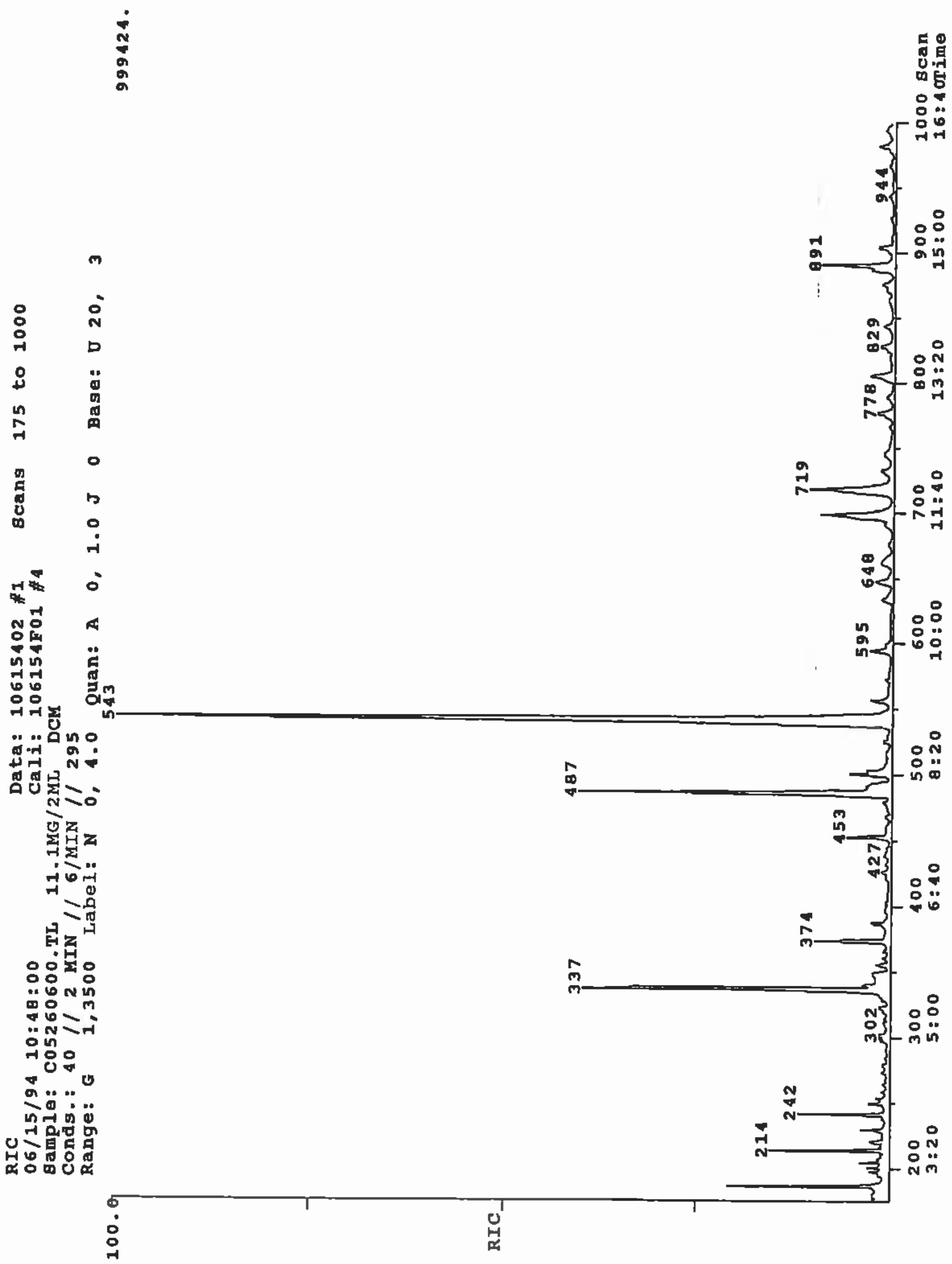
TENTATIVELY IDENTIFIED COMPOUNDS
SAMPLE CO5260600.TL

Scan #	Tentative ID			Area	Area %
1195	unknown diene			42584	0.35
1203	tridecene	$C_{13}H_{26}$	MW=182 or isomer	40953	0.34
1208	tridecene	$C_{13}H_{26}$	MW=182	158546	1.32
1216	methyl naphthalene			62516	0.52
1219	alkane	$C_{13}H_{28}$	MW=184	74423	0.62
1239	methyl naphthalene			33640	0.28
1337	biphenyl	$C_{12}H_{10}$	MW=154 or isomer	40793	0.34
1341	mono unsaturated	$C_{14}H_{28}$	MW=196	38396	0.32
1353	tetradecene	$C_{14}H_{28}$	MW=196	149820	1.25
1363	alkane	$C_{14}H_{30}$	MW=198	34887	0.29
1409	methyl biphenyl	$C_{13}H_{12}$	MW=168	13337	0.11
1479	mono unsaturated	$C_{15}H_{30}$	MW=210	30849	0.26
1490	mono unsaturated	$C_{15}H_{30}$	MW=210	112586	0.94
1500	alkane	$C_{15}H_{32}$	MW=212	31832	0.26
1520	mono unsaturated alkene coeluting with methyl-9H flourene	$C_{14}H_{12}$	MW=180	9825	0.08
1610	mono unsaturated	$C_{16}H_{32}$	MW=224	27454	0.23
1620	mono unsaturated	$C_{16}H_{32}$	MW=224	93447	0.78
1630	alkane	$C_{16}H_{34}$	MW=226	28447	0.24
1699	benzene; (propanediyl)Bis-	$C_{15}H_{16}$	MW=196	29358	0.24
1735	mono unsaturated	$C_{17}H_{34}$	MW=238	18192	0.15
1744	mono unsaturated	$C_{17}H_{34}$	MW=238	72404	0.60
1753	alkane	$C_{17}H_{36}$	MW=240	25998	0.22
1852	mono unsaturated	$C_{18}H_{36}$	MW=252	17978	0.15
1860	mono unsaturated	$C_{18}H_{36}$	MW=252	69695	0.58

TENTATIVELY IDENTIFIED COMPOUNDS
SAMPLE CO5260600.TL

Scan #	Tentative ID			Area	Area %
1868	alkane	$C_{18}H_{38}$	MW=254	29535	0.25
1938	phenylmethylene indene	$C_{16}H_{12}$	MW=204	7769	0.06
1964	mono unsaturated	$C_{19}H_{38}$	MW=266	17869	0.15
1971	mono unsaturated	$C_{19}H_{38}$	MW=266	60249	0.50
1978	alkane	$C_{19}H_{40}$	MW=268	27321	0.23
2063	phenyl naphthalene	$C_{16}H_{12}$	MW=204	15293	0.13
2070	mono unsaturated	$C_{20}H_{40}$	MW=280	19685	0.16
2077	mono unsaturated	$C_{20}H_{40}$	MW=280	55915	0.46
2083	alkane	$C_{20}H_{42}$	MW=282	23485	0.20
2173	mono unsaturated	$C_{21}H_{42}$	MW=294	17401	0.14
2179	mono unsaturated	$C_{21}H_{42}$	MW=294	44761	0.37
2185	alkane	$C_{21}H_{44}$	MW=296	23117	0.19
2271	mono unsaturated	$C_{22}H_{44}$	MW=308	12783	0.11
