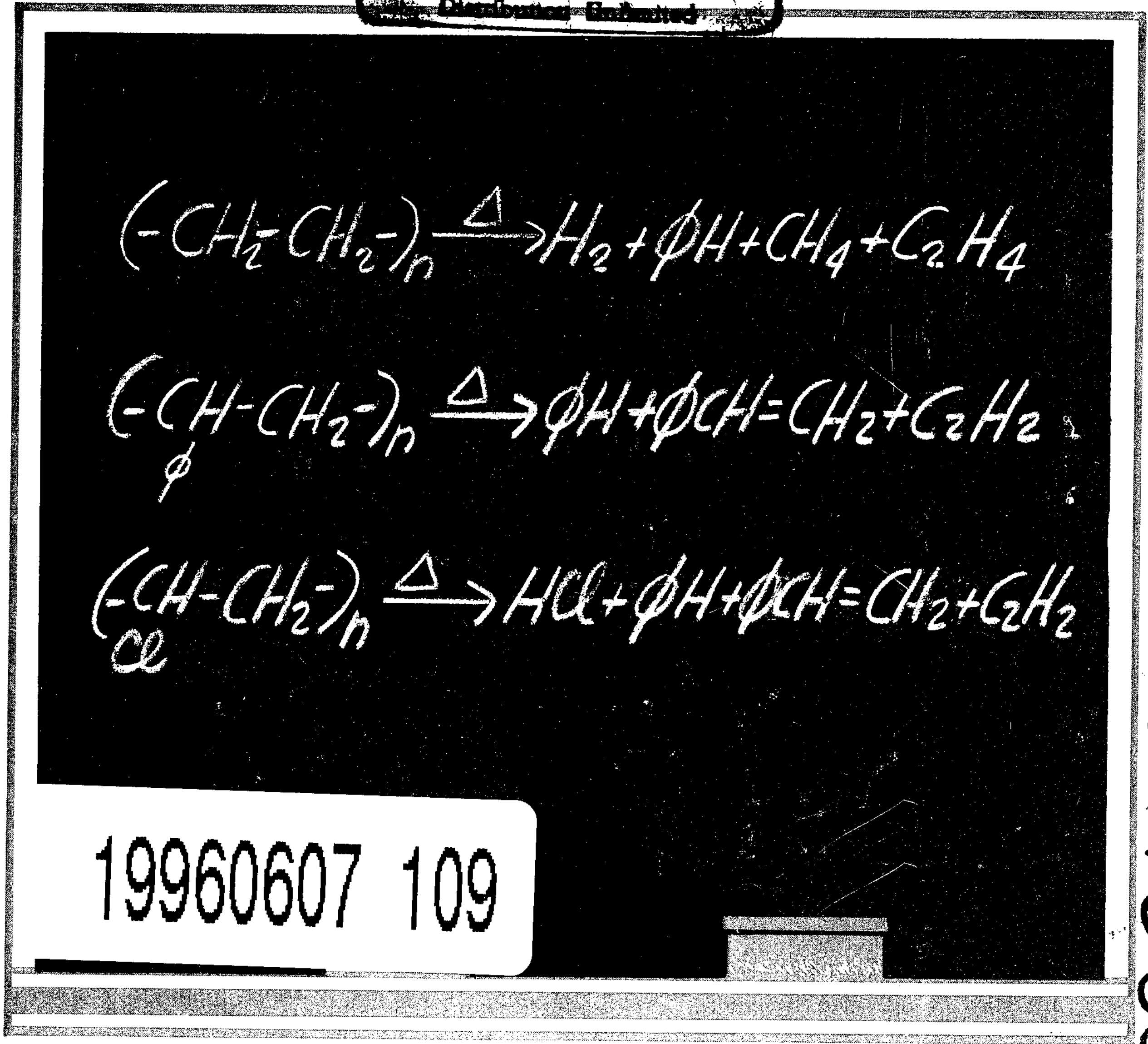
NEW CHEMICAL CONCEPTS FOR UTILIZATION OF WASTE PLASTICS



$$(-CH_2-CH_2-)_n \xrightarrow{\Delta} H_2 + \phi H + CH_4 + C_2H_4$$

$$(-\underset{\phi}{CH}-CH_2-)_n \xrightarrow{\Delta} \phi H + \phi CH=CH_2 + C_2H_2$$

$$(-\underset{Cl}{CH}-CH_2-)_n \xrightarrow{\Delta} HCl + \phi H + \phi CH=CH_2 + C_2H_2$$

An Analytical Investigation

NEW CHEMICAL CONCEPTS FOR UTILIZATION OF WASTE PLASTICS

This report (SW-16c) was prepared for
the Federal solid waste management program
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TRW Systems Group, Redondo Beach, California
under Contract No. PH 86-68-206

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FOREWORD

A MAJOR EMPHASIS of the Solid Waste Disposal Act, Title II of Public Law 89-272, October 20, 1965, was directed toward the conservation of natural resources through the recovery and utilization of the potential resources in solid wastes. Plastic wastes are a growing concern among the variety of solid wastes produced in this country. These materials are difficult to dispose of and are expected to serve an even larger role in the future.

The Federal solid waste management program has decided to investigate the possibility of reacting waste plastic with various reagents in a high-temperature, gas-phase reactor in order to produce chemicals for eventual commercial use. The first step in the overall study has involved the computer simulation of the thermodynamics and kinetics of various reaction systems. This has produced design parameters and economic data for various systems. This report represents the results of Contract No. PH 86-68-206, which was prepared by TRW Systems Group, Redondo Beach, California. The Federal solid waste management program was represented by Dr. Daniel F. Bender during the implementation of the contract and the preparation of the report.

–RICHARD D. VAUGHAN
Deputy Assistant Administrator
for Solid Waste Management

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NEW CHEMICAL CONCEPTS FOR UTILIZATION OF WASTE PLASTICS

1. INTRODUCTION AND SUMMARY

In June 1968, TRW Systems Group, under contract to the U.S. Department of Health, Education, and Welfare's Bureau of Solid Waste Management,* undertook a project to investigate analytically the use of waste plastic materials for the production of high-volume process chemicals. The objectives of the analysis were as follows: to identify waste plastic/coreactant reaction products with potential commercial value; to identify waste plastic/air combustion products that are potential air pollutants; to conceive of and provide technical and economic evaluations for chemical processes utilizing waste plastics as raw materials; and to identify potential R&D programs leading to the development of commercially viable chemical processes.

The approach developed by TRW Systems Group for this contract uses the first two phases of a generalized technique for the development of chemical processes. This technique starts with the formulation of a process concept, followed by the analysis of the proposed process using technical-economic simulation models, laboratory development of the process, pilot plant operation, and commercialization (Figure 1). Throughout this procedure management is provided information about the technical and economic implications of various results upon which they can base an informed, intelligent decision for continuing the procedure. At any stage, each of which calls for an increasingly large investment, a proposed process concept is measured against criteria based on earlier results. New information on the technical and economic feasibility is used to update the criteria for the next stage of development.

In using the first two stages of the chemical process development procedure, TRW Systems analyzed the technical and economic aspects of a wide variety of process concepts involving the use of waste plastic materials. In order to provide a maximum amount of information at minimum cost, the analyses of the chemical systems of interest were performed with literature information where available and with estimates where direct information could not be found. The technical-economic analysis was divided into two phases as follows: phase I, thermochemical equilibrium analyses; phase II, reaction kinetic analyses and preliminary design and economic analyses. Similar to the overall chemical process development procedure, this division of the technical-economic analysis into two phases with different sections was designed to provide decision points to project management where the number of systems to be considered in the subsequent analyses could be limited to those demonstrating technical feasibility at the end of the previous analysis. This approach converges on those systems demonstrating both technical and economic feasibility for laboratory investigation (Figure 2). The various portions will now be described in detail.

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*During this project, the Federal solid waste management program was a part of the U.S. Department of Health, Education, and Welfare, although the program is now in the U.S. Environmental Protection Agency.

The thermochemical equilibrium analysis (phase I) was initiated with three thermoplastic materials, polystyrene, polyethylene, and polyvinyl chloride, together with five coreactants, ammonia, hydrogen chloride, chlorine, steam, and air, plus heat without air. The various plastic/coreactant systems were examined in the gas phase by use of the TRW chemical analysis program. The product distributions resulting from the various systems under a wide range of reactant mixture, pressure, and temperature conditions were used for the identification of commercially important products. The systems in which no significant quantities of commercial-quality products were predicted were eliminated at this stage of the analysis. This procedure eliminated the following two coreactants from further consideration: ammonia, which has a very high tendency to decompose; and hydrogen chloride, which shows no tendency to react with plastics to form anything other than itself. A general approach developed by TRW Systems for this study was used to determine thermochemically feasible reaction paths for the remaining chemical systems. This second treatment considerably narrowed the range of reaction intermediates to be considered in the reaction kinetic analysis.

The management information generated in the thermochemical equilibrium analysis was used first to limit the number of chemical systems to be considered in subsequent analyses and second to determine the scope of the reaction kinetic analysis, that is, the number of species to be considered, the products desired, and the approximate operating conditions. The reaction kinetic analysis (phase II, part 1), which employed mathematical representations of the rate relationships of the various reactions occurring in the chemical system of interest, was used to determine the product distribution-time history of that system. The models and the parameters contained therein were derived from current theory and the literature. Where information was not available, estimating techniques were used to provide the necessary data. The models were formulated for the computer and used to analyze the systems of interest.

On the basis of reaction kinetic analysis it was possible to eliminate the plastics/chlorine system from further consideration, since it was not possible to identify conditions producing a commercially attractive product mix. Steam was also eliminated as a reactant although it was retained as a heat carrier. The parameters resulting from the reaction kinetic analysis, including residence times, flow rates, reactor sizing, and heat requirements, were provided to the subsequent analyses.

The data resulting from the reaction kinetic analysis were used to perform the final phase of the technical-economic analysis, preliminary design and economic analysis (phase II, part 2). The objective of this final analysis was to provide information about the economic behavior of the proposed chemical process. The analysis was based on the development of a preliminary process design corresponding to the material and energy relationships of the major process components. The various components of the process system were sized by use of data from the reaction kinetic analysis. The operating costs were then derived in terms of depreciation, utilities costs, and labor and used to define an "upgrading cost" per unit of product or raw material. This information is to be used by management together with other data, such as market analyses, to select the processes to be continued into the laboratory development phase.

The following chapters present the approaches, methods, and results of the various phases of the technical-economic analyses performed on waste plastic utilization systems. Chapter 2 presents the general approach and analytical tools employed by TRW Systems Group. The determination of the equilibrium species distributions and reaction path analyses may be found in chapter 3. Chapters 4 and 5 present the kinetic analyses and preliminary design and economic analyses, respectively. These results provide the basis for the conclusions and recommendations of chapter 6. The conclusions and recommendations include not only the proposed selection of processes for further application, but also other implications, for air pollution, for example, of the results of the TRW analysis.

2. TECHNICAL APPROACH

The technical approach taken by TRW Systems in meeting the project objectives consisted of two interrelated phases described in this chapter (Figure 3).

Phase I

Phase I of the theoretical study of waste plastics utilization employed the TRW-developed chemical analysis program (CAP). Cap is a thermochemical equilibrium computer program used to provide the following information:

1. The equilibrium product distribution of the chemical reactions of plastics with selected chemical reactants under various conditions

2. The potential air and water pollutants associated with each chemical system

3. The thermodynamically feasible reaction paths from the reaction of plastic materials with selected reagents to produce desirable end products

The approach for the first part of phase I was to apply thermochemical principles to determine the behavior of plastics/chemical agent reaction systems. The following three plastics representative of the families of plastics expected to have large-scale future consumer usage were investigated in the program: polyethylene, polystyrene, and polyvinyl chloride. Chemical agents to react with these plastics, such as oxygen (air), and steam, hydrogen chloride, chlorine, and ammonia, were selected on the basis of cost, availability, and possible reactivity with the selected plastics. The TRW thermochemical equilibrium program computed the distribution of chemical species produced at equilibrium from specified reactants as a function of temperature, pressure, and reactant composition. The program is capable of describing systems containing gases, pure liquids, pure solids, and solutions. It requires as inputs only the chemical formulas, entropies, and enthalpies of the reaction products. Given the selected plastics and chemical agents, possible reaction products were selected, and the necessary thermodynamic data for these products obtained. For the waste plastics analysis, only a small number of chemical elements are involved in the possible products as follows: carbon, hydrogen, oxygen, nitrogen, and chlorine.

After all the necessary information was collected and placed on the program input tapes, the analysis was conducted as follows: (1) by calculating rapidly and inexpensively the product distribution for a broad range of initial compositions and temperature and pressure conditions; and (2) by examining the outputs for economically significant product concentrations and potentially harmful air or water pollutants. Further calculations were made to determine quantitatively the effects of the reaction conditions on the concentrations of important products.

The second part of phase I applied the thermochemical computer program to determine the thermodynamically feasible reaction paths. In the equilibrium analysis performed during the first part of phase I, the reactant systems were essentially reduced to an elemental composition and recombined into the products according to thermodynamic principles describing equilibrium. It was then necessary to determine if an actual chemical reaction path could be described, that is, whether or not some required intermediate reaction step was likely to occur thermodynamically.

The thermochemical equilibrium program was applied to reaction path analysis simply by limiting the number of products considered at each stage to those that were possible intermediates for the next stage. For example, the polyethylene/chlorine coreactant system predicted benzene, methane, hydrogen, and hydrogen chloride as the principal equilibrium products. The first stage of the reaction path analysis eliminated these from consideration and found ethane, propane, and toluene as the next most feasible intermediates. A subsequent deletion found ethylene, pentadiene, butane, and other products as the next higher feasible intermediate stage. Following this stage, ethylene was predicted. In sum, the feasible reaction path was scoped from ethylene to the final equilibrium products through two reaction stages.

Phase II

Phase II of the theoretical study employed mathematical models for describing the various time-dependent characteristics of plastics-containing chemical reaction systems. The information generated with the models included the following: (1) quantitative data describing the time dependence of various steps in the reaction path; (2) quantitative descriptions of product distribution as a function of time and temperature; (3) parametric functions relating cost factors such as plastics pretreatment, reactants used with the plastics, value of products, and reactor design and control capabilities.

The first task of phase II was the formulation of the general physical and chemical properties of waste plastics and the waste plastics reaction chemistry into a chemical model. This was followed by the synthesis of a mathematical model that restated the chemistry model in analytical expressions. The mathematical model was translated into an equivalent computer model that described the time-dependent characteristics of each plastic containing chemical reaction system.

The second task of phase II was the application of the mathematical models developed under phase II (part 1) to the analysis of the selected reaction systems. The analysis of the reacting systems required the knowledge of (1) the reaction paths and chemical reaction equations for each step in the reaction path (phase I), (2) the parameters describing the various chemical and physical reaction rates at each step, (3) the pressure, and the temperature environment throughout the reactor, and (4) the flow velocity (or residence time) in the reactor. As mentioned already, only those reactions that appeared important from either an economic or pollution viewpoint were analyzed with the simulation models. The reaction rate parameters required to complete the description of the reactions were taken from the available literature. Where data were not available in the literature, they were estimated from data on similar systems or calculated by use of theoretical-empirical techniques.

The temperature environment and the flow rates through the reactors are parameters that were varied to determine the effects on the reaction corresponding to the desirable product distributions investigated under phase I. These conditions were varied to assess the effects on product distribution in the kinetically controlled systems. The data resulting from the variations of parameters provided the necessary information on the dependence of the reaction on residence time in the reactor.

Finally, the data resulting from these analyses were interpreted to develop relationships describing disposal costs in terms of the reactants used with the plastics, the value of the products, the complexity of the reactor and process, and the control capability requirements.

3. THERMODYNAMIC ANALYSES

The objectives of the analyses of the waste plastic systems equilibrium were to determine the following: the thermal decomposition equilibrium products for polystyrene, polyethylene, and polyvinyl chloride; the equilibrium reaction products formed by combustion of waste plastics with air; the potential pollution products of waste plastic reactions; the useful products resulting from the reactions of waste plastics with other chemical materials; and the feasible reaction paths for each system in order to scope kinetic analysis. The approach taken by TRW Systems Group to reach these objectives includes application of the chemical analysis program (CAP) computer program. This program is capable of calculating possible reaction products and reaction paths by determining the thermodynamic equilibrium of each system. The principal purpose of the CAP application is to eliminate from further consideration those systems that will not yield useful products. In addition, CAP is used to determine for each coreactant system the products that may form. The specific methods of and results for each CAP application are presented in what follows.

TRW Chemical Analysis Program and Thermochemical Data Base

Determination of theoretically expected thermochemical equilibrium product and of reaction path species distribution requires appropriate thermochemical data for each potential product. In addition, a mathematical model is required to combine these data in order to ascertain the equilibrium quantities of each product. The data and model are used under various conditions of temperature, pressure, and reactant combination to stimulate each equilibrium chemical system and reaction stage.

The mathematical model necessary to compute these equilibrium product distributions is embodied in the TRW chemical analysis program. This program is capable of simultaneously considering a maximum of 200 gaseous products together with a maximum of 20 condensed species. The basic variables considered by the program are the partial pressures of the elemental gases, such as monatomic hydrogen gas, monatomic carbon gas, and the total moles of gas in the system. These variables are used to solve a system of simultaneous equations, including mass balances for each element and a pressure match. The concentrations of the other species in the system are computed from the partial pressure of the elemental gas. The program requires curvefit coefficients (a ninth-order orthogonal polynomial is used) for the standard enthalpy and standard entropy of each species as a function of temperature. These data are used by the program to determine standard free energies from which equilibrium constants are computed for reactions of the type

$$aA + bB + cC + ... \quad A_a B_b C_c ....$$

These constants are used in the mass balance relationships to provide the appropriate weighting factors to each elemental gas.

