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by

Procedyne Corp.

221 Somerset St.

New Brunswick, NJ 08903

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CONVERSION OF ATACTIC POLYPROPYLENE WASTE
TO FUEL OIL

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INTRODUCTION

1.0

CONVERSION OF ATACTIC POLYPROPYLENE
WASTE TO FUEL OIL

1.0 INTRODUCTION

1.1 General Background

Polypropylene was introduced as a new commercial plastic in 1959. The volume of polypropylene produced in the United States in 1963 was less than 200 million pounds. The 1974 production level in the United States was 2.25 billion pounds and the level for 1979 was in excess of 4.5 billion pounds. An historical record for this plastic is shown in Table I.

TABLE I

U.S. PRODUCTION AND SALES OF POLYPRO
POLYPROPYLENE RESINS

(Millions of Pounds)

	<u>Production</u>	<u>Sales</u>
1960	41	35
1961	97	57
1962	145	107
1963	197	173
1964	270	261
1965	374	377
1966	554	545
1967	662	650
1968	878	925
1969	1,090	972
1970	1,031	996
1971	1,339	1,294
1972	1,731	1,685
1973	2,165	2,200
1974	2,249	2,201
1975	1,902	1,903
1976	2,632	2,536
1977	2,747	2,698
1978	3,074	3,055
1979	3,841	3,893
1980	3,648	3,790*

*Estimated consumption based on market trends.

Because of the strong acceptance of polypropylene in the marketplace, the industry generally regards the prospects for this plastic to remain excellent in the long run. Table II lists projected demand over the next three years, based on present market trends. Plants planned or under construction will give the United States the capacity to meet the demand.

1.1 General Background (cont'd)

TABLE II

Projection of U.S. Polypropylene
Production and Demand
(Millions of Pounds)

	<u>Capacity</u>	<u>Demand</u>
1981	5,740	4,208
1982	5,915	4,628
1983	6,015	5,090

Fig. 1, pg. 3, is a graphical summary of Tables I and II showing Capacity, Production, and Sales in the United States only. The above data are all given on a dry weight basis including colorants, stabilizers, and fillers. Also included are copolymers and modified homopolymers containing more than 50% polypropylene. The numbers do not include sales and production of atactic polypropylene.

1.2 Description of Compounds

Propylene

Propylene ($\text{CH}_3\text{CH}=\text{CH}_2$; molecular weight - 42.08) is a gas under standard ambient conditions and can be readily liquified under pressure and/or reduced temperatures. Polymer-grade propylene contains more than 99% propylene, usually up to 99.5%, with catalyst poisons such as water, oxygen, carbon dioxide, hydrogen sulfur, acetylene, and others removed.

Polypropylene

The development of the catalyst system which led to synthesis of a highly crystalline polypropylene was reported by Nobel Prize winner, Giulio Natta, of Italy in 1954. The crystallinity of polypropylene was discovered to be due to "steriospecific"* arrangement of the polymer molecules. Polypropylene, by virtue of the methyl group, is asymmetric with respect to axis of the polymer chain and can assume two geometrically "sterioregular" (i.e., geometrically regular spatial arrangements). As shown by Figures 2, 3, and 4, isotactic refers to the arrangement in which all of the methyl groups are aligned on the same side of the

FOOTNOTE: * Sterioregular or stereoregular species refers to the isotactic and syndiotactic arrangement of substituents respectively. In the isotactic placement, all substituents have the same configurational position and in the syndiotactic placement there exists a regular alternation between the positions over the entire molecule. Any deviation from these two cases is called Atactic.

Figure 2: Isotactic Polypropylene

Figure 3 Syndiotactic Polypropylene

Figure 4 Atactic Polypropylene

1.2 Polypropylene (cont'd)

polymer chain; syndiotactic is the arrangement in which methyl groups are alternately aligned on opposite sides of the chain. When the methyl group is randomly arranged along the chain, the polymer is in the atactic form. The only form of commercial importance is the isotactic form. Atactic polypropylene is produced as a by-product in the polymerization of isotactic polypropylene and only a limited amount finds use as an adhesive base. Syndiotactic polypropylene has been synthesized in the laboratory but production has not been commercialized.

1.3 Process

Several processes exist for the production of polypropylene. The desired form, isotactic polypropylene, is linear and stereoregular and therefore capable of crystallization when cooled from a melt. (It is the presence of crystallinity that imparts the commercially useful strength and toughness characteristics to polypropylene). The preferred process is the "SLURRY PROCESS", which is typically as shown in the flowsheet of Figure 5, pg. 6. In this process, the atactic polypropylene is a waste stream which runs about 7% to 10% by weight of the total useful process yield.

A lower cost "GAS PHASE" process has been introduced by BASF AG (West Germany) but it has not yet gained acceptance because of difficulties in matching of properties of presently available commercial grade polypropylene. The Gas Phase process, interestingly, produces substantially more atactic polymer than the Slurry Process.

1.4 Atactic Polypropylene - Waste Polymer

During the past ten years, attempts have been made to find a commercially useful product path for the atactic polymer. To date, these efforts have yielded a few limited successes in hot melt adhesives for some atactic types; however, the general industrial conclusion is that the optimum route to handling a major part of this waste stream is to convert it to a useful energy source.

The atactic polymer is a relatively pure wax like polymer which is a soft solid at room temperature and melts to a viscous liquid at temperatures above 135°C. The polymer contains traces of aluminum, chlorides, and titanium.

Attempts to burn the polymer directly or in blends with fuel oil have given difficulties because of its high molecular weight which yields a highly viscous melt at relatively high temperature.

A laboratory scale process involving thermal cracking (pyrolysis) of the atactic polypropylene to useful liquid and gaseous fuels has been demonstrated. It was the objective of this work to extend the process technology to larger scale operation and to demonstrate the technical and economic feasibility of this process on a commercial scale.

Figure 5 Slurry Process for Manufacture of Polypropylene

1.5 Polymer Cracking Processes

The atactic polypropylene (APP) has been converted to heavy industrial fuel oil on a laboratory scale. The resulting fuel oil contains practically no sulfur and is clean burning. Corrosivity is very low - it is anticipated that the burner tips will be mildly affected by the trace presence of residual chlorides, but this is expected to be of negligible consequence on a commercial scale.

Two cracking processes have been successfully employed on a laboratory scale; a thermal cracking and a catalytic cracking process.

1.5.1 Thermal Cracking of Atactic Polypropylene

1.5.1a Introduction and Background

Studies on thermal cracking of atactic polypropylene have been carried out in Proceadyne's laboratories for the past four years, with the objective of producing commercially useful products. Thermal cracking of organic polymers, in general, has aroused considerable interest in the recent years from a waste disposal as well as an energy conservation viewpoint. Such studies are of importance from a scientific point of view, also, because they shed light on the molecular structure and the strength of the various bonds holding together the polymer molecules and on the effects of time, temperature, pressure and other variables, on rates and products of degradation, and the kinetics involved in the reactions during pyrolysis.

Much of the experimental work on pyrolysis reported in the literature is in the temperature range of 400 - 600 °C although, studies have been carried out at temperatures up to 1200 °C. As would be expected, the studies indicate that the higher the temperature, the greater the fragmentation of the degradation products. Pyrolysis studies, which aim to recover useful hydrocarbons, would by necessity have the temperature range dictated by the desired product mix. Numerous researchers have studied the rate of thermal cracking of commercially important polymers. For instance, the rate of degradation of teflon, which is one of the most thermally stable polymers, tends to double for every 10°C rise in temperature in the range of 200 - 500 °C. (1) In actual practice, the rate is considerably lower because polytetrafluoroethylene like most organic polymers, cracks endothermically and hence, the low rate of delivery of heat to the reaction site is bound to reduce the reaction rate considerably. Another complication to rate studies is the fact that some of the sample degrades and vaporizes during the heat up period, so that the reaction does not take place at a constant temperature.

1.5.1a Introduction and Background (cont'd)

Pyrolysis studies described in literature often report work done in a vacuum. This is due to the gaseous atmosphere retarding the diffusion out of the sample of viable products so that these products can undergo secondary reactions.

1.5.1b Mechanism of Thermal Cracking

Researchers have finally established that thermal cracking proceeds by a free radical mechanism. The main body of research originated from pyrolysis of hydrocarbons such as ethane, propane, isobutane and isopentane (2). There is general agreement that these reactions can basically be described in terms of the Rice-Herzfield radical chain mechanisms (3) and that in general the chains are long. In the case of polyolefins thermal decomposition occurs as in model short chain paraffins. However, the appropriate Rice-Herzfield scheme must be extended and modified to account for the products observed. Also, it is established that the effect of surfaces and impurities must be taken into consideration.

The steps of formation of free radicals and abstraction of hydrogen by the radicals, a process which continues until equilibrium sets in are represented as follows by Madorsky (1);

a. Initiation - This is a unimolecular process consisting of the rupture of C-C bonds of a chain to yield free radicals. In the case of a pure linear polymer like polymethylene, the rupture of bonds anywhere in the chain would be the only path by which free radicals could form:

1.5.1b Mechanism of Thermal Cracking (cont'd)

However, most polymers contain impurities, either incorporated in the backbone of the chain or attached to it at random as side groups along the chain, thus forming weak links, or at the ends.

b. Propagation - This step is the reverse of the propagation step in addition polymerization* and results in the formation of monomers at the free-radical ends of chains. However, in polypropylene this step is not predominant.

c. Free-radical transfer - This step is two types: inter-molecular, in which a free radical abstracts a hydrogen from another chain, and intra-molecular, in which a free radical abstracts a hydrogen from its own chain. The results in either case consist in the formation of one saturated end, one unsaturated end, and a new free radical:

d. Termination - This occurs when two free radicals combine to form one polymer chain:

2 radicals 1 polymer chain

*FOOTNOTE: In addition Polymerization, the individual monomers add to each other directly without any change in composition and form a long chain. For instance, ethylene C_2H_2 is converted into Polyethylene $(\text{C}_2\text{H}_2)_n$, according to the scheme:
 $\text{CH}_2 = \text{CH}_2 -\text{CH}_2 -\text{CH}_2 -\text{CH}_2 -\text{CH}_2 -\text{CH}_2 -\text{CH}_2$ (generally = 1000)

Addition Polymerization is distinguished from condensation Polymerization in which two or more monomers react with each other with elimination of a small part of them - usually water, to form a linear chain molecule.

1.5.1b Mechanism of Thermal Cracking (cont'd)

With regard to a free radical formed in the initiation or in any of the other steps, one or two competing reactions may follow: (1) propagation (unzipping) to yield monomers and (2) free-radical transfer involving an abstraction of hydrogen from a polymer chain and resulting in the formation of one saturated end, one unsaturated end, and a new free radical, as indicated above. Which of these alternative reactions will prevail, will depend on the amount of hydrogen on the chain.

Thus in Polypropylene:

The hydrogen atom on the tertiary carbon is more reactive and is abstracted in preference to the one on a secondary carbon. The CH group is small and does not present much of an obstacle to a hydrogen transfer. As a result, the scissions of C-C bonds in the chains are predominantly of a type involving a hydrogen transfer at the site of scissions. In contrast, it is of interest to know that in pyrolysis of polyisobutylene where every alternate carbon of the chain is quarternary and no reactive hydrogen atoms are present, a large number of scissions result in the formation of free radicals which unzip to yield monomers:

According to the hydride transfer mechanism, fragments having saturated and unsaturated ends result and obviously, there is very little propagation to yield the monomer. In general, the more substituted hydrocarbon structures give higher monomer yield. Leo Wall (4) has published data on monomers yield from decomposition of polymers. Polystyrene yields 42% monomer as compared to 2% from polypropylene and 0.1% from polyethylene. As apparent from the cracking mechanism, the more substituted polymers would also be less stable thermally. Figure (6), pg. 11, outlines the effect of side groups on thermal stability of various polyolefins (7).

FIG. 6 The effect of side-groups on the thermal stability of various polyolefins: 1: polyisobutylene, 2: at. and lt. PP, 3: linear PE, 4: polyvinylcyclohexane(x), poly-4-methyl-1-butene(Δ)⁹

1.5.1c Effect of Tacticity - The discussion of reaction mechanisms so far has revolved around polyolefins in general and polypropylene in particular. Since this work is concerned primarily with atactic polypropylene, the effect of tacticity on pyrolysis must be investigated. Preliminary experimental work performed at Procedyne on isotactic polypropylene indicates that a significant departure in cracking behavior does not exist. From the limited data available in literature (6) it seems that changes in tacticity do not have a significant effect on the mechanism of decomposition of polymers of the type which degrade by random breaking of polymer backbone to yield small fragments such as polypropylene and polyethylene or by depolymerization (such as polymethacrylate). Some differences in energies of activation on kinetic coefficients are expected. The differences in the energies of formation between the various tactic structures are reported to be only a few hundred small calories (1); however, different synthesis routes for preparing polymers may sometimes obscure the effects of tacticity. The activation energy of decomposition of polypropylene has been reported to be around 58 Kcal/mole.

1.5.1d Affect of Abnormalities - One of the practical problems in pyrolysis studies of polymers is the sensitivity of the polymer to concentrations of abnormal structures which are often too low to be detected by conventional means. This is due to the susceptibility of polymers to radical chain reactions. For example, the anionically synthesized polystyrene is considerably more stable than the free radical material and this is considered to be due to thermolabile structures in the latter.

1.5.1d Affect of Abnormalities (cont'd)

Polypropylene, like many other polymers, is subject to slow oxidative degradation at ambient temperatures. Van Scooten et al (8) have suggested that degradation of polypropylene is influenced by oxidation products such as hydroperoxide presumably formed by oxidation at the tertiary hydrogen atoms which are a more sensitive site for oxidation.

Besides irregular structures chemically bonded to the polymer chain, there are often contaminants physically mixed with the polymer, such as residues of polymerization catalysts. This and the above factors result in conflicting data on polymer studies and often preclude safe transfer of reaction parameters from one make of polymer to another and in some instances may even result in different pyrolyzate. This factor is also attributed as the cause of much of the conflicting data which has appeared in the literature.

1.5.2 Catalytic Cracking of Atactic Polypropylene

1.5.2a Introduction and Background

Catalytic cracking of hydrocarbons is a widely used process in the Petroleum and Petrochemical industry. The advantages of catalytic cracking over thermal cracking are traceable to specific chemical changes in Petroleum hydrocarbons. The catalytic reactions do not take place by an acceleration of thermal cracking reactions by the catalyst, but are brought about by the specific capacity of the cracking catalysts to promote reactions qualitatively different from thermal cracking reactions, most probably because of the difference in the principal intermediates formed - radicals in thermal cracking, and carbonium ions in catalytic cracking. Thus catalytic cracking gives rise to a more selective cracking. Emmet (9) lists the characteristics of catalytic cracking as (a) a more selective cracking and relatively less of the smaller (C_1 & C_2) fragments, (b) more olefin isomerization, (c) a more controllable saturation of double bonds, especially in the fractions of higher molecular weight, (d) greater production of aromatics, (e) less diolefin production, (f) relatively more coke.

Atactic polypropylene has been cracked over a catalyst bed to yield a variety of paraffin and olefin mixtures and gas losses. The catalysts used have been mainly solid acid catalysts such as a silicated alumina or chromia-alumina. The silica-on alumina catalyst was reported to be quite specific in obtaining the desired liquid fuel oil (10). Other alumina based catalysts containing, for example, tungsten trioxide catalyze the formation of substantial amounts of volatile products.

1.5.2b Mechanism of Catalytic Cracking

Catalytic cracking over solid acid catalysts occurs by a carbonium ion mechanism yielding an olefin molecule and carbonium ion for each carbon-carbon bond broken. Equations, on the next page, show the mechanism over an acid catalyst to

1.5.2b Mechanism of Catalytic Cracking (cont'd)

yield an olefin and a carbonium ion, after tertiary hydrogen abstraction by the acid catalyst and rupture of the carbon-carbon bond.