2277	mono unsaturated	$C_{22}H_{44}$	MW=308	38445	0.32
2282	alkane	$C_{22}H_{46}$	MW=310	18700	0.16
2366	mono unsaturated	$C_{23}H_{46}$	MW=322	10786	0.09
2371	mono unsaturated	$C_{23}H_{46}$	MW=322	29616	0.25
2376	alkane	$C_{23}H_{48}$	MW=324	18933	0.16
2457	mono unsaturated	$C_{24}H_{48}$	MW=336	8347	0.07
2462	mono unsaturated	$C_{24}H_{48}$	MW=336	25701	0.21
2466	alkane	$C_{24}H_{50}$	MW=338	14813	0.12
2544	mono unsaturated	$C_{25}H_{50}$	MW=350	7130	0.06
2549	mono unsaturated	$C_{25}H_{50}$	MW=350	23826	0.20
2552	alkane	$C_{25}H_{52}$	MW=352	13722	0.11
2628	mono unsaturated	$C_{26}H_{52}$	MW=354	5835	0.05

TENTATIVELY IDENTIFIED COMPOUNDS SAMPLE CO5260600.TL					
Scan #	Tentative ID			Area	Area %
2632	mono unsaturated	$C_{26}H_{52}$	MW=364	22257	0.18
2636	alkane	$C_{26}H_{54}$	MW=366	14101	0.12
2709	mono unsaturated	$C_{27}H_{54}$	MW=378	4725	0.04
2712	mono unsaturated	$C_{27}H_{54}$	MW=378	16719	0.14
2716	alkane	$C_{27}H_{56}$	MW=380	14265	0.12
2790	2 mono unsaturated coeluting	$C_{28}H_{56}$	MW=392	18913	0.16
2793	alkane	$C_{28}H_{58}$	MW=394	11686	0.10
2865	2 mono unsaturated coeluting	$C_{29}H_{58}$	MW=406	17317	0.14
2868	alkane	$C_{29}H_{60}$	MW=408	11160	0.09
2903	Quaterphenyl	$C_{24}H_{18}$	MW=306	3731	0.03
2938	mono unsaturateds $C_{30}H_{60}$ MW=410 coeluting with alkane	$C_{30}H_{62}$	MW=422	19815	0.16
3015	mono unsaturateds $C_{11}H_{62}$ MW=424 coeluting with alkane	$C_{31}H_{64}$	MW=436	15607	0.13
3098	mono unsaturateds $C_{32}H_{64}$ MW=438 coeluting with alkane	$C_{32}H_{66}$	MW=454	14544	0.12
3196	mono unsaturateds $C_{33}H_{66}$ MW=452 coeluting with alkane	$C_{33}H_{68}$	MW=468	10368	0.09
3310	mono unsaturateds $C_{34}H_{68}$ MW=466 coeluting with alkane	$C_{34}H_{70}$	MW=482	7897	0.07
3449	mono unsaturateds $C_{35}H_{70}$ MW=480 coeluting with alkane	$C_{35}H_{72}$	MW=496	4334	0.04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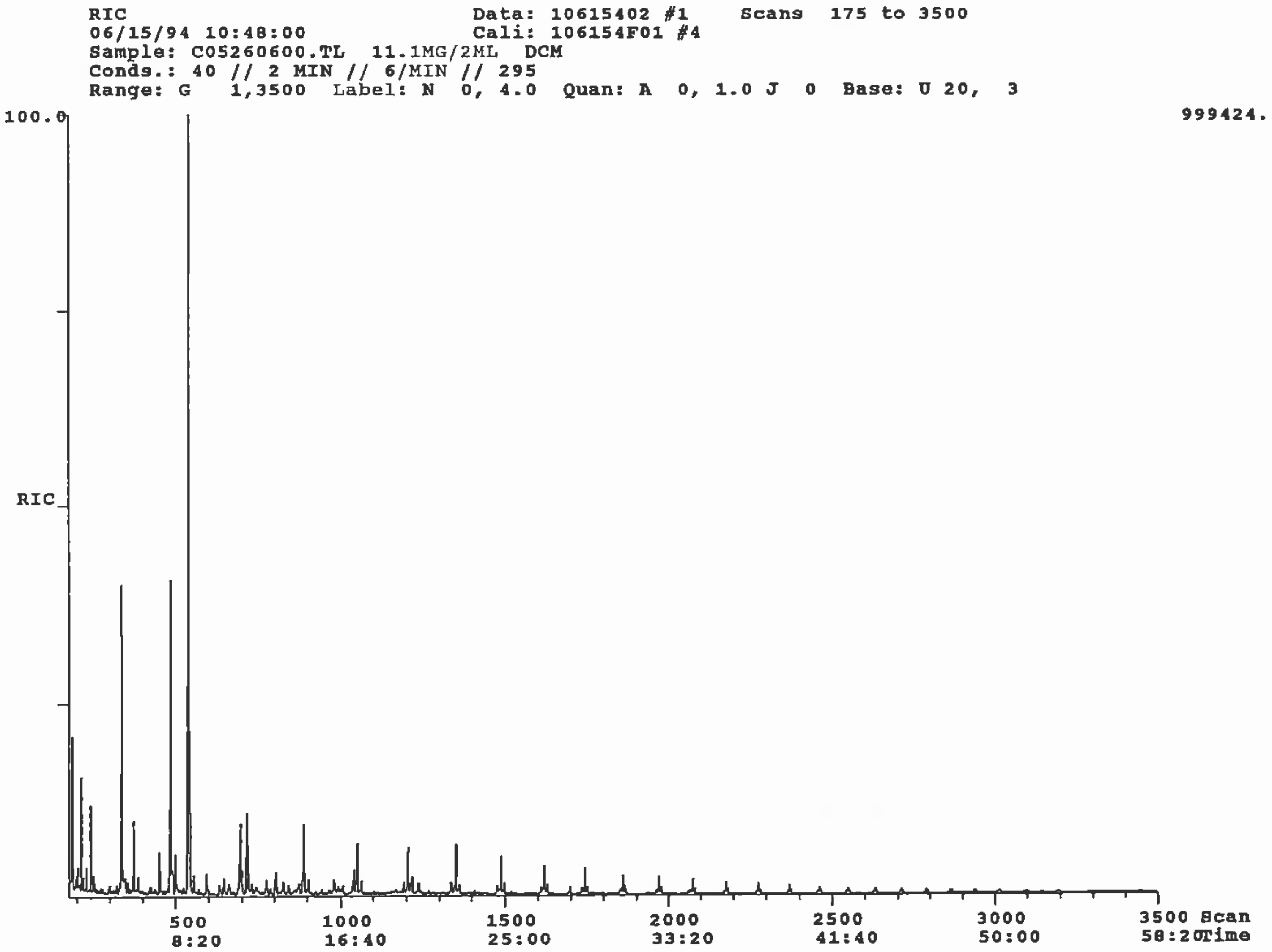
06/15/94 10:48:00
Sample: C05260600.TL 11.1MG/2ML DCM
Conds.: 40 // 2 MIN // 6/MIN // 295
Range: G 1,3500 Label: N 0, 4.0 Quan: A 0, 1.0 J 0 Base: U 20, 3
Data: 10615402 #1
Cali: 106154F01 #4
Scans 175 to 1000
999424.