The program is capable of providing equilibrium calculations for a complete set of thermodynamic constraints input as pairs, as follows: constant pressure, energy; temperature, volume; temperature, enthalpy; temperature, entropy; temperature, energy; volume, enthalpy; volume, entropy; enthalpy, energy; and entropy, energy. The program accepts the weight percents of the various reactants together with their molecular formulas and enthalpies of formation. Other data, such as T and P, are input corresponding to the constraints. The quantities of each element (100 g total system being assumed) are computed and species corresponding to the combinations of elements selected from the thermochemical data tape. The mass balances are set up for each element and the equilibrium compositions computed under the stipulated thermochemical constraints.

The equilibrium distribution is computed only among the species selected from the thermochemical data tape. Under the normal operating mode, data for all listed potential products of the reactant elements are selected from the species tape. The program is, however, designed to accept specifications on the product list considered, allowing specific deletions and selections of potential products. The classes of problems that can be analyzed are, therefore, expanded to include competitive reaction analysis as well as general system equilibrium.

The proper use of the mathematical model requires accurate data describing the thermochemical behavior of the various species considered as resulting from the reaction of the starting materials. The thermochemical data required by the TRW chemical analysis program for the waste plastic systems are the enthalpy and entropy as a function of temperature. These data are used not only to compute the necessary equilibrium constants but also to provide the information necessary to satisfy the thermochemical constraints.

The primary data base used by the TRW chemical analysis program was provided by the JANAF thermochemical tables prepared by the Dow Chemical Corporation.[1] These data include information on a broad range of chemical species containing a very representative selection of the common elements. The JANAF tables emphasize species that could be significant in chemical rocket exhausts. Since rocket conditions are very severe, complex organic molecules are unlikely and are not included.

In order to perform an adequate equilibrium product distribution analysis, it was necessary to develop a thermochemical data set containing additional species representative of the products expected under the less severe conditions characteristic of industrial reactors. The JANAF tables include the potential products methane, acetylene, ethylene, ethylene oxide, formaldehyde, and the various methyl chlorides among the organics; no higher organics are represented. Data for classes of compounds were required to represent the products expected with the waste plastics coreactants. The classes are the following:

(1) higher saturates, e.g., ethane;
(2) higher unsaturates, e.g., propylene;
(3) alcohols;
(4) glycols;
(5) higher aldehydes, e.g., acetaldehyde;
(6) ketones;
(7) ethers;
(8) higher chlorides, e.g., ethyl chloride;
(9) amines;
(10) higher epoxides, e.g., propylene oxide;
(11) aromatics.

Data for the first two classes were available from a compilation prepared by the American Petroleum Institute Project (API) 44.[2] The thermochemical data selected were limited to compounds having six carbons in the case of aliphatics and nine carbons in the case of aromatics since higher molecular weight materials are not found in significant quantities under the conditions planned for study.

Heat capacity (CP) data for some of the alcohols, glycols, aldehydes, chlorides, and epoxides were available from the recent compilations prepared by R. W. Gallant and published in *Hydrocarbon Processing*.[3-12] In order to compute the necessary enthalpy and entropy data as a function of temperature, data for the enthalpy of formation ($H^o{}_{f,298}$) and entropy at 25 C ($S^o{}_{298}$) are combined with the heat capacity data. These data were obtained from the literature when available.[13,14] Data not available from these sources were estimated with the techniques of S. W. Benson.[15] A computer program was written for the TRW time-sharing system to compute the appropriate enthalpies and entropies from the heat capacity, heat of formation, and reference entropy data.

Data for the ketones, ethers, amines and certain compounds of interest in the other classes were not available in compiled sources; therefore, the technique of S. W. Benson was again used to estimate heat capacity as well as heat of formation and reference entropy.[15] Whenever possible, computed data were compared with individual data available in the literature. The estimated data were used together with the time-sharing program to generate the necessary entropies and enthalpies.

Equilibrium Product Distribution Analyses

The purpose of the equilibrium product distribution analyses is to provide a sound thermochemical basis for the determination of the species resulting from the reaction of waste plastic materials with various coreactants. Three plastic materials, polyethylene, polystyrene, and polyvinyl chloride, were considered with five coreactants, hydrogen chloride, ammonia, water, air, and chlorine, as well as with no coreactants (thermal decomposition). In the following sections the products resulting with each coreactant are discussed with emphasis on the general characteristics of the reaction systems. The numerical results for each system and the equilibrium chemical species considered were summarized (Appendix A).

Thermal Decomposition Reaction Systems. The equilibrium product distributions resulting from each of the three plastic systems were examined at two pressures, 68 and 1 atm, and three temperatures, 1,472, 1,073, and 773 K. Thermal decomposition provides a basis for comparison of the effects of the coreactants on the product distribution. The primary products produced at equilibrium for the three plastic types vary with carbon-hydrogen ratio in the original plastic material (Figure 4). The relative amounts of the various products naturally vary also as a function of temperature and pressure–the amounts of the unsaturated aliphatics increasing as temperature increases and decreasing with increasing pressure. Benzene appears to be particularly favored in the polystyrene and polyvinyl chloride systems. The polystyrene $(C_8H_8)_n$ is stoichiometric to benzene, and the polyvinyl chloride $(CH_2CHCl)_n$ is also stoichiometric to benzene if hydrogen chloride is formed. Under the temperature and pressure conditions considered, the polyethylene system indicated a tendency toward dehydrogenation to acetylene and benzene. At temperatures lower than those examined in the analysis, it would be expected that ethylene would become the most favored decomposition product.

Hydrogen Chloride Reaction System. The set of pressure-temperature conditions used for the thermal decomposition was the basis of comparison for the subsequent analyses. The hydrogen chloride system represented the first coreactant analysis. For the analysis, reactant concentrations were chosen such that complete reaction would not result in large excesses of the initial materials since excesses tend greatly to promote kinetic rather than equilibrium effects. The concentrations selected were 70 weight percent polymer/30 percent coreactant, 50 percent polymer/50 percent coreactant, and 20 percent polymer/80 percent coreactant.

The hydrogen chloride systems analyses indicated that hydrogen chloride does not react significantly under the conditions examined, primarily because of the favoring of equilibrium toward the aromatic compounds (Figure 5). The product distribution is, therefore, essentially the same as is seen in the thermal decomposition analysis. It is possible, therefore, to eliminate this system from specific consideration.

Ammonia Reaction Systems. The ammonia systems were examined to indicate whether amine compounds were feasible products from waste plastic reactions. Under equilibrium conditions at the compositions, pressures, and temperatures selected, the analysis showed that ammonia formation equilibrium

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

was completely reversed supplying free hydrogen to the system (Figure 6). The hydrogen released from the ammonia severely decreased the concentrations of the unsaturated compounds, both aliphatic and aromatic. The most significant organic reaction product under these conditions is methane.

The production of methane from the waste plastics/ammonia systems is not an economically significant result. Ammonia is prepared commercially by a process including the partial oxidation of methane or other saturated hydrocarbon with air to produce hydrogen and nitrogen, which are further reacted to give ammonia. The results of the ammonia equilibrium analysis further indicate that direct hydrogenation would also be economically limited since the hydrogen is produced from similar reactions.

Water Reaction Systems. The water (steam) coreactant systems were investigated primarily to determine whether partially oxidized compounds, e.g., alcohols, were potential products of waste plastics utilization. The equilibrium product distributions were computed under the previously stated environmental and compositional conditions. Partially oxygenated product types represented in the calculations included alcohols, glycols, ethers, aldehydes, and ketones in addition to the various carbon oxides.

Under the conditions studied, no significant quantities of the various oxyorganic compounds were found in the major product distributions (Figure 7). The analyses indicated, however, the potential of a steam reforming reaction system's producing carbon monoxide and hydrogen with the waste plastics. A steam-fed catalytic reactor could eliminate the bulk plastic and produce reducing gas products. Recovery equipment would be necessary to collect the hydrogen chloride generated by the polyvinyl chloride system.

Air Reaction Systems. The steam reaction system represents a relatively inexpensive reactant that when combined with waste plastics might have economic potential as a disposal technique. The air reaction system described in this section also uses a very inexpensive reactant. The purposes of this analysis were twofold. First, the systems were examined to indicate conditions that limit the formation of products, representing a potential air pollution hazard. These analyses are concentrated on a current technology used in many places to eliminate bulk waste, substituting a potential pollution problem for the immediate bulk waste disposal problem.

Commercially significant products for these systems are absent in the temperature-pressure and composition ranges examined (Figure 8). The primary products are the expected combustion products; however, certain potential pollutants are indicated in the analyses. In the fuel-rich combustion range examined, the equilibrium analyses show significant quantities of hydrogen cyanide gas, HCN, present in all the plastics systems. Temperatures higher than those examined show a further preference for this product. This would indicate that the reactor (combustor) design used for the burning of plastic materials must include specific provision for the adequate mixing of the reactants eliminating hot spots in fuel-rich zones.

A second potential pollutant whose quantity is dependent only upon the original quantity of plastics is hydrogen chloride gas, HCl, produced from polyvinyl chloride. Its presence indicates that plastics combustion equipment must have provision for the recovery of this gas, which certainly is comparable with the sulfur oxides in potential corrosive effects on biological, metallic, and other systems exposed to it.

Chlorine Reaction Systems. Chlorine gas represents a relatively expensive reactant but one whose reactivity was considered likely to produce economically significant products. Organic chlorides have found a wide variety of commercial applications. The chlorine/plastics systems were examined in equilibrium under the usual conditions in order to predict the product mix obtained (Figure 9). As was expected, significant quantities of chloro-organic products were predicted under equilibrium conditions. The simulation of the chemical-kinetic behavior of these systems defined conditions that allowed chlorine to produce several different chlorine derivatives.

Reaction Path Analyses

The purpose of this analysis was to determine the general types of possible thermodynamically feasible intermediate species for each chemical reaction. The resulting information from this analysis was used to scope the chemical-kinetics model. A separate analysis from that of the equilibrium results reported earlier is necessary since its data are calculated by reducing the reactant system to elements and recombining them into products according to equilibrium thermodynamic principles. Calculations of this type give no hint about the possible reaction paths and species to consider. Possible intermediate species at a given step are identified by rerunning the equilibrium program and deleting all major equilibrium products found by the previous run.

Significant products are formed from polyethylene, polystyrene, and polyvinyl chloride by reacting them thermally and with the coreactants air and chlorine. These system paths and their possible intermediates were studied, and the results are now reported.

Thermal Decomposition Reaction Path Analysis. The polystyrene thermal decomposition equilibrium results indicate that benzene is in equilibrium with styrene at 1,073 K and 1 atm pressure. This equilibrium mixture represents a minimum of the relative system's free energy, or in other words the most probable distribution of species at equilibrium. When benzene is not allowed to form, the reaction yielded a new product distribution (Figure 10), which represents a higher system's free energy. This result may be interpreted to mean that these products are similar to the actual intermediates in the benzene from polystyrene reaction. The possible intermediates include toluene, the cis-trans 1-phenyl-1-propylene and the ortho-meta-para methyl-styrene.

Polyethylene equilibrium results, like polystyrene results, predict conversion of the given plastic to benzene at 773 K and 1 atm. The feasible reaction intermediates are, however, for the most part different (Figure 10). Toluene is the only species that appears in both cases. In addition to toluene, the feasible intermediates include ethane, propane, ethyl-benzene, and ortho-meta-para dimethyl-benzene.

The major coproducts of the thermal decomposition of polyvinyl chloride at 773 K and 1 atm pressure are benzene and hydrogen chloride. This is similar to the polystyrene and polyethylene decomposition, except that no hydrogen chloride can be formed in the first two systems. The polyvinyl chloride decomposition path analysis consisted of two equilibrium runs, the first excluding benzene from forming. The results of this run indicate that chlorine-substituted ethylenes and toluene are formed. A second run deleting these as possible products yielded ethyl benzene as the next level of feasible product.

Air-Plastic Reaction Path Analysis. The reaction path analyses for the determination of feasible intermediate species for the air-plastic reactions are presented in this section. As in the thermal decomposition equilibrium analysis and reaction path analysis, benzene is one of the major coproducts formed from the three waste plastics (773 K, 1 atm, and with 70 percent plastic material and 30 percent air by weight). In addition to benzene, carbon monoxide, carbon dioxide, and methane are formed at equilibrium from the polystyrene-air system. When these products are not allowed to form in the polystyrene system, toluene appears to be the next most feasible product. After all previous products are deleted, the styrene monomer is the most feasible species (Figure 11).

Polyethylene-air reaction equilibrium products include hydrogen as well as those products found in the polystyrene-air reaction system under similar conditions. Although the equilibrium results are similar, a number of differences are found in the distribution of feasible intermediate species. In addition to toluene, which is found in both systems, propane, ethylbenzene, and ortho-meta-para-dimethyl benzene are formed. When these are excluded, propylene, ethanal, and dimethyl ketone are found to comprise the next level of feasible products (Figure 11).

The polyvinyl chloride equilibrium products are similarly distributed to those previously listed except that in place of hydrogen, hydrogen chloride is formed. The first level of feasible products includes toluene and styrene. After deletion of these products, ortho-meta-para methyl-styrenes and xylenes, and ethanal become feasible products (Figure 11).

Chlorine Reaction Path Species Analysis. Reacting polystyrene with chlorine at 773 K, 1 atm, and 70 percent plastic to 30 percent chlorine (on a weight basis) results in the reaction products benzene and tetrachloroethylene with hydrogen chloride as a coproduct (Figure 12). The styrene monomer comprises a secondary level of feasible materials when the previous product formations are suppressed. After styrene, the next level of feasible products includes toluene and tetrachloroethane.

The polyethylene reaction path equilibrium analysis identified benzene, methane, and hydrogen along with hydrogen chloride as the major products. These were formed at 773 K, 1 atm, and 70 percent polyethylene by weight. After suppression of the products, a rerun of the chemical equilibrium program predicted ethane, propane, and toluene as the next set of feasible intermediates. A second product suppression and rerun yielded 1,4 pentadiene; 1,3 butadiene; ethylene; and butane as feasible intermediate products.

The final path analysis studied polyvinyl chloride and chlorine reacting at 773 K and 1 atm pressure with a mixture of 70 percent by weight polyvinyl chloride to chlorine. The final equilibrium mixture under these conditions gave methane, benzene, tetrachloroethylene, and hydrogen chloride as products. Feasible intermediate products included toluene, the three isomers of dichloroethylene, isomers of tetrachloroethane, and ortho-meta-para dimethylbenzene. A rerun of the equilibrium program gave styrene as a feasible intermediate after all previous major products were suppressed (Figure 12).

4. KINETIC ANALYSES

Phase I of the waste utilization program was based on the application of a TRW-developed thermochemical equilibrium computer program. This program determined equilibrium reaction species concentrations resulting from chemical reactions of plastics in various environments. In addition, the program selected thermochemically feasible reaction paths from the total number possible. The kinetic analysis expanded the phase I equilibrium data base by determining residence times, flow rates, reactor sizing, and heat requirements for each system. Emphasis of the kinetic analysis was placed on identifying reaction systems of an economic potential that would lead to the development of commercially attractive chemical processes. The primary purpose of the kinetic analysis is to provide time-dependent data resulting in a consistent characterization of each system.

The information compiled from phase I and from the literature was used to delineate those reactions and reaction mechanisms that would yield the identified final products. The reactions were combined with a heat and material balance to complete the chemical-kinetics model. In some cases, the rate parameters, and the enthalpy and heat capacity data for the models were not obtainable. For these, the data were estimated by methods developed by Benson.[15] This information resulted in the formulation of mathematical models describing the time and temperature behavior of chemically reacting waste plastic systems.

Following the formulation stage, the models were programmed into equivalent computer programs capable of simulating a broad range of operating conditions. The resulting computer programs were used to simulate the process unit operations for determining technical-economic characteristics of the total system. The results of these analyses are interpreted in terms of the following: cost factors associated with various reaction processes, performance criteria necessary for research on new reaction process concepts, and the design of chemical reactors capable of providing desired product distributions.

The results of the polystyrene, polyethylene, and polyvinyl chloride thermal decomposition kinetic analyses using nitrogen gas as the heat source are presented now, followed by the waste plastics/chlorine gas coreactant analyses and the coreactant system analyses of the three waste plastics with water and with air.

Thermal Decomposition Kinetic Analysis

The approach for the kinetic analysis of thermally decomposing polystyrene, polyethylene, and polyvinyl chloride waste plastics consisted of the following: (1) determining the physical and chemical properties of the reactants, (2) determining the decomposition mechanism, (3) formulating a chemical model, (4) translating the chemical model into a mathematical model, (5) programming the mathematical model into an equivalent computer program, and (6) simulating each reaction system under various reaction conditions. The results are presented as concentrations of reaction products and nitrogen gas (heat source) as a function of time. From these data the reactor geometry and heat requirements were defined.

Polystyrene. The kinetic behavior of a chemical system is strongly dependent upon the physical and chemical properties of the reactants. In order to treat realistically these time-dependent characteristics of the polystyrene decomposition reaction, the following physical and chemical properties of waste polystyrene were postulated from information reported in the literature: (1) polystyrene waste plastic contains thermally active sites ("weak links"), which are randomly distributed within each molecule; (2) waste polystyrene is heterogeneous with respect to initial chain size; (3) the reactant plastic can be characterized by an initial "most probable" molecular weight distribution; (4) plastic fed to the reactor is selected at random, that is, no distinction is made on the basis of degree of polymerization, molecular weight, etc; (5) it is homogeneous with respect to monomer type, i.e., polystyrene only.

Initially, the decomposition of commercial polystyrene occurs by a random mechanism owing to weak links formed in the polymerization reaction. When a weak link is broken, a number of monomers are split off. This phase continues until the weak links are exhausted. During this rapid initial period, inhibitors are produced to give rise to an induction period that is very pronounced at 625 K and below. Above 675 K the induction period is not experimentally evident for either unfractionated or fractionated samples.