The secondary carbonium ion can then undergo several possible reactions. The ion can lose a proton and form an internal olefin as shown in the equation below:

The final result is two olefin terminated molecules from one carbon-carbon bond scission. Alternately, the carbonium ion could decompose by beta scission to the positive center giving a propylene molecule and a new carbonium ion as shown by the equation on the following page.

1.5.2b Mechanism of Catalytic Cracking (cont'd)

Obviously, this new ion can undergo any of the above reactions. However, depolymerization as shown above is a low probability reaction for polypropylene. In the presence of acid catalysts, double migration also occurs to some extent, but this would not reduce the overall yields of olefin. Since catalytic cracking is normally carried out in the range of 350°- 550°C., the thermal cracking reaction with its formation of saturated hydrocarbon fragments is a side reaction.

Catalysts vary in the direction and range of their activity. The silica-alumina catalyst has a high cracking capability but no dehydrogenation activity. Catalysts falling into the class of acid dehydrogenation catalysts are chromia aluminas, tungsten oxide on alumina and molybdenum oxide on alumina. Clearly, the latter group would be the preferred catalysts if the goal of the cracking operation is to maximize olefin yield whereas the silica on alumina would be preferred for fuel oil production. Catalyst choice may further be dictated by the necessity to minimize formation of coke or gaseous fractions.

1.6 Previous or On-Going Related Work

There has been considerable interest in the general problem of converting waste plastics to useful energy for two decades. For the first decade, the level of interest was greater in Europe and Japan because the cost of energy was substantially higher in these countries than the United States. With increasing energy costs in the United States in recent years, interest level increased rapidly.

In 1970 and the years following, there was a substantial amount of laboratory and small pilot scale work done by Matsumoto et al and Oda et al (15,16). The latter did most of their work on PVC pyrolysis while the former group emphasized the polyolefines; polypropylene and polyethylene. Kitaoka et al (14), Shimizu et al (18) and Speth, (20) have worked on the process of useful fuel from polyethylene.

Mitsubishi Heavy Industries set up a pilot plant to pyrolyze polyolefins to fuels (15). A pilot plant operating at Yoga, Japan, was a pyrolysis process on polystyrene bottles.

In Germany, at the University of Hamburg, Kaminsky et al (12,13), Sinn et al (19) and others have been working on laboratory and pilot plant scale studying the pyrolysis of various plastics to useful energy. Their general conclusions are that it is feasible from a technical and economical point of view.

1.6 Previous or On-Going Related Work (cont'd)

In the United States there has been recent work on the pyrolysis of plastics by the Bureau of Mines (17), West Virginia University (11), and others.

The technical literature of these researchers generally supports the thesis that waste plastic can be thermally cracked to useful fuel and chemicals and that steadily increasing energy costs insure that this type of industrial approach is a necessity.

With respect to atactic polypropylene, there has been interest on the part of most of the major polypropylene producers to convert the waste atactic material to useful fuel that could be used on the producing plant site. There have been efforts to melt the material and feed it to a burner; however, this approach has not proven to be technically feasible because of the problems associated with handling the melt.

Some companies in Europe have resorted to pumping the atactic polymer waste on top of coal piles and burning the polymer with the coal. This has proven to be suitable in a few cases but has generally caused handling problems in the incinerators and has not found general acceptance.

2.0 PILOT PLANT PROGRAM

2.0 Pilot Plant Program

2.0 PILOT PLANT PROGRAM

2.1 Objectives of Work

The objectives of this work were:

1. to extend the present laboratory scale technology on thermal cracking of atactic polymer to a pilot plant operation,
2. to demonstrate the commercial feasibility of the process and,
3. to develop sufficient design data and operating experience to design, engineer, and operate a fullscale commercial processing plant.

2.2 Pilot Plant Processes

1. Continuous Pilot Plant - Large Scale
2. Benchscale Pilot Plant - Batch
3. Benchscale Pilot Plant - Continuous

2.2.1 Process Description - Continuous Pilot Plant - Large Scale

A pilot plant cracking process based on the flowsheet shown in Drawing No. E-09880, (See Appendix), was designed.

The operating design basis for the waste feed rate of atactic polymer to the pilot plant was 100 gallons per hour.

The waste atactic polymer was received in block mold form, and the blocks were fed to a melt surge tank TK-2, an 800 gallon agitated tank equipped with a heating jacket. TK-2 contained a sufficient amount of atactic polymer for one steady state operation under specified operating conditions.

The waste polymer melt was held at 400 °F using circulating 450 °F heat transfer oil through the jacket of TK-2. The melt was pumped through hot oil traced lines to the reaction coil, RE-1, submerged in fluidized bed furnace, HE-3, using gear pump, PL-2.

HE-3 is a 24 inch diameter fluid bed reactor furnace which serves as a constant temperature heat source for reactor coil RE-1. Fluidizing air is supplied by compressor PB-1, which also provides the air supply for the burner system. Heat to HE-3 is supplied by burner system, X-2, which is fuel oil fired.

The hot combustion gases combine with the fluidizing air, pass through the distributor plate of HE-3, and fluidize the silica sand serving as the fluid bed. The furnace off gas is passed through Cyclone, C-1, for particulate removal before discharge to the atmosphere. HE-3 is typically operated at 900 °F to supply the heat requirements of pyrolysis coil RE-1 operating at about 820 °F.

2.2.1 Process Description - Continuous Pilot Plant - Large Scale (cont'd)

The atactic polymer melt is heated to 820°F at 50 psig where it is cracked to liquid and gas phase components. These pyrolysis products pass through a pressure reducing station, PIC-1, and are flashed into Flash Distillation unit, TK-5. The overhead vapor from TK-5 is the light oil fraction, (LOF), and is sent to Condenser, HE-3, where it is condensed and cooled below 100°F. The LOF is then sent to storage tank, TK-4. This storage tank is nitrogen blanketed to insure a safe condition at all times.

The gas phase product from TK-5 remains with the LOF until condenser HE-3. When the LOF is condensed, the non-condensable gas phase is sent to afterburner, FL-1, where it is flared before discharge to the atmosphere.

The liquid phase from TK-5 Flash Distillation is the heavy oil fraction, (HOF), which is directed through product cooler, HE-2, where its temperature is dropped below 100°F before being sent to the HOF storage tank, TK-3, also nitrogen blanketed.

Both LOF and HOF can be pumped from the respective storage to drums or to melt tank, TK-2, for flushing and/or dilution. Table III, below, is an equipment list.

TABLE III
CONTINUOUS PILOT PLANT
MAJOR EQUIPMENT LIST

TK-2	Melt Tank
PL-2	Waste Polymer Melt Pump
HE-3	Fluid Bed Heating Furnace
RE-1	Reactor Pyrolysis Coil
C-1	Furnace Cyclone
TK-5	Flash Distillation Unit
HE-3	Light Oil Fraction Condenser
HE-2	Heavy Oil Fraction Cooler
TK-4	Light Oil Fraction Storage Tank
TK-3	Heavy Oil Fraction Storage Tank
PL-4	Oil Products Pump
FL-1	Off Gas Afterburner

2.2.2 Process Description - Benchscale Pilot Plant - Batch

The process flowsheet for the Benchscale Pilot Plant support unit is shown in Fig. 7, pg. 19. The design basis for this facility is a batch charge of atactic polypropylene. The polymer is charged to Pyrolysis Reactor RE-10. This reactor is submerged in fluid bed furnace, HE-10, which provides a high temperature uniform heating source for RE-10.

HE-10 is typically operated at 850°F yielding a pyrolysis reaction to temperature of approximately 800°F. The pyrolysis gaseous evolution is sent to condenser, HE-11, where the light oil fraction, (LOF), is condensed. The non-condensable fraction is separated from the LOF and sent to an afterburner to be flared.

The heavy oil fraction, (HOF), is the liquid phase remaining in HE-10.

This benchscale process, being a batch operating non-steady state, and run at lower pressure than the continuous pilot plant process was not intended to duplicate the processing results of the continuous unit, but rather to provide useful reproducible information that could be used to guide and anticipate performance of the continuous unit. This benchscale process was used in the earlier work on Hercules feedstock and runs 1 through 4 on Novamont feedstock described later.

The above process was modified somewhat for all other benchscale batch pyrolysis work at Procedyne and this modified process is currently the standard process. The reactor, for this modified process, consists of a 304 SS reactor, 2" x 36" with a 24" length freeboard section flanged to it. The freeboard section contains a relief valve set at 50 psig. This reactor simulates the commercial process more realistically in that the operating pressure of 50 lbs., (built up due to volatiles generation as the reaction proceeds), prevents a large proportion of low boiling pyrolyzates from escaping, thus, preventing a highly unsteady state run. Fig. 8, pg. 20, shows the modified test apparatus.

The upper 2 ft. of the reactor was wrapped with cooling coil to prevent the relief valve from being damaged. It should be noted that this coil also acted as the reflux condenser and as such introduced additional heat load to the process. The off gases were again led to the afterburner.

2.2.3 Process Description - Benchscale Pilot Plant - Continuous

The continuous benchscale pilot plant is essentially a simulation of the large scale pilot plant. Fig. 9, pg. 21, details the basic process flowsheet. The polymer is charged to the jacketed melt tank M1, the molten polymer is fed to the Pyrolysis reactor, R₁/R₂, by a gear pump, (P₁), which is hot oil jacketed. The lines up to the inlet feed pipe of the reactor are heat traced. The inlet feed pipe is coiled and dipped in the furnace 1530 along with the pyrolysis reactor to also serve as a preheater. The pyrolysis reactor has a nitrogen purge and typically operates under

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NEXT ASSEMBLY							
USED ON				JOB NO.			
DO NOT SCALE DRAWING				DR. <i>MARYANN</i>		CHK.	
RFI FASED				DATE <i>6-27-79</i>		DATE	
				DATE		DATE	
				TITLE <i>FIG. 7 BENCHSCALE PILOT PLANT FLOW DIAGRAM</i>			
				SCALE		DRAWING NUMBER	
				<i>B-10627</i>		SHEET	
						OF	
						REV.

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NEXT ASSEMBLY							
USED ON				JOB NO. DR. MARY ANN CHK. APPD.			
DO NOT SCALE DRAWING				DATE 8-23-79 DATE - - DATE - -			
RELEASED - -				TITLE BENCH SCALE PYROLYSIS REACTOR			
				SCALE DRAWING NUMBER SHEET REV.			
				A-11000 OF			
REV	DESCRIPTION	BY DATE	APPD. DATE				

REF.

P -
S -
PS -

REV.

(M)

FIGURE 9

Procedyne CORPORATION
NEW BRUNSWICK, NEW JERSEY

DR. MARY ANN	CHK.	APPD.
DATE 8-13-80	DATE - -	DATE - -

**BENCH SCALE POLYMER
CRACKING SYSTEM**

JOB NO.	DRAWING NUMBER B-11874	SHEET OF	REV.
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2.2.3 Process Description - Benchscale Pilot Plant Continuous (cont'd)

a pressure of 50 psig. The pressure is monitored by a manually controlled needle valve at the outlet.

The reactor is operated around 850°F and the pyrolysis gaseous products are flashed in a Cyclonic Separator. The condensate from the cyclone (which operates at temperatures from 300°F to 400°F) is collected in a glass jar H₁ (the heavy oil collector). The fraction of pyrolyzate having a boiling point lower than the flash temperature is condensed in the glass condenser, C₁, before being collected in the flask L₁. The non-condensibles are flared in an afterburner, (AB-25), after being monitored for gas flow rate through a wet test meter. Gas samples are collected in between the wet test meter and the afterburner.

The duration of the run length varies from 60 to 180 minutes. The feed rate is controlled by the RPM setting on the gear pump. Thermocouples monitor the temperature of the inlet feed as well as at three points in the reactor. The reactor temperature is controlled by controlling the temperature of the 1530 furnace in which the pyrolysis reactor is dipped for heat input. The 1530 furnace is a fluid bed furnace which acts as a constant temperature heat source to aid in isothermal cracking. However, due to the substantial endotherm of the pyrolysis reaction, temperature gradients do exist along the length of the reactor. The 1530 furnace has a standard ProceDyne screw plate design distributor and is fluidized on N₂ for the pyrolysis experiments.

The pyrolysis reactor is charged with 5mm and 6mm pyrex beads for thermal cracking and with suitable catalyst beads in case of catalytic cracking.

This pilot plant has also been utilized to study catalytic cracking. The catalyst used was the well known silica-on-alumina cracking catalyst. The catalyst or the pyrex beads are supported on a stainless steel screen. Wire mesh is used in the freeboard position to prevent the beads from moving.

2.3 EQUIPMENT DESCRIPTION

1. Continuous Pilot Plant - Large Scale
2. Batch Benchscale Pilot Plant
3. Continuous Benchscale Pilot Plant

2.3 Equipment Description (Major Equipment Listed in Table III)

2.3.1.1 Continuous Pilot Plant - Large Scale

2.3.1.2 Continuous Pilot Plant - Modifications

2.3.1.1a Melt Tank TK-2

This tank is detailed in Drawing No. C-09904 (See Appendix)

The tank specifications are summarized on the following page.

2.3.1.1a Melt Tank TK-2 (cont'd)

Capacity: 800 gallons
Type: Vertical, jacketed, agitated, insulated.
Operating Temperature: 400°F
Design Pressure: Internal; 12 inches
Jacketed; 12 psig
Material of Construction: 304 Stainless Steel
Agitator: Lightnin Mixer
Mixco Model 72-c-5
Top entering Turbin Type
Mixco 70 Sines Solid Shaft:
2" dia.; 54" long
Agitator Speed: 68 rpm
Agitator: Mixco 36" axial flow turbine;
4 blades, 45° pitch
Motor: 5 HP 230/460/60/3 phase 1750 rpm

Bottom Discharge Valve:

1" Ram Type Drain Valve (Strahman Valves, Inc.)
150 lb. ANSI flanged
316 Stainless Steel construction
6" piston extension
Equipped with centroheat jacket

Tank Instrumentation: (Drawing No. E-09880 - See Appendix)

System No.	Function
T1-2	Temperature Indicator
L1-13	Level Measurement
P1-5	Pressure Indicator

2.3.1.1b Waste Polymer Melt Pump - PL-2

Viking
Model: H-124 Jacketed
Capacity: 5 gpm
Head: 70 ft.

2.3.1.1b Waste Polymer Melt Pump - PL-2 (cont'd)

Internal Pressure Relief: 120 psig
Pump Speed: 520 rpm
Motor: 1-1/2 HP, 220/60/3 phase
1750 rpm

2.3.1.1c Fluid Bed Heating Furnace - HE-3

Furnace Dia. (I.D.): 24"; 36" freeboard dia.
Bed Depth: 5 ft.
Freeboard Height: 5 ft.
Plenum Height: 2 ft.
Insulation Thickness: 6"
Distributor Plate: 14 Tuyeres
Material of Construction: RA 330 Stainless Steel

2.3.1.1c Fluidizing Air Blower - PB-1

Gardner Denver Company

Model: 3DDR6 with BMA-2 silencer and BWDA85US
inlet filter
Motor: 10 HP, 220/60/3 phase, 1750 rpm

Major Furnace Instrument Systems -(See Drawing No. E-09880 in Appendix)

System No.	Function
TRC-4	Temperature Recorder Controller (Fluid Bed Temperature)
PI-3	Plenum Pressure Indicator
FIA Burner System, X-2 Instrumentation	Control and Safety Instru- mentation for the plenum burner system.