100.0
RIC
214
242
302
337
374
427
453
487
543
595
648
719
778
829
891
944
200 3:20
300 5:00
400 6:40
500 8:20
600 10:00
700 11:40
800 13:20
900 15:00
1000 Scan
16:40 Time



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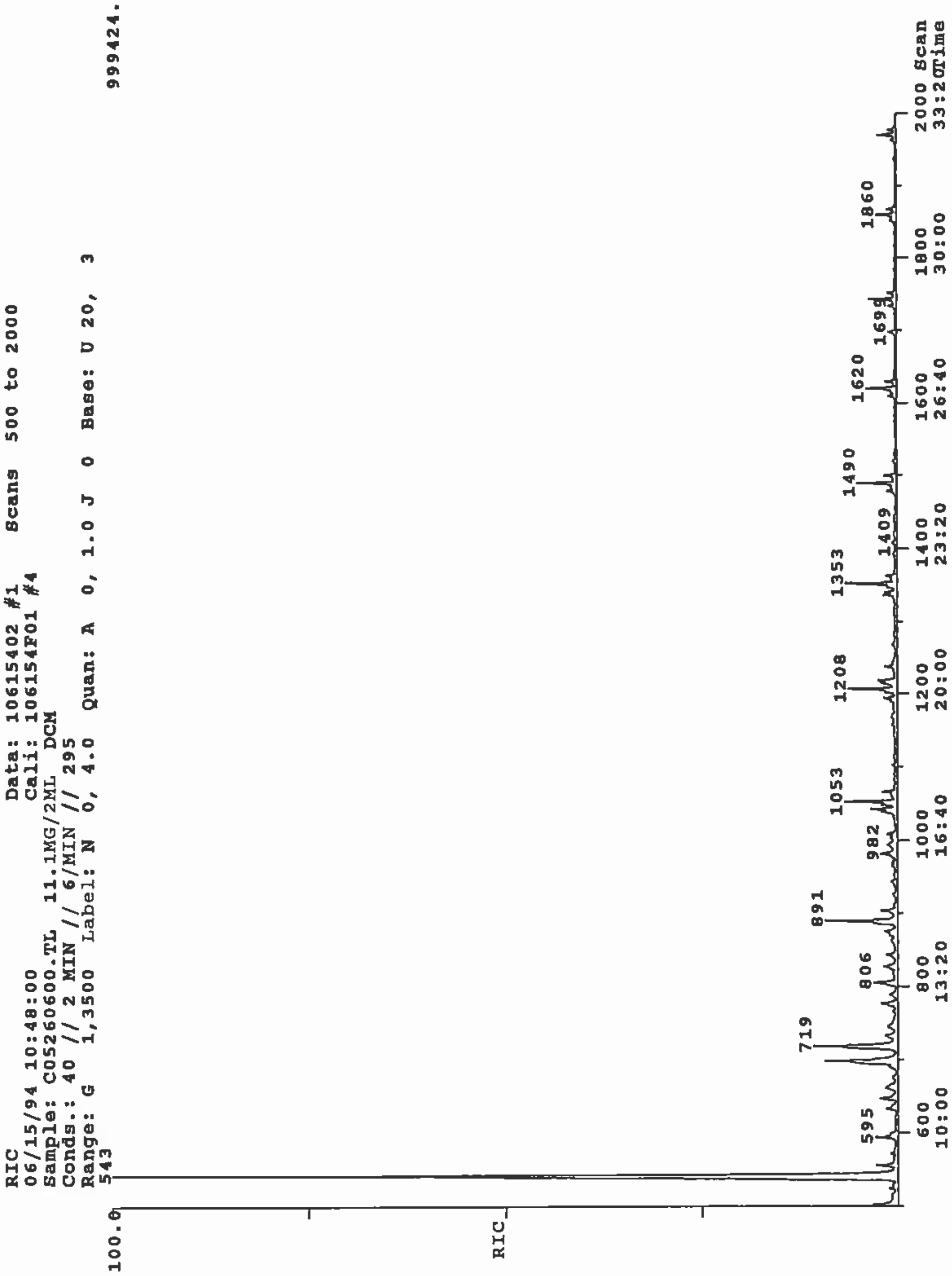
RIC                                Data: 10615402 #1    Scans  175 to 3500
06/15/94 10:48:00                  Cali: 106154F01 #4
Sample: C05260600.TL  11.1MG/2ML  DCM
Conds.: 40 // 2 MIN // 6/MIN // 295
Range: G   1,3500  Label: N  0, 4.0  Quan: A  0, 1.0 J  0  Base: U 20,  3
```



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RIC                                Data: 10615402 #1      Scans  500 to 2000
06/15/94 10:48:00                     Cali: 106154F01 #4
Sample: C05260600.TL  11.1MG/2ML  DCM
Conds.: 40  // 2 MIN // 6/MIN // 295
Range: G   1,3500  Label: N  0, 4.0  Quan: A  0, 1.0 J  0  Base: U 20,  3
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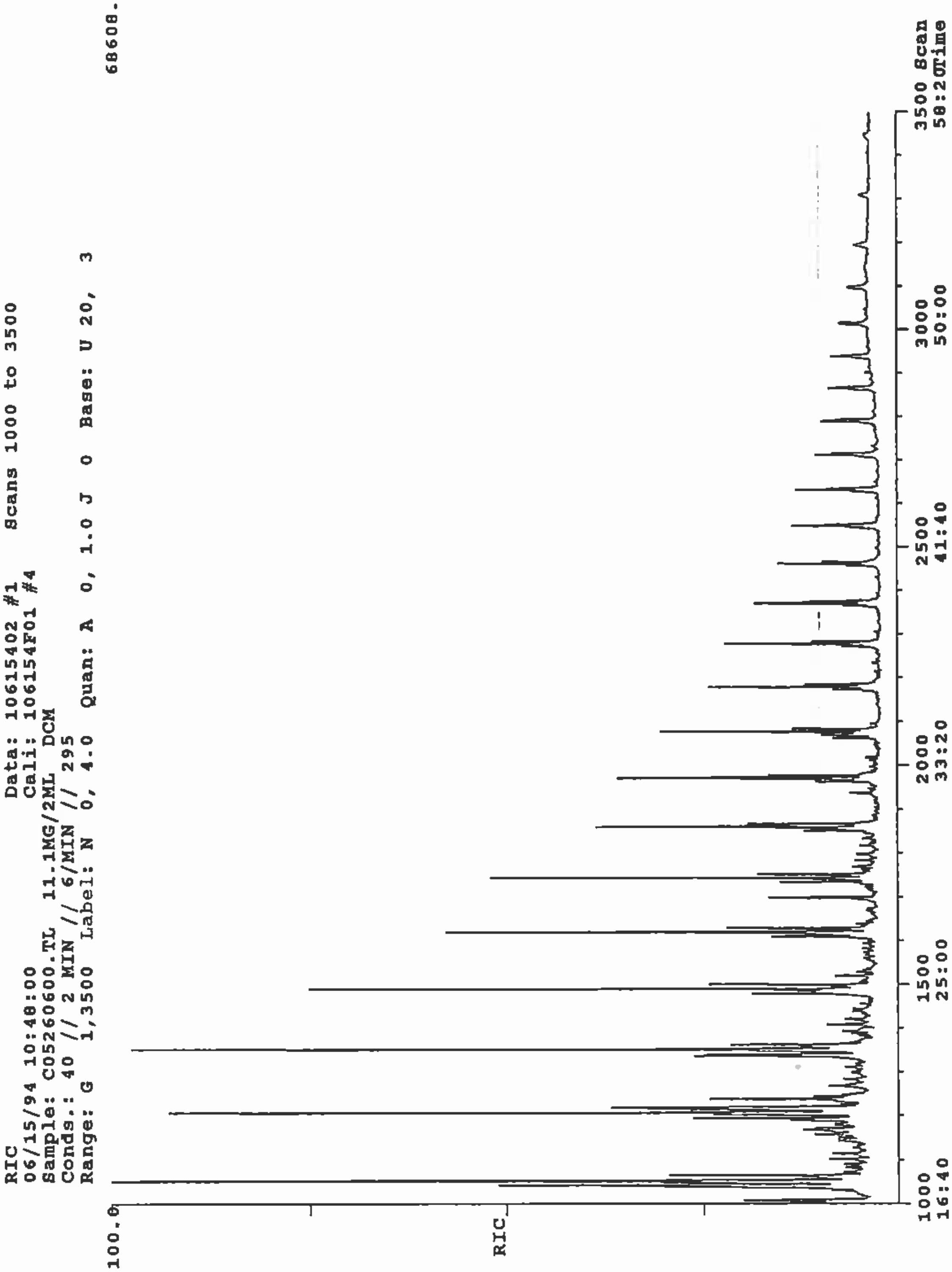
RIC
06/15/94 10:48:00
Sample: C05260600.TL 11.1MG/2ML DCM
Conds.: 40 // 2 MIN // 6/MIN // 295
Range: G 1,3500 Label: N 0, 4.0 Quan: A 0, 1.0 J 0 Base: U 20, 3
Data: 10615402 #1 Scans 1000 to 3500
Cali: 106154F01 #4
68608.