A depolymerization reaction occurs at the end of the induction period by the following mechanism: chain end initiation reaction, transfer reactions, propagation reaction, termination reaction. Transfer reactions are at a trace level for temperatures between 700 and 1,000 K, which means high styrene monomer yield with 100 percent selectivity.

This chemical model was reformulated in terms of a mathematical model that describes the time-dependent or kinetic behavior of waste plastic chemical reactions. It is composed primarily of systems of interdependent ordinary differential equations. For waste plastic thermal degradation models, these equations describe the rates of product formation as a function of time and distance within a chemical reactor. Usually, these equations can be solved numerically only by high-speed computing machines. It is for this reason that the waste plastic mathematical models are coded into equivalent computer programs. The computer programs are written in a general format in order to facilitate conversion from one set of differential equations describing polystyrene into another set describing either polyethylene or polyvinyl chloride.

The grams of styrene produced per gram of polystyrene as a function of the solid residence time (that is, the residence time of the solid waste plastic material) were computed for a broad range of temperatures (Figures 13, 14, and 15). As expected, the higher the temperature the faster the rate; however, the increase in rate must be balanced against heat requirements. The heat necessary to maintain an isothermal reactor is supplied by hot nitrogen gas that is preheated to 1,500 K. At 92 percent conversion the reactor requires a total of 15.5 g of nitrogen per gram of styrene when the initial nitrogen is 1,500 K. This may be compared with 82.0 g of nitrogen per gram of styrene at 1,000 K initial nitrogen temperature. The quantity of nitrogen (at 1,500 K) required per gram of styrene produced increases with reactor temperature at fixed conversion (Figure 16). The economies in nitrogen gas at the higher conversion are due to the fixed amount of nitrogen (1,500 K) required to bring the waste plastic from ambient temperature to reactor temperature.

The reactor residence time-heat requirement tradeoffs, the required conversion, and the physical properties of unreacted waste plastic dictate the necessary solid residence time and as such the total volume. From this, an economical reactor system and associated process were designed and used to estimate the costs for processing each pound of waste polystyrene.

Polyethylene. As expected in a kinetic study, the physical/chemical properties of waste polyethylene are important in characterizing its time-dependent nature. Spectroscopic investigations show that polyethylene is not strictly a straight polymethylene chain but contains methyl, carbonyl, and peroxide groups. Moreover, it has been determined that polyethylene is branched with one branch point present on the average for every 50 carbon atoms. Additional physical properties of waste polyethylene are equivalent to the ones listed for polystyrene. The decomposition reaction mechanism for polyethylene proceeds, however, in a different fashion from that of polystyrene. Polystyrene degrades into monomer styrene between 700 and 1,000 K. Reaction products resulting from polyethylene contain little monomer but primarily paraffins with as many as 50 carbon atoms, depending on the temperature. The degradation reaction for temperatures between 660 and 710 K appears to be of zero order over a large range of percent weight loss. The mechanism probably consists of splitting off large molecular fragments in rapid succession once the chain is initiated.

After the chemical and mathematical models were derived, the necessary simulation model was programmed and an analysis was completed that characterized the system. The quantity of product produced versus residence time with a polymer of 822 average degrees of polymerization varies strongly with temperature (Figures 17 and 18). Temperatures between 685 and 710 K were found to be practical reactor temperatures, heat input requirements and residence times being considered. Complicating the analysis is the fact that the rate was found to be affected by the average degree of polymerization (ADP). Inasmuch as it is impossible to determine waste polyethylene ADP a priori, its effect must be considered parametrically in designing the reactor. The effect of ADP over a range of 571 to 3,000 units was examined in the present study (Figure 19). As in the polystyrene analysis, the heat versus rate or conversion was studied for the reaction design (Figure 20). The product distribution for a polyethylene thermal degradation system was calculated at 710 K (Table 1). The relative concentrations of species are approximately constant at each conversion.

Polyvinyl Chloride. Polyvinyl chloride is essentially a linear polymer of "head to tail" configuration. A small amount of branching is present composed probably of carbon and chlorine atoms. The general properties of waste polyvinyl chloride material are the same as those presented for polystyrene.

The thermal degradation of polyvinyl chloride is primarily a dehydrochlorination reaction. After a short initial period, hydrogen chloride is evolved under a mechanism of approximately 3/2 order in the fraction of undegraded units. Following hydrogen chloride evolution, a secondary decomposition occurs that yields numerous organic products (Table 2). The effects of temperature on the hydrogen chloride and on the hydrocarbon reaction were examined to determine feasible reaction conditions (Figures 21, through 24). The net result is that the reaction is commercially feasible above 675 K. The hydrogen chloride and hydrocarbon product evolution was examined as a function of solid residence time (Figure 25), 723 K being selected as the nominal case. Here the hydrogen chloride is the predominant product at all residence times. The overall reaction is exothermic owing to the predominance of the exothermic hydrogen chloride stage over the endothermic organic evolution stage. As such, no nitrogen is required after the initial 1.2 g/g of waste plastic polymer necessary to raise the temperature from 300 to 723 K.

Thermal Decomposition Preliminary Reactor Designs. The thermal decomposition reactor mathematical models were based on engineering design of a semicontinuous moving-bed reactor. The reactors are to be operated isothermally by supplying "hot" nitrogen gas at various points within the reactor. Waste plastic is fed continuously from above. Any unreacted material is removed in a batch fashion by switching to auxiliary reactors.

Resulting data from the reactor models are used to develop relationships describing plastic-processing costs as a function of coreactants, value of reaction products, capital costs and operating costs. A schematic diagram of the designed plastic thermal decomposition reactor was prepared (Figure 26), and the specific dimensions of the reactor for each of the decomposition systems were summarized (Table 3).

Waste Plastics/Chlorine Kinetic Analysis

Polystyrene. This section describes the results of the polystyrene/chlorine kinetic analysis. Reactions of polystyrene waste plastic and chlorine gas were kinetically simulated with two different reactor configurations. The first configuration consisted of a two-stage reactor; the first reactor used hot nitrogen gas to decompose the polymer thermally, followed by a second reactor that reacted the monomer with chlorine gas (Figure 27). The second configuration consisted of a single reactor using chlorine gas reactant as the heat carrier. This reactor is equivalent to the thermal decomposition reactor presented earlier (Figure 26).

Kinetic results of the first-configuration second reactor indicated that the monomer/chlorine reactions proceed slowly in the presence of excess nitrogen. A modification to this configuration was proposed whereby nitrogen was removed before the second reactor. Subsequent analyses calculated more favorable kinetics. In addition, the volume of the second reactor without nitrogen was found to be approximately 3 percent that of an equivalent reactor with nitrogen at equal conversions. The product analysis of the second reactor (Table 4) and the product produced per gram reactant (Figure 28) were calculated for both systems (with and without nitrogen at 900 K).

The second configuration consisted of a single reactor where polystyrene reacts with chlorine gas directly. Here chlorine acts as the heat source as well as the coreactant. The kinetic analysis of this reactor indicated an almost total conversion of waste polystyrene gas phase products to hydrogen chloride and heavily chlorinated styrene with some chlorinated toluene and methane derivatives.

From a kinetic or reaction control standpoint, the practical system would be the first configuration, where chlorine gas is reacted with styrene monomer after the nitrogen-waste plastic decomposition reaction (first reactor) and after nitrogen removal. Further analyses of this two-stage reactor indicated that increasing chlorine/styrene ratio (or temperature) favors formation of (ortho, meta, para) 1,2 dichloro-ethyl chlorobenzene over 1,2 dichloro-ethyl benzene as the major product (Figure 29). Both systems were found to be impractical from an economic and product yield point of view (see what follows).

Polyethylene and Polyvinyl Chloride. Kinetic analyses similar to the polystyrene/chlorine analysis were completed for polyethylene and polyvinyl chloride waste plastics reacting with chlorine. Both waste plastic systems were modeled with the two configurations already described.

The results of these analyses were analogous to the results reported in the previous section, where the two-reactor configuration was found to be favored from a process control standpoint. Various mixtures of hydrocarbons and chlorinated hydrocarbons could be produced by varying feed concentrations of nitrogen and chlorine. The second configuration (single reactor) gave hydrogen chloride as the major product for both plastics. In addition, the mixed-feed alkane-alkene stream of polyethylene produced a mixture of carbon tetrachloride, hexachloroethane, etc., whereas chlorinated toluene and styrene, along with carbon tetrachloride, hexachloroethane, etc., were produced from the polyvinyl chloride decomposition stream.

The general usefulness of the waste plastic/chlorine system is limited by the fact that chlorine reactions are not very selective. All types of alkane hydrogens are attacked with almost equal probability. Introduction of one chlorine atom does not appreciably affect the replacement rate of a second or third, etc., hydrogen atom. The net result is that all possible products are obtained when the reaction is chlorine limited. Excess chlorine replaces all available alkane hydrogens at a very rapid rate.

In summary, kinetic analyses of the three waste plastic/chlorine coreactant systems demonstrated the usefulness of the two-reactor configuration from a control or final product standpoint. From an economic point of view, however, this configuration is unfavorable, since it requires the heating of waste plastic to the decomposition temperature followed by cooling to remove part or all of the nitrogen. Subsequently, the stream must be reheated to react with chlorine. Most importantly, the value of the final chlorinated products (including upgrading costs) is less than the value of the thermal decomposition products. Commercially, it would be possible to hydrolyze the mixed chlorides to produce mixed alcohols. Reactions with ammonia would yield amines and with sodium hydrosulfide would yield mercaptans and sulfides. For reactions such as these to be commercially rewarding, a market for these chemicals would have to be identified.

Waste Plastics/Steam Kinetic Analysis

Presented in this section are the results of the kinetic analyses of polystyrene/steam, polyethylene/steam, and polyvinyl chloride/steam digestion systems. The objective of these studies was to determine the feasibility of using steam-fed reactors to eliminate bulk waste plastics and supply products valuable for fuel. Results indicate processes could be designed for thermal decomposition using steam that would be more economical than corresponding waste plastics/nitrogen thermal decomposition systems.

Waste plastics/steam digestion systems were analyzed with use of equilibrium thermodynamics in phase I of the waste plastics utilization study. The purpose was to determine whether partially oxidized compounds such as alcohols, glycols, ethers, aldehydes, and ketones were potential products. Results of phase I showed that no significant quantities of these chemicals will be found under the conditions studied. They did, however, indicate the potential of steam-reforming reaction systems' producing carbon monoxide and hydrogen. These reforming systems were not kinetically simulated, since the reactor would require a catalyst development that would be outside the scope of this study. A system without catalysis was, however, modeled that would thermally decompose the bulk plastics with steam as the heat source.

The analyses of the waste plastic/steam systems without catalysts gave kinetic results similar to those of the waste plastics/nitrogen systems in that the product distributions were essentially the same for each system. There are however, advantages in using steam as a source of heat in place of nitrogen. This is due to the larger heat capacity of steam as compared with nitrogen, which reduces the carrier gas concentrations, and hence, the reactor gas volume. For example, the polyvinyl chloride decomposition reactor operating isothermally at 723 K requires 0.9 mole of nitrogen at 1,500 K as compared with 0.7 mole of steam at 1,500 K. A nitrogen/steam comparison was calculated for a variety of thermal decomposition systems and conditions (Table 5).

A fourth waste plastic/steam system was simulated wherein an equal-weight mixture of polystyrene, polyethylene, and polyvinyl chloride was fed to the reactor. The product distribution (Table 6), the reactor design (Figure 30), the geometries (Table 7), and steam (as a heat carrier) requirements (Figures 31 and 32) were calculated for the composite feed system as necessary for the economic analysis.

Waste Plastics/Air Kinetic Analyses

The phase I equilibrium analysis and reaction path analysis indicated the possibility of reacting waste polystyrene, polyethylene, and polyvinyl chloride with air. From the point of view of the technologic and economic importance of hydrocarbon oxidation, the air oxidation of waste plastics was considered an important system for analysis. The utilization of oxidized waste plastics could be important in two separate applications as follows: partial oxidation to synthesize important industrial compounds, and complete oxidation to produce energy. In this light, the waste plastics/air reactor systems were modeled for an adiabatic reactor and an isothermal reactor with two configurations.

The adiabatic reactor system was simulated to determine the value of using waste plastic materials as a source of energy. Four separate systems were simulated as follows: polystyrene/air, polyethylene/air, polyvinyl chloride/air, and an equal-weight mixture of the three plastics with air. The system consisted of an adiabatic reactor with plastic material and air input at ambient temperature (298 K). A preliminary kinetic analysis indicated the lack of usefulness of rate data (by itself) for determining reactor geometry.

For the waste plastic systems considered, the observed products are very near equilibrium for any reasonable reactor geometry. For this reason, the complete simulation model was not formulated. Rather, the preliminary kinetic analysis was expanded by use of the CAP program to determine reactor heat requirements. These requirements along with estimated heat transfer coefficients allowed the determination of a heat transfer area. As is customary with combustion reactors, the preliminary reactor design and estimated costs are based on this surface area. A preliminary reactor design was prepared for the waste plastic/air system (Figure 33), and the product distribution, reactor exit temperature, and air input were calculated for the four systems (Table 8). Polystyrene and polyethylene yielded heat value products; polyvinyl chloride and the mixture yielded heat value products and hydrogen chloride.

The isothermal reactor was modeled in two separate configurations. The first configuration consisted of a single reactor using air as the heat source as well as the reactant. The second configuration consisted of two reactors; the first reactor thermally decomposes waste plastics into products, using nitrogen or steam as the heat source. Following this reactor, a second reactor is used to react the decomposition products with air under mild conditions. The first configuration was found to be impractical from a reaction control standpoint. In addition to the all but uncontrollable heat transfer problems, local hot spots encourage the formation of air pollutants such as hydrogen cyanide. The second isothermal configuration was found controllable and without pollutants, but owing to the thermal decomposition product mix, the partially oxidized product mix from the second reactor was found commercially unattractive.

In summation, the isothermal reactor configurations were found to be commercially unattractive. The polystyrene and polyethylene adiabatic reactors were found to be commercially feasible for energy production. Polyvinyl chloride and the waste plastic adiabatic reactors were found to yield hydrogen chloride and heat.

5. PRELIMINARY DESIGN AND ECONOMIC ANALYSES

The objective of this portion of the investigation was to provide information regarding the economic potential of proposed chemical processes for waste plastics utilization. The analyses were based on preliminary process designs accomplished by use of chemical engineering principles together with material and energy relationships supplied by reaction kinetic analyses.

Three of the originally proposed coreactants survived the screening and evaluation phase following the chemical reaction analyses. Specifically, those coreactants were nitrogen, air (oxygen), and water (steam). The results of the economic analyses for waste plastic/nitrogen systems, wherein the nitrogen is used as a heat carrier for the thermal decomposition of polystyrene, polyethylene, polyvinyl chloride, and a mixture of equal portions of all three, are given in what follows. In the next section, the economic analyses for the four waste plastic/air (oxygen) systems are presented. In those analyses, air was used as a source of oxygen for combusting the selected waste plastics. Finally, the economic analyses for the waste plastic/water (steam) systems are discussed. In those cases, water, rather than nitrogen, was used as a source of heat for the thermal degradation of waste plastics.

Waste Plastic/Nitrogen Processes

The first process concept analyzed for the utilization of waste plastics involved using hot nitrogen to decompose thermally the selected waste plastics in a semicontinuous moving-bed reactor, followed by recovery of the reactor effluent and separation of the useful products. This section presents the results of economic analyses accomplished for proposed processes to decompose polystyrene, polyethylene, polyvinyl chloride, and a mixture of equal portions of all three. The economics for each waste plastics utilization system are presented in what follows.

Polystyrene/Nitrogen. This first proposed process for waste polystyrene utilization was based on the thermal degradation of scrap polystyrene to form pure styrene monomer (Figure 34).

The degradation is accomplished in a stainless steel reactor at 600 C in the presence of nitrogen, which is used to carry the heat required for the endothermic styrene-producing reactions. Nitrogen at 1,230 C is fed to the reactor through a number of inlets so that the temperature will remain constant throughout. A lower cost system might be based on the direct use of burner product gases to provide the heat and eliminate the need for the gas-gas heat exchanger. This configuration, however, was not considered for the economic analyses, since the effect of the oxygen carried in the heating gas would first have to be determined. The costs presented herein are therefore probably higher than what could be determined following laboratory development.

After leaving the reactor, the gaseous reaction products are cooled to 250 C by heat exchange with the nitrogen recycle from the refrigeration step and then sent to the secondary heat exchanger, where the reaction products are further cooled with water to 50 C. Refrigeration is used to cool the stream to 20 C, removing all but 0.6 percent of the styrene monomer from the gaseous nitrogen. The stream is then sent to a phase separator, and an inhibitor is added to the liquid monomer before it is pumped to the product storage tank.

The nitrogen leaving the refrigerator is recycled to the direct fired heater, cooling the effluent reactor gases on the way. In the direct fired heater step, make-up nitrogen is added to the recycle nitrogen stream (now at 460 C) and heated up to 1,230 C by means of oil/gas combination burners.

Overall capital and operating costs were estimated with the aid of computer subprograms written for the process as well as of modified existing subprograms. When the installed process equipment costs and hourly operating costs were summarized (Table 9) for a plant designed to process 12.5 million lb of scrap polystyrene per year, it was found that at current market values, the plant would gross a cost-price differential of 6.1 cents/lb of pure polystyrene processed. No estimate was made for potential waste plastic separation costs although a good part of the cost-price differential might be applied thereto.

A similar analysis was performed with use of nitrogen at 730 C to heat the polystyrene feed. It was found that the reduced temperature necessitated increasing the size of many pieces of the process equipment by a factor of five with no increase in production. Increasing the size of pieces of process equipment would have a detrimental effect on the process economics, and hence, the higher temperature was used in modeling and costing the proposed process.