2.3.1.1d Reactor Pyrolysis Coil - RE-1

Design: Helical Coil (Dwg. B-09965)
(See Appendix) 3" diameter
schedule 40 pipe.
Coil Diameter: 19" outside
Length of Pipe: 35 feet
Material of Construction: 316 L Stainless Steel

2.3.1.1d Reactor Pyrolysis Coil - RE-1 (cont'd)

Major Reaction Coil Instrument Systems - (See Drawing No. E-09880 in Appendix)

System No.	Function
TR-1	Temp. Indicator - Product Feed
TR-3	Temp. Indicator - Product Out
PL-1	Pressure Indicator - Coil Pressure

2.3.1.1e Furnace Cyclone - C1

Capacity:	500 scfm; 1884 acfm
Pressure Drop:	6 inches w.c. @ 1500°F
Temperature of Operation:	1600°F Max.
Material of Construction:	RA 330 Stainless Steel

2.3.1.1f Flash Distillation Unit - TK-5 (See Dwg. B-09898 in Appendix)

<u>Feed:</u> (before flashing)	
Rate:	800 lbs/hr.
Composition:	Pyrolysis gas 80/lb/hr.
	LOF 160 lb/hr.
	HOF 560 lb/hr.

Temperature:	800°F
Pressure:	50 psig

Discharge Conditions:

Temperature:	400°F
Pressure:	2 psig
Overhead:	Pyrolysis Gases plus LOF
Bottom Discharge:	HOF

Equipment Details: (See Dwg. B-09898 in Appendix)

Dia.:	12 inches
Straight Side Height:	30 inches
No. Trays:	4
Holding Trays with 2-3/8" drain holes	
Material of Construction:	Carbon Steel

2.3.1.1f Flash Distillation Unit - TK-5 (cont'd)

(See Dwg. E-09880 in Appendix)

System	Function
Tl-6	Temperature Indicator - flash temperature
Pl-2	Pressure Indicator - flash distillation pressure

2.3.1.1g LOF Condenser - HE-3 (See Dwg. C-09829 in Appendix)

Shell diameter:	6 inch nom. pipe
Shell length:	47 - 3/4 inch
Tubes:	0.5 inch OD, 0.035 inch wall
No tubes:	31
Material of Construction:	304 Stainless Steel

Major LOF Condenser Instrument Systems

(See Dwg. E-09880 in Appendix)

System No.	Function
Tl-8	Temperature Indicator: LOF discharge tempera- ture
Tl-10	Temperature Indicator: Cooling water discharge temperature
F1-5	Flow Indicator: Cool- ing water flow

2.3.1.1h HOF Cooler - HE-2 (See Dwg. C-09829 in Appendix)

Shell diameter:	6 inch nom. pipe
Shell length:	47 - 3/4 inches
Tubes:	0.5 inch OD, 0.035 inch wall
No. Tubes:	31
Material of Construction:	304 Stainless Steel

System No.	Function
Tl-7	Temperature Indicator, HOF discharge temp- erature

2.3.1.1h Major HOF Cooler Instrument Systems (cont'd)

System No.	Function
T1-14	Temperature Indicator, Cooling Water discharge temperature
F1-4	Flow Indicator - Cooling water flow

2.3.1.1i LOF Storage Tank - TK-4

Type:	Horizontal Cylindrical
Capacity:	275 gal.
Temp.:	160°F (max.)
Pressure:	6 inch w.c. (max.)
Material of Construction:	Steel

Major LOF Storage Tank Instrument Systems

System No.	Designation
L1-2	Level Indicator
P1-10	Pressure Indicator

2.3.1.1j HOF Storage Tank TK-3

Type:	Horizontal Cylindrical
Capacity:	1000 gal.
Temp.:	160°F (max.)
Pressure:	6 inch w.c. (max.)
Material of Construction:	Steel

System No.	Designation
L1-1	Level Indicator
P1-9	Pressure Indicator

2.3.1.1k Oil Products Pump - PL-4

Allis Chalmers

Model 01

Type:	1.5 x 1.3 x 5 RR3
Capacity:	5 gpm
Head:	10 ft.
Motor:	3/4 HP, 220 volt/60 Hz 3 phase

2.3.1.1L Off Gas Afterburner - FL -1 Procedyne Model AB-30

The Model AB-30 Afterburner is designed to eliminate hydrocarbons and carbon monoxide produced by the incomplete combustion of organic materials. When operated within specifications, the gases are retained at temperatures between 1200°F and 2000°F from 0.3 to 0.5 seconds.

Process off gas is fed directly to the flame of a gas burner. Additional air is drawn into the Afterburner and residence time is such that all combustible gases are incinerated as they travel through the Afterburner chambers. Temperatures in the Afterburner are between 1200°F and 2000°F depending upon the heat content of the input gas stream.

Utilities Requirements

Model AB-30

Fuel Supply - Liquid Propane (LP Gas) at delivery pressure from 1 psig is the standard fuel for the AB-30. Natural Gas at delivery pressure from 4.0 - 7.0 inches of water can be used as an alternate fuel. Burner fuel requirement is 300,000 BTU/Hr. (max.)

Electrical Supply - 220/440 volt, 3 phase, 60 Hz
Total load - 3 HP for Burner Blower

Major Afterburner Instrument System

System No.	Function
TIC-11	Temperature Indicating Controller controls afterburner temperature by controlling flow of dilution air.
PIC-2	Pressure Indicating Controller Back pressure control of feed to afterburner.
FIA Burner System	Burner instrumentation controlling and monitoring burner in the afterburner.

2.3.1.1m Services

1. Cooling Water

a. Cooling Temp

Carborundum Corp.

Delta Cooling Tower

Model No. 3-20

Capacity: 30 gpm

Inlet Temp.: 105°F

Outlet Temp: 85°F Wet Bulb: 78°F

Material of Construction: PVC

Motor: Fan: 2 HP, TEFC
220 volt/60 Hz/3phase

b. Cooling Water Circulating Pump

Capacity: 20 gpm

Head: 50 ft. w.c.

Material of Construction:

Motor: 1 HP, 220 volt/ 60 Hz
3 phase

System No. Tl-5

Function Temperature Indicator

Tl-5

Temperature Indicator -
Cooling & water

PSL-1

Low Pressure Switch
Cooling Water supply
pressure

2. Heating Oil System

a. Circulating Oil Tank: (See Dwg. A-09828 in Appendix)

Capacity: Nominal 100 Gallons

Material of Construction: Steel

b. Circulating Heater: HE-1

Chromalox No. NWHO-6251-5

Capacity: 25 KW @ 480 volt/60 Hz
3 phase

2.3.1.1m Services (cont'd)

Material of Construction:	Steel
c. Circulating Oil Pump:	PL-1
Viking Self Priming	
Capacity:	20 gallons/Minute
Head:	20 psig
Internal Pressure relief:	30 psig
Material of Construction:	Steel
Motor:	1 HP Direct Drive 220 volt/60 Hz/3 phase

Heating Oil System Instrument Systems

System No.	Function
PL-6	Pressure Indicator - Heating Oil Supply
TIC-1	Temperature Indicating Controller Circulating heating oil temp.
FL-1	Flow Indicator - Circulating heating oil
Tl-15	Temperature Indicator Heating oil return
Pl-4	Pressure Indicator Surge Tank

3. Nitrogen Supply

Cylinder Bank

Capacity:	8 cylinders
Regulated:	15 psig

Nitrogen Supply Instrument Systems

System No.	Function
PC-4	Pressure Regulators - nitrogen
Pl-8	Pressure Indicator - nitrogen supply
PC-5	Pressure regulator - nitrogen supply

2.3.1.2 Continuous Pilot Plant - Modifications

After the successful completion of pilot runs, described later, it was felt that the plant needed to be modified prior to further operation to enable the plant to be operated over a wider range of the key process variables, primarily with respect to reduced residence time and higher reactor pressure. A detailed description of the modifications carried out is given below.

2.3.1.2a Increased Pump Capacity

Because some atactic polypropylene waste is of a very high molecular weight, and because solvents which are inherent in the waste stream are lost in shipment and storage, the viscosity is higher than anticipated so that the primary pump out of the hot melt tank was limiting the flow that can be achieved through the reaction coil. With a fixed reaction coil volume, this pump limitation prevented operation at short residence times and limited the total plant throughput. A larger pump with a vari-drive and an enlargement of the tank discharge port would aid in the handling of this high viscosity material. The new pump has a capacity of up to 15 gpm molten feed with a viscosity of up to 10,000 cp.

2.3.1.2b Back Pressure Capacity Increase

There is an automatic back pressure control loop on the reaction coil which maintains a constant pressure in the reaction coil during the cracking operation. The pilot plant appeared to be much more effective as a cracking operation than was anticipated by the results of the bench scale testing program. Even at the lower temperatures, cracking appeared very efficient with a tendency to produce more light ends. Operating at a higher back pressure would keep the light ends in solution thereby allowing better residence time control. The back pressure capacity was increased to enable operation at 100 psig.

2.3.1.2c Flowmeter Relocation and Calibration

The flowmeter was relocated and the flow bypass was installed prior to the measuring circuit. This eliminated the problem of measurement of flow out of the primary hot melt tank by permitting on line checks.

Flashtank Cooling

The flash tank was natural convection cooled. By adding water cooling jacket capability, it will be possible, during further runs, to remove more heat at this stage in the process and reduce the gas phase product yield in favor of increased liquid oil yield.

2.3.1.2d Reactor Burn-Out System

After a number of runs, it may be necessary to remove residual coke that may form in the reaction coil during the cracking reaction. Because of the fluidized bed as the

2.3.1.2d Reactor Burn-Out System (cont'd)

heating medium and its high heat removal capability, it is possible to clean the coil in place easily without any chance of damage to the coil. This can be done by controlled injection of air through the coil. By monitoring the gas discharge, it will be possible to not only clean the coil, but, also to determine the extent of coking without dismantling the system. A 79.5 scfm air flow meter, along with an air inlet nozzle were added for this purpose.

2.3.1.2e Improved Roof Ventilation

Two roof vents, 24" diameter each, were installed to relieve heat build up in the ceiling.

2.3.1.2f Propane to Natural Gas

The plenum burner and the Afterburner AB-30 were changed from propane fired to Natural Gas fired burners.

2.3.2 Batch Benchscale Pilot Plant

The Benchscale pilot facility is shown schematically in Fig. 10, pg. 80. An Equipment List is given in Table IV, below.

TABLE IV

BATCH BENCHSCALE PILOT PLANT EQUIPMENT
LIST

RE-10	Pyrolysis Reactor
HE-10	Pyrolysis Reactor Heater
HE-11	Distillate Condenser
M-10	Condensate Receiver
AB-20	Off-gas Afterburner

2.3.2a Pyrolysis Reactor RE-10

The basic pyrolysis reactor is 3 inches in diameter and 24 inches in length. It is equipped for monitoring temperature and pressure.

Material of Construction: 304 SS

2.3.2b Pyrolysis Reactor Heater - HE-10

The pyrolysis reactor is heated by submerging it in a temperature controlled fluid bed furnace - Procedyne Model 1530. The specifications of this furnace are summarized on pg. 35

2.3.2c Distillate Condenser - HE-11

The distillate condenser was 18 feet of 1/2 inch tubing submerged in a cooling water shell.

2.3.2c Distillate Condenser - HE-11 (cont'd)

Material of Construction:

Initially:

Copper

Changed to:

304 Stainless Steel

2.3.2d Condensate Receiver - M-10

This unit is a 4 liter glass flask.

2.3.2e Off-Gas Afterburner

The off-gas afterburner used was a Procedyne Model AB-20.

MATERIALS OF CONSTRUCTION:

MODEL 1530 FURNACE

Retort —	Stainless Steel
Exhaust Sleeve —	Stainless Steel
Cover —	Stainless Steel
Cabinet —	Steel with medium blue finish
Heaters —	Indirectly heated electric resistance clamp-on band type
Insulation —	Ceramic
Fluidized Bed Medium —	150 mesh Al_2O_3
Dimensions:	See diagram
Shipping Weight:	985 Lbs. (approx.) 447.7 Kg. (approx.)

MODEL 1530

Furnace Volume: 15" diameter x 30" deep (5300 cu. inches) 38.1 cm diameter x 76.2 cm deep (86.7 liters)

Loading Capacity: (typical) 1770 cubic inches - Max. wt. 241 kg. (loading capacity based on hardware weight in steel)

Temperature Range: Ambient to 1000 °F (538 °C)

Heatup Time: 5 hours, ambient to 850°F (454°C)

Temperature Control: Automatic, thermocouple actuated controller

Temperature Readout: 4" meter - thermocouple actuated - accuracy $\pm .5\%$ of full scale

Gas Flow Control: Manual valve adjust - rotameter indication

Protection Systems:

- Gas Flow: shuts down system if gas supply fails
- Overtemperature: shuts down heaters and gas supply if limited temperature is exceeded

Utility Requirements:

- Electrical: 9 KW (Max.) at 220 V, Single phase, 60 Hz (alternate voltages available)
- Gas Supply: 9 cfm (Max.) -30-160 psig, plant air is acceptable .2548 meters³/min. (Max.), -2.109 - 11.249 Kg/cm²

Afterburner - Model AB-20 Series

The model AB-20 Afterburner has been designed to eliminate visible smoke produced by the incomplete combustion of organic materials. When operated within specifications, the gases are retained at temperatures between 1200 °F and 2000 °F for from 0.3 to 0.5 seconds which is considered adequate to produce a stack discharge which, in most areas, is acceptably non-polluting with respect to combustible components.

The principle of operation of the afterburner is quite direct. Smoke emanating from a process is fed directly to the flame of a 1000,000 BTU per hour gas burner. Additional air is drawn into the afterburner and residence time is such that all combustible gases are incinerated as they travel through the afterburner chambers. Temperatures in the afterburner are between 1200 °F and 2000 °F depending upon the heating value of the input gas stream.

2.3.2e Afterburners Model AB-20 Series (cont'd)

An exhaust blower is required with the system. Since the gases leaving the afterburner can be as high as 2000°F, it is necessary to cool them before the blower. The cooling can be accomplished by dilution with ambient air through an adjustable intake section, or by water cooling. Proce-dyne can supply an air cooled or water cooled afterburner exhaust system. For the air cooled system, a 1000 scfm blower is required and a dampered tee is supplied to permit dilution in the ratio of approximately 9:1. This reduces the exhaust gas temperature to approximately 300°F. The water-spray gas cooling system contains 4 water spray nozzles mounted inside a stainless steel spray tower. The hot exhaust gases from the afterburner are contacted by the water spray which cools the gases which are then fed into the blower.

Specifications

Capacity: Model AB-20 Afterburners are designed to handle a maximum of 100 scfm of Off-gases.

Combustion
Capability: Model AB-20 can process combustibile vapors having an energy content not to exceed a maximum instantaneous rate of 100,000 BTU/hr.

Exhaust Gas
Temperatures: Exhaust gases from the Afterburner may reach temperatures as high as 2000°F based on the energy content and input rate of off-gases from the cleaning furnace. The original fumes from the process and the final exhaust gases must be drawn through and into the Afterburner by a positive ventilation system. The hot exhaust gases must be cooled prior to reaching the typical blower used.

A smaller twin-dampered tee and a Water Spray Tower provide necessary cooling and some scrubbing of the exhaust gases prior to passage through a smaller Exhaust Blower.

Utility

Requirements: Model AB-20

Fuel Supply: Liquid Propane (LP Gas) at delivery pressure of 20 psig (max.) is the standard fuel for the AB-20. Natural Gas at delivery pressure of 1 psig (max.) can be used as an alternate fuel. Burner fuel requirement is 100,00 BTU/hr. (Max.)