100.0
RIC
1000
16:40
1500
25:00
2000
33:20
2500
41:40
3000
50:00
3500 Scan
58:20 Time

TABLE XXXV Original APC/Conrad Industries Test Plan

Week	Run#	Objective	Hours	Temp	Feed Consumed	Rate (pph)	Feed (lbs)	Oil (gal)	Comments	Test Sample	Retain (gal)	Retain (gal)
1	1	Polymer Shakedown	52	High	Base	300	15,600	1040	Check Operability	No	N/A	N/A
1	2	Polymer Shakedown	26	Seek Low	Base	300	7,800	832	Maximize Liquid Yield	No	N/A	N/A
2	3	Polymer Shakedown	78	Low	Base	300	23,400	2496	Observe system behavior	No	5	1
3	4	Polymer Shakedown	26	Low	Base	150	3,900	416	Study Rate Effects	No	5	1
3	5	Polymer Shakedown	26	Low	Base	300	7,800	832	Study Rate Effects	No	5	1
3	6	Polymer Shakedown	26	Low	Base	400	10,400	1109	Study Rate Effects	No	5	1
4	7	Final Shakedown	78	Low	Base	Best	23,400	2496	Benchmark Base Run	Yes	5	1
5	8	High LDPE	26	High	B + LDPE	300	7,800	520	High LDPE effects at 2 temps.	Yes	5	1
5	9	High LDPE	26	Low	B + LDPE	300	7,800	832	High LDPE effects at 2 temps.	Yes	5	1
5	10	High PS	26	High	B + PS	300	7,800	520	High PS effects at 2 temps.	Yes	5	1
6	11	High PS	26	Low	B + PS	300	7,800	832	High PS effects at 2 temps.	Yes	5	1
6	12	High PET	26	High	B + PET	300	7,800	416		Yes	5	1
6	13	High PET	26	Low	B + PET	300	7,800	728		Yes	5	1
7		Shutdown for preventative maintenance and install caustic scrubber										
8		Same as "7"										
9	14	Shakedown	26	Low	Base	300	7,800	832	Check Operability	No		
9	15	PVC Shakedown	52	High	B + PVC1	300	15,600	1040		No		
10	16	PVC -1	26	High	B + PVC1	300	7,800	520	Low PVC Blend Study	Yes	5	1
10	17	PVC - 1	26	Low	B + PVC1	300	7,800	832	Low PVC Blend Study	Yes	5	1
10	18	PVC - 1	26	Low	B + PVC1	400	10,400	1109	Low PVC Blend Study	Yes	5	1
11	19	PVC - 2	26	High	B + PVC2	300	7,800	489	High PVC Study	Yes	5	1
11	20	PVC - 2	26	Low	B + PVC2	300	7,800	780	High PVC Study	Yes	5	1
11	21	Purge Run	26	Low	Base	300	7,800	832	Purge System	No	N/A	N/A
12	22	Reserve for Extra Runs	26	?	?	300	7,800	832		Yes	5	1
12	23	Reserve for Extra Runs	26	?	?	300	7,800	832		Yes	5	1
12	24	Reserve for Extra Runs	26	?	?	300	7,800	832		Yes	5	1
13	25	Synthetic PCP Run	26	Tune	?	Vary	7,800	520	Simulate 1st PCP composition	Yes	5	1
13	26	Synthetic PCP Run	26	Best	?	Best	15,600	1664		Yes	5	1
14	—	Shutdown for Prvnt. Maint.	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
15	27	1st PCP Feed	26	Tune	PCP1	Vary	7,800	520	Run 1st (low PVC) PCP feed	Yes	5	1
15	28	1st PCP Feed	52	Best	PCP1	Best	15,600	1664		Yes	5	1
16	29	2nd PCP Feed	26	Tune	PCP2	Vary	7,800	520	Run 2nd (High PVC) PCP Feed	Yes	5	1
16		2nd PCP Feed	52	Best	PCP2	Best	15,600	1664		Yes	5	1
17-24		Contingency										

Table XXXVI Material balance and yield data

RUN	PRODUCTION DATA (lbs)				CALCULATED YIELDS[1] (wt %)				NORMALIZED YIELDS (%)			
#	FEED	LIQUID[2]	COR.GAS[3]	CARBON	LIQUID	GAS	CARBON	TOTAL	LIQUID	GAS	CARBON	TOTAL
11	4059	2876	†		70.8	25.5	0	96.3	73.7	26.3	0	100
12	6368	4259	2156		66.9	33.9	0	100	66	34	0	100
13	6703	454	2080		67.3	31	0	96	67.7	32.3	0	100
14	5943	4531	1375		81.3	23.1	0	104	77.9	22.1	0	100
15	6844	4664	1171		68.1	17.1	0	86	80.2	19.8	0	100
16	4331	3653	1344		84.3	31	0	115	73	27	0	100
17A	1983	1235	†	0	62.3	37.7	0	100	62	38	0	100
17B	2119	1699	†	0	80.2	19.8	0	100	80	20	0	100
18A	1433	513	†	43	35.8	61.2	3	100	36	61	3	100
18B	1805	946	†	0	52.4	47.6	0	100	52	48	0	100
18C	1964	1504	†	0	76.6	23.4	0	100	77	23	0	100
19A	2484	4	†	75	41	56	3	100	41	56	3	100
19B	1446	651	†	0	45	55	0	93	48.4	51.6	0	100
19C	5289	4342	†	0	82.1	17.9	0	100	82	18	0	100
20	1342	432	†	13	32.2	66.8	1	100	32	67	1	100
21A	1132	396	†	45	35	61	4	100	35	61	4	100
21B	1003	632	292	0	63	29.1	0	92	68.5	31.5	0	100
21C	1024	809	243	0	79	23.7	0	102.7	76.9	23.1	0	100
22	9333	N/A	4528	0	51.4	48.6	0	100	51.4	48.6	0	100
23	N/A										0	
24	1393	⊕	764	47	41.8	54.8	3.4	100	41.8	54.8	3.4	100
25	3041	⊕	1260	♦	58.6	41.4	N/A	100	58.6	41.4	0	100
26	4585	⊕	1783	♦	61.1	38.9	N/A	100	61.1	38.9	0	100
27	3826	⊕	1789	♦	53.2	46.8	N/A	100	53.2	46.8	0	100
28	(Aborted)										0	
29	6285	3750	2132	♦	59.6	33.9	N/A	93.5	63.7	36.3	0	100
30	1900	1134	579	♦	59.6	30.2	N/A	89.8	66.4	33.6	0	100
31	6806	4334	2081	♦	63.7	30.6	N/A	94.3	67.6	32.4	0	100
32	6840	4199	2574	♦	59.9	37.6	N/A	97.5	61.4	38.6	0	100
33	(Aborted)											
34	7188	4610	3024	♦	64.1	42.1	N/A	104.2	59.6	40.4	0	100
35	5802	2324	2938	♦	40.1	50.6	N/A	90.7	44.2	55.8	0	100
36	3074	1189	1427	♦	38.7	46.4	N/A	85.1	45.5	54.5	0	100
37	5392	2354	2506	0	43.7	46.5	0	90.1	48.4	51.6	0	100
38	1550	396	973	♦	25.5	62.8	N/A	88.4	29	71	0	100
39	4514	2035	2043	♦	45.1	45.3	N/A	90.4	49.9	50.1	0	100
40	5607	2571	3415		45.9	60.9	7.6	106.8	43	57	0	100
41	1925	1285	551	♦	66.8	28.6	N/A	95.4	70	30	0	100
42	860	⊕	373	♦	56.6	43.4	N/A	100	56.6	43.4	0	100
43	1832	985	847	♦	53.8	46.2	N/A	100	53.8	46.2	0	100
44	10927	6357	4300	♦	58.2	39.4	N/A	97.6	59.6	40.4	0	100
45	2493	1623	756	♦	65.1	30.3	N/A	95.4	68.2	31.8	0	100
46	(Aborted)											
47	4356	1992	1612	♦	41.4	51.1	N/A	101.7	49.8	50.2	0	100
48	(Aborted)											
49	3212	1394	1818	♦	43.4	56.6	N/A	100	43.4	56.6	0	100
50	8173	7495	280	70	91.7	3.4	0.9	96	95.5	3.5	0.9	100
51	2653	2492	161	♦	93.9	6.1	N/A	100	94	6	0	100
52	3030	1823	1207	♦	60.2	39.8	N/A	100	60.2	39.8	0	100
53	4533	1488	♦	96	32.8	65	2.2	100	32.8	65	2.2	100
54	5971	3359	2042	♦	56.2	36.9	N/A	93.1	60.4	39.6	0	100
55	4365	3468	977	13	79.4	22.4	0.3	102.1	77.8	21.9	0.3	100
56	4379	1496	2396	575	34.2	54.7	N/A	102	33.5	53.6	12.8	100
57	448	N/A	230	♦	49	51	N/A	100	49	51	0	100
58	4042	2522	1028	♦	63	40	N/A	103	61.2	38.8	0	100
59	1778	1106	797	♦	62	45	N/A	107	57.9	42.1	0	100
60	3645	2151	1434	♦	59	39.3	N/A	98	60.2	39.8	0	100
61	7535	4636	3538	♦	57.9	47	N/A	104.9	55.2	44.8	0	100
62	(Aborted)						N/A					
63	3767	951	2596	♦	30.6	68.9	N/A	99.5	30.8	69.2	0	100
64	2361	406	2101	♦	17.2	89	N/A	106.2	16.2	83.8	0	100

RUN	PRODUCTION DATA (lbs)				CALCULATED YIELDS[1] (wt %)				NORMALIZED YIELDS (%)			
#	FEED	LIQUID[2]	COR.GAS[3]	CARBON	LIQUID	GAS	CARBON	TOTAL	LIQUID	GAS	CARBON	TOTAL
65A	4293	2612	1814	♦	60.8	42.3	N/A	103.1	59	41	0	100
65B	1057	636	414	♦	60.1	39.2	N/A	99.3	60.5	39.5	0	100
66	3960	1373	2863	♦	34.7	72.3	N/A	107	32.4	67.6	0	100
67	5940	5199	2316	♦	87.5	39	N/A	126.5	69.2	30.8	0	100
68	4936	3176	1516	♦	64.4	31.6	N/A	96	67.1	32.9	0	100
69	(Aborted)											
70	6808	3679	3536	♦	54	51.9	N/A	105.9	51	49	0	100
71	1039	686	377	♦	66	36.3	N/A	102.3	64.5	35.5	0	100
72	1015	615	340	♦	60.5	33.5	N/A	94	64.4	35.6	0	100
73	1143	728	429	♦	63.6	37.5	N/A	101.1	62.9	37.1	0	100
74	(Aborted)											
75	2612	865	1839	♦	33.1	70.4	N/A	103.5	32	68	0	100
76A	747	382	395	17	51.1	52.8	2.3	106.2	48.1	49.7	2.2	100
76B	1135	754	354	39	66.4	31.2	3.4	101	65.7	30.9	3.4	100

1 Waxes collected in carbon system were combined with actual liquids collected to give total liquids

2 Including waxes

3 Gas production corrected for the presence of nitrogen (added as a sweep gas)

⊛ Oil yield calculated by difference due to lack of operating data.