Polyethylene/Nitrogen. The first proposed process for waste polyethylene utilization was based on the thermal degradation of scrap polyethylene to form useful hydrocarbons (Figure 35).

Nitrogen, used as an inert heat carrier, is preheated to 1,230 C in a direct fired heater using oil/gas combination burners. The hot nitrogen stream is then fed to the semicontinuous stainless steel reactor, where thermal degradation of the polyethylene is accomplished at a constant temperature of 440 C. The reactions are only slightly endothermic, most of the heat carried by the nitrogen being used to elevate the temperature of the polyethylene feed.

After leaving the reactor, the gaseous reaction products are cooled to 110 C by heat exchange with cold water and then sent to the secondary heat exchanger (condenser), where the stream is further cooled to 45 C (again with cold water). Phase separation is used to separate the hydrocarbons that have condensed from those that are still gaseous. Fuel credit was taken for the effluent gaseous stream and gasoline credit was taken for the condensed hydrocarbon stream.

Overall capital and operating costs were estimated by use of computer subprograms written for the polystyrene process as well as of subprograms created specifically for this process. The installed process equipment cost and hourly operating costs were summarized (Table 10) for a plant designed to process 12.5 million lb of scrap polyethylene per year, including contingencies and contractor's fee. Even with the credits taken for all products and with the separation costs ignored, the process was found to be uneconomical, and it was concluded that the process should be compared to other disposal techniques to determine its overall value.

Polyvinyl Chloride/Nitrogen. The first proposed process for waste polyvinyl chloride utilization was based on the thermal degradation of scrap polyvinyl chloride with nitrogen to yield hydrogen chloride as the major product, hydrocarbon streams receiving fuel and gasoline credit (Figure 36).

Nitrogen, used as an inert heat carrier, is preheated to 1,230 C in a direct fired heater using oil/gas combination burners. The hot nitrogen stream is fed to the semicontinuous stainless steel reactor, where thermal degradation of the polyvinyl chloride is accomplished at a constant temperature of 450 C. The overall system is exothermic, the heat carried by the nitrogen being used to elevate the temperature of the polyvinyl chloride feed.

After leaving the reactor, the gaseous reaction products are sent to the scrubbing system, which is capable of removing 99 percent of the hydrogen chloride from the reactor effluent.[15] The scrubber process allows recovery of the hydrogen chloride either as acid, at 18 Baume, or, with the aid of a simple stripping system, as anhydrous hydrogen chloride.

The installed process equipment cost and hourly operating costs were summarized (Table 11) for a plant designed to process 12.5 million lb of scrap polyvinyl chloride per year, including contingencies and contractor's fee. At current market values there is no gross cost-price differential for the processing of pure polyvinyl chloride, and this indicates that further information is required for determining the potential profitability of this process.

Mixed Waste Plastics/Nitrogen. This proposed process involves the thermal decomposition of a mixture of equal portions of polystyrene, polyethylene, and polyvinyl chloride, using hot nitrogen (Figure 37).

Nitrogen, again used as an inert heat carrier, is preheated to 1,230 C in a direct fired heater using oil/gas combination burners. The hot nitrogen is fed to the semicontinuous stainless steel reactor, where thermal degradation of the waste plastics mixture is accomplished at a constant temperature of 600 C.

After leaving the reactor, the gaseous decomposition products are cooled by heat exchange, incoming nitrogen being sent to the direct fired heater for preheating. The stream temperature is then lowered to 90 C with a water spray quench that removes the hydrogen chloride and water from the stream. The condensed hydrogen chloride/water stream is sent to a phase separator for recovery of heavy hydrocarbons for gasoline credit and then on to a hydrogen chloride distillation column.

The gaseous stream leaving the quench is cooled to 50 C with a cold water heat exchanger, sent to a phase separator to remove fuel grade organics, and then refrigerated to 20 C, which removes all but 0.6 percent of the styrene monomer from the gas stream. The condensed styrene stream is further purified in a vacuum finishing column, treated with an inhibitor, and sent to storage.

When the installed process equipment costs and hourly operating costs for a plant designed to treat 12.5 million lb of mixed waste plastics per year were summarized (Table 12), with contingencies and contractor's fee included in the plant costs, it was found that the gross cost-price differential for the mixed plastic-heat system is approximately -0.1 cents/lb of plastics processed, credits based on current market values being used. This again indicated that further research is required for determining profitability.

Waste Plastic/Air (Oxygen) Processes

The second method studied for waste plastics utilization proposes reacting (combusting) the specified plastics with oxygen (air). Presented in this section are the results of analyses performed for the four waste plastic/oxygen (air) systems. Specifically, the waste plastics treated are polystyrene, polyethylene, polyvinyl chloride, and a mixture of equal portions of all three. The economics for each system of waste plastic disposal will now be discussed.

Polystyrene/Air and Polyethylene/Air Systems. The proposed process for reacting polystyrene or polyethylene with air is based on controlled combustion of the plastic in an air (oxygen) environment. Once combustion is initiated, the reaction is perpetuated by continuous addition of plastic.

Economic analysis of the polystyrene/air and polyethylene/air systems indicates that a plant designed to process 12.5 million lb of scrap polystyrene or polyethylene per year would yield about 1.5 million Btu of recoverable heat per hour.

The process cost summary for either a polystyrene/air or polyethylene/air system (Table 13) indicates that the relatively small amount of heat liberated by either system would probably not justify the purchase of process equipment to make use of it to produce steam. The alternative to steam production would be to consider the polystyrene or polyethylene to be a general fuel, fit for burning as a source of heat with a process value of $0.25 per million Btu. Contingencies and contractor's fee were included in the installed boiler unit cost.

Polyvinyl Chloride/Air and Mixed Plastics/Air Systems. The polyvinyl chloride/air and mixed plastics/air systems were considered together since the combustion products of the two systems are nearly identical and require the same process for recovering usable process heat and valuable hydrogen chloride.

The proposed process for reacting polyvinyl chloride or mixed plastics with air was based on controlled combustion of the plastic in air to yield hydrogen chloride (Figure 38).

Air and chlorinated waste plastics are fed to the semicontinuous stainless steel reactor, where combustion is accomplished at a constant temperature of 930 C for the polyvinyl chloride/air system and 1,600 C for the mixed plastics/air system. Both systems are exothermic and self-perpetuating.

From this point in the process, the steps taken to recover the hydrogen chloride are the same as those described in the economic analysis of the process for thermal degradation of polyvinyl chloride. After leaving the reactor, the gaseous reaction products are sent to the scrubbing system which is capable of removing 99 percent of the hydrogen chloride contained in the reactor effluent.[16] The scrubber process allows recovery of the hydrogen chloride either as acid, at 18 Baume, or, with the aid of a simple stripping system, as anhydrous hydrogen chloride.

The installed process equipment cost and hourly operating costs, including contingencies and contractor's fee, were summarized (Table 14) for a plant designed to process yearly 12.5 million lb of scrap polyvinyl chloride or a blend of equal portions of polystyrene, polyethylene, and polyvinyl chloride. The gross cost-price differential per pound of polyvinyl chloride reacted is 0.7 cents/(credit).

Waste Plastic/Water Processes

The third coreactant system investigated in this analysis involves the use of water (steam) as a heat carrier in the thermal degradation of the waste plastics. The chemical reaction analyses for the waste plastic/water systems without catalysts produced results similar to those of the waste plastic/nitrogen systems in that the distributions of reactor products were essentially the same. Since water has a larger heat capacity than nitrogen has, the volume of steam required in each system is significantly less than the amount of nitrogen required for the waste plastic/nitrogen reaction systems. This property of water (steam) results in the size reduction of some process equipment and hence reduces the overall process cost. The results of economic analyses completed for each of the four waste plastic/water coreactant systems are now discussed.

Polystyrene/Water. This process proposes the direct substitution of water (steam) for nitrogen in the polystyrene/nitrogen process (Figure 34). Low-pressure steam is fed to the direct fired heater (furnace), where its temperature is raised to 1,230 C. The steam is then fed to the reactor in the same manner as nitrogen is fed in the polystyrene/nitrogen process already described.

With the steam for nitrogen substitution, this process is analogous to the rest of the process for polystyrene/nitrogen. The installed process equipment cost and hourly operating costs for a plant designed to process 12.5 million lb of waste polystyrene per year (1,580 lb/hr), including contingencies and contractor's fee, were summarized (Table 15). The gross cost-price differential was found to be 6.1 cents/lb of feed.

Polyethylene/Water. The proposed process for reacting polyethylene with water again involves the substitution of steam for nitrogen (Figure 35). The remarks in the previous section concerning the preparation of steam also apply here. The process costs were summarized (Table 16), and the byproduct credits are reflected in the cost-price differential of -0.6 cents/lb of feed.

Polyvinyl Chloride/Water. The substitution of steam for nitrogen in the degradation of plastic is again the essence of this proposed process. Steam is preheated and sent to the reactor in the same manner as described for the polystyrene/water system.

Since the reaction products for this process are essentially the same as those for the polyvinyl chloride/nitrogen system (Figure 36), the reactor effluent is treated in exactly the same manner. The process cost summary was seen to vary only slightly, owing to the similarities of the two processes (Table 17).

Mixed Plastics/Water. This process is again analogous to its mixed plastics/nitrogen counterpart. Low-pressure steam is sent through the direct fired heater (furnace) and heated to 1,230 C prior to being sent to the reactor. The reactor effluent would not be first cooled by the incoming nitrogen, but the rest of the process is the same as the process to decompose a mixture of waste plastics with hot nitrogen, as already described (Figure 37). The economic analysis indicated that the gross cost-price differential for this proposed process would be 0.3 cents/lb of feed (Table 18).

6. CONCLUSIONS AND RECOMMENDATIONS

The present study has successfully demonstrated the value of computer-based simulation and analysis of proposed chemical processes. The information resulting from the analyses provides HEW management with an evaluation of a large number of chemical process concepts for the use of waste plastics as raw materials for the production of commercially valuable process chemicals. In addition to these direct results, the project has also provided information applicable to other related process techniques that might be applied to waste disposal as well as to the assessment of potential air pollution problems resulting from the incineration of waste plastic materials.

The chemical process development technique was used to analyze 18 separate concepts for the use of various plastics as raw materials in the production of commercially valuable process chemicals. The various stages of the analysis have provided the information required for narrowing the concepts to those that should be continued into the laboratory development phase of the chemical process development technique as follows: polystyrene-thermal decomposition, polyvinyl chloride-thermal decomposition, mixed plastics-thermal decomposition, and mixed plastics-combustion with air. The individual characteristics of the various systems to be examined in the laboratory development phase are now presented.

The polystyrene-thermal decomposition system produces styrene by using an inert gas as a heat source. The particular information required from the laboratory is related to the design of an efficient reactor system capable of volatilizing a maximum amount of the plastic materials. Process variables to be examined include initial solid particle size, heating gas temperature-volume tradeoffs, heating gas duct locations, reactor design, solid residence times, heating gas (the direct use of combustion products in place of nitrogen or steam reduces the costs considerably), and separation of styrene from the heating gas.

The polyvinyl chloride-thermal decomposition system produces a hydrocarbon mixture and hydrogen chloride. The parameters to be examined include those listed already, plus the identification of reactor conditions leading to a more desirable hydrocarbon mixture. The separation of the various components of the reactor effluent stream must also be examined in detail.

The mixed plastic-thermal decomposition system eliminates a major economic shortcoming of the first two separate processes in that it does not require a prereaction separation of the plastic materials. The laboratory development, however, is more complex since it would require the examination of both the individual systems and the mixed system. The depth of the examination of the individual systems would be less than that required for the first two. The information described earlier would still be required for the mixed system, but the individual system examinations would limit the regions examined.

The mixed plastics combustion with air system is essentially a chemical processing approach to a commonly used waste disposal technique. The laboratory development would be primarily concerned with the design and testing of efficient combusters and with the separation of the effluent hydrogen chloride from the combustion products. This system is of particular importance since it has been indicated throughout the analysis that specific measures are required to prevent hydrogen chloride pollution resulting from the incineration of polyvinyl chloride and other chlorinated organics.

The contract effort provides, in addition to the laboratory development recommendations already mentioned, a more general set of chemical engineering guidelines applicable to the scope of research and development programs related to waste disposal. The approach used in this study has identified materials that appear to have little or no value in the gas phase reaction of organic-chemical-based waste systems. These coreactants, hydrogen chloride and ammonia, should be considered for further research and development effort only where specific reaction technology is previously known. It has further been demonstrated that chlorine gas is highly nonselective in reactions with mixed organic systems while, of course, it still has great value in individual process systems. The lack of selectivity greatly limits its value for using waste in the production of marketable organic chlorides. The contract effort has also indicated that future R&D efforts relative to incineration should be concerned both with the design of efficient combustion reactions and with the recovery of valuable and noxious combustion effluents such as hydrogen chloride from chlorocarbons and hydrogen fluoride from fluorocarbons. Finally, the economic analyses have consistently indicated that labor is an important cost factor in both the utilization and the disposal by combustion of waste materials. The labor costs and capital costs per pound of product would be reduced significantly in large plant sizes. This indicates that strong consideration should be given to the establishment of a network of regional waste treatment plants not only for economic reasons but also for prevention of a considerable pollution problem.

The use of waste materials for the production of process chemicals has demonstrated both economic and technical feasibility under appropriate conditions (partial or complete separation and large plant size). Further R&D efforts in this general area should concentrate on the further examination of the waste plastics systems that appear promising and on the technical-economic analysis of concepts related to other specific waste constituents such as cellulosics. Simultaneously, concepts involving stage-by-stage preprocessing and separation techniques should also be examined.

7. REFERENCES

1. JANAF thermochemical tables. 3 v. (loose-leaf). Midland, Michigan, Dow Chemical Company, Dec. 31, 1960-Mar. 31, 1965. Quarterly supplement. 1 v. (loose-leaf). Sept. 30, 1962. First addendum. 1 v. (loose-leaf). Aug. 1966. Second addendum. 1 v. (loose-leaf). Aug. 1967.

2. Rossini, F. D., K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel. Selected values of physical and thermodynamic properties of hydrocarbons and related compounds. Comprising the tables of the American Petroleum Institute Research Project 44, Extant as of Dec. 31, 1952. Pittsburgh, Carnegie Press, 1953. 1050 p.

3. Gallant, R. W. Physical properties of hydrocarbons. Part 6. Chlorinated ethylenes. Hydrocarbon Processing, 45(6):153-160, June 1966.

4. Gallant, R. W. Physical properties of hydrocarbons. Part 7. Chlorinated aliphatics. Hydrocarbon Processing, 45(7):111-118, July 1966.

5. Gallant, R. W. Physical properties of hydrocarbons. Part 8. Primary alcohols. Hydrocarbon Processing, 45(10):171-182, Oct. 1966.

6. Gallant, R. W. Physical properties of hydrocarbons. Part 10. C3-C4 alcohols. Hydrocarbon Processing, 46(1):183-189, Jan. 1967.

7. Gallant, R. W. Physical properties of hydrocarbons. Part 11. Miscellaneous alcohols. Hydrocarbon Processing, 46(2):133-139, Feb. 1967.

8. Gallant, R. W. Physical properties of hydrocarbons. Part 12. C2-C4 oxides. Hydrocarbon Processing, 46(3):143-150, Mar. 1967.

9. Gallant, R. W. Physical properties of hydrocarbons. Part 13. Ethylene glycols. Hydrocarbon Processing, 46(4):183-196, Apr. 1967.

10. Gallant, R. W. Physical properties of hydrocarbons. Part 14. Propylene glycols and glycerine. Hydrocarbon Processing, 46(5):201-215, May 1967.

11. Gallant, R. W. Physical properties of hydrocarbons. Part 19. Chlorinated C2's. Hydrocarbon Processing, 46(12):119-125, Dec. 1967.

12. Gallant, R. W. Physical properties of hydrocarbons. Part 24. C1-C4 aldehydes. Hydrocarbon Processing, 47(5):151-160, May 1968.

13. Lange, N. A., comp. and ed. Handbook of chemistry. 9th ed. Sandusky, Ohio, Handbook Publishers, Inc., 1956. 1969 p.

14. Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Baily, and R. H. Shumm. Selected values of chemical thermodynamic properties. Tables for the first thirty-four elements in the standard order of arrangement. U.S. National Bureau of Standards Technical Note 270-3 (This Technical Note supersedes Technical Notes 270-1 and 270-2). Washington, U.S. Government Printing Office, Jan. 1968. 264 p.

15. Benson, S. W. Thermochemical kinetics. Methods for the estimation of thermochemical data and rate parameters. New York, John Wiley and Sons, Inc., 1968. 223 p.

16. Solving waste problem profitably. Chemical Week, 104(24):38-39, June 14, 1969.

17. Madorsky, S. L. Thermal degradation of organic polymers. New York, Interscience Publishers, 1964. 315 p. (Polymer Reviews, 7).

18. Jellinek, H. H. G. Degradation of vinyl polymers. New York, Academic Press, Inc., 1955. 329 p. (Physical chemistry. A series of Monographs, III).

19. Tsuchiya, Y., and K. Sumi. Thermal decomposition products of polyvinyl chloride. Journal of Applied Chemistry, 17(12):364-366, Dec. 1967.

8. BIBLIOGRAPHY

Bejuki, W. M. Degradation. In Encyclopedia of polymer science and technology. Plastics, resins, rubbers, fibers. v. 4. New York, Interscience Publishers, 1966. p. 647-725.

Benson, S. W. The foundations of chemical kinetics. New York, McGraw-Hill Book Company, Inc., 1960. 703 p. (McGraw-Hill Series in Advanced Chemistry).

Boyd, R. H. Theoretical depolymerization kinetics in polymers having an initial "most probable" molecular weight distribution. Journal of Chemical Physics, 31(2):321-328, Aug. 1959.

Bush, R. W., T. Park, and C. L. Kehr. Polymer oxidation process and emulsion therefrom. U.S. Patent 3, 322, 711, May 30, 1967.