Continuous Bench Scale Test Apparatus

Batch - Bench Scale Test Apparatus

2.3.2e Afterburners Model AB-20 Series (cont'd)

Electrical Supply: 120 volt, single phase,
60 Hz, 0.5 amps

Water Cooling Tower: The Exhaust Blower
used has the following
specifications:

200 scfm at 4.0 inches
of water static dis-
charge pressure, 1HP,
240/280 volts, 3 phase,
60 Hz., provided with
shaft extension and
Teflon seals. Dampered
Tee, Water Spray Tower
and interconnection
adapters are supplied.
Water flow requirement
for Spray Tower and in-
terconnection adapters
are supplied. Water flow
requirement for Spray
Tower is approximately
1 gpm.

2.3.3 Continuous Benchscale Pilot Plant

The following is the equipment description for the Contin-
uous Benchscale Pilot Plant: (Equipment List - Table V)

TABLE V

CONTINUOUS BENCHSCALE PILOT PLANT EQUIPMENT LIST

M1	Melt Tank
P1	Feed Gear Pump
R1	Reactor
R2	Reactor
F1	Flash Separator
H1	Heavy Oil Collector
C1	Condenser
L1	Light Oil Collector
W1	Wet Test Meter
AB-25	Afterburner

2.3.3a Melt Tank - M₁

Specifications:

Material:

316 Stainless Steel-
all welded construction.
Jacketed for oil heat.

Capacity:

2.5 gallons. Temperature sensor is type J thermocouple. Nitrogen purged. Pressure indicator. Pressure relief valve.

2.3.3b Gear Pump - P₁

Specifications:

Capacity:

Zenith High Temperature Metering Pump. Jacketed for oil heat. Controlled by Zenith variable speed digital drive system.

1.752 cc per rev. Range 6.0 to 99.9 RPM. Control and display - 0.2 RPM. Temperature for pump housing is type J Thermocouple sensor.

2.3.3c Reactor - R₁

Specifications:

Material:

1" nps x 18" 316 Stainless Steel all welded construction

Multipoint temperature sensors by type J thermocouples. Flanged top. Pressure indicator. Pressure relief valve. Manual control valve.

2.3.3d Reactor - R₂

Specifications:

Material:

1"nps x 36" 316 Stainless Steel all welded construction.

2.3.3d Reactor - R₂ (cont'd)

Multipoint temperature sensors by type J thermocouples. Flanged top. Pressure indicator. Pressure relief valve. Manual control valve.

2.3.3e Flash Separator - F₁

Specifications:

Cyclone 3" x 18" material-316 stainless steel. Temperature sensor is type J thermocouple Pressure indicator.

2.3.3f Heavy Oil Collector - H₁

Specifications:

Capacity:

316 stainless steel or graduated glass.

1.25 gallons. Temperature sensor is type J thermocouple.

2.3.3g Condenser - C₁

Specifications:

Glass apparatus 2" x 40". Water flow appx. 30 gals. per hr.

2.3.3h Light Oil Collector - L₁

Specifications:

Capacity:

Glass apparatus

1 gal. Temperature indicator.

2.3.3i Wet Test Meter - W₁

Specifications:

Capacity:

Precision Scientific Co. Model 63125

20 cu. ft. per hour.

2.3.3j Afterburner AB-25

See following pages:

2.3.3 Continuous Benchscale Pilot Plant (cont'd)

Further Notes:

Heat for melt tank and pump is from Dowtherm Heat Transfer Oil Circulating System. Heat source for reactor is a standard Procedyne Fluid Bed Furnace Model 1530, described in the section on batch tests. Off gas on line sampling is obtained by an intricate network of valving (as shown in Fig. 9, pg. 2). Off gases are combusted in a standard Procedyne afterburner Model AB-25 meeting and surpassing all EPA requirements.

2.3.3j Afterburner - Model AB-25 Series

The Model AB-25 Afterburner has been designed to eliminate visible smoke produced by the incomplete combustion of organic materials. When operated within specifications, the gases are retained at temperatures between 1200 °F and 2000 °F for from 0.3 to 0.5 seconds which is considered adequate to produce a stack discharge which, in most areas, is acceptable nonpolluting with respect to combustible components.

The principle of operation of the afterburner is quite direct. Smoke emanating from a process is fed directly to the flame of a 150,000 BTU per hour gas burner. Additional air is drawn into the afterburner and a residence time is such that all combustible gases are incinerated as they travel through the afterburner chambers. Temperatures in the afterburner are between 1200 °F and 2000 °F depending upon the heating value of the input gas stream.

An exhaust blower is required with the system. Since the gases leaving the afterburner can be as high as 2000 °F, it is necessary to cool them before the blower. The cooling can be accomplished by dilution with ambient water cooling. Procedyne can supply an air cooled or water cooled afterburner exhaust system. For the air cooled system, a 3000 scfm blower is required and a dampered tee is supplied to permit dilution in the ratio of approximately 9:1. This reduces the exhaust gas temperature to approximately 300 °F. The water -spray gas cooling system contains 4 water spray nozzles mounted inside a stainless steel spray tower. The hot exhaust gases from the afterburner are contacted by the water spray which cools the gases which are then fed into the blower.

Afterburner Model AB-25 Series

Specifications:

Capacity:

Model AB25 Afterburners are designed to handle a maximum of 300 scfm of Off-gases from the incineration cleaning of polymer from metal parts in a typical Procedyne Fluidized Bed Cleaning Furnace.

2.3.3j Model AB25 Series (cont'd)

Combustion Capability:

Model AB25 can process combustible vapors having an energy content not to exceed a maximum instantaneous rate of 300,000 BTU/hour.

Exhaust Gas Temperatures:

Exhaust gases from the Afterburner may reach temperatures as high as 2000 °F based on the energy content and input rate of offgases from the cleaning furnace. The original fumes from the process and the final exhaust gases must be drawn into and through the Afterburner by a positive ventilation system. The hot exhaust gases must be cooled prior to reaching the typical blower used.

A smaller, twin-dampered, tee and a Water Spray Tower provide necessary cooling and some scrubbing of the exhaust gases prior to passage through a smaller Exhaust Blower.

Scrubbers:

A conventional Scrubber was used to provide removal of particulate matter and cool the off gas before feeding to Exhaust Blower.

Utility Requirements:

Fuel Supply:

Liquid Propane (LP Gas) at delivery pressure of 20 psig (maximum) is the standard fuel for the AB25. Natural Gas at delivery pressure of 1 psig (maximum) can be used as an alternate fuel. Customer to specify desired fuel at time of purchase. Burner fuel requirement is 150,000 BTU/hr. (max.)

Electrical Supply:

120 volt, single phase, 60 Hz, 0.5 amps

2.3.3j Afterburner Model AB25 Series (cont'd)

Specifications (cont'd)

Ventilation System:

WATER COOLING METHOD

The Exhaust Blower used in this case has the following specifications:

600 scfm at 4.0 inches of water static discharge pressure, 1 HP, 240/480 volts, 3 phase, 60 Hz., provided with shaft extension and Teflon seals. Dampered Tee and Water Spray tower are supplied, Water Flow requirement for Spray Tower is apprx. 3 GPM.

Equipment Size:

When used with Water Cooling Method, the apprx. requirement for the AB25 is 38" x 63" x 143" high.

A typical AB25 Afterburner with Water Cooling is shown in Dwg. No. E-08805, Rev.E, (See Appendix).

2.4 OPERATING PROCEDURE

1. Continuous Pilot Plant - Large Scale
2. Benchscale Pilot Plant - Batch
3. Benchscale Pilot Plant - Continuous

Thermal

Catalytic

2.4.1 Continuous Pilot Plant - Large Scale

2.4.1.1 Startup

- a. The heating oil system was started by starting circulating pump P1 and electric heater, HE-1. The heating oil was circulated from heating oil tank, TK-1 through the jacket of TK-2 and back to TK-1. The heating oil was also circulated through the tracing lines back to TK-1. The system is circulated with heating oil system at 400 °F.
- b. Blocks of atactic polymer were charged to TK-2 with the agitator off. Some LOF was pumped from TK-4 to assist in melting the blocks and to reduce the viscosity of the resulting solution when operating on high viscosity atactic types of material. For the high viscosity types, the ratio of LOF to atactic polymer was 1/1.
- c. When the temperature in TK-2 exceeded 350 °F, the agitator was started and the atactic blocks were melted into a viscous solution.
- d. Fluid Bed Furnace, HE-3, was started by starting the fluidizing air blower, PB-1, and starting burner system, X-2. Fuel to X-2 was supplied from oil tank, TK-6, by fuel oil pump, PL-5. The burner system was controlled by temperature control system, TRC-4. Typical operating temperature for HE-3 was 900 °F.
- e. Afterburner, FL-1, burner system was started and the temperature controlled at 1300 °F in FL-1.

2.4.1.1 Startup (cont'd)

- f. Cooling water tower, PB-3, and circulating pump, PL-3, were started and cooling water flow was applied to heat exchangers, HE-3, and HE-2.
- g. The flow of melted atactic polymer was started from TK-2 through gear pump, PL-2, and directed back into TK-2. When it was apparent that design circulation rate was achieved, the polymer flow was directed to reactor coil, RE-1, with some flow back to TK-2 maintained.

The flow rate to RE-2 was manually adjusted and monitored on flow indicator FI-2.

- h. Back Pressure control system, PIC-1, was adjusted to approximately 50 psig and secondary back pressure control system, PIC-2, was adjusted to 2 psig.
- i. The atactic feed was continued and the system permitted to approach steady state operating conditions.

2.4.1.2 Operating - Continuous Pilot Plant - Large Scale

- a. The feed of atactic polymer was monitored on flow indicator, FI-2.
- b. The pyrolysis temperature was controlled by controlling the temperature of HE-3 and monitoring the pyrolysis temperature on temperature recorder TR-3.

2.4.1.3 Shutdown - Continuous Pilot Plant - Large Scale

- a. The atactic feed to the reactor coil, RE-1, was discontinued by recycling the stream back to TK-2.
- b. The plenum burner of fluid bed furnace HE-3 was shut down.
- c. Some of the LOF was pumped from TK-4 into the suction line of pump PL-2 to flush polymer out of the bottom drain valve of TK-2, pump PL-2, and the feed line back to TK-2. Then the bottom drain valve of TK-2 was closed.

A small amount, (typically 5 gallons), of LOF was then sent through the feed line to reactor coil RE-1 and through reactor coil RE-1 to the condensers.

2.4.1.3 Shutdown - Continuous Pilot Plant - Large Scale

- d. Pumps PL-2 and LOF pump PL-4 were then shut down.
- e. Heating oil circulating system was shut down by shutting down heater HE-1 and circulating pump PL-1.
- f. The agitator on tank TK-2 was shut down.
- g. The fluidizing air blower, PB-1, was shut down.
- h. After thirty minutes time elapsed, afterburner FL-1 was shut down.
- i. After an additional thirty minutes, the cooling water circulating pump, PL-3, and the cooling tower for PB-3 was shut down.

2.4.2 Benchscale Pilot Plant - Batch

2.4.2.1 Startup - Benchscale Pilot Plant - Batch

- a. Fluid bed furnace, HE-10, was started up and temperature controlled at 850°F, (typically).
- b. A predetermined amount of atactic polypropylene was charged to test reactor RE-10.
- c. Cooling water was started to cooler condenser HE-11 reservoir.

2.4.2.2. Operating - Benchscale Pilot Plant - Batch

- a. Batch reactor, RE-10, was submerged in fluid bed furnace, HE-10. The temperature in the RE-10 was monitored.
- b. In the modified design of the reactor, the pressure build-up was also monitored. The pressure relief valve was set at 50 psig. The course of the reaction could be monitored by observing the condensate.
- c. The LOF was condensed and collected and the non-condensable gases burned in the afterburner.
- d. This reaction arrangement was continued for the required residence time - typically twenty minutes.

2.4.2.3 Shutdown - Benchscale Pilot Plant - Batch

- a. The reactor, RE-10, was removed from fluid bed furnace, HE-10, and allowed to cool.
- b. The reactor was opened and the residue was poured out.

2.4.2.3 Shutdown - Benchscale Pilot Plant - Batch (cont'd)

- c. The reactor was cleaned by dipping in the fluid furnace and incinerating the residue.

2.4.3 Operating Procedure - Continuous Benchscale Pilot Plant

- a. The fluid bed furnace 1530 was started up and was temperature controlled around 900°F or as dictated by the particular reaction temperature desired.
- b. Hot oil, (at around 400°F), was introduced to the jacket of the melt tank, (M_1) and the gear pump, (P_1).
- c. The pyrolysis reactor, (R_1 or R_2), was charged with the desired grade of catalyst beads for the catalytic cracking runs and with pyrex beads for the thermal cracking runs. It was purged with N_2 prior to feed input.
- d. The gear pump, P_1 , was calibrated for each variety of feedstock. The throughput was controlled by the pump r.p.m.
- e. Cooling water was introduced to the cooler condenser.
- f. Afterburner AB-25 was started.

2.4.3.2 Operating - CAC

- a. Pyrolysis reactor was dipped in the fluid bed furnace 1530.
- b. The temperature at various points in the reactor was monitored.
- c. The reactor was observed for pressure buildup.
- d. The observed viscosity of the heavy oil fraction was used as an indication of the degree of cracking.
- e. The apparatus was allowed to reach steady-state and run for required length of time, generally varying from 60 - 180 minutes.

2.4.3.3 Shutdown - Continuous Benchscale Pilot Plant

- a. The feed pump was shut-off.
- b. The reactor was allowed to be cleaned of all product by letting the pyrolysis to proceed until no more condensate was observed.

2.4.3.3 Shutdown - Continuous Benchscale Pilot Plant (cont'd)

- c. The reactor was purged with N₂.
- d. The two oil fractions were collected and weighed. The reading on the wet test meter was noted.
- e. The reactor was opened and the contents, (beads or catalyst), weighed to determine the amount of coke formed.
- f. The reactor was rinsed with hexane which was filtered to collect all the coke.

2.5 Operating Results

- 1. Continuous Pilot Plant - Large Scale
- 2. Benchscale Pilot Plant - Batch
- 3. Benchscale Pilot Plant - Continuous

2.5.1 Continuous Pilot Plant - Large Scale

2.5.1.1 Preparation

The continuous process was described in Section 2.2.1. The equipment used for these tests was also outlined.

a. Initial Testing

The various items of equipment and instrumentation were checked out carefully.

- b. The melt tank, TK-2, was charged with 265 gals. of kerosene. The nitrogen blanket system for this tank was initiated.
- c. The off gas burner, FL-1, was started and allowed to stabilize at a temperature of approximately 1200°F.
- d. The heating oil system, TK-1, HE-1, and PL-1, (Flow-sheet Drawing No. E-09880, in Appendix), was started up and the heating oil temperature controlled at 400 F. The heating oil was circulated through melt tank, TK-2. The kerosene was heated to 290 F.
- e. Blocks of atactic polymer, (each weighing approx. 150 lbs.), were added to the melt tank with the agitator off. After the blocks softened, the agitator was started. The softening process took approximately two hours. Each time a block was added, the agitator

2.5.1.1 Preparation (cont'd)

e. (cont'd)

was turned off and the block was permitted to soften.

A nitrogen purge was maintained to the tank during the loading operation. A total of 2160 lbs. of atactic polymer was added to the system making a polymer solution of approximately 55 wt. % atactic. With a melt tank temperature between 350°F and 400°F, the atactic polymer was pumpable even when operating on the high viscosity copolymer material.

f. The fluid bed heating furnace, HE-3, was then started up and heated to 1200°F using the plenum burner. The furnace was put on automatic temperature control with a plenum burner temperature of approximately 1400°F.

g. Water cooling was started to condenser, HE-3, and product cooler, HE-2. The system was ready for the first continuous run.

2.5.1.2 Continuous Run No. 1.

Started product feed to pyrolysis coil, RE-1. There was a rapid build up in reactor coil pressure. In addition, the afterburner FL-1 showed a rapidly increasing temperature suggesting an overload of non-condensibles.