† Gas meter was non-functional, therefore, gas yield calculated by difference.

♦ Collected solids were an unknown mixture of spent lime and carbon

TABLE XXXVII Run Classifications

Run #	Dates	Run Classification	Hours of Operation	Feedstock	Objective	Results and Comments
1	5/5/93	shakedown/abort	4	base	demonstrate operability	Run aborted due to too much partially converted plastic plugging carbon outfeed screw conveyor.
2	5/6/93	shakedown/abort	7	base	prove operability	Higher furnace temperature (1450°F) and lower feed rate resulted in smooth operation
3	5/7/93	shakedown/abort	7.5	base	prove operability	Determined that furnace temperatures of 1350-1450 °F favored gas production.
4	5/12/93	shakedown/abort	2	base	prove operability	Mechanical problems terminated run before feed could be started.
5	5/13/93	shakedown/abort	14	base	prove operability	Unreliable material balance information. Furnace temperature still too high.
6	5/17/93	shakedown/abort	3	base	prove operability	Mechanical problems terminated run before stable operating conditions could be established.
7	5/18/93	shakedown/abort	19	base	prove operability	Emphasis on smooth furnace operation for environmental stack testing (AM Test).
8	5/19/93	shakedown/abort	10	base	prove operability	Second stack test conducted, but no estimate of liquid and solids production possible.
9	6/8/93-6/9/93	shakedown	24	base	prove operability	First successful operation of DART without forced abort. Ran for 24 hours (longest to date) with highest oil yield to date.
10	6/14/93-6/16/93	shakedown	54	base	high oil yield	With low feed rate of 50 lb/hr, furnace temperature lowered from 1300 °F to 1000 °F. Oil yield increased to ~80%. Light and heavy oil tanks calibrated.
11	6/29/93-7/1/93	shakedown	66	base	increase feed rate	Feed rate slowly increased from 44 lb/hr to 120 lb/hr. Continuous problems with wax production at high oil yields and low temperature operations.
12	7/6/93-7/8/93	shakedown	56	base	reduce wax production	Wax production not reduced by establishing temperature gradient in furnace . Furnace effluent sampling started. Furnace mid-auger temperature monitored routinely.
13	7/12/93-7/15/93	shakedown	64	base	reduce wax production	Wax production not reduced by establishing temperature gradient in furnace . Infeed reamer failed due to leaking oil seals.
14	7/19/93-7/22/93	shakedown	59	base	reduce wax production	Wax production not reduced by establishing temperature gradient in furnace . Furnace auger shaft thermocouples installed to measure temperature at 7 points.
15	7/26/93-7/29/93	shakedown	64	base	reduce wax production	Wax production not reduced by establishing temperature gradient of 300 °F in furnace .

Run #	Dates	Run Classification	Hours of Operation	Feedstock	Objective	Results and Comments
16	8/2/93-8/4/93	shakedown	47	base	reduce wax production	Wax production not reduced by establishing temperature gradient in furnace . Temperature gradient experiments abandoned.
17A-B	8/9/93-8/12/93	parametric study	76	base + 20% PET	study effect of 20% PET	Pyrolysis of base resin with 20% PET studied at two different temperatures. TPA levels in oil as high as 4%.
18A-C	8/16/93-8/19/93	parametric study	67	base + 20% PS	study effect of 20% PS	Pyrolysis of base resin with 20% PS studied at three different temperatures.
19A-C	8/23/93-8/27/93	parametric study	100	base + 20% LDPE	study effect of 20% LDPE	Pyrolysis of base resin with 20% LDPE studied at three different temperatures.
20A-B	8/29/93-9/3/93	parametric study	75.5	base + 20% PET	study affect of high furnace temp on TPA production	No TPA found in oil at 1450 °F furnace control temperature. Did attempt capacity operation with base plastic, but furnace auger stalled.
21A-C	9/8/93-9/10/93	parametric study	37	base	comparison run with base resin	Pyrolysis of base resin studied at three different furnace temperatures (1100, 1200, 1300 °F)..
22	9/13/93-9/16/93	parametric study	62	base	capacity	Capacity determination hindered by incomplete pyrolysis of resin.
23	9/21/93	abort	6	base	demonstration	Demonstration run for visitors.
24	10/20/93-10/21/93	shakedown	23	base	test acid gas scrubber	Using water circulation only, the caustic scrubber operated well.
25	10/25/93-10/28/93	parametric study	38	base + 3% PVC	study effect of 3% PVC without lime hydrate	AM-TEST on site to test flare stack for HCl, NOx, CO, hydrocarbons.
26	11/8/93-11/11/93	parametric study	41	base + 3% PVC	study effect of lime hydrate	Oil organochloride levels – 4000 ppm. Run terminated early by power outage.
27	11/17/93-11/18/93	parametric study	39	base (terminated before PVC)	study affect of lime hydrate	Cold weather resulted in blockage of heavy oil circulation to air coolers located outdoors and lacking winterization.
28	11/24/93	down	0	down	down	Unit down for winterizing and other repairs.
29	11/29/93-12/2/93	parametric study	55	base + 3% PVC	reduce organochlorides in oil	Oil organochloride levels ~7000 ppm. (Poor control of lime hydrate feeder.) Run terminated by blockage in acid gas scrubber.
30	12/7/93-12/9/93	abort	11	base + 3% PVC	reduce organochlorides in oil	Heavy oil circulation problems because of cold weather. Relocating heavy oil piping from outside to inside of building. Also planning to build enclosure around air coolers..
31	12/13/93-12/16/93	parametric study	72	base + 0.5% PVC	reduce organochlorides in oil	Organochlorides reduced to ~100 ppm. Heavy oil contained 5% lime solids because of blockage of inlet to screw conveyor for removing coke and lime from furnace and bell.

Run #	Dates	Run Classification	Hours of Operation	Feedstock	Objective	Results and Comments
32	1/3/94-1/6/94	parametric study	71	base + 0.5% PVC	reduce organochlorides in oil	Organochlorides reduced to <10 ppm. Acid gas scrubber by passed in planned experiment, relying on lime hydrate to react with HCl.
33	1/14/94	abort	15	base + 0.5% PVC + 2% PET	study effect of lime hydrate on capture of CO2 from PET	Run terminated because of apparent high pressure drop across oil condensing towers. Furnace pressure control valve at discharge of vacuum blower malfunctioning.
34	1/18/94-1/20/94	parametric study	66	base + 0.5% PVC + 2% PET	study effect of lime hydrate feed rate	Reducing the lime hydrate addition rate showed significant reaction of sodium hydroxide to sodium carbonate in the acid gas scrubber.
35	1/25/94-1/27/94	parametric study	60	base + 1% PVC & 5 &10% PET	determine any operating problems at high PET	No indication of terephthalic acid (TPA) in product oil for furnace temperature of 1350 °F. Without lime hydrate, furnace temperature of 1450 °F needed to avoid TPA.
36	1/31/94-2/1/94	parametric study	28	base + 1% PVC & 10% PET	determine minimum lime hydrate requirements	Using a lime hydrate feed rate corresponding to 1 - 2 times the stoichiometric requirements for reaction with CO2 (from PET) and HCl, stalling of the furnace auger drive occurred.