Cameron, G. G. Mechanism of volatile production during pyrolysis of polystyrene. Makromolekulare Chemie, 100:255-261, Jan. 13, 1967.

Cameron, G. G., and J. R. MacCallum. The thermal degradation of polystyrene. Journal of Macromolecular Science, Part C: Reviews in Marcomolecular Chemistry, C1(2):327-359, 1967.

Flory, P. J. Configurational statistics of chain molecules. In Proceedings; the Robert A. Welch Foundation Conferences on Chemical Research. X. Polymers, Houston, Nov. 21-23, 1966. p. 133-149; discussion, p. 149-166.

Geddes, W. C. Mechanism of PVC degradation. Rubber Chemistry and Technology, 40(1):177-216, Feb. 1967.

Gilbert, J. B., J. J. Kipling, B. McEnaney, and J. N. Sherwood. Carbonization of polymers I--Thermogravimetric analysis. Polymer, 3:1-10, Mar. 1962.

Halstead, M. P., and C. P. Quinn. Thermal hydrogenation of ethylene. Transactions of the Faraday Society, 64(6):1560-1567, June 1968.

Hansel, J. G., and R. F. McAlevy, III. Energetics and chemical kinetics of polystyrene surface degradation in inert and chemically reactive environments. AIAA [American Institute of Aeronautics and Astronautics] Journal, 4(5):841-848, May 1966.

Houilleres du Bassin du Nord et du Pas-de-Calais. Process for measuring the speed of thermal decomposition of polymers. British Patent 1,080,438, Aug. 23, 1967.

Imoto, M., and T. Otsu. Studies on polyvinylchloride. III. On dehydrochlorination of polyvinylchloride by heating. Journal of the Institute of Polytechnics, Osaka City University, Series C: Chemistry, 4(1):124-128, Apr. 1953.

Jellinek, H. H. G. Degradation-termination reactions. Journal of Polymer Science, Part B: Polymer Letters, 2(4):457-459, Apr. 1964.

Jellinek, H. H. G. Depolymerization. In Encyclopedia of polymer science and technology. Plastics, resins, rubbers, fibers. v. 4. New York, Interscience Publishers, 1966. p. 740-793.

Jellinek, H. H. G. Photodegradation and high temperature degradation of polymers. Pure and Applied Chemistry, 4(2):419-458, 1962.

Jenkins, R. K., N. R. Byrd, and J. L. Lister. Chlorination of polystyrene. Journal of Applied Polymer Science, 12(9):2059-2066, Sept. 1968.

Joshi, R. M., and B. J. Zwolinski. Heats of combustion studies on polymers. Macromolecules, 1(1):25-30, Jan./Feb. 1968.

Joshi, R. M., B. J. Zwolinski, J. M. O'Reilly, and F. E. Karasz. Configurational enthalpy of polystyrene. Journal of Polymer Science, Part A-2: Polymer Physics, 5(3):705-710, May 1967.

Joshi, R. M., B. J. Zwolinski, and C. W. Hayes. Correlation procedures for estimating the enthalpies of vaporization, formation, and polymerization and certain physical properties of *a*-olefin polymers. Macromolecules, 1(1):30-36, Jan.-Feb. 1968.

Kerr, J. A., and A. F. Trotman-Dickenson. The reactors of alkyl radicals. In Porter, G., and B. Stevens, eds. Progress in reaction kinetics. v. 1. New York, Pergamon Press, 1961. p. 105-127.

Knight, G. J. Thermal degradation of polystyrene. Journal of Polymer Science, Part B: Polymer Letters, 5(9):855-857, Sept. 1967.

McAlevy, R. F., III, and J. G. Hansel. Linear pyrolysis of thermoplastics in chemically reactive environments. AIAA [American Institute of Aeronautics and Astronautics] Journal, 3(2):244-249, Feb. 1965.

MacCallum, J. R. The mechanism of initiation of random degradation. Makromolekulare Chemie, 99:282-286, 1966.

Madorsky, S. L. Rates of thermal degradation of organic polymers. SPE [Society of Plastics Engineers] Journal, 18(12):1482-1490, Dec. 1962.

Mandelkern, L., A. L. Allou, Jr., and M. Gopalan. The enthalpy of fusion of linear polyethylene. Journal of Physical Chemistry, 72(1):309-318, Jan. 1968.

Molera, M. J., and F. J. Stubbs. The kinetics of the thermal decomposition of olefins. Part II. Journal of the Chemical Society, London, 381-391, 1952.

Petersen, J., and B. Ranby. Structure and properties of polyvinylchloride. 1. Molecular structure of chlorinated PVC. Makromolekulare Chemie, 102:83-93, Mar. 1967.

Pinner, S. H., ed. Weathering and degradation of plastics. Based on a symposium at the Borough Polytechnic, London. New York, Gordon and Breach, Science Publishers Inc., 1966. 131 p.

Polymer degradation mechanisms. Proceedings; U.S. National Bureau of Standards Semicentennial Symposium on Polymer Degradation Mechanisms, Washington, Sept. 24-26, 1951. U.S. National Bureau of Standards Circular 525. Washington, U.S. Government Printing Office, Nov. 16, 1953. 280 p.

Rabinovitch, B. Regression rates and the kinetics of polymer degradation. In Tenth Symposium (International) on Combustion, University of Cambridge, Cambridge, England, Aug. 17-21, 1964. Pittsburgh, The Combustion Institute, 1965. p. 1395-1404.

Simha, R., L. A. Wall, and P. J. Blatz. Depolymerization as a chain reaction. Journal of Polymer Science, 5(5):615-632, Oct. 1950.

Simha, R., and L. A. Wall. Some aspects of depolymerization kinetics. Journal of Polymer Science, 6(1):39-44, Jan. 1951.

Simha, R., L. A. Wall, and J. Bram. High-speed computations in the kinetics of free-radical degradation. I. Random initiation. Journal of Chemical Physics, 29(4):894-904, Oct. 1958.

Smith, D. A. Modification of a thermogravimetric balance for pyrolysis in a controlled atmosphere. Rubber Chemistry and Technology, 37:934-935, 1964.

Stull, D. R. Physical properties of styrene monomer. In Boundy, R. H., and R. F. Boyer, eds. Styrene. Its polymers, copolymers and derivatives. New York, Reinhold Publishing Corporation, 1952. (American Chemical Society Monograph Series). p. 47-82.

Talamini, G., and G. Pezzin. Kinetic study on the reaction of polyvinyl chloride thermal dehydrochlorination. Makromolekulare Chemie, 39(1-2):26-38, July 1960.

Valko, L. Kinetic study of thermal dehydrochlorination of poly(vinyl chloride) in the presence of oxygen. Part II. Correlations of derived equations with experimental results. Journal of Polymer Science, Part C: Polymer Symposia, No. 16(Part 1):545-554, 1967.

Venn, R. G. A. Physical degradation of polyethylene due to oxidation. Plastics Institute, Transactions and Journal, 35(118):601-605, Aug. 1967.

Vidotto, G. A. Crosato-Arnaldi, and G. Talamini. Determination of transfer to monomer in the vinyl chloride polymerization. Makromolekulare Chemie, 114:217-225, May 1968.

Wall, L. A., and J. H. Flynn. Degradation of polymers. Rubber Chemistry and Technology. 35:1157-1221, 1962.

Wall, L. A. Polymer decomposition. Part 1. Thermodynamics, mechanisms, and energetics. Part 2. Energetics of polymer decompositions. SPE [Society of Plastics Engineers] Journal, 16(8):810-814, Aug. 1960; 16(9):1031-1035, Sept. 1960.

Wall, L. A., S. Straus, J. H. Flynn, D. McIntyre, and R. Simha. The thermal degradation mechanisms of polystyrene. Journal of Physical Chemistry, 70(1):53-62, Jan. 1966.

Williams, J. L., and K. J. Cleereman. The general physical properties of polystyrene. In Boundy, R. H., and R. F. Boyer, eds. Styrene. Its polymers, copolymers and derivatives. New York, Reinhold Publishing Corporation, 1952. (American Chemical Society Monograph Series). p. 448-516.

Wunderlich, B., and C. M. Cormier. Heat of fusion of polyethylene. Journal of Polymer Science, Part A-2: Polymer Physics, 5(5):987-988, Sept. 1967.

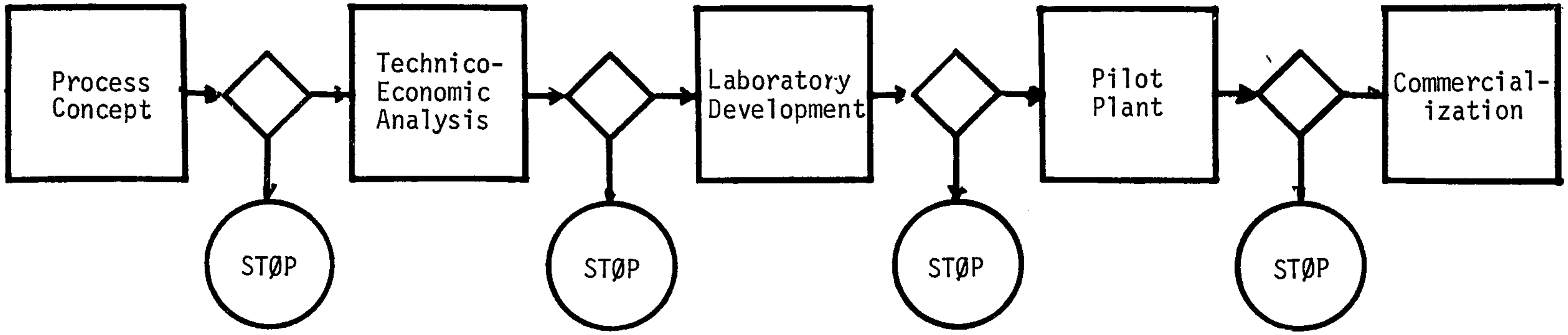
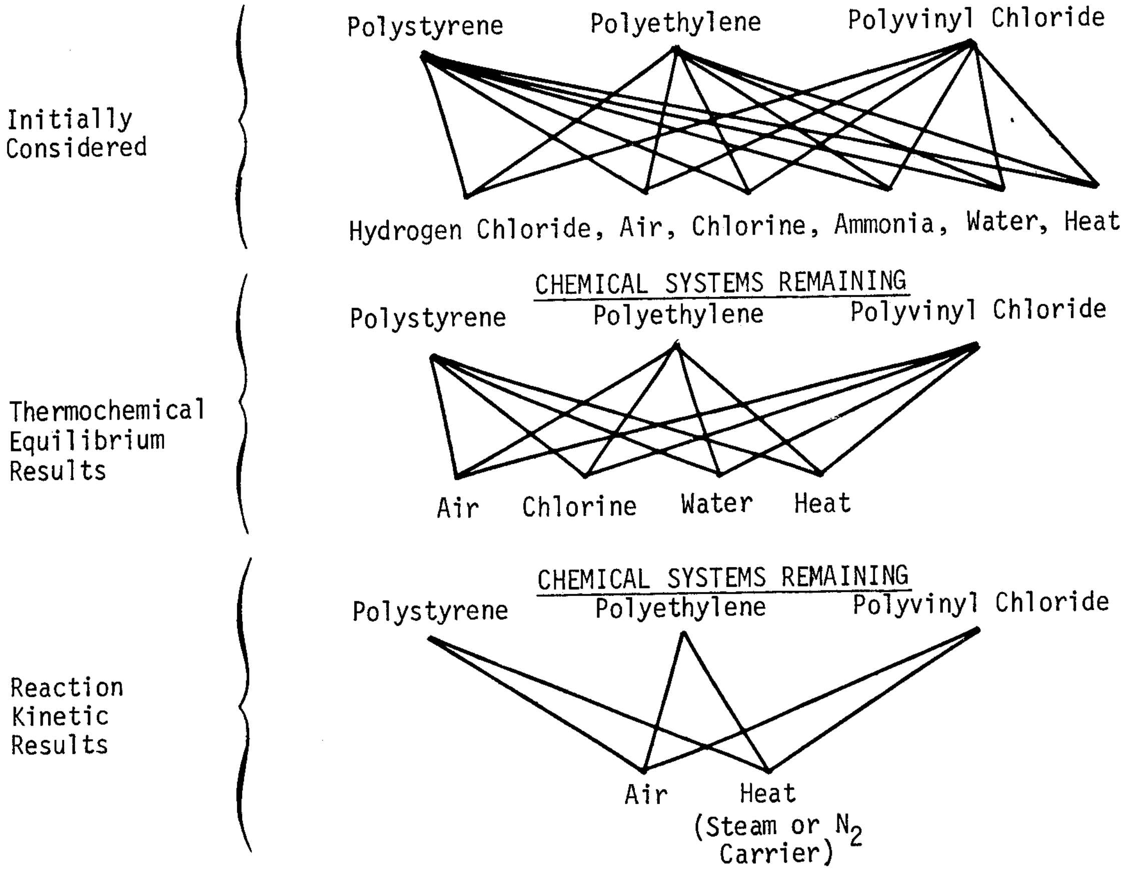


Figure 1. Generalized technique for chemical process development. Management decisions (diamonds) about continuing the process development are made on the basis of the results in the previous steps.



Preliminary Design and Economic Results

System	Product
Polyvinyl chloride - Air	Heat - HCl
Polystyrene - Heat	Styrene monomer
Polyvinyl Chloride - Heat	HCl - Hydrocarbon

Recommended For Laboratory Development

Mixed Plastics - Air	to give HCl and Heat
Polystyrene - Heat	to give Styrene
Polyvinyl Chloride - Heat	to give HCl - Hydrocarbon Mixture
Mixed Plastics - Heat	to give HCl, Styrene and Hydrocarbons

Figure 2. Technical-economic analysis for plastic/coreactant chemical processes. The analysis effort converges on those processes demonstrating both technical and economic feasibility for laboratory investigation.

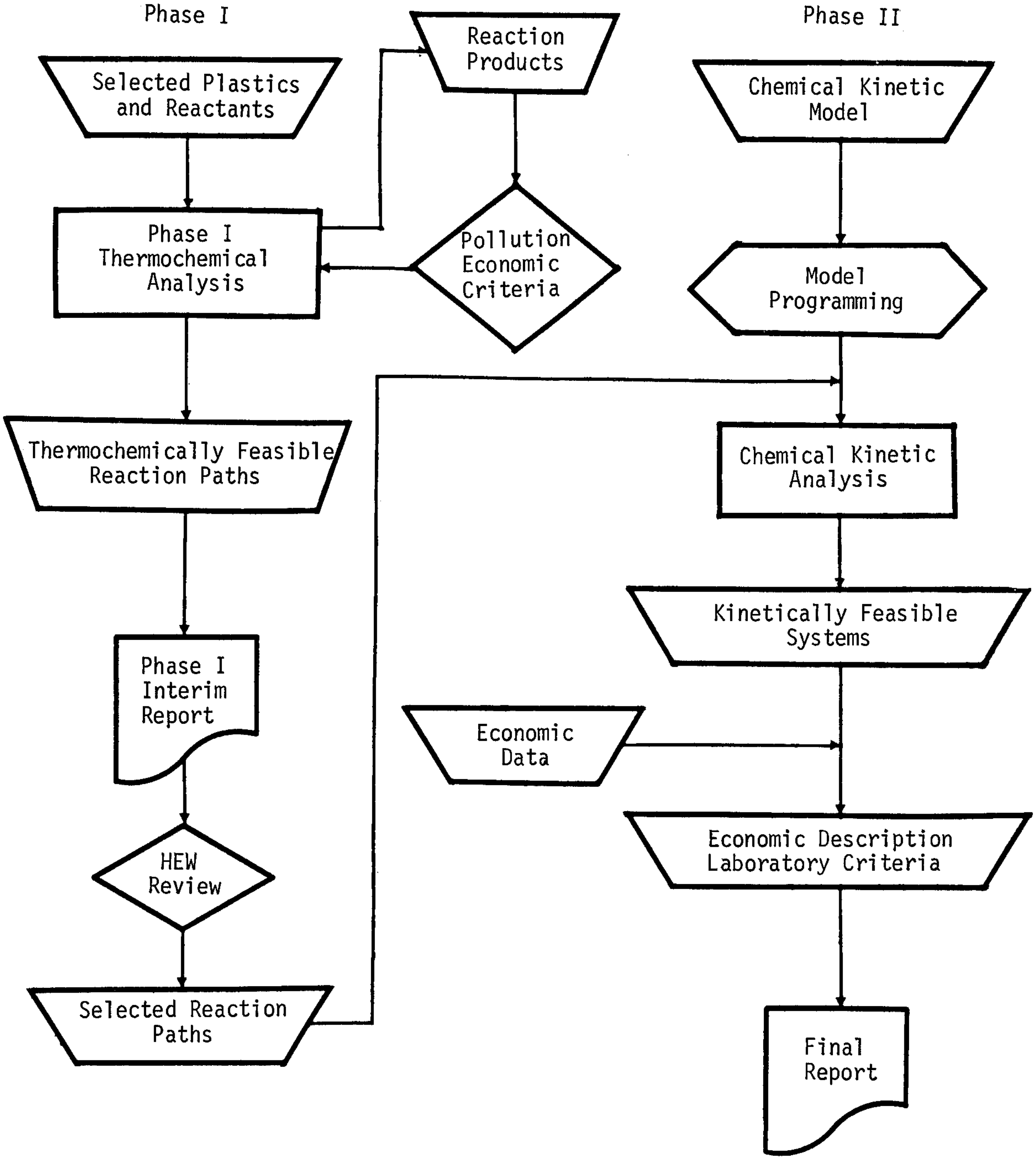


Figure 3. Project flow diagram. Step-by-step diagram of the approach applied to this study.