The system was shut down after running 15 minutes with polymer feed.

The following two modifications were made following the Run 1 attempt:

- a. A second condenser was put in series with HE-3, designated HE-3A, to provide greater capacity for condensation of light liquid fraction.
- b. It was concluded that 1200°F in the Reactor Furnace yielded too high a pyrolysis temperature which resulted in high gas yield.

2.5.1.3 Continuous Run No. 2

This continuous pyrolysis run was made using the facilities described in Section 2.3.1 and the process was described in Section 2.2.1.

The temperature of the fluid bed furnace was controlled at 850°F.

The process was operated for approximately four hours under the conditions shown in Table VI, pg. 51.

2.5.1.3 Continuous Run No. 2 (cont'd)

Some difficulty was encountered keeping the coil pressure from climbing above the setpoint pressure of 30 psig. The feed rate had to be reduced to maintain the pressure below 45 psig.

2.5.1.4 Continuous Run No. 3

This continuous pyrolysis operation was similar to Run No. 2 except that the reaction coil temperature was reduced to 730°F and the polymer feed rate was decreased to 50 lbs/hr.

No problem was encountered in controlling coil pressure at 30 psig. Product yield was reasonably good.

Operating conditions are summarized in Table VI, pg.51.

2.5.1.5 Continuous Run No.4

The continuous pyrolysis operation was again started; however, a leak developed in one of the pyrolysis product pipes.

The run was discontinued immediately.

2.5.1.6 Continuous Run No. 5

This continuous pyrolysis operation was made at substantially higher feed rate without operating difficulties.

The process was stable and the product yield was high.

Operating conditions are Summarized in Table VI, pg.51.

2.5.1.7 Continuous Run No.6

This continuous pyrolysis operation was made at conditions similar to Run No. 5.

The operation was stable and product yield was high.

Operating conditions are summarized in Table VI, pg.51.

2.5.1.8 Conclusions from Continuous Plant Test Operations

a. Preparation Testing

1. The basic preparation testing emphasized the importance of maintaining adequate tracing on polymer melt handling lines to prevent solid-

TABLE VI

RUN NO.	POLYMER FEED RATE LBS/HR	PYROLYSIS FURNACE TEMP °F	POLYMER FEED PRODUCT DIS- CHARGE TEMP °F	PYROLYSIS PRODUCT DISCHARGE TEMP. °F	PYROLYSIS COIL PRESSURE PSIG	FLASH DISTIL- LATION TEMP °F	DISTILLATE TOTAL, LBS.	HEAVY OIL PHASE, HRS. LBS.	NO. OPER. HRS.	REMARKS
1	----	1200	350	----	----	----	----	----	----	Overload gas hand- ling sys- tem immedi- ately upon starting feed
2	200	850	375	652	25 to 45	490	----	----	4	Shutdown at close of shift
3	55	730	378	535	30	420	15	281	6	Good run at low feed rate
4	----	1000	---	---	---	---	---	---	---	Leak de- veloped in piping. Run aborted
5	406	930	335	785	50	700	674	1620	6	Shutdown end of shift
6	487	950	395	740	46	600	928	1253	5.5	Shutdown end of shift

2.5.1.8 Conclusions from Continuous Plant Test Operations (cont'd)

a. Preparation (cont'd)

fication.

2. The operating stability of the fluid bed furnace was excellent; however, some temperature control problems were encountered in operating the tower at the lower temperatures due to difficulties in turning the plenum burner down to a low enough capacity.

b. Continuous Test Runs 1,2,3

1. Suction line to the polymer feed pump was limiting the feed capacity of the operation.

The suction line was increased in size and the tracing detail was improved.

2. The capacity of the Light Oil Fraction Condenser, HE-3, was too low.

A second condenser was installed in a series with the original one.

3. When the temperature of the heavy oil fraction product leaving the Heavy Oil Fraction Cooler, HE-2, dropped too low, (below 100°F), there was some tendency to plug the cooler tubes with viscous product and drive heavy oil product overhead.

This was avoided by controlling cooling water flow rate to HE-2.

4. The pressure reducing station controlling coil pressure was capacity limiting.

A by-pass was installed around this station.

c. Continuous Test Runs 5 and 6

1. A stable process was achieved under basic design conditions and could be operated with little difficulty.
2. Process performance was close to the design basis and liquid phase products were produced with a high degree of yield.
3. The reactor coil was disassembled after these runs and found to be clear.

2.5.1.9 Pyrolysis Product Quality

a. Liquid Phase Properties

The basic characteristics of the liquid phase components are summarized in Table VII.

The pyrolysis products, (liquids), from the process were burned in commercial burners. No problems were encountered in these tests.

b. Gas Phase Properties

The gas phase products produced during the various test operations were all burned in a commercial burner.

No problems were encountered in these tests.

TABLE VII

Typical Liquid Phase Product Characteristics

PRODUCT	VISCOSITY at 150°F Centistokes	FLASH PT °F	DENSITY GMS/CC @ 80°F
Light Oil Fraction (LOF)	2.8	92-112	0.78
Heavy Oil Fraction (HOF)	3.0 to 10,000	118-122	0.86

2.5 OPERATING RESULTS (cont'd) Benchscale Pilot Plant - Batch

2.5.2 Test Operations

The process used for the Benchscale Pilot Plant Operations has been detailed earlier.

2.5.2.1 Hercules Feedstock- Cracking & Viscosity Tests

a. Initial Testing

A series of five test runs were made on Hercules high viscosity atactic copolymer under the conditions described in Table VIII, pg. 55.

The Hercules atactic polypropylene had the properties estimated in Table IX, pg. 56. The atactic melt was poured into drums at the Hercules polypropylene producing plant, and permitted to solidify.

It was established that a pyrolysis temperature range of 780 to 880 °F gave liquid phase products with good yield.

In Run No. 1, there was a substantial amount of distillate refluxing back into the reactor because the vapor line between reactor and distillate condenser was not insulated. Residence time was 53 minutes and pyrolysis started at a temperature of 575 °F which was increased to 800 °F during the run.

Run No. 2 was made with a heavily insulated vapor line between the reactor and distillate condenser. Residence time was reduced to 34 minutes. Pyrolysis temperature range covered 600-800 °F. Yield of liquid phase from atactic polymer feed was 81.76% by weight. Pyrolysis proceeded to yield a distillate to residue ratio of 27.6.

It was noted during Run No. 2 that the line connecting the reactor with the distillate condenser was of copper. There was concern that copper could have a catalytic effect on the pyrolysis reaction.

This line was replaced with 316 Stainless Steel and it was decided to proceed with Run No. 3 at the same conditions as Run No. 2.

Run No. 3 results were similar to Run No. 2 - except that the yield of liquid phase from feed was increased to 88.2% by weight.

TABLE VIII

ATACTIC THERMAL CRACKING - BENCHSCALE TESTING

Date	Run No.	Drum No.	Amount of Feed-Grams	Pyrolysis Temp Range °F	Decomposition Time, Min.	Distillate (D) grams	Residue (R) grams	D/R	Comments
5/16/78	1	1	not recorded	575 - 800	53	340	117	1.9	Substantial reflux Long Cu tubing between retort & condenser
5/18/78	2	1	910	600 - 800	34	718	26	27.62	No reflux. Insu- lated the copper tubing
5/18/78	3	1	910	590 - 880	35	757	46	16.46	S.S. pipe in place of copper tubing
5/19/78	4	1	905	720 - 880	20	382	175	2.18	Substantial loss of gases when re- actor was pulled out of the furnace. Pressure built up to 30 PSIG on closing the valve leading to the condenser. Solids found in the flask.
5/19/78	5	2	900	650 - 780	25	372	307	1.21	Used sample from a different drum to compare with Run 4. No air in the furnace for 5 min.

2.5.2.1 Hercules Feedstock - Cracking & Viscosity Tests (cont')

a. Initial Testing (cont'd)

In Run No. 4, it was decided to reduce the residence time to 20 minutes in an attempt to increase the yield of the residue, (heavy oil fraction), i.e. decrease the ratio of distillate to residue. Run No.4 successfully accomplished the objective, however, it was found that the reaction was being stopped at a high rate point causing some operating difficulties during the time it took to cool down the reactor i.e. there was a pressure buildup when the vapor line was closed until the reactor was cooled down.

TABLE IX

ATACTIC POLYPROPYLENE PROPERTIES

MELT VISCOSITY (400°F):	700,000 - 1,000,000 cp (est.)
MELTING POINT:	250 - 320°F
MOLECULAR WEIGHT:	100,000 - 250,000
SPECIFIC GRAVITY:	0.88
COLOR:	White
VOLATILE CONTENT:	< 4 wt. %

The ratio of distillate to residue was successfully reduced to 2.18 for Run No. 4. However, the overall liquid phase yield dropped to 61.5% because of operating difficulties during cool down which required venting some distillate to prevent an unacceptable pressure build up.

Run No. 5 was a replicate of Run No. 4, using a different drum of atactic feed product to establish whether there was significant variation from drum to drum in the same lot of material.

2.5.2.1 Hercules Feedstock - Cracking & Viscosity Tests (cont'd)

a. Initial Testing (cont'd)

Run No. 5 successfully duplicated Run No. 4 with a higher overall liquid phase yield of 75.4% by weight because of a more rapid cool down at the conclusion of the run.

b. Conclusions of Initial Benchscale Test Program

1. The fluid bed furnace heating concept appeared to yield reproducible, controllable results.
2. The range of thermal pyrolysis reaction was 600 to 880° F.
3. A residence time of approximately 20 minutes gave indications of a good yield of heavy oil fraction.
4. The feedstock appeared to remain in a highly viscous form at temperatures well over 450° F. It was concluded that it would be difficult to pump the atactic polymer to the pyrolysis reactor when operating on atactic polymer by-product from the polymerization of high viscosity copolymer polypropylene/polyethylene.

The decision was made to study the possibility of reducing viscosity of the feed polymer by blending back some pyrolysis product distillate when operating on the high viscosity copolymer atactic product. The program objective was established to reduce the viscosity below 20,000 cp. at 400° F to facilitate handling the melt.

c. Viscosity Reduction Test Program

1. 250 gms. of pyrolysis distillate was added to 250 gms. of the high viscosity copolymer atactic and the mixture was heated to 400° F.

The resulting solution viscosity was well below 20,000 cp. at 400° F and was clearly a pumpable liquid phase.

2. 200 gms. of kerosene was added to 200 gms. of the high viscosity copolymer atactic and the mixture heated to 420° F.

The resulting solution viscosity was well below 20,000 cp. at 400° F and was clearly a pumpable liquid phase.

2.5.2.1 Hercules Feedstock - Cracking & Viscosity Tests (cont'd)

c. Viscosity Reduction Test Program (cont'd)

3. 200 gms. of pyrolysis distillate was added to 250 gms. of the high viscosity copolymer atactic and the mixture heated to 400 °F.

The resulting solution viscosity was well below 20,000 cp. at 400 °F and was clearly a pumpable liquid phase.

d. Conclusions of Viscosity Reduction Test Program

1. A 55 wt. % atactic solids solution in pyrolysis distillate yielded a pumpable liquid phase at 400 °F with a viscosity well below 20,000 cp. for atactic polypropylene by-product from the polymerization of high viscosity copolymer commercial type of polypropylene/polyethylene.
2. Kerosene could be used to perform the same function as pyrolysis distillate. The property provided a mechanism to startup the plant on the high viscosity copolymer atactic when pyrolysis distillate was not available.

e. Benchscale Pilot Plant Operations - Atactic Solutions

A series of two pyrolysis test runs were made on high viscosity atactic copolymer, one using 50% by wt. solution of atactic and pyrolysis distillate and one using 100% atactic to observe the influence on the pyrolysis reaction of forming the solution. The one with 100% atactic was a duplicate of test Run No. 2 in Table VIII, pg. 55. The conditions employed and the results obtained are summarized in Table X, pg 59 .

f. Conclusions of Atactic Solutions Test Program

1. Run No. 6 duplicated the results of Run No. 5 in Table VIII, pg. 55 with the exception that overall yield was down to 51.7%. The yield problem continued to be associated with cooldown procedure of the batch reactor at the end of the run.
2. Run No. 7 showed light ends distilling over in a temperature range of 415 to 600 °F with very little pyrolysis reaction.

Essentially, all of the atactic feed and the pyrolysis distillate were accounted for giving a closure of the material balance without gas phase losses.

TABLE X

Date of Test	Run No.	Drum No.	Amount of Feed Grams	Pyrolysis Temp Range °F	Decomposition Time, Min.	Distillate (D) Gms.	Residue (R) Gms.	D/R	Comments
6/19/78	6	1	906	650 - 810	23	258	210	1.228	
6/19/78	7	1	906	415 - 600	24	513	403	1.27	

2.5.2.1 Hercules Feedstock - Cracking & Viscosity Tests (cont'd)

f. Conclusions of Atactic Solutions Test Program (cont'd)

The residue material was a tacky solid on cooling rather than liquid phase. The nature of the material suggested little pyrolysis distillate.

It was concluded that it would be necessary to increase the pyrolysis conditions of pressure to prevent distillation of light phase from the solution at temperatures below the significant pyrolysis range to be able to pyrolyze atactic polypropylene solubilized in pyrolysis distillate.

g. Viscosity Determinations

Viscosity measurements were run on samples of the residue pyrolysis products, (heavy oil), from various runs. All viscosities were run at 150° F using Canon Fenske Capillary Tube Vicometers.

Viscosity results were determined at the conclusion of the test run and then repeated 48 hours later. Results are summarized in Table XI, pg. 61

Part of the samples were treated with 5% by weight methyl alcohol. Viscosity results were determined at the conclusion of the test run and then repeated 48 hours later. Results are summarized in Table XI, pg. 61

After 48 hours, the viscosities showed no more change.

h. Conclusions of Viscosity Determination Test Program

It was concluded that the viscosity of higher boiling liquid phase, (residue), decreased during the first 48 hour period after pyrolysis. The samples treated with methyl alcohol showed the same behavior suggesting that the variation was not due to latent catalyst activity in the polymer.

It was decided that this behavior be checked during continuous operations. There was the consideration in these batch benchscale operations that the break between distillate and residue when the reaction was terminated by cooling was contaminated and this was influencing viscosity behavior.

There was the additional possibility that oxidation of the samples, (the samples were in sealed containers under an air atmosphere), was taking place.

TABLE XI

VISCOSITY DETERMINATIONS

on

DISTILLATE AND RESIDUE

SAMPLE FROM RUN NO.	UNTREATED SAMPLES		SAMPLES TREATED WITH 5% METHANOL AFTER INITIAL VISCOSITY MEASUREMENT	
	<u>End of Test Viscosity-CS</u>	<u>Viscosity 48 hrs later-CS</u>	<u>End of Test Viscosity-CS</u>	<u>Viscosity 48 hrs later-CS</u>
1	157	96	145	90
3	54	50	44	41
6	1680	1440	1200	1024
7	880	440	776	472

2.5.2.1 Hercules Feedstock - Cracking & Viscosity Tests (cont'd)

- h. After 48 hours, the additional viscosity drop was negligible.

2.5.2.2 Novamont Feedstock - Thermal Cracking & Viscosity Tests

2.5.2.2 Novamont Feedstock - Thermal Cracking & Viscosity Tests

a. Background & Objectives

Extended batch pyrolysis tests were performed on homopolymer feedstock from Novamont's plant at Houston, TX as well as on copolymer produced by Novamont in its European plant in support of Procedyne's engineering effort on the Houston plant. The purpose of this testwork was to compare cracking characteristics of various batches of feedstock produced by Novamont. These batches vary in viscosity and volatiles content. Since the Novamont polypropylene facility at Houston is still in a startup phase, operating problems often result in atactic polypropylene of varying impurities.