37	2/7/94-2/10/94	parametric study	53	base + chlorinated oil	determine effect of lime hydrate for oil cleanup	For the first time 40 gal. of product oil containing more than 3,000 ppm organochlorides (Cl only) was fed to the furnace over 7 hours to produce oil with less than 45 ppm Cl.
38	2/14/94-2/17/94	parametric study	40	base + 0.5% PVC + 2% PET	lower operating temperature of heavy oil tower from 185oF to 145oF	Run terminated early because of blockage at inlet to carbon screw conveyor. This was also a practice run for the environmental test (Run 39-B).
39A	2/22/94-2/23/94	private study		PP Bale Wrap from Amoco	PP Bale Wrap	Run aborted because of inability to feed material to furnace at uniform rates.
39B	2/24/94-2/25/94	regulatory requirement	32	base + 0.5% PVC + 2% PET	AM-TEST for environmental air permit	Furnace operated at 1400 °F.
40	2/28/94-3/1/94	parametric study	48	base + 2% PET	effect of lime hydrate feed rate on CO2 content of pyrolysis gas	Acid gas scrubber was by-passed so that CO_2 content of pyrolysis gas could be correlated with lime hydrate to plastic feed ratio.
41	3/8/94-3/10/94	parametric study	22	base + 3% PVC	effect of lime hydrate on organochloride in product oil	With better control of lime hydrate feed, repeated earlier tests to confirm expected organochloride content of product oils.
42	3/14/94-3/18/94	control study	8	base + 3% PVC	study effect of lime hydrate stoppage on organochloride levels	Test results might be useful for possible stream analyzer application to indicate need to vary lime feed rate. Run terminated early because of furnace auger malfunction.
43	3/29/94-4/1/94	parametric study	54	base + chlorinated oil	determine furnace capacity to handle chlorinated oil	Base plastic was a new mix which, at furnace temperatures of 1250-1350 °F, filled wax drum in 9 hours. This "base" plastic contained ultra high molecular weight polyethylene which should be avoided.
44	4/9/94-4/13/94	parametric study	98	base + chlorinated oil	repeat Run 43	Product oil at feed rates of 50-75 lb/h was successfully dehydrochlorinated along with lime and base plastic. No further parametric studies for oil cleanup needed.
45	4/19/94-4/21/94	parametric study	58	base + 1% PVC & 3% PET	determined furnace capacity at gas yield below 20%	Furnace capacity for base resin limited to 175 lb/h, with furnace control temperature at 1450 °F. Earlier forecast of 250 lb/h placed in doubt.
46	4/25/94-4/26/94	aborted	10	base + 1% PVC & 3% PET	repeat of Run 45 capacity test	Head of inactive reamer, formerly used to push solids along bottom of furnace below plastic feed point, broke loose and jammed furnace auger. Repairs involved removal of inlet end bell.

Run #	Dates	Run Classification	Hours of Operation	Feedstock	Objective	Results and Comments
47	5/9/94-5/12/94	parametric study	34	base + 1% PVC & 3% PET	repeat of Run 45 capacity test	Furnace capacity of 150-175 lb/h could only be achieved by starting up furnace at lower feed rate to avoid discharge of partially pyrolyzed solids into carbon conveyor.
48	5/19/94	abort	2	PCP-OR		Lack of safety equipment for HCN detection.
49	5/24/94-5/26/94	post-consumer plastic	58	PCP-OR	determine behavior of PCP in furnace	PCP is in flake form; requiring screw conveyors to move it. (Base resin is in pellet form suitable for pneumatic conveyor.)
50	5/31/94-6/3/94	parametric study	61	100% PS	determine optimum furnace conditions	Polystyrene pyrolyzes at a lower temperature than base plastic and at feed rates of 240 lb/h. Very low gas yields.
51	6/7/94-6/10/94	parametric study	61	100% PS from Mobil	test PCP consisting of 100% PS	Slabs of compressed PS from used foamed PS food service ware were crushed into irregular shaped and sized solids; very difficult to feed to furnace.
52	6/14/94-6/16/94	parametric study	40	base + 4% paper	effect of paper from PCP on yields.	Paper was mixed with base plastic to simulate PCP. No problems, just more CO2 produced from cellulose.
53	6/20/94-6/23/94	parametric study	47	base + high PET	confirm earlier tests on TPA destruction	TPA in oil from base plastic with 20% PET was 0.4% at 1400 °F. For 40% PET in base, TPA in oil was 4%.
54	6/27/94-7/1/94	parametric study	63	base + 5% PVC & 5% PET	what is organochloride content of product oil?	Increasing PVC and PET to 10% of feed resulted in higher organochloride yields.
55	7/6/94-7/7/94	parametric study	36	base	establish operating conditions for 80% liquid yields	Liquid yields of 78% achieved at furnace temperature of 1100 °F and TC-12 of 780 °F for plastic feed rate of 120 lb/h.
56	7/12/94-7/15/94	private study	45	3M Magnetic tape	determine product yields and oil quality	Magnetic tape was fed in pelletized form along with virgin polypropylene pellets to reduce PET content to 20%. Evidence for hydrocracking (high hydrogen yields).
57	7/19/94-7/21/94	parametric study	49	PP	determine produce yields for pure PP	Left over PP from Run 56 was fed to furnace for 5 hours. Pyrolysis gas composition results obtained, but no liquid composition data. Processed left over odd lots of plastic - too small for required tests.
58	7/25/94-7/29/94	parametric study	39	base + 1% PVC & 3% PET	testing new resin feed bin weighing system	New feed bin weighing system provided improved tracking of feed utilization.
59	8/1/94-8/5/94	post-consumer plastic	17	PCP-NJ	maximum oil yield, minimum wax	Oil yields of 56% ;oil was very viscous and waxy at room temperature and may have caused plugging of nozzles in the oil quenching system, particularly during startup (no heat tracing).
60	8/8/94-8/12/94	post-consumer plastic	30	PCP-NJPCP-GW	maximum oil yield	Plugging of oil lines and spray nozzles were problems. PCP--NJ contains more HDPE than base plastic, giving higher wax yields.
61	8/15/94-8/19/94	post-consumer plastic	70	PCP-IN	maximum oil yield	Oil yields were less than 60%. Concern that higher oil yields would increase viscosity of circulating heavy oil.
62	8/22/94-8/26/94	abort	19	PCP-GW	produce oil with no TPA	Run was terminated early because inlet to outfeed carbon conveyor was plugged. Also feed system required cleaning.

Run #	Dates	Run Classification	Hours of Operation	Feedstock	Objective	Results and Comments
63	8/29/94-9/2/94	post-consumer plastic	51	PCP-GW	produce oil with no TPA	PCP-GW contains 30-35% PET. Together with lime, the oil yield was only 30%, but no TPA was evident.
64	9/6/94-9/9/94	post-consumer plastic	35	PCP-IN	study effect of high furnace temperature on wax production	At low feed rates of 67 lb/h and furnace temperatures ranging from 1300 °F to 1450 °F, the oil yield was only 16% with no evidence of wax constituents.
65	9/12/94-9/16/94	parametric study	10	base + FCC catalyst	study effect of cracking catalyst on product composition	Pyrolysis gas showed twice the normal concentration of cis & trans 2-butene with a significantly higher aromatics concentration in the product oil.
66	9/19/94-9/23/94	post-consumer plastic	57	PCP-IN	demonstration run for APC television production	At feed rates of 100 lb/h and furnace temperature of 1200 °F, the carbon discharge showed some incompletely pyrolyzed plastic.
67	9/26/94-9/30/94	parametric study	61	chlorinated oil	upgrade product oil with high organochlorides	Feeding high chloride-containing oil with lime hydrate produced oil with <25 ppm Cl. 25-40% of oil was gasified.
68	10/3/94-10/7/94	parametric study	37	chlorinated oil	commission new wax feed system	Attempts to feed molten wax (from early runs) abandoned because wax could not be completely melted in 55 gal. drums. Recycled 15 drums oil.
69	10/17/94-10/21/94	abort	0	chlorinated oil and wax	reprocess off- spec oil and wax from early runs	Run terminated early because of problems with feed pump. Wax melted slowly (inadequate facilities).
70	11/8/94-11/10/94	parametric study	60	base + 1% PVC & 3% PET	determine minimum lime hydrate feed rate	New "loss in weight" feed system for lime hydrate tried out for first time. Could produce low chloride oil with only 40% of lime used in previous runs as long as PVC content did not exceed 1%.