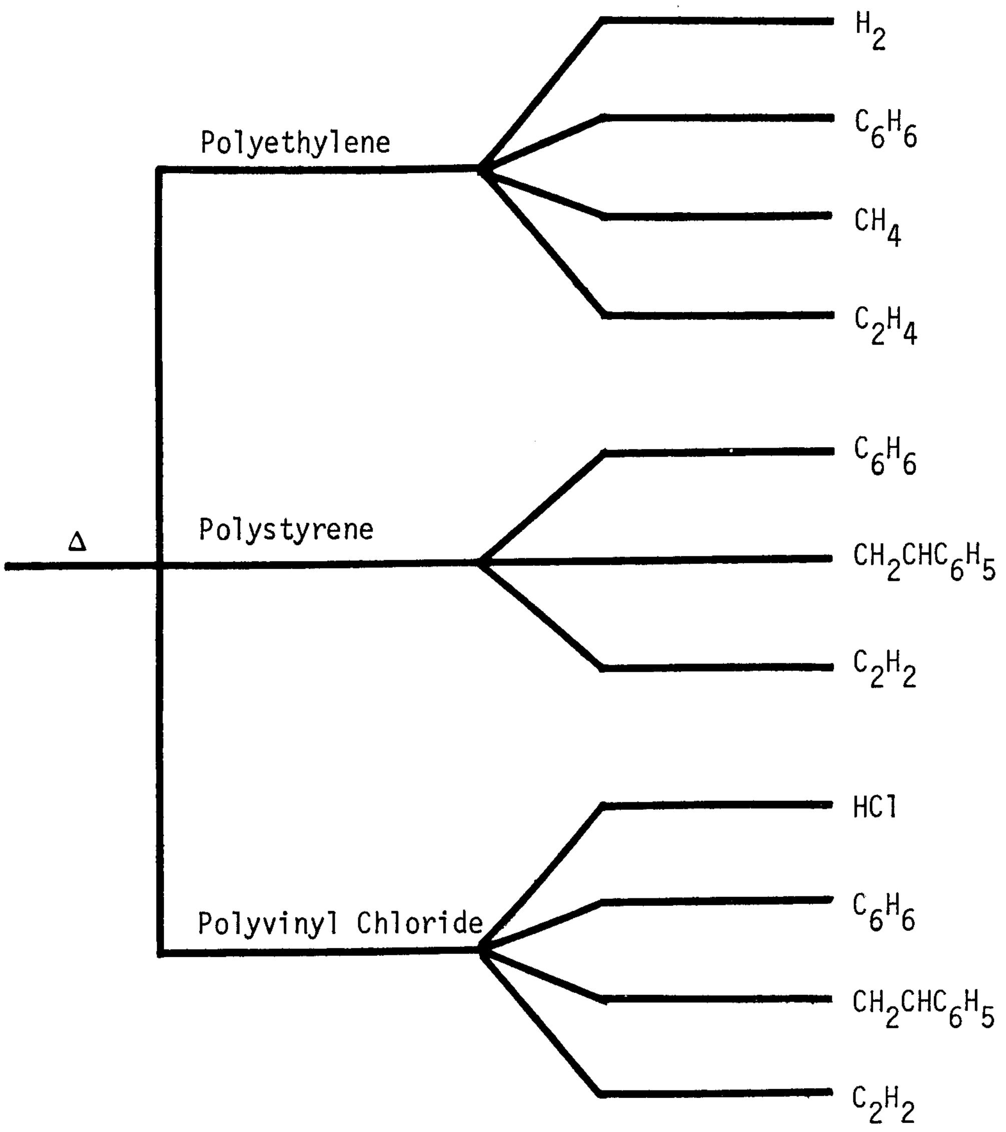


Figure 4. Thermal decomposition: major products analysis. Product species favored depend on the plastic's carbon-hydrogen ratio.

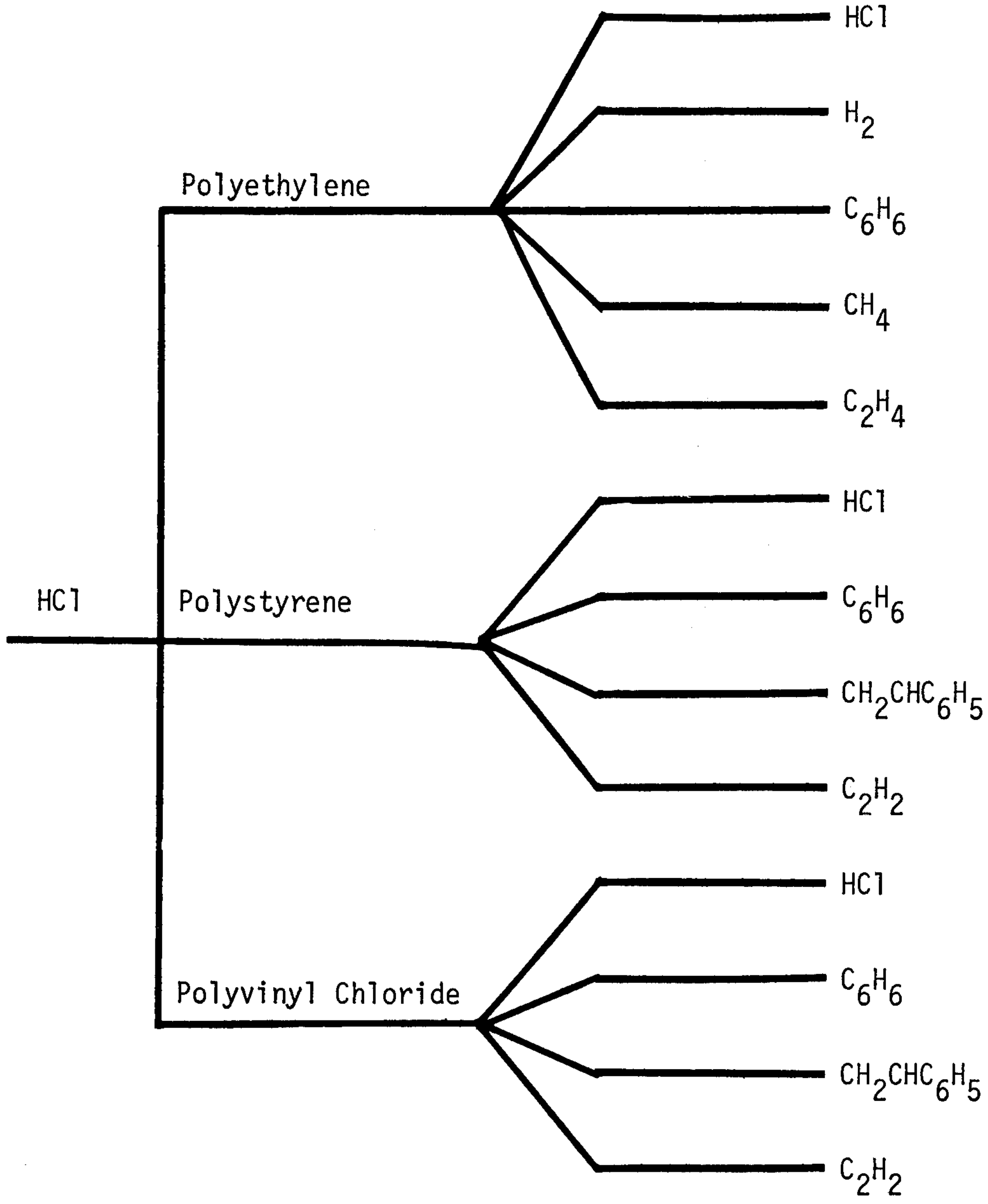


Figure 5. Hydrogen chloride: major product analysis. The addition of hydrogen chloride to the plastics system does not lead to the formation of chlorinated addition products under the conditions examined.

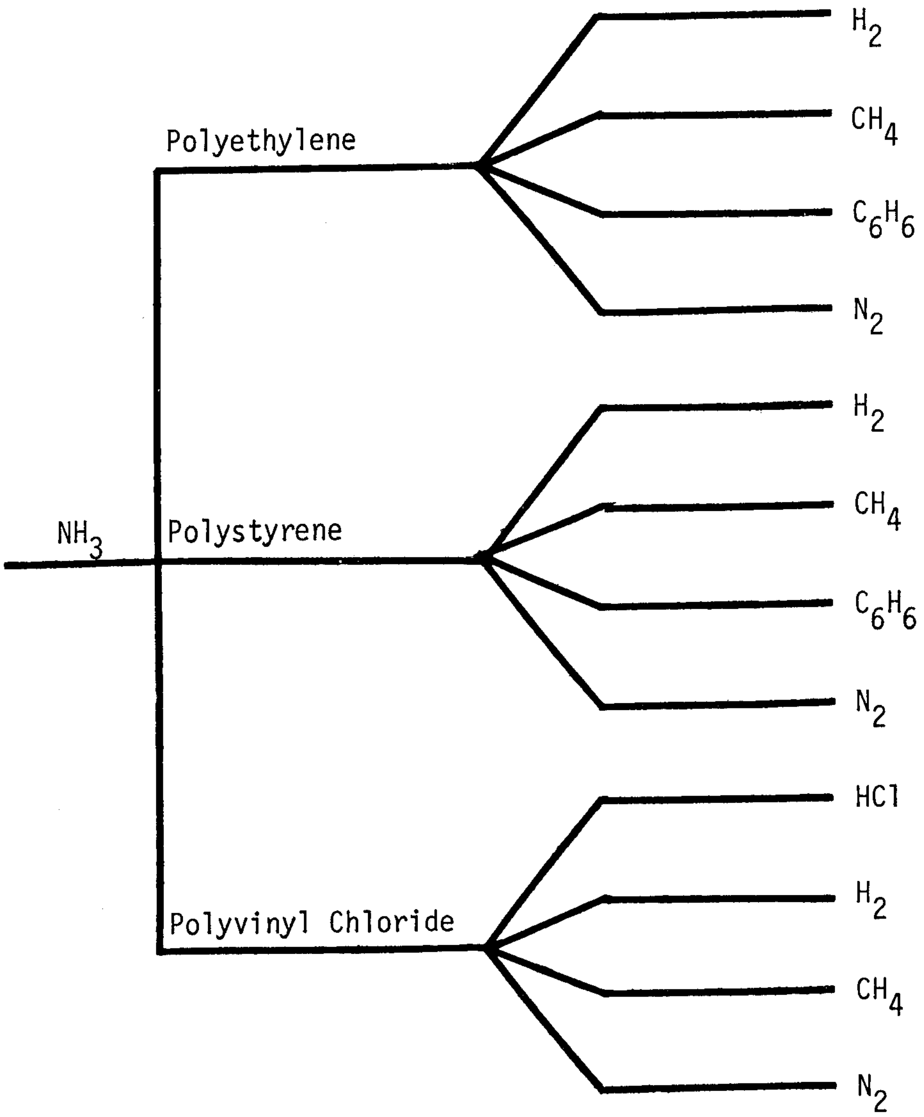


Figure 6. Ammonia: major product analysis. Ammonia is decomposed to nitrogen and hydrogen under the equilibrium conditions examined.

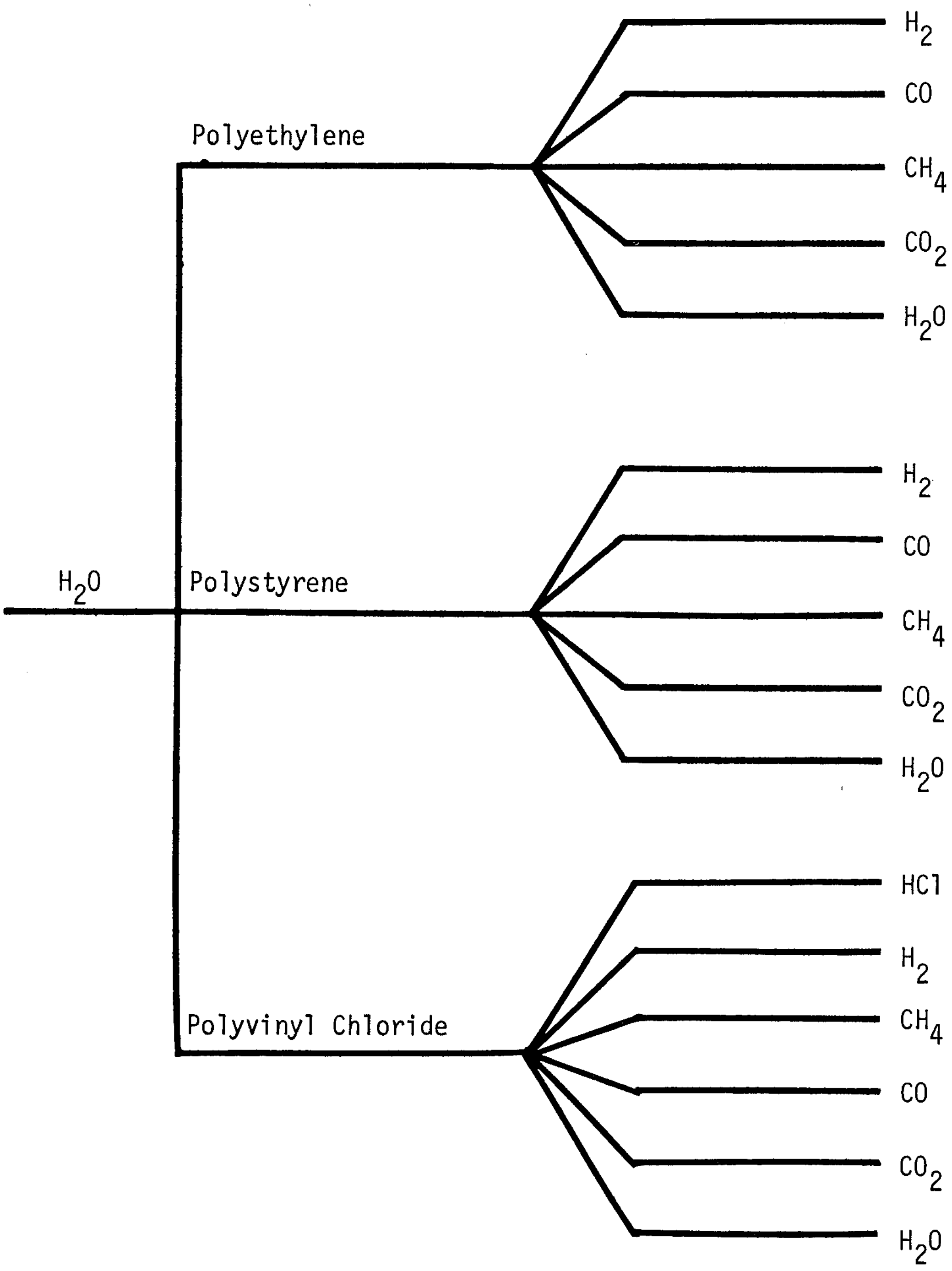


Figure 7. Water: major product analysis. Under the reaction conditions examined, the major products of the reactions between the plastics and water included no oxyorganic compounds.

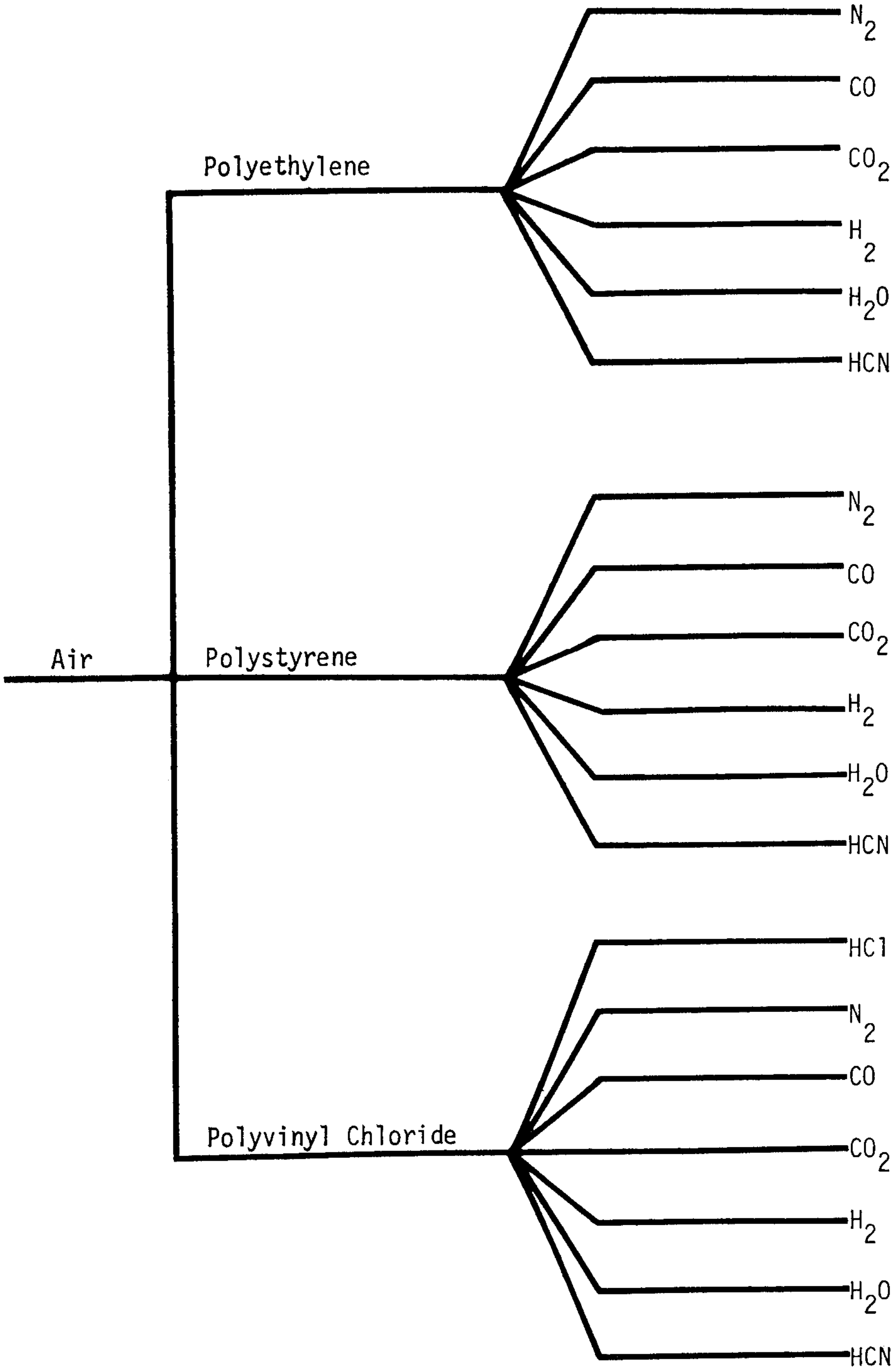


Figure 8. Air: major product analysis. As was the case with water, no oxyorganic compounds were favored under the conditions examined.