The test facilities for runs 1 through 4 and procedure for this testwork were as described in the previous section.

Runs 5 through 11 were made on the modified altered test apparatus, (Fig. 8 pg.20), described earlier. The reactor for these tests consisted of a 304 Stainless Steel vessel, 2" by 36" with a 24" length free-board section flanged to it and containing a relief valve set at 50 lbs. pressure. This reactor simulated our commercial process, (described earlier in this report), more realistically in that the operating pressure of 50 lbs., (built up as the reaction proceeds due to volatiles generation), prevented a large proportion of low boiling pyrolyzates from escaping, thus preventing a highly unsteady state run.

Table XII, pg.63, is a summary of test data and results. The pertinent comments for this part of the testwork are found in this table.

b. Viscosity Checks

Blending of atactic feedstock with various cuts of pyrolysis product was studied in order to observe their strength as solvents for the Novamont product. The following is a description of this testwork:

TABLE XII

NOVAMONT ATACTIC POLYPROPYLENE: BATCH TEST PYROLYSIS DATA

RUN #	DATE	WT. OF SAMPLE AND FEED CHARACTERISTICS	CRACKING TEMP °F	CRACKING TIME MINS.	HEAT SOURCE TEMP °F	REACTOR PRESSURE DURING CRACKING PSIG	DISTILLATE COLLECTED GRAMS	RESIDUE COLLECTED GRAMS	COMMENTS
1	4/12/79	450 gms (copoly- mer from Nova- mont's plant in Europe	250	30	850	0	217	158	The unusual results of this test are attributed to large amounts of sol- vent or water from steam stripping.
2	4/12/79	450 gms (feed as in Run #1)	735-790	23	700-710	--	---	---	A residue of thick paste was recovered from the vessel.
3	5/12/79	450 gms. (feed as in Run #1)	780-790	--	-----	--	144	88	Good cracking.
4	5/17/79	910 gms. (feed as in Run #1)	-----	--	850	--	---	---	Purpose of this test was to obtain material for diluting the Novamont feed to obtain viscosity data
5	4/7/80	450 (viscosity approx. 10,000c.p. 2% hexane) homo- polymer feed	850	40	980	50 - 52	---	---	Product was in one large lump. No cracking.
6	4/7/80	450 (feed same as for Run #5)	850	80	1000	50 - 54	70	300	Heavies had hardened by 4/8/80
7	4/8/80	450 (feed same as for Run #5)	950	40	1050	50 - 56	16	305	Best run of this series. Heavies still liquid on 4/25/80.
8	4/8/80	450 (feed same as for Run #5)	850	40	980	50 - 56	50	335	Heavies had hardened by 4/9/80

TABLE XII (cont'd)

NOVAMONT ATACTIC POLYPROPYLENE: BATCH TEST PYROLYSIS DATA

RUN #	DATE	WT. OF SAMPLE AND FEED CHARACTERISTICS	CRACKING TEMP °F	CRACKING TIME MINS.	HEAT SOURCE TEMP °F	REACTOR PRESSURE DURING CRACKING PSIG	DISTILLATE COLLECTED GRAMS	RESIDUE COLLECTED GRAMS	COMMENTS
9	4/8/80	450 gms. (feed same as for Run #5)	850	80	980	42 - 56	10	380	Heavies had hardened by 4/9/80
10*	6/17/80	450 gms.	850	15	1000	50 - 52	275	33	Heavies still liquid
11*	6/17/80	450 gms.	800	20	915	48 - 52	211	198	Heavies set up

Runs 5 through 9 - Viscosity approximately 10,000 C.P. 2% hexane

* Different raw material - lower viscosity approximately 5,300 C.P. homopolymer.

2.5.2.2 Novamont Feedstock - Thermal Cracking & Viscosity Tests (cont'd)

b. Viscosity Checks

1. The feed material was mixed with an equal weight of residue from Run #3.

The product was found to be sufficiently fluid at 400°F so as to be pumpable using a gear pump.

2. The feed material was mixed with the 75% cut, (heavy fraction), obtained from Run #4 above on a 50-50 weight basis and heated up to a temperature of 400°F. It was found to be quite fluid.
3. The new sample obtained from Novamont was used this time. This sample already had been mixed with fifty-percent, (50%), by weight with some solvent; however, it was quite viscous. It was mixed with ten percent, (10%), by weight of the heavy cut from Run #4. The viscosity was found to be higher than desirable.
4. The same sample as used for Run #3 was this time mixed with an equal weight of the heavy fraction obtained from Run #4. This sample was found to be fluid enough at 400°F to be pumpable.

NOTE:

- (I) Viscosity checks 2 through 4 were made with a small N₂ bleed into the mixing flask.
- (II) Direct measurement of viscosity using the Cannon-Ubbelohde viscosity tubes, was exceedingly difficult due to the high temperatures at which viscosity data was desired. However, visual checks were made and viscosity estimated by pouring the molten liquid out of a glass flask. The viscosity of samples from tests 2 and 4 above, could be around 8000 C.P., whereas the viscosity of the sample obtained from test #3 above, (i.e. viscosity Test #3), was estimated around 12,000 C.P.

2.5.2.2 Novamont Feedstock- Thermal Cracking & Viscosity Tests (cont'd)

c. Conclusions of Novamont Benchscale (batch) Testing

1. The Novamont atactic polypropylene varies in consistency, solvent content and possibly residual catalyst content. These factors resulted in a marked difference in the cracking characteristics (temperature, residence time) of these grades of feed when tested on a batch basis.
2. However, since there is indication that except for the residual catalyst content, the above factors do not influence the cracking rates appreciably, the variation in residence time is attributed to the lower heat transfer rates prevailing during the cracking.
3. Heat transfer coefficients as low as 2 to 3 BTU/hr, $^{\circ}\text{F ft.}^2$ were previously calculated for the commercial plant in Texas. The coefficients in the batch test mode are likely to be even lower. This reasoning would also explain the variation in cracking rates observed from Procedyne's batch and continuous (described later in this report) benchscale cracking units.
4. The heavy oil fraction from cracking of Novamont atactic polypropylene could serve adequately as a solvent for the polymer.

2.5.2.3 ICI Feedstock - Thermal Cracking Tests

- a. Batch tests were conducted on atactic polypropylene produced by ICI, England to convert it to liquid fuel by the Thermal Cracking Process developed by Procedyne. This testwork involved bench scale experiments designed to serve as screening tests. It was the objective to gain information on the cracking characteristics of the product and to compare them with the material on which the earlier process development work had been carried out. The sample cracked at Procedyne was a homopolymer with a 15% residual diluent, (C_{12} para-fin), 7-10 ppm titanium as oxide or chloride, 20-30 ppm aluminum as hydroxide or chloride, and 24-45 ppm other chlorides.

Test apparatus and procedure used was the same as used for Run #5 through #11 on the Novamont product described in the last section.

2.5.2.3 ICI Feedstock - Thermal Cracking Tests (cont'd)

a. Background and Objective (cont'd)

A total of three tests were conducted. The total residence time varied from twenty minutes to forty minutes and the product temperature from 780°F to 870°F.

The cracked product from these tests was a liquid with low viscosity. Test #3 resulted in a somewhat pastier product. Test #1 resulted in a product which appeared to have visually the best characteristics.

Table XIII is a summary of the test data and results. (pg. 67)

b. Conclusions

The atactic polypropylene produced by ICI cracked readily to a low viscosity product at temperatures in the neighborhood of 800°F.

2.5.3 Benchscale Pilot Plant Operations - Continuous

2.5.3.1 Thermal Cracking

a. Background and Objectives

Continuous thermal cracking apparatus was set up in Proceadyne's Process laboratories. The process and equipment for this effort has been described in Section 2.3.3.

This facility was initially set up for studying the cracking behavior of Novamont feed and possible use of catalytic cracking. Its use was soon extended to other feedstocks. This facility is now the standard mode of evaluating cracking characteristics of waste polymers because of its steady state operation, ability to afford accurate and valid data and visible products during pyrolysis.

The primary process variables investigated were pyrolysis temperature and residence time. The reactor pressure was maintained close to 50 psig. The important test results consisted of the weight fraction of heavy and light oil produced as well as levels of gas and coke formation. Feedstock of Hercules origin was tested for comparison purposes.

TABLE XIII: THERMAL CRACKING OF ICI APP

<u>Test No.</u>	<u>Weight of Charge</u>	<u>Product Temp. Range (°F)</u>	<u>Heat Source Temp (°F)</u>	<u>Cracking Period (min.)</u>	<u>Reactor Pressure</u>	<u>Comments</u>
1	450 gms.	790-- 812	900 - 930	30	29-53 PSIG	This test was quite successful.
2	450 gms.	865 - 870	935 - 950	26	22-57 PSIG	The total yield was about sixty percent (60%). Product was somewhat more viscous than from Run #1.
3	450 gms.	750 - 800	880 - 900	23	21-56 PSIG	The product was quite viscous. Time/Temperature was apparently too low for good cracking.

2.5.3.1 Thermal Cracking (cont'd)

a. Background and Objectives (cont'd)

Table XIV, on the following pages is an exhaustive summary of this testwork. The column headed comments and conclusions provides the pertinent test details. The product temperature varied considerably along the reactor length. This is ascribed to the strongly endothermic reaction.

b. Test Analysis and Discussion

1. Residence Time and Temperature

Table XIV shows that with reactor temperatures in the range of 830-860 °F, good cracking of Novamont atactic polypropylene was attainable with residence time as low as 4.6 minutes. The residence time was varied from 18.4 minutes to 4.6 minutes. The actual retention time is lower because the gas formation in the reactor has not been accounted for in the residence time computation.

The coke level decreased from 0.8% to 0.22% with a decrease in residence time from 18.4 to 4.6 minutes. It is likely that the coke levels recorded are more than the actual coke formed due to the difficulty in collecting all the coke from the tubular reactor.

It was found in subsequent runs that some coke had accumulated and hardened below the screen which served as support for the glass beads. Coke levels reported later on in this program are likely to be more representative.

The product temperature during Run #12 varied from 734 - 753 °F in the bottom of the reactor to 810-830 °F in the top. The residence time was 4.6 minutes. The run resulted in a very viscous product. The top and bottom temperatures obtained during Run #13 are somewhat comparable to those obtained during Run #12. However, the retention time was doubled through the use of a longer reactor. The viscosity of the heavy product was found to increase significantly. It can be inferred that a residence time as low as 4.6 minutes can be used provided the product temperature (as measured at the top) is at least 830 °F, (as in Run #11).

TABLE XIV

THERMAL CRACKING RUNS: CONTINUOUS BENCHSCALE APPARATUS

R U N #	FEED STOCK	VESSEL AND PACKING	FEED RATE cc/min.	TOTAL RUN LENGTH	RES. TIME mins.	REACTOR TEMP °F BOTTOM	REACTOR TEMP. TOP °F	INLET FEED TEMP °F	HEAT SOURCE TMP. °F	HEAV. WT. % CONS.	LIGHTS WT. % CONS.	GAS %	COKE %	COMMENTS & CONCLUSIONS
9	Nova- mont 4000- 9000cp	Pyrex 6MM beads 18" vessel	5	82 min.	18.4	820-843 (SS Con- dition)	875-860	808-825	866-880	91.35 A	216	6.49	0.8	Very little coke on beads, more coke on sides.
10		" "	10	72 min.	9.2	793-817	850-860	778-788	880	76 A	13	10.65	34	Wet test meter added. Note: More ΔT between top and bottom of react- or with higher feed rate. Purpose of this run was to compare effect of resi- dence time. However, the purpose was not fully realized because of diffi- culty in controlling pro- duct temperature.
NOTE: Runs 4-10: APP might have been partially oxidized during melting.														
11	Same as above	18" vessel (6 mm Py- rex bead)	20	45 min.	4.6	768-803 (Steady state)	830-860	716-722	903-916	63% B	30%	6.78	0.22*	Note: decrease of coke with decrease in residence time at approx. same temp- erature. *It is likely that all the coke was not col- lected.
12	Same as above		20 CCM	45 min.	4.6	734-753 (Steady state)	810-830	700	854-857		40 732	apprx. 7%	0.5%	Obj: 50°F lower tempera- ture. Not met due to er- ratic offset. Temp. too low, very heavy product. Compare with 11. Could be gas of different densi- ty.
13	Same as above	5MM pyrex bead 36" vessel (1" dia.)	20 CCM	105 min.	9.2	700-800B 810-840 (center)	808-821	765-800	847-818* toward end	83.0 B	apprx. 6.4%	apprx. 11%	apprx. .46%	Generally inconclusive run compared with 11, beads a little wet.

TABLE XIV (Cont'd)

THERMAL CRACKING RUNS: CONTINUOUS BENCHSCALE APPARATUS

R U N #	FEED STOCK	VESSEL AND PACKING	FEED RATE cc/min.	TOTAL RUN LENGTH	RES. TIME mins.	REACTOR TEMP °F BOTTOM	REACTOR TEMP °F TOP OF	INLET FEED TEMP °F	HEAT SOURCE TMP. °F	HEAV. WT. % CONS.	LIGHTS WT. % CONS.	GAS %	COKE %	COMMENTS & CONCLUSIONS
14	Same as above	5MM py- rex bead 36" ves- sel (1" dia.)	20 CCM	85 min.	9.2	818-828 (B) 810-830 (Center)	---	782	844- 848	apprx. 5%	apprx. 24	apprx. 25	apprx. 0.3%	Note: BC temps. tracking 3 SCFH air add- ed. Good material bal- ance not possible due to gas leaks. Water in lights approx. 10%. No significant exotherm observed with air. Coke is less but needs to be double checked. Note effect on gas formation.
15	As in 14	Pyrex 5MM	20	88 min.	9.2	821-829 860-868 (C)	891 (top)	812- 830	897	apprx. 57% A	apprx. 29 A	14	0.309	Good steady state con- ditions. This run made at higher temp. to com- pare coking and gas for- mation. NOTE: A.B.C. are quali- tative viscosity levels with A being the light- est - (Comparable to #2 fuel oil) and C being the heaviest (comparable to machine oil)
16	Hercu- les Low viscos- ity	Same as 15	20	20 mins.	9.2	786-800 810-840 (Center)	808- 821	780	800-761	-----	-----	-----	-----	Run aborted. Basically uncracked product con- tinued the run (#17) with higher heat source temperature. NOTE: No temperature gradient in the reactor.

TABLE XIV (Cont'd):

THERMAL CRACKING RUNS: CONTINUOUS BENCHSCALE APPARATUS

R U N #	FEED STOCK	VESSEL AND PACKING	FEED RATE cc/min.	TOTAL RUN LENGTH	RES. TIME mins.	REACTOR TEMP °F BOTTOM	REACTOR TEMP °F TOP OF	INLET FEED TEMP °F	HEAT SOURCE TMP. °F	HEAV. WT.% CONS.	LIGHTS WT.% CONS.	GAS %	COKE %	COMMENTS & CONCLUSIONS
17	Same as above	Same as 15	20	80 min.	9.2	838-840	830-840	830	840-850	858	5.4	8.78	---	Coke level not appli- cable because the re- actor was not cleaned between runs 16 & 17. This run proves that there is not an enor- mous difference in cracking characteristics between high and low viscosity APP.
*Gas Percent is by difference between feed and liquid.														
18	Same as Run 15	36" py- rex bead	20	24 min.	9.2	847-868 865-890 (Center)	833-877	826- 866	876	79	5	16	0.61	Objective of this run was to duplicate Run #15 and establish Process parameters for compar- ison. Run was aborted because of leaks but data shows coke level with time. The higher coke level could indi- cate that coke levels are high initially and then fall off due to a coke layer on walls.
19	Same as Run 15	36" py- rex bead	20		9.2	830-860 (bottom) 840-880 (center)	866-886	830- 868	870- 890					Material balance cannot be reliable due to leaks and frequent stoppages.