71	12/12/94-12/16/94	parametric study	67	base + PU	study effect of PU in feed, monitor HCN production	HCN in pyrolysis gas varied from 0-20 ppm. Significant production of ammonia. Cyanide not detected in oil or scrubber water. Cyanide detected at 40 ppm in spent carbon/lime. Run progressed smoothly at 5% PU.
72	12/19/94-12/22/94	parametric study	19	base + 5% ABS	study effect of ABS in feed, monitor HCN production	No HCN was detected in any gas samples. Ammonia detected at 1 - 2% in the gas. No cyanide was detected in the oil, spend lime/carbon or scrubber water. The run progressed smoothly.
73	11/17/95-11/18/95	parametric study	18	base + 5% nylon	study effect of nylon in feed, monitor HCN production	No HCN was detected in the gas, oil, spend lime/carbon or scrubber water. The run progressed smoothly.
74	2/6/95-2/10/95	shakedown abort	42	PCP-GW	effect of furnace and lime hydrate temperature on TPA destruction	Run terminated because of problems with ram feed system.
75	2/13/95-2/17/95	post-consumer plastic	34	PCP-GW	effect of furnace temperature on TPA destruction	Found TPA in furnace effluent sample when furnace temperature dropped to 1350 °F from 1400 °F. (Oil yield ~30%.)
76	2/21/95-2/24/95	parametric study	38	100% PP	determine yield pattern for oil and gas	Pyrolysis gas was predominately isobutylene and propylene. PP was easier to pyrolyze than base plastic (no wax problems).

TABLE XXXVIII Run Data Summary

	Feedstock					Operating Conditions			Yields[2] (wt %)		Pyrolysis Gas Componential Yield (wt %)										Retort Oil Componential Yield (wt%)								
Run Number[1]	Base Blend	PET	PVC	Other	Feed Rate (lb/hr)	Lime Hydrate Feed Rate (lb/hr)	Furnace Temperature (°F)	Retort Temperature (°F)	Liquid	Gas	Hydrogen	Methane	Ethane	Ethylene	Propane	Propylene	Total C4's	Carbon Monoxide	Carbon Dioxide	Other	Aliphatics	≤C10 Aliphatics	C11-C20 Aliphatics	>C20 Aliphatics	Aromatics	Benzene	Toluene	Styrene	Unidentified
17A	80	20			124	0	1300	970	62.0	38.0	0.04	2.1	3.2	4.1	1.1	6.3	7.9	1.7	1.7	9.9	29.2	16.4	9.3	3.5	25.2	1.9	4.5	5.5	6.7
17B	80	20			117	0	1200	910	80.0	20.0	0.02	0.8	1.4	1.7	0.7	2.8	4.0	1.4	1.7	5.5	36.9	12.4	16.7	7.8	28.8	0.9	3.0	6.4	10.7
18A	80			20[2]	110	0	1300	1100	36.0	61.0	0.12	4.4	3.2	7.3	1.8	13.6	16.8	0.4	0.2	13.2	6.9	3.8	2.2	0.9	25.6	2.1	5.8	7.6	3.5
18B	80			20[2]	113	0	1200	1000	52.0	48.0	0.04	1.7	2.2	3.4	1.4	8.0	12.1	0.3	0.2	18.7	14.8	7.7	5.6	1.5	31.5	1.1	5.6	12.8	5.7
18C	80			20[2]	110	0	1100	910	77.0	23.0	0.02	0.7	1.1	1.4	0.9	4.2	6.4	0.3	0.2	7.8	24.9	11.2	8.1	5.6	38.7	0.9	6.2	16.9	13.4
19A	73			27[3]	108	0	1300	1100	41.0	56.0	0.10	4.5	3.0	8.4	1.8	12.9	13.8	0.4	0.1	11.0	10.9	7.0	3.0	0.9	25.8	3.1	6.4	6.4	4.3
19B	73			27[3]	111	0	1200	1000	52.0	48.0	0.05	2.4	2.9	5.3	1.9	9.7	13.5	0.3	0.1	11.9	19.1	11.5	6.0	1.6	27.0	1.5	5.8	9.0	5.9
19C	73			27[3]	104	0	1100	910	82.0	18.0	0.02	0.7	0.9	1.5	1.0	3.1	5.2	0.3	0.2	5.1	32.3	15.3	8.6	8.4	35.4	0.8	6.4	12.1	14.3
20	80	20			100	0	1450	1200	32.0	67.0	0.30	8.5	3.7	11.8	1.3	12.3	8.8	2.9	4.4	13.0	5.8	1.8	3.1	0.9	22.8	5.5	5.3	4.1	3.4
21A	100				126	0	1300	1100	35.0	61.0	0.12	4.6	1.0	8.8	2.0	14.6	16.7	0.4	0.3	12.5	9.0	4.8	2.9	1.3	22.2	1.9	5.3	6.5	3.8
21B	100				125	0	1200	980	63.0	37.0	0.04	2.0	0.8	4.5	1.7	8.1	11.2	0.3	0.2	8.2	23.9	12.0	6.6	5.3	29.0	1.2	5.5	10.0	10.1
21C	100				128	0	1100	890	79.0	21.0	0.02	0.7	0.4	1.7	1.1	3.7	5.9	0.5	0.2	6.8	27.2	11.9	7.4	7.9	36.9	0.7	6.9	14.4	14.9
22	100				153	0	1300	990	51.4	48.6	0.10	3.3	1.3	5.7	1.8	11.9	14.1	0.5	0.3	9.6	17.3	8.8	5.6	2.8	28.6	1.8	6.2	9.7	5.5
25	97		3		81	0	1350	1225	58.6	41.4	0.29	8.0	NA	8.1	0.6	7.4	4.9	0.4	0.0	11.7	7.9	1.1	4.6	1.9	46.8	10.2	10.8	9.6	3.9
26	97		3		88	bad	1050	870	61.1	38.9	0.19	2.8	1.1	5.2	1.2	9.0	10.8	0.2	0.2	8.2	20.7	9.3	6.9	4.3	32.6	1.3	5.1	11.6	7.8
29	97		3		143	0	1250	956	65.6	34.4	0.03	1.5	1.5	3.1	2.3	6.7	10.9	0.4	0.5	7.5	23.6	11.9	7.9	3.5	33.7	1.4	5.4	13.3	8.3
30	97		3		100	bad	1200	851	59.6	30.2	0.09	0.9	0.1	1.7	1.8	5.0	9.7	0.1	0.0	10.8	29.0	12.3	10.7	5.6	24.7	0.8	3.9	8.6	5.9
31	99.5		0.5		110	bad	1250	842	67.6	32.4	0.06	1.6	0.4	3.2	1.6	6.5	11.0	0.2	0.0	7.8	34.3	20.6	10.0	3.4	28.4	1.5	5.3	8.8	4.9
32	99.5		0.5		107	12	1250	947	61.4	38.6	0.12	1.9	0.7	4.1	1.7	8.1	12.2	0.1	0.0	9.7	26.4	14.8	7.4	3.7	29.4	1.3	4.9	11.4	5.6
34	97.5	2	0.5		126	9	1300	933	59.6	40.4	0.08	1.8	0.6	4.1	1.5	8.1	11.7	0.1	0.0	12.4	31.8	15.0	10.5	5.6	25.9	1.5	4.9	10.0	1.9
35	94.5	5	0.5		120	15	1350	975	44.2	55.8	0.22	3.7	1.3	6.9	1.6	12.2	16.0	0.4	0.0	13.5	18.2	8.3	6.7	2.9	24.8	2.2	3.9	9.2	1.2
36	89	10	1		110	12	1300	980	45.5	54.5	0.22	3.4	1.7	6.6	1.5	11.3	14.7	0.5	0.0	14.6	14.9	8.7	4.9	1.2	28.9	5.1	5.7	7.2	1.7
37	Base + oil				117	10	1300	964	48.4	51.6	0.10	2.7	1.5	5.9	1.7	11.1	15.5	0.2	0.0	12.9	19.9	10.6	7.6	1.7	25.8	1.4	4.3	10.9	2.7
38	97.5	2	0.5		129	17	1350	900	29.0	71.0	0.28	6.5	2.3	10.8	1.8	16.3	15.8	0.4	0.0	16.8	6.3	3.4	2.3	0.5	21.5	3.9	4.3	6.3	1.2