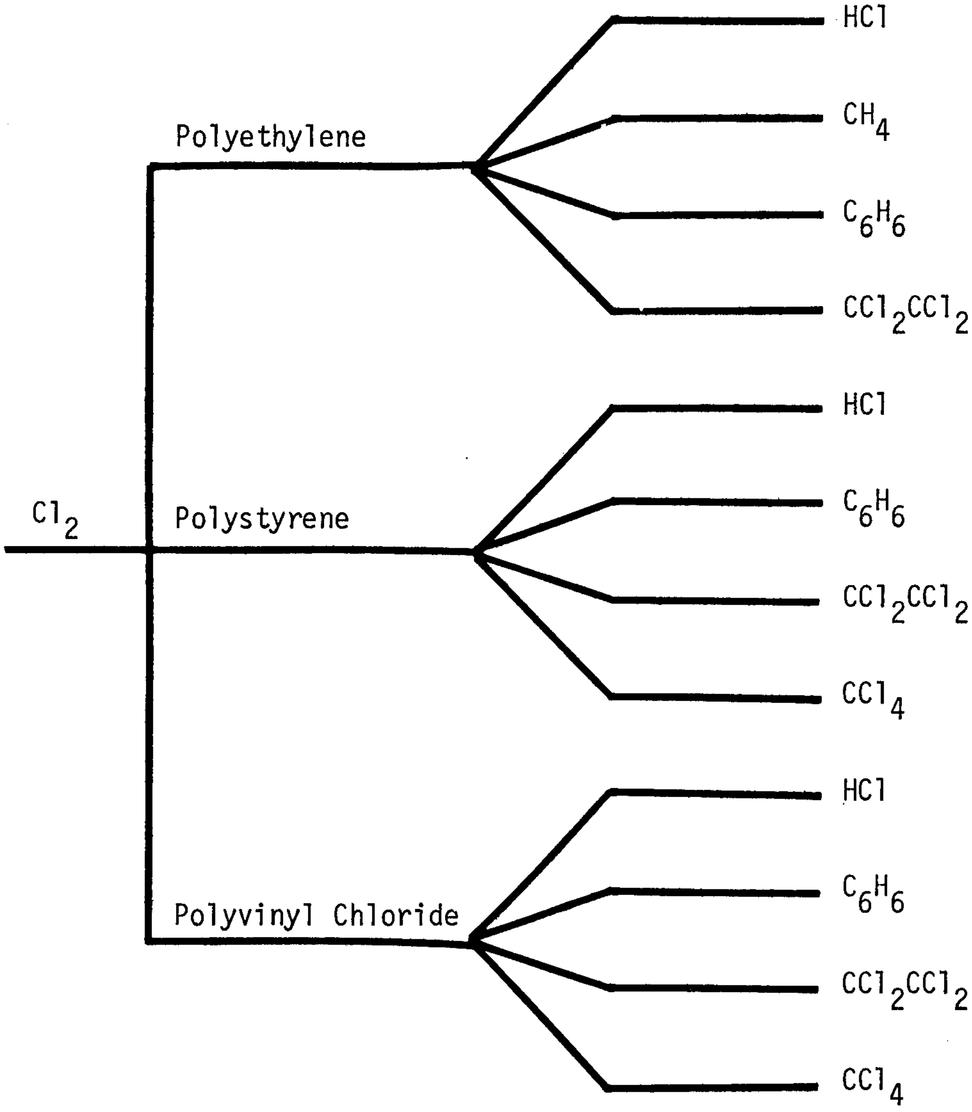


Figure 9. Chlorine: major product analysis. Under the equilibrium conditions examined, the plastics/chlorine systems favored the formation of various chlorinated organic compounds.

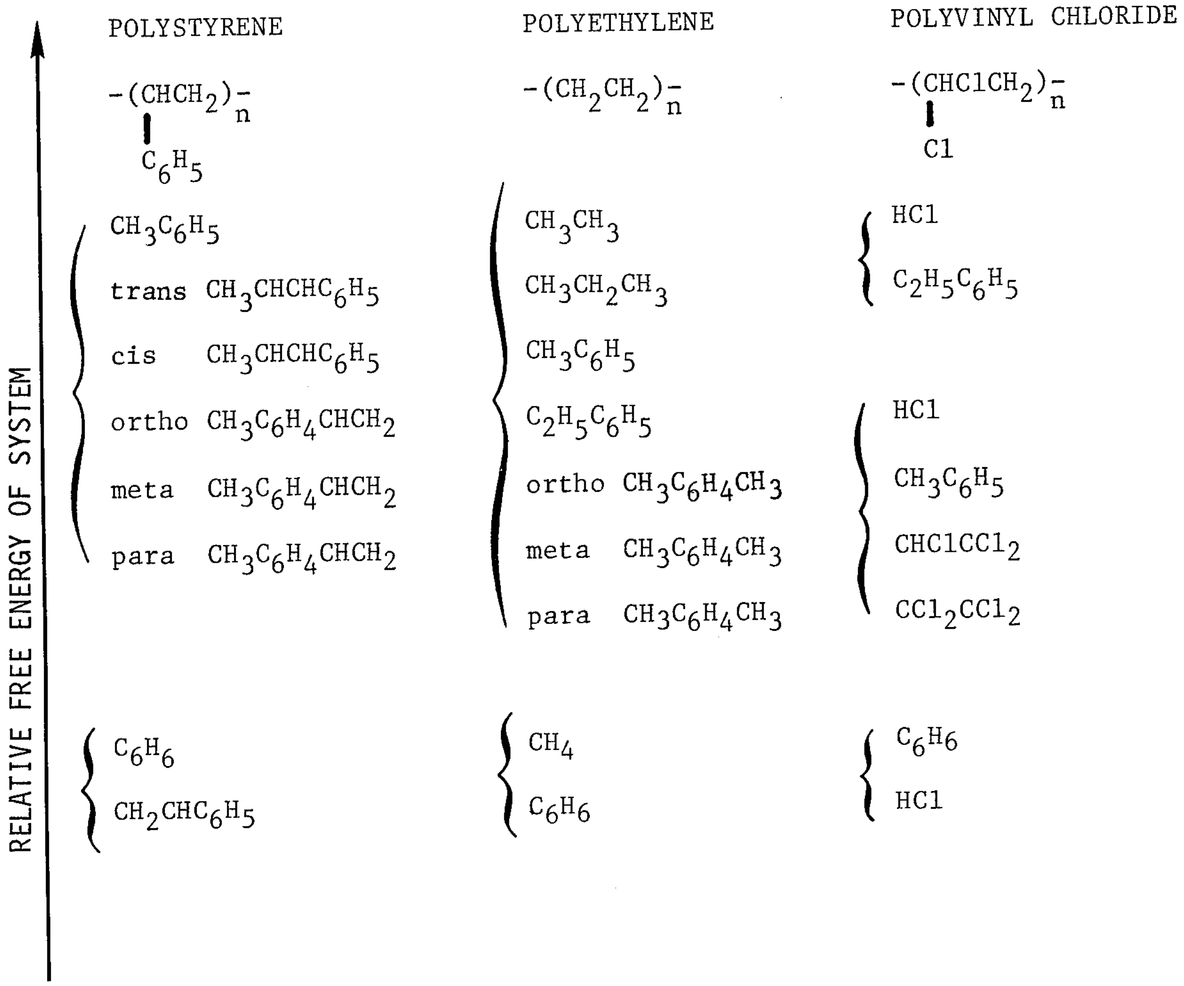


Figure 10. Feasible reaction path species, thermal decomposition, 773 K, 1 atm. The compounds in the higher relative free-energy ranges are found in significant quantities at equilibrium only when the lower energy products are deleted from consideration. (Polystyrene at 1,073 K in place of 773 K.)

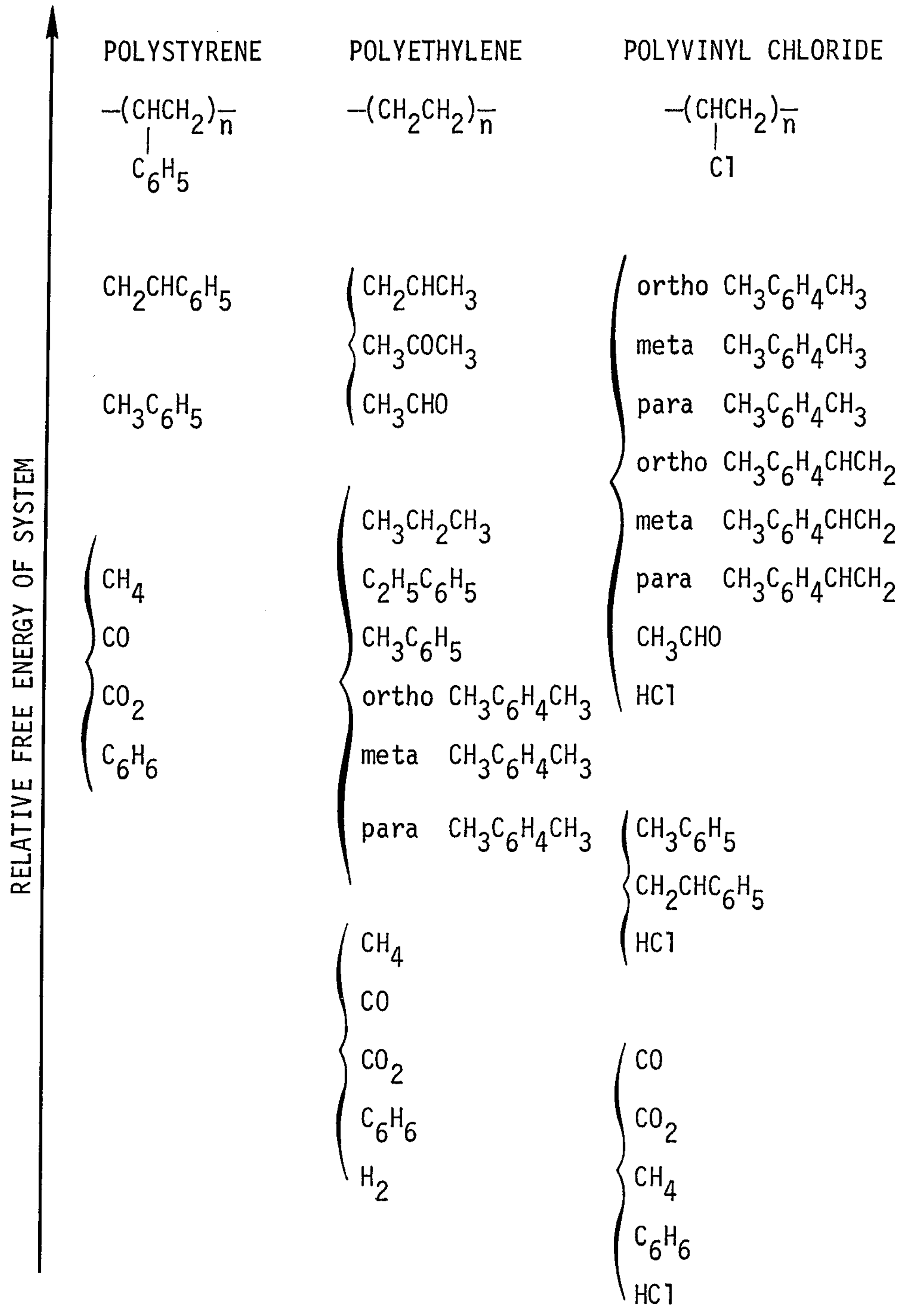


Figure 11. Feasible reaction path species, air, 773 K, 1 atm, 70 percent plastic material. Deletion of the normal combustion products from consideration leads to product distributions similar to those from thermal decomposition. Deletion of these compounds gives some oxyorganic products.

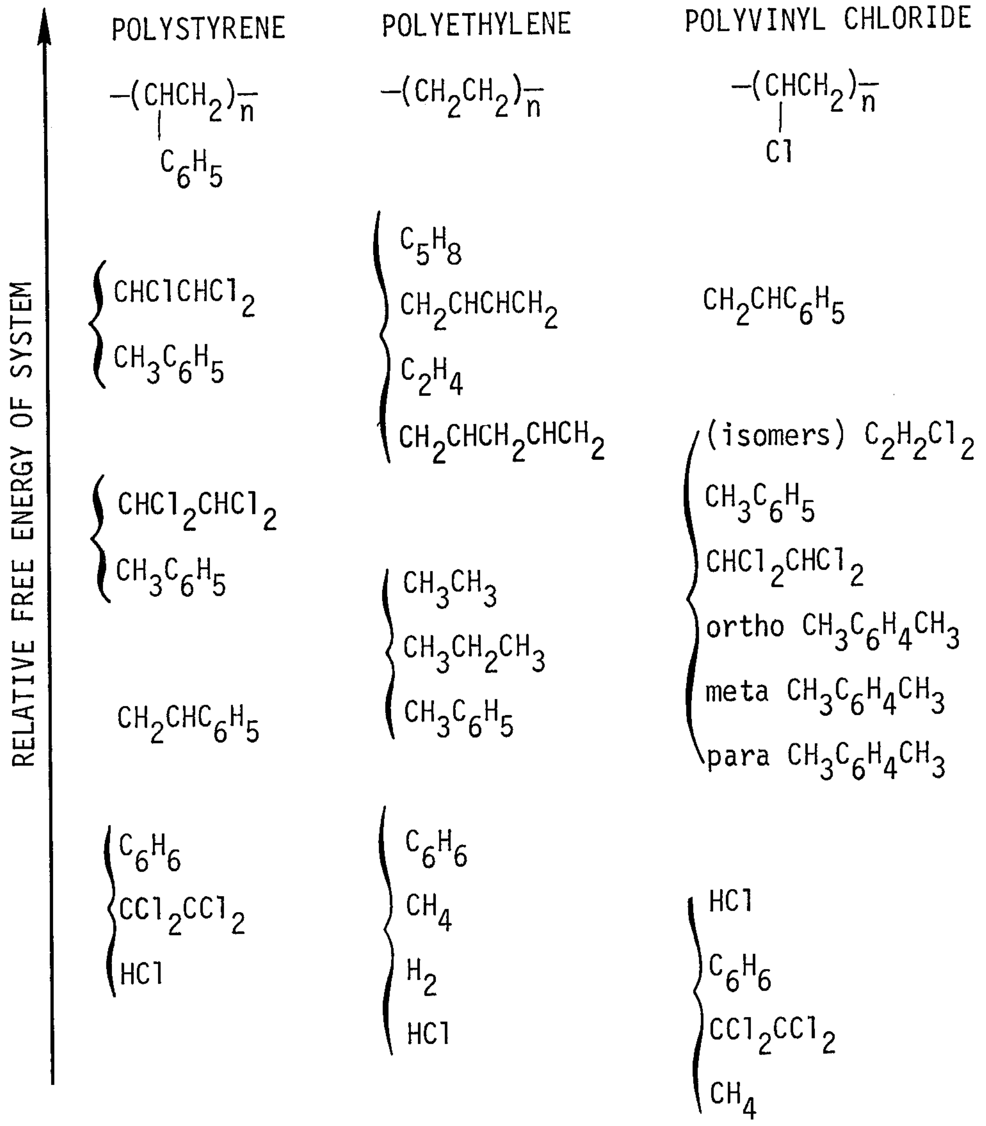


Figure 12. Feasible reaction path species, chlorine, 773 K, 1 atm, 70 percent plastic material. Many different chlorinated products are favored following the deletion of the lowest energy products.