2.5.3.1 Thermal Cracking (cont'd)

b. Test Analysis and Discussion (cont'd)

2. Gas Formation

The percent gas formed varied from 6.5% to 11%. The levels of gas are around 7% at low residence time and seem to increase to 11% at retention time of 9.2 minutes. Run #9 with a higher residence time, (18.4 minutes), and a higher product temperature also resulted in less than 7% gas formation. Since gas flow measurement in this run was not done by a wet test meter, this reading can be ignored. Run #15, which was a good steady state run confirmed higher gas formation, (14%), figure at a higher temperature and intermediate retention time.

3. Oxidative Pyrolysis

Run #14 was an attempt at oxidative pyrolysis. It was the intent to evaluate the effect of introducing oxygen into the pyrolysis reactor in terms of reaction rates and coke formation. The operating conditions were comparable to other thermal cracking runs but 3 SCFH air was introduced to the feed.

Studies on oxidative pyrolysis of hydrocarbons such as propane (2) suggest that oxygen can greatly accelerate the pyrolysis, especially in reactors with low surface to volume ratios. It has been reported that in pyrolysis and partial oxidation of n-butane, an O_2 concentration as low as 1 ppm could significantly affect pyrolysis rates and a concentration of 0.5% increased the rate a hundred-fold.

In general, the presence of oxygen produces peroxide radicals which increases the rate of free radical formation; so H_2O_2 has a self-accelerating effect which could appear very early in the reaction. O_2 could also have an inhibiting effect. This is considered to be due to the appearance of new chain termination processes which are heterogeneous and unlike alkyl radicals, the oxygenated radicals (especially HO_2) are easily destroyed on solid surfaces.

2.5.3.1 Thermal Cracking (cont'd)

b. Test Analysis and Discussion (cont'd)

3. Oxidative Pyrolysis (cont'd)

Furthermore, it has been reported that during Thermal oxidation of polymers, that the rate of oxygen uptake is inversely proportional to the percentage of crystallinity. Since the tacticity of a polymer is related to its crystallinity, the atactic polymer would be more susceptible to oxidation than the stereoregular polymer. The difference may be attributed to the formation and decomposition of hydroperoxide blocks in the atactic polymers.

Run #14, is considered inconclusive due to gas leaks and inadequacy of the bench scale apparatus, however, the lights contained significant amounts of water due to the peroxide condensation mentioned earlier. An analysis of lights and gas indicated that the lights had 7.2% water and the gas samples contained 1.5% O_2 and 11% CO_2 and CO.

Since most commercial atactic polypropylene feedstock contains chlorides, this route was not explored further. However, it could become worth exploring as a means of accelerating the pyrolysis rate or obtaining different products of pyrolysis.

The present run does indicate somewhat lower coke formation. However, the effect of O_2 preferentially attacking the free radicals is likely to predominate over its effect in combustion of coke. It may, however, be useful as a tool for preventing formation of coke precursors. This can be part of a future study when analytical data on coke precursors is available.

4. Rate Data

Table XIV indicates space times used. The decomposition of organic polymers is in general said to be a function of the dissociation rates of bonds in the molecular structure and is generally regarded as a first order reaction. The space times indicated in Table XIV appear to be in general agreement with predicated rate data (1). An Arrhenius plot from this source leads to the residence times of around 3 minutes at the temperatures used (approximately 845°F). Run #11, at this temperature resulted in good cracking at 4.6 minutes.

2.5.3.1 Thermal Cracking (cont'd)

b. Test Analysis and Discussion (cont'd)

4. Rate Data (cont'd)

A very accurate rate equation can not be derived from this work due to temperature gradients along the length of the reactor. Another difficulty in comparing rate data is that during the current phase of testwork the degree of cracking varied from run to run and the cracked product has not yet been characterized by a function such as the average molecular weight. However, since any commercial design is likely to be based on heat load considerations, the actual residence time will be greater than the required residence time for the particular temperature. A heat load calculation assuming an endotherm of 250 BTU/lb. did not allow for adequate heat transfer into the reactor, particularly at lower pyrolysis temperatures.

Another complication to rate studies, as noted earlier, is the fact that some of the sample degrades and vaporizes during the heat up period, so that the reaction does not take place at a constant temperature.

5. Effect of Feed Molecular Weight

Polymer viscosity is a function of its weight average molecular weight. Runs 16 and 17 were conducted to study the relative cracking characteristics of atactic polypropylene of different viscosity. The feed for these runs was Hercules atactic polypropylene with a viscosity in the neighborhood of 1000 cp at 350 °F.

It is important to note that an additional 24" of coil length was added to the inlet feed pipe from Run 16 onward to serve as feed preheater. Runs 16 and 17 indicate there is not substantial variation in cracking characteristics between low and high viscosity polymers. There appears to be a minimum temperature (around 830 °F) which the product, regardless of its viscosity must achieve in order to crack into a relatively low viscosity product. Apparently, the rate of decomposition of low viscosity polymer at lower temperatures, (apprx. 800 °F) is not significantly lower.

This is also confirmed by pyrolysis experiments conducted on low molecular weight and high molecular weight polyisobutylene. (1) The rate curves in

2.5.3.1 Thermal Cracking (cont'd)

b. Test Analysis and Discussion (cont'd)

5. Effect of Feed Molecular Weight (cont'd)

the latter case showed rapid initial rates in the case of low molecular weight polymer due undoubtedly to the abundance of short chains, but, overall the initial molecular weight or the molecular weight distribution had little effect on the rate beyond several percent. Thus, in one series of experiments the rate of decomposition, (%/min.), varied from .0736 to .062 with a corresponding molecular weight variation of 4,800,000 to 700,000.

The Hercules atactic polypropylene, besides being a lower viscosity feed, is also produced by a different synthesis route and as such may consist of different impurities.

6. Batch versus Continuous Data

As observed earlier, the pyrolysis reaction rate using a batch process was considerably slower than that carried out on a continuous basis. This effect is ascribed largely to the lower rates of heat input to a batch reactor. Calculations assuming a heat of reaction of 250 BTU/lb. and a heat transfer rate of 3BTU/hr.^oF ft² showed that the product would need a residence time far in excess of that necessary for continuous pyrolysis.

It may be useful to note that besides heat transfer, diffusion effects are also likely to retard the overall pyrolysis and volatilization phenomenon. On the studies of depolymerization of teflon, for instance (4), it has been reported that rates were enhanced as the samples were made thinner. In a batch reactor containing a one pound sample, it is obvious that the escape of pyrolysis products will be retarded, although, there is no effect on the pure thermal decomposition.

The escape of small radicals at the surface leaves a high surface concentration of large radicals and consequently a high rate of decomposition at the surface. Thus, even though the rate of decomposition is determined by the rate of bond rupture and is proportional to the weight of the polymer, diffusion or evaporation can also be rate controlling. If every molecule leaves the exposed surface immediately then the rate of arrival of molecules at the surface would determine the rate of vapor-

2.5.3.1 Thermal Cracking (cont'd)

b. Test Analysis and Discussion (cont'd)

6. Batch versus Continuous Data (cont'd)

ization. It is of interest to know that diffusivity of small molecules in polymers is of the order of $10^{-6} \text{ cm}^2 / \text{second}$.

7. Products of Pyrolysis

Products from Run #9 were analyzed by a local laboratory. The heavy liquid fraction which constituted a majority of the pyrolyzate showed 8% alkane of carbon numbers from C_5 to C_8 and 91.2% alkenes of carbon numbers varying from C_6 to C_{20} . No aromatics were detected, although aromatics have been reported in analysis performed on products from batch pyrolysis tests. Since the alkenes content of the heavy fraction was as high as that of a similar catalytic cracking test, (described later under Catalytic Cracking), there is a strong indication that the reaction mechanism is not entirely that of thermal cracking. As seen earlier under the discussion on cracking mechanism, every thermal scission results in one saturated and one unsaturated molecule.

Most of the runs at cracking temperatures above 800°F resulted in what appeared to be a relatively low viscosity well cracked product. The product was generally of a lower viscosity than that obtained from batch tests. A majority of the product was collected in the "heavies" jar indicating low formation of lower boiling components, (the temperature in the cyclone flash separator varied from 300°F to 400°F).

It is the intent to analyze the pyrolyzate, (liquid and gas), samples in terms of their saturated paraffinic, olefinic and aromatic content. The tables on the following pages, (Tables XV through XVIII), contain the results of analysis on a few selected liquid and gas amples as well as characterization of cracked products as fuel oil candidates.

TABLE XV ANALYSIS OF SELECTED SAMPLES:
CONTINUOUS BENCHSCALE PILOT PLANT*
 (CONTINUED)

TABLE XV ANALYSIS OF LIGHT FRACTION

<u>Run 14</u>		<u>Run 15</u>	
	<u>% (W/W)</u>		<u>% (W/W)</u>
Water	7.2	Water	0.7
Alkanes (C5-C26, predominantly C5-C8)	3.0	Alkanes (C5-C13, predomi- nantly C5-C10)	22.8
Alkenes (C6-C30)	89.8	Alkenes (C6-C10)	75.5
Alcohols	ND	Alcohols	ND
Aldehydes	ND	Aldehydes	ND
Aromatics	ND	Aromatics	ND
		Other	1

*Analysis performed by Princeton Testing Labs

TABLE XVI ANALYSIS OF SELECTED SAMPLES:

CONTINUOUS BENCHSCALE PILOT PLANT*

(CONTINUED)

TABLE XVI ANALYSIS OF HEAVY FRACTION

	Run #9	Run #17
	<u>% (W/W)</u>	<u>% (W/W)</u>
Water	--	.02
Alkanes	8.8 (C5-C8)	ND
Alkenes (C5-C30)	91.2 (C6-C20)	99.98 (C5-C30)
Alcohols	ND	ND
Aldehydes	ND	ND
Aromatics	ND	ND

*Analysis performed by Princeton Testing Labs

TABLE XVII ANALYSIS OF SELECTED SAMPLES:

CONTINUOUS BENCHSCALE PILOT PLANT*

TABLE XVII ANALYSIS OF GAS SAMPLES

	#9	#14	#15
Carbon Monoxide	--	3.1	--
Carbon Dioxide	--	7.9	--
Oxygen	--	1.5	--
Methane	.5	2.0	6.1
C ₂ as Ethane	10	2.5	8.0
C ₃ as Propane	44	14	45
C ₄ as Butane	7	1.1	4.4
C ₅ as Pentane	7	3.5	6.6
C ₆ as Hexane	3	1.3	.9

*Analysis performed by Princeton Testing Labs

TABLE XVIII: FUEL OIL CHARACTERISTICS OF CRACKED PRODUCT*

Gravity:	49.2 - 44.8
(API at 60°F)	
Heat of Combustion:	
(BTU/lb)	19,702 - 19,829
(BTU/gal)	128,434 - 132,497
Flash Point:	70°F - 68°F
Viscosity	33.2 - 67.6
(Saybolt Universal at 100°F, in seconds)	
Kinematic Viscosity at 100°F. in c.s.	2.10cs - 12.96cs
Aluminum (ppm)	3 - 71
Sulfur	Nil Nil
Magnesium (ppm)	1 - <1
Titanium (ppm)	<1 - <1
Vanadium (ppm)	<1 - 1
Sodium (ppm)	<1 - 1
Chlorides (ppm)	Analysis not available

*Tests performed by E. W. Saybolt, Kenilworth, NJ

*Two (2) samples of varying consistency were analyzed for this data.

2.5.3.1 Thermal Cracking (cont'd)

b. Test Analysis and Discussion (cont'd)

8. Melt Viscosity

Polyolefin melts deviate considerably from ideal Newtonian flow characteristics. However, at small shear stresses and correspondingly small shear rates the flow approaches Newtonian behavior. The melt viscosities on atactic polypropylene feeds of various origins investigated during the testwork are plotted as a function of temperature. Figures 10, 11, pgs. 80&81 show this relation. The viscosity existing at the pyrolysis condition can be extrapolated from this data. The viscosity data shown was taken at low spindle speeds.

2.5.3.2 Catalytic Cracking

a. Background and Objectives

The Continuous benchscale polymer cracking facility described earlier was used to investigate Catalytic Cracking. The Catalyst consisted of 3/8" to 3/16" cylindrical beads of alumina on silica catalyst supplied by Harshaw Chemicals. Table XIX gives the properties of the Harshaw Catalyst AL602, which was studied for this phase of the testwork.

It has been reported, (10), that the use of the above catalyst enables cracking of Atactic Polypropylene to a fuel oil product of relatively low viscosity. The cracking process was developed in apparatus similar to one used here at temperatures in the vicinity of 450°C. Among the claimed advantages of this process was that cracking proceeded with the formation of minimal amounts of gaseous and volatile liquid products. Space times in the range of 5 to 15 gms of the catalyst per gram of the polymer fed to the reactor per minute were used. The catalyst has to be periodically regenerated to remove the organic material and carbon deposited on its surface during continued operation by passing a stream of air over the catalyst at temperatures over 650°C.

All the catalytic runs described herein were made on Novamont Feedstock. As indicated in Table XX, feedstocks of two different viscosities were examined.

The purpose of studying catalytic cracking was to evaluate the commercial viability of this route versus thermal cracking.

FIGURE 10

FIGURE 11

Viscosity Determination Apparatus

TABLE XIX: PROPERTIES OF CATALYST AL602

Surface areas:	210-240
m ² /g	
Pore volume:	0.48
cc/g	
Average pore:	.87
diameter ^o A	
Components:	19% AL ₂ O ₃ with 6% SiO ₂
Pellet size:	3/8" to 3/16"
	cylindrical pellets

TABLE XX

CATALYTIC CRACKING RUNS: OPERATING DATA

R U N #	FEED STOCK	CATALYST GRADE AMOUNT	FEED RATE cc/min.	TOTAL RUN LENGTH mins.	RES. TIME mins.	REACTOR TEMP. BOTTOM OF	REACTOR TEMP. TOP OF	INLET FEED TEMP OF	HEAT SOURCE TEMP OF	HEAV. WT. %	LIGHTS WT. %	GAS %	COKE %	COMMENTS
1	Black approx. 2000 cp at 350° homo-polymer	Al 602 Silica on Alumina 190 gms. (3/8")	20 cc/mm	88 min	4.6 (based on 40% voids)	766-811	790-811	---	897-905		22%	15%	Did not check	The heavy fraction was quite fluid. Some uncracked residue at bottom of the jar could be the initial product before steady state. Gas flowmeter too small.
2	RUN ABORTED -- PRESSURE CONTROL VALVE FROZE													
3	Same as above	Al 602 190 gms. (3/8")	20	35 min.	4.6	775	850-902	706-795	850-860	See comment	---	---	---	Run aborted. Pressure fluctuated and blew relief valve. 80% uncracked greenish liquid in heavies jar.
4	High visc. 4000-9000 CP at 350° homo-polymer	Al 602 190 gms. (3/8")	11	60 min.	10 min.	765-777	880	813-819	915	32.25	28.75	33	---	Note difference in top and bottom reactor.
5	Same as #4	Al 602 190 gms. (3/8")	11	LEAK AT FLANGE IN 19 MINUTES		10 min.	766	815	----	861	---	---	---	Approx. 6% coke for runs 4 & 5 combined

(84-a)

1. No conclusions can be drawn with respect to material balance.
2. Catalyst had not been examined or re-activated between runs 4 & 5.