39	97.5	2	0.5		129	12	1400	995	49.9	50.1	0.20	3.5	1.4	6.8	1.5	11.4	14.3	0.4	0.0	10.6	15.1	8.5	4.8	1.6	31.0	3.7	6.1	10.4	3.8
40	98	2			117	var.	1400	1117	43.0	57.0	0.23	5.3	2.9	8.7	1.5	13.3	12.6	0.3	0.3	11.9	11.2	6.2	4.0	0.9	29.2	3.1	5.5	10.3	2.6
41	97		3		137	12	1250	923	70.0	30.0	0.06	1.4	0.9	3.2	1.4	6.7	9.7	0.2	0.0	6.4	27.3	14.7	9.7	2.5	35.6	1.1	4.6	18.1	7.1
43	Base + oil				72	10	1350	958	53.8	46.2	0.14	2.8	2.4	5.4	1.6	10.1	13.7	0.2	0.0	9.9	19.4	9.0	7.6	2.6	30.6	1.1	5.2	12.3	3.8

	Feedstock					Operating Conditions			Yields[9] (wt %)		Pyrolysis Gas Componential Yield (wt %)										Retort Oil Componential Yield (wt%)								
Run Number[1]	Base Blend	PET	PVC	Other	Feed Rate (lb/hr)	Lime Hydrate Feed Rate (lb/hr)	Furnace Temperature (°F)	Retort Temperature (°F)	Liquid	Gas	Hydrogen	Methane	Ethane	Ethylene	Propane	Propylene	Total C4's	Carbon Monoxide	Carbon Dioxide	Other	Aliphatics	≤C10 Aliphatics	C11-C20 Aliphatics	>C20 Aliphatics	Aromatics	Benzene	Toluene	Styrene	Unidentified
44	Base + oil				71	10	1300	927	59.7	40.3	0.16	2.5	2.2	4.3	1.3	8.8	12.2	0.1	0.0	8.7	NA	NA	NA	NA	NA	NA	NA	NA	
45	96	3	1		178	14	1450	929	68.2	31.8	0.10	1.9	1.7	4.0	1.0	7.0	9.1	0.2	0.1	6.7	28.5	14.2	10.1	4.5	33.0	2.5	5.4	13.0	6.7
47	96	3	1		97	21	1350	1002	49.9	40.4	0.12	2.6	2.7	5.1	1.2	8.9	11.2	0.2	0.0	8.4	16.8	7.9	6.4	2.4	31.5	3.2	5.7	11.0	1.6
49	PCP-Oregon				100	10	1250	1000	43.4	56.6	0.20	3.2	3.7	6.2	1.7	11.2	15.3	1.0	0.2	13.9	14.4	7.2	5.6	1.6	26.4	2.2	4.5	7.4	2.6
50				100[2]	250	0	1250	1000	95.6	3.5	0.02	0.2	0.0	0.3	0.0	0.1	0.1	1.0	0.8	0.9	8.8	0.8	6.0	2.0	85.4	0.5	8.7	57.7	1.4
51				100[4]	49	0	1250	1069	94.0	6.0	0.14	1.0	0.4	0.9	0.1	1.0	0.9	0.3	0.3	1.0	6.2	1.0	3.8	1.3	87.0	1.1	12.0	47.7	0.8
52	96			4[5]	100	0	1250	1029	60.2	39.8	0.10	2.3	3.0	4.7	1.3	8.9	11.5	1.2	1.0	5.8	19.1	9.3	7.4	2.0	36.2	1.0	5.9	14.7	4.9
53	60	40			100	0	1400	1125	32.8	65.0	0.30	6.0	4.5	8.6	1.4	12.2	12.9	3.6	4.8	10.7	8.4	2.6	4.9	0.7	21.6	4.4	3.4	3.8	2.8
54	90	5	5		92	18	1250	870	60.4	39.6	0.16	2.1	2.7	4.0	1.4	7.3	10.2	0.3	0.2	11.2	27.1	12.1	10.0	4.3	30.0	2.4	4.5	12.1	3.3
58	96	3	1		106	12	1300	945	60.8	39.2	0.12	1.8	2.6	3.8	1.3	7.7	10.9	0.3	0.1	10.6	24.3	17.0	6.9	0.5	34.4	1.8	5.7	15.7	2.1
59	PCP-New Jersey				105	8	1300	950	57.9	42.1	0.10	1.9	2.9	4.2	1.8	7.9	11.8	0.4	0.2	10.9	37.8	16.0	15.4	6.4	12.7	1.0	1.8	0.7	7.4
60	PCP-New Jersey				121	20	1300	942	60.2	39.8	0.10	1.8	2.7	4.4	1.5	7.3	11.2	0.4	0.2	10.2	41.6	13.8	17.9	9.9	12.1	0.7	1.3	0.7	6.5
61	PCP-Indiana				108	7	1300	970	55.2	44.8	0.10	1.9	2.7	4.0	1.4	8.2	12.2	0.8	0.3	13.2	31.6	15.3	11.5	4.8	14.4	1.1	2.2	4.1	9.2
63	PCP-Goodwill				74	10	1350	1095	30.8	69.2	0.60	5.6	4.1	7.5	1.5	10.9	12.9	4.2	5.7	16.2	5.8	2.4	2.8	0.6	23.1	3.8	3.3	4.6	1.9
65	Base + Catalyst				106	0	1150	983	59.0	41.0	0.08	1.8	2.4	2.7	1.7	7.3	12.2	0.6	0.6	11.6	21.5	12.4	6.8	1.9	34.7	1.4	4.7	11.3	2.8
67	Oil and wax				97	10	1350	984	69.2	30.8	0.22	1.9	1.6	3.5	0.6	4.8	7.6	0.6	1.0	9.0	19.8	9.0	8.7	2.1	41.6	2.8	8.0	9.8	7.8
68	Oil and wax				133	5	1450	1096	67.1	32.9	0.26	3.4	2.4	5.0	0.6	6.8	6.9	0.5	0.5	6.5	10.7	5.8	3.9	1.1	53.6	7.1	14.3	11.9	2.8
70	96	3	1		125	4	1350	969	51.0	49.0	0.10	2.5	3.3	5.0	1.5	9.4	13.0	0.6	0.8	12.8	18.6	9.8	2.9	2.4	29.9	1.9	4.4	10.2	2.5
71	95			5[6]	103	4	1250	964	64.5	35.5	0.14	2.0	2.7	4.3	1.5	7.4	9.6	0.6	0.4	6.9	24.8	7.7	9.5	6.8	35.2	0.7	4.6	14.3	4.5
72	95			5[7]	127	4	1300	990	64.4	35.6	0.11	1.8	2.5	3.4	1.2	7.7	10.2	0.2	0.1	8.4	20.0	9.1	7.4	3.3	39.2	1.3	6.6	15.6	5.2
73	95			5[8]	114	4	1300	1050	62.9	37.1	0.04	2.0	2.8	3.9	1.3	8.1	10.9	0.2	0.1	7.8	18.5	9.7	5.9	2.9	40.3	2.1	7.8	15.0	4.1
75	PCP-Goodwill				119	20	1400	1054	32.0	68.0	0.40	5.2	4.3	7.2	1.8	11.6	14.3	4.3	6.7	12.2	11.0	5.6	4.0	1.4	17.3	5.2	2.4	2.1	3.7
76A	PCP-Polypropylene				94	0	1200	931	48.1	49.7	0.10	1.7	3.2	1.8	1.7	12.3	15.4	0.6	0.6	12.3	28.9	21.0	5.9	2.0	10.2	1.0	1.3	1.4	9.0
76B	PCP-Polypropylene				103	0	1100	843	65.7	30.9	0.00	0.9	2.0	0.8	1.1	7.6	8.7	0.6	0.5	8.7	44.7	28.7	11.5	4.5	14.0	0.9	1.8	1.7	6.9

[1] Refer to Table 8.7 for information regarding runs not included on this table
[2] PS
[3] LDPE
[4] Ground, post-consumer PS
[5] Paper
[6] PU
[7] ABS
[8] Polyamide
[9] See Table 8.6 for further yield information

9. Supporting Documents

Following is a list of the supporting documents for this report:

- Extended Run Summary "Archive" Reports For All Runs
- All Outside Plant Analyses Organized By Sample Type
- Plant Industrial Hygiene Plan
- Hydrogen Cyanide Safety Guidelines and Emergency Response
- Pre-Manufacture Notice
- Plant Operating Manual
- Lab and Plant Computer Data Files
- State of Washington Air Permit
- Analytical Results Table
- Engineering Assessment Report
- Waste Water Discharge Permit
- Activated Carbon Recycling Permit
- Initial Safety Review Document
- Corrosion Coupon Evaluations
- Record of GC Analyses Listed Out of Sequence in "Archive" Reports

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