TABLE XX (Cont'd)

CATALYTIC CRACKING RUNS: OPERATING DATA

R U N #	FEED STOCK	CATALYST GRADE AMOUNT	FEED RATE cc/min.	TOTAL RUN LENGTH mins.	RES. TIME mins.	REACTOR TEMP. BOTTOM OF	REACTOR TEMP. TOP OF	INLET FEED TEMP OF	HEAT SOURCE TEMP OF	HEAV. WT. %	LIGHTS WT. %	GAS %	COKE %	COMMENTS
6	Same as #4	Al 602 3/8" cyl. 190 gms.	11	75 min.	10 min.	754-764	760-802	756- 783 (last 60 min)	862 (light liquid)	51.3	26%	17.7	5	Catalyst reactivated. Note: Bottom reactor temp. is lower than feed by 13-20°F as in run #4. Material balance is ap- proximate because no feed for an unknown per- iod of time.
7	As in #4	Al 602 155 gms. reactiva- ted (3/16") & 35 gms. fresh 190 gms. total	11	94 min.	10 min.	719-746*	755-770	726- 792	822-787	58 Very heavy liquid	14	24	3.34	Purpose was to observe cracking and coking be- havior at a lower temp. (compared to #6) Cyclone plugged with heavy liquid toward the end with lowering of temperature.

*Toward the end the temperature
at steady state (last 50 mins.)
Lowered 1530 temperature half-
way through the run.

2.5.3.2 Catalytic Cracking (cont'd)

b. Analysis and Discussion

Runs 1 through 3 were made using a Space time of 11gms catalyst per gram/min polymer feed, whereas Runs 4 through 7 were made using a Space time of 21 grams catalyst/gm/min polymer feed. The feedrate for Runs 1 and 3 was too high to result in sufficient cracking at the temperatures used. A great deal of difficulty was experienced in controlling the reactor pressure, (desired around 50 psig).

Run #1: A space time of 11 grams catalyst/per gm per min. polymer feed was used. The reactor temperature varied from 766 to 811°F. This was the first run on the Continuous benchscale pilot plant and this run proved the need for the following modifications to the apparatus:

1. The gas flowmeter was too small. It was changed for the next run.
2. The LOF glass condenser was too small. It was doubled in length for the next run.
3. A relief valve, (100 psig), was added to the reactor before the next run to guard against excessive pressure buildup. The relief valve was connected to the Afterburner.

The HOF of the cracked product consisted of about 70% fluid liquid and the rest uncracked residue at the bottom. It is likely that some of the uncracked residue was obtained initially before the plant had gained steady state operation.

Runs 2 and 3: These runs were aborted due to pressure buildup problems in the reactor. However, the limited data obtained from Run #3 indicated poor cracking, even though the reactor temperatures were higher than that used for Run #1.

Run #4: The lowered feed rate resulted in a Space time of 21 gm catalyst per gram polymer feed per minute. The feedstock was of high viscosity, The cracking operation resulted in a well cracked product. However, the higher temperatures employed resulted in very high gas formation, (39%). The temperature gradient along the length of the reactor was about 100°F. This could be due to severe Coking. Although no precise Coking data is available, (since the catalyst was not examined between Runs 4 and 5), the Coking

2.5.3.2 Catalytic Cracking (cont'd)

b. Analysis and Discussion (cont'd)

Run #4 (cont'd): levels appeared to be higher than 6%. A material balance indicates that the average molecular weight of the gaseous fraction was close to 70.

Run #5: The reactor temperature varied from 766 to 815°F. The run was terminated after a period of 19 minutes due to a leak at the reactor flange.

Run #6: The feedstock and the feed rate were the same as for Runs 5 and 4. The reactor temperature varied from 754 to 802°F. The ΔT between the top and the bottom of the reactor was 30-40°F at steady state as compared to the 100°F ΔT during #4. The material balance for this run is only approximate because there was no feed to the reactor for an unknown period of time. The Coke level was again significant, (5.0%).

Run #7: The purpose of this test was to study the feasibility of operating at a lower temperature than used for Run #6 to minimize Coke formation. Although, a reduction in Coke levels was seen, the operating temperature, (746-77°F), was not high enough to permit good cracking. The Coke level, though less than from previous runs was still very high, with 3.3% of feed being converted to Coke.

2.5.3.2

c. Conclusions of Catalytic Cracking Program

1. Catalytic Cracking of Atactic Polypropylene does not occur at temperatures significantly lower than those needed for Thermal Cracking.
2. The gas formation appears to be higher than that obtained from Thermal Cracking.
3. The Coking problem with Catalytic Cracking is very severe. The Coke levels were as much as ten times those obtained from Thermal Cracking.

CONCLUSIONS AND RECOMMENDATIONS

3.0

3.0 Conclusions and Recommendations

3.1 Conclusions and Recommendations - The following broad based conclusions can be drawn from the work reported here.

- a. A stable, convenient thermal pyrolysis process was demonstrated on a large scale pilot plant. The process successfully converted high viscosity copolymer atactic polypropylene to predominantly liquid fuels which could be burned in commercial burners.

Energy yield of the process was very high - in excess of 93% including gas phase heating value.

Design and operating data were obtained to permit design of a commercial size atactic conversion plant.

- b. Atactic polypropylene can be cracked to produce a low viscosity product with potential as a fuel oil candidate at temperatures around 850°F and residence time of 5 minutes. The viscosity of the cracked product increases with decrease in time/temperature. A better control of reactor temperature profile should be attempted in future runs. Since the rate of reaction rises rapidly with temperature, the effect of reduced residence time at temperatures between 850°F and 1200°F should be studied in terms of the formation of coke and gas.
- c. A majority of the pyrolysis was carried out at a pressure of 50 psig. Effect of pressure was not studied. Since the effect of pressure on enhancing the rate of pyrolysis is reported to be at least as high as that of temperature, this aspect should be investigated in a future study.
- d. Thermal cracking of atactic polypropylene is seen to result in significant coke formation (0.4% to 0.8% on a weight of feed basis) although the coke levels were of an order of magnitude lower than those obtained during catalytic cracking. Studies on the coking phenomenon with the aim of alleviating this problem are being continued.
- e. The discrepancy between batch and continuous test data can be attributed to lowered heat transfer and diffusion rates.
- f. Oxidative pyrolysis is not seen as a viable commercial alternative due to a significant amount of water formation. However, introduction of controlled quantities of oxygen at lower temperatures to affect change

3.1 Conclusions and Recommendations (cont'd)

- f. (cont'd) in feedstock viscosity could be considered. This is also indicated by the fact that the activation energy of pyrolysis of an oxidized polymer molecule is significantly lower. Oxidative pyrolysis can be carried out by treatment with oxygen or by treatment of hydrocarbon solutions of atactic polypropylene with peroxides.
- g. There is no indication of a strong effect of feed viscosity on cracking rates. The lower rates on high viscosity product obtained on batch pyrolysis can be due to a retarded heat transfer or diffusion mechanism.
- h. It is essential to have a complete characterization of the polymer composition and structure in order to obtain useful and duplicable data because the pyrolysis products and probably the pyrolysis kinetics are affected by introduction of abnormalities into the polymer structure during polymerization.
- i. The polymer products from continuous testing contained an olefinic content of 80% or higher. This suggests that the pyrolysis products be investigated for use as olefinic raw materials. Their use as a solvent for atactic polypropylene has already been demonstrated in the case of Novamont feed.
- j. Catalytic Cracking does not seem to result in any advantage over the Thermal Cracking process in terms of reaction rates or temperature of operation. The limited testwork on Catalytic Cracking undertaken highlighted the inherent drawbacks of Catalytic Cracking in terms of enhanced Coke formation and the need to frequently regenerate the Catalyst bed.

However, use of Catalysts other than the Silica on Alumina used should be investigated. For instance, some of the new Catalysts used in the coal to gasoline cracking process, (Mobil process), are reported to operate relatively free of Coke formation.

3.2 Recommendations for Continued Work

- a. Study the suitability of different catalysts in terms of their cracking efficiency and Coke formation.
- b. Continue Benchscale Continuous Pilot Plant work to minimize Coke formation.
- c. Extend the use of the continuous benchscale pilot plant to develop a process for conversion of high salt atactic

3.2 Recommendations for Continued Work (cont'd)

- c. (cont'd) polypropylene to useful products. This type of waste product is generated by three major producers of polypropylene and there is little likelihood that it can find any significant commercial applications.
- d. Increase the energy recovery potential of this basic processing approach by extending the process applicability to waste plastics rather than limiting it to atactic polypropylene.
- e. Incorporate a major analytical input during the next phase of testwork.

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4 . 0

4.0 REFERENCES

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APPENDIX

5.0

DRAWING LIST

5.1

<u>DRAWING #</u>	<u>TITLE OF DRAWING</u>
B-10627	Benchscale Pilot Plant Flow Diagram
A-11000	Benchscale Pyrolysis Reactor
B-11874	Benchscale Polymer Cracking System
C-09904	Atactic Polymer Melt Tank Assembly
B-09965	Atactic Furnace Reactor Coil
E-09880	Atactic Polymer Process Flow Diagram
B-09898	Atactic Polymer Flash Drum
C-09829	Atactic Heat Exchanger
A-09828	Circulating Oil Tank
E-08805	AB/25 Installation

BILL OF MATERIAL

ITEM	QUAN.	PART NO. OR DRAWING NO.	DESCRIPTION	MATERIAL	REMARKS
1	1	C-09907	TANK JACKET	C STEEL	
2	1	C-09906	MAIN BODY	304 ST ST	
3	4	B-09902	MOUNTING LUG	HRS	
4	4	C-09903	LEG	HRS	
5	1	C-09905	COVER DETAILS	304 ST ST	
6	60		1/2"-13 BOLTS 1" LONG	CAD PLATED STEEL	
7	60		1/2"-13 NUTS	CAD PLATED STEEL	
8	As Req		1/16" ASBESTOS GASKET 500°F OPERATION		
9	1	C-09912	LOADING DOOR	304 ST ST	
10	1	C-09907	JACKET RING	304 ST ST	
11	4		1/2"-13 BOLTS 1" LONG	304 ST ST	
12	4	C-09913	BAFFLES	304 ST ST	

NOTES !

- ITEM 6 ROLLED ANGLE MUST BE DRILLED TO MATCH COVER DWG NO. C-09905 (60 HOLES)
- MAINTAIN ORIENTATION OF JACKET (ITEM 1) AS DEFINED BY LOCATION OF 2" NPT HALF COUPLING AND OF JACKET RING (ITEM 10) AS DEFINED BY LOCATION OF 3/8" NPT HALF COUPLING. SEE TOP VIEW.
- NOTE ORIENTATION OF BAFFLES ITEM 12 WITH RESPECT TO COVER (ITEM 5)

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TOLERANCES EXCEPT AS NOTED DECIMALS ± FRACTIONS ± ANGLES ±					
NEXT ASSEMBLY					
USED ON 4502					
DO NOT SCALE DRAWING					
RELEASED					
JOB NO. 1123		DR. HKS		CHK. APPD.	
DATE 1-6-78		DATE		DATE	
TITLE ATACTIC POLYMER MELT TANK ASS'BL					
SCALE 3/4"=1'		DRAWING NUMBER C-09904		SHEET OF	
REV.	DESCRIPTION	BY DATE	APPD. DATE	REV.	

REF.

P -
S -

BILL OF MATERIAL

ITEM	QUAN.	PART NO. OR DRAWING NO.	DESCRIPTION	MATERIAL	REMARKS

- NOTES:
- 1. MATL - SCH 40 PIPE 316L STAINLESS STEEL, SEAMLESS
 - 2. ALL WELDS TO BE FULL PENETRATION & X RAY

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NEXT ASSEMBLY									
USED ON:				JOB NO.		DR. <i>RBR</i>	CHK.	APPD.	
DO NOT SCALE DRAWING				1123		DATE 2-13-78	DATE -- --	DATE -- --	
RELEASED				-- --					
				TITLE					
				ATACTIC FURNACE REACTOR COIL					
				SCALE		DRAWING NUMBER		SHEET	REV.
				1/4" = 1"		B - 09965		OF	
REV.	DESCRIPTION			BY	DATE	APPD.	DATE		

BILL OF MATERIAL

ITEM	QUAN.	PART NO. OR DRAWING NO.	DESCRIPTION	MATERIAL	REMARKS

TUBESHEET DETAIL SHOWN FULL SCALE 1 MAT'L $\frac{1}{4}$ " 304 SS

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DECIMALS [±]		FRACTIONS [±]						ANGLES [±]		
NEXT ASSEMBLY				JOB NO. 4508						
USED ON										
DO NOT SCALE DRAWING				DR. <i>RSR</i>		CHK.		APPD.		
RELEASED		— —		DATE 11-17-77		DATE — —		DATE — —		
				TITLE ATACTIC HEAT EXCHANGER						
				SCALE						
				DRAWING NUMBER C-09829						
				SHEET OF						
REV	DESCRIPTION		BY DATE	APPD. DATE	REV.					

BILL OF MAT'L

- 1 12" SCH 40 PIPE X 24"
- 2 12" SLIP-ON FLANGE (2)
- 3 12" WELDNECK FLANGE (2)
- 4 12" PIPE CAP (2)
- 5 2" STUB END X 6" (2)
- 6 2" BACKUP FLANGE (2)
- 7 1" THREADED HALF COUPLING
- 8 $\frac{1}{8}$ " GRAPHITE FILLED TEFLON GASKET (2)

ALL MAT'L MILD STEEL

ATACTIC POLYMER FLASH DRUM

PROJECT 1123 RBR 1/3/78

TANK TK 5

DWG #13-09878
1-7-78-MS

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DECIMALS ±	FRACTIONS ±	ANGLES ±	
NEXT ASSEMBLY			
USED ON			
DO NOT SCALE DRAWING			
RELEASED	—	—	
REV.	DESCRIPTION	BY DATE	APPD. DATE

Procedyne CORPORATION NEW BRUNSWICK, NEW JERSEY			
JOB NO. 4500	DR. <u>JKS</u> DATE <u>11-15-77</u>	CHK. DATE — —	APPD. DATE — —
TITLE <u>CIRCULATING OIL TANK</u>			
SCALE 3/4" = 1'	DRAWING NUMBER A-09828	SHEET OF	REV.

REF.

P —
S —
PS —

COOLER

L.P. NITROGEN
COMPRESSOR

H.P. NITROGEN
COMPRESSOR

TO CHEMICAL IMPURITY
REMOVAL SYSTEM
DUO 52-38-1102

(B)

POINT	Pound Moles Per Hour		
	A	B	C
He	50	50	-
H ₂	5.2 x 10 ⁻⁴	5.2 x 10 ⁻⁴	-
Ne	10.4 x 10 ⁻⁴	10.4 x 10 ⁻⁴	-
N ₂	2	2	5.40 x 10 ⁻⁴
CO	5.2 x 10 ⁻⁴	0.52 x 10 ⁻⁴	4.68 x 10 ⁻⁴
A	0.52 x 10 ⁻⁴	-	0.52 x 10 ⁻⁴
K ⁺ , Xe	0.20 x 10 ⁻⁴	-	0.20 x 10 ⁻⁴
CO ₂	0.52 x 10 ⁻⁴	-	-
H ₂ O	0.12 x 10 ⁻⁴	-	-

* ADDED TO SYSTEM
FROM N₂ SUPPLY

PRELIMINARY
OCTOBER 25, 1960

PEACH BOTTOM ATOMIC POWER STATION PHILADELPHIA ELECTRIC COMPANY			
DR	CHK	APP	APP
HAYS	10-25-60		
PROCESS FLOW DIAGRAM HELIUM PURIFICATION SYSTEM LIQUID NITROGEN WASH PROCESS			
32-SK-1503		SHEET	OF
SCALE		IN/IN	WT
REV			
GENERAL DYNAMICS GENERAL ATOMIC DIVISION P.O. BOX 400 - SAN DIEGO 16, CALIFORNIA			

RECEIVED BY TIC 4-13-91