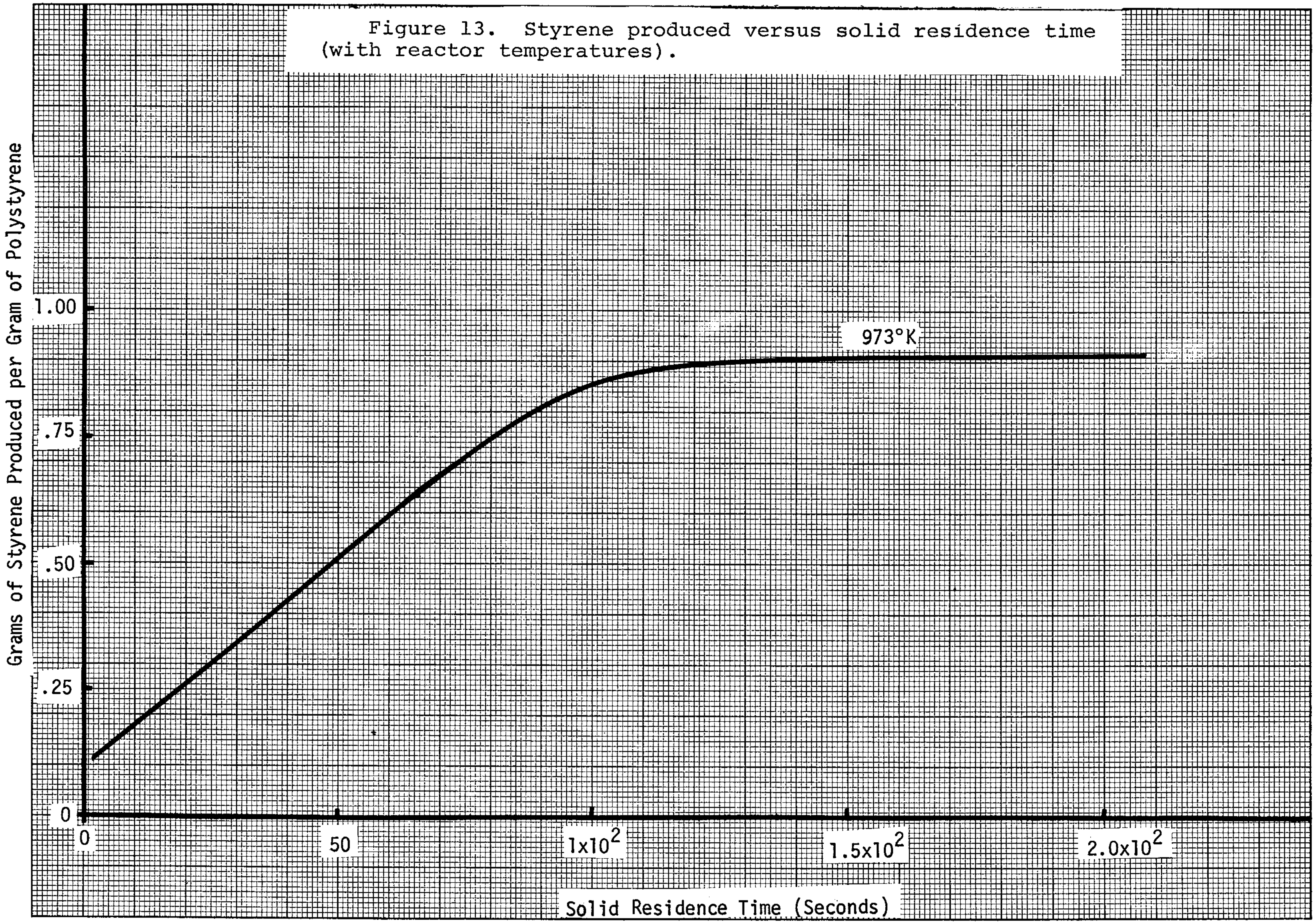
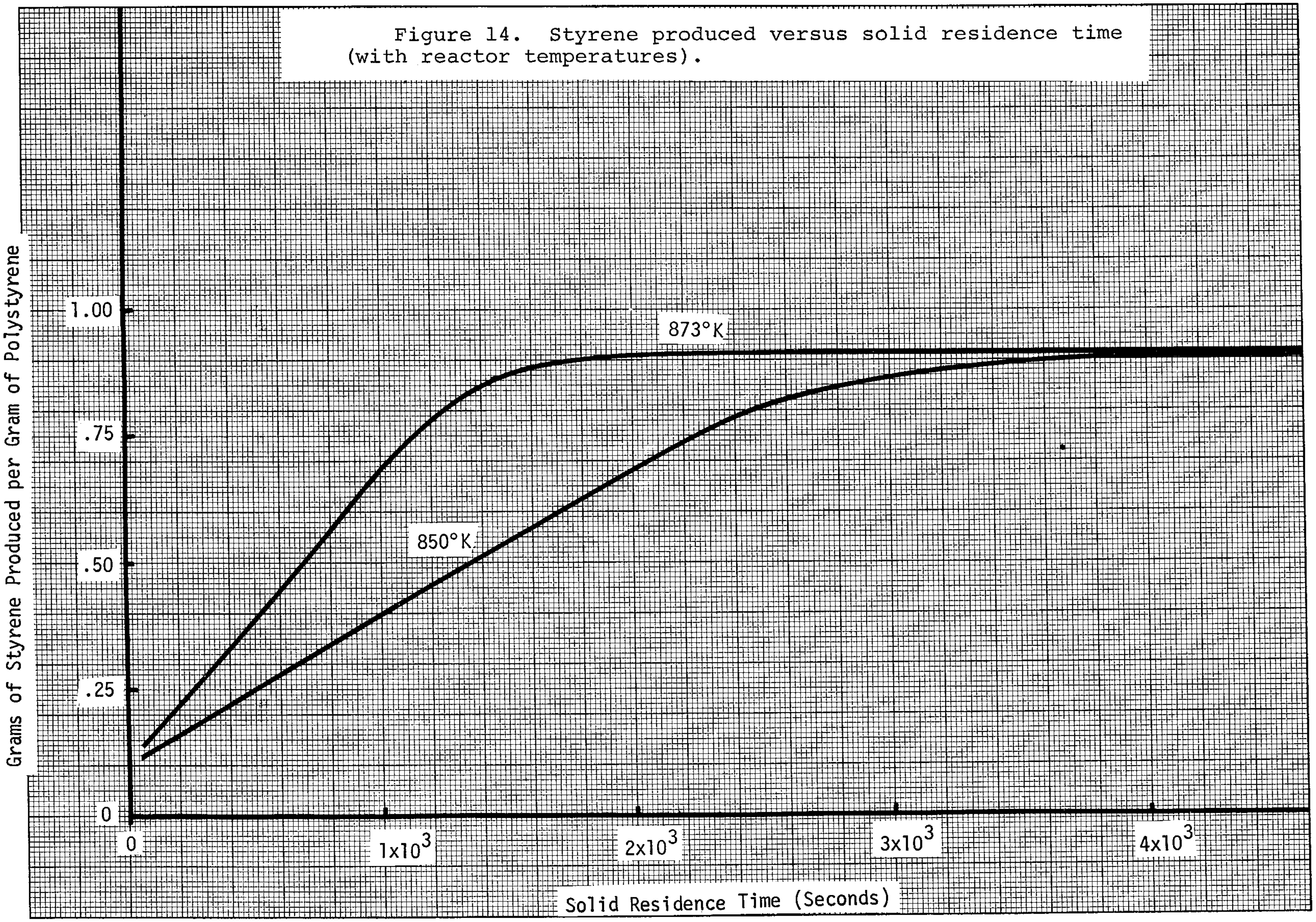


Figure 13. Styrene produced versus solid residence time (with reactor temperatures).

Figure 14. Styrene produced versus solid residence time (with reactor temperatures).



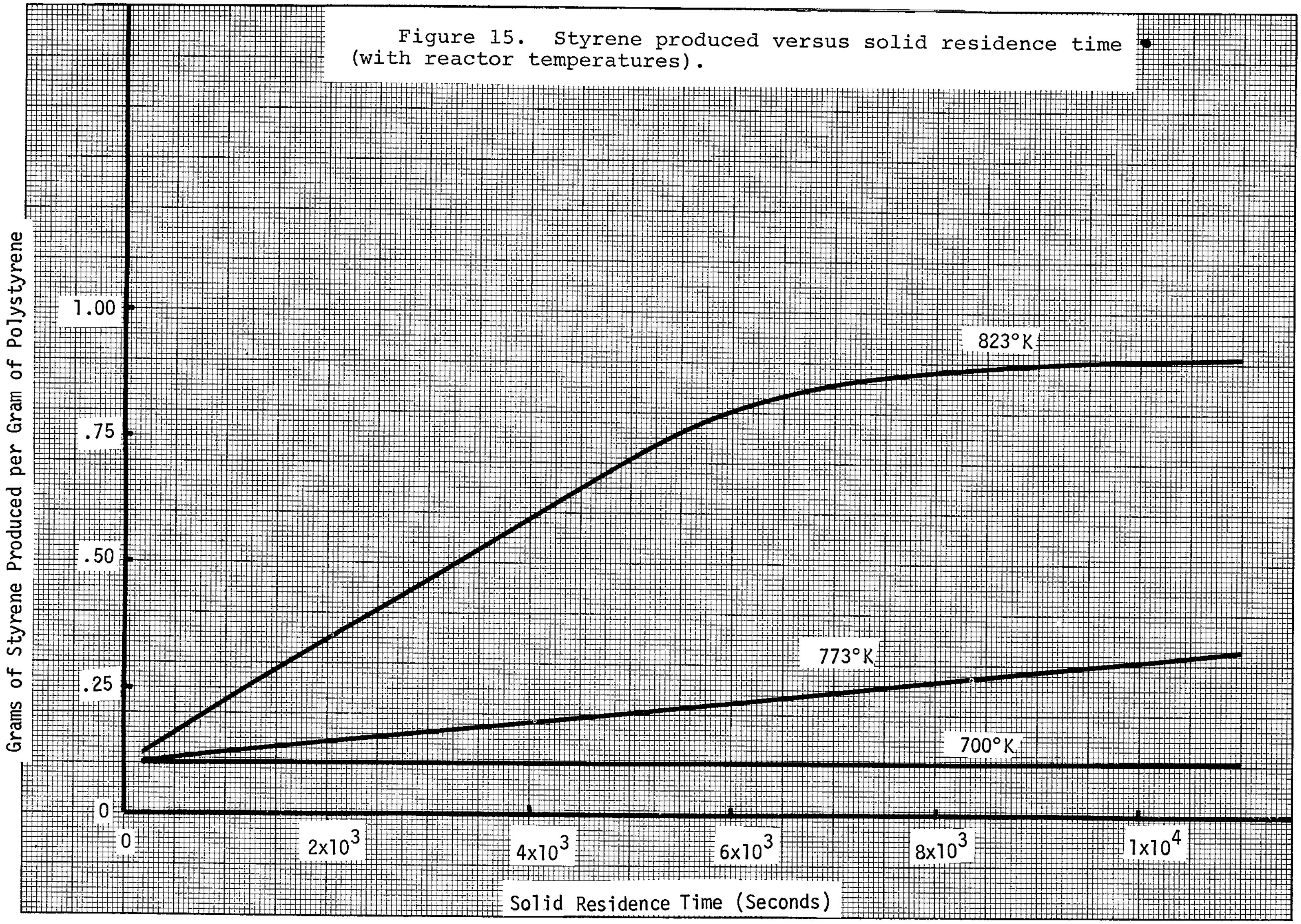
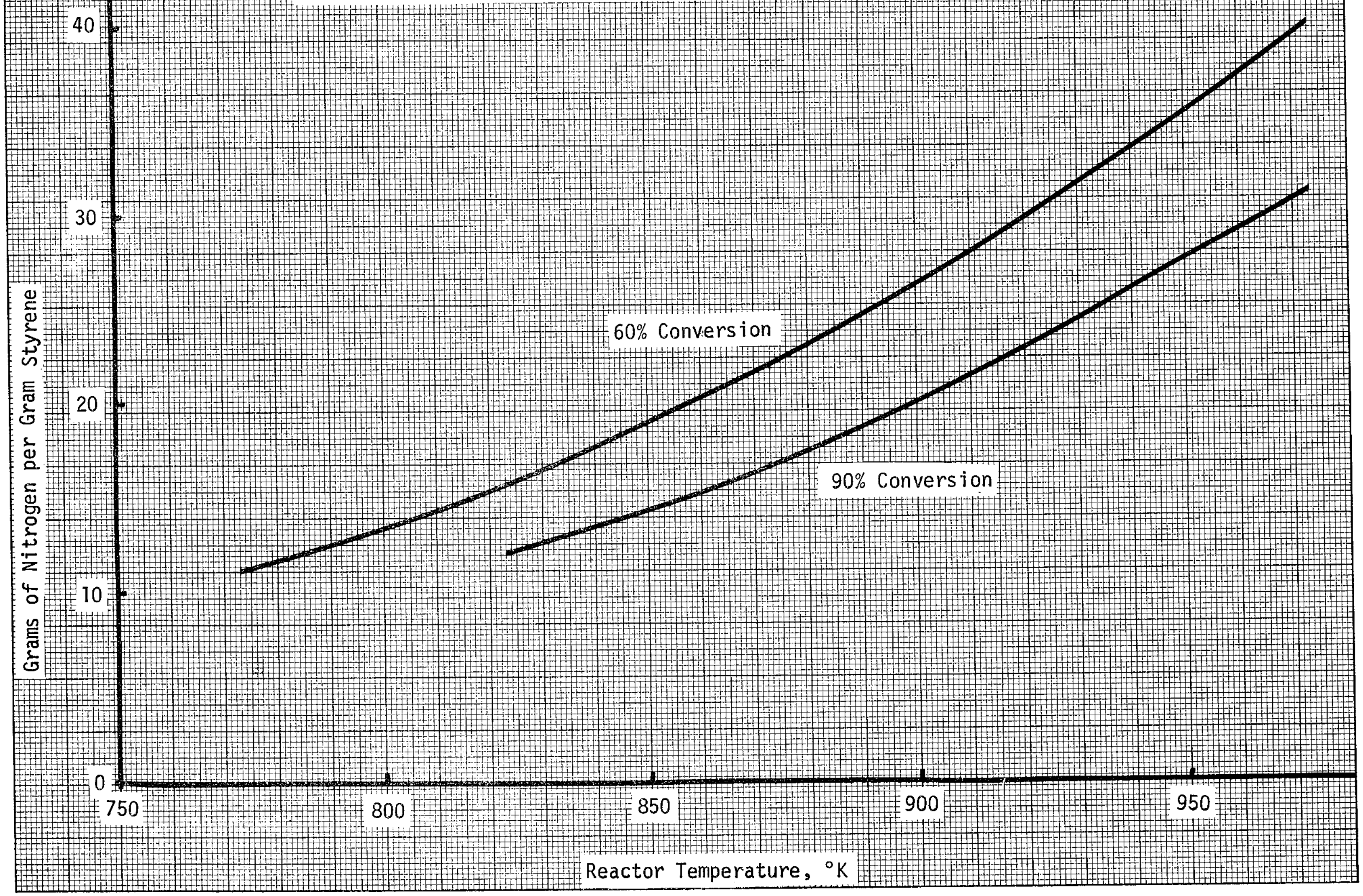


Figure 15. Styrene produced versus solid residence time (with reactor temperatures).

Figure 16. Nitrogen necessary per g of styrene (nitrogen at 1,500 K).



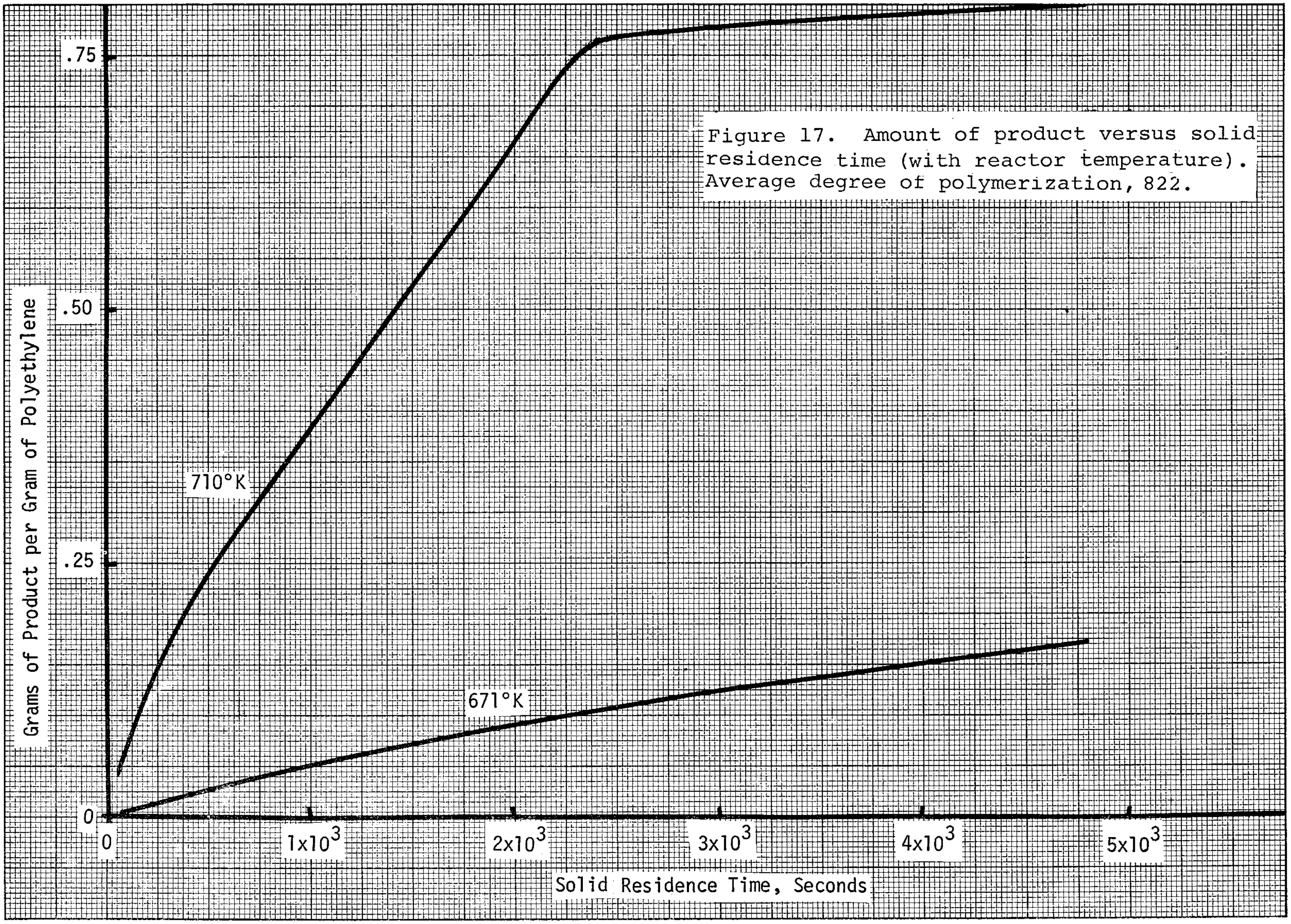


Figure 17. Amount of product versus solid residence time (with reactor temperature). Average degree of polymerization, 822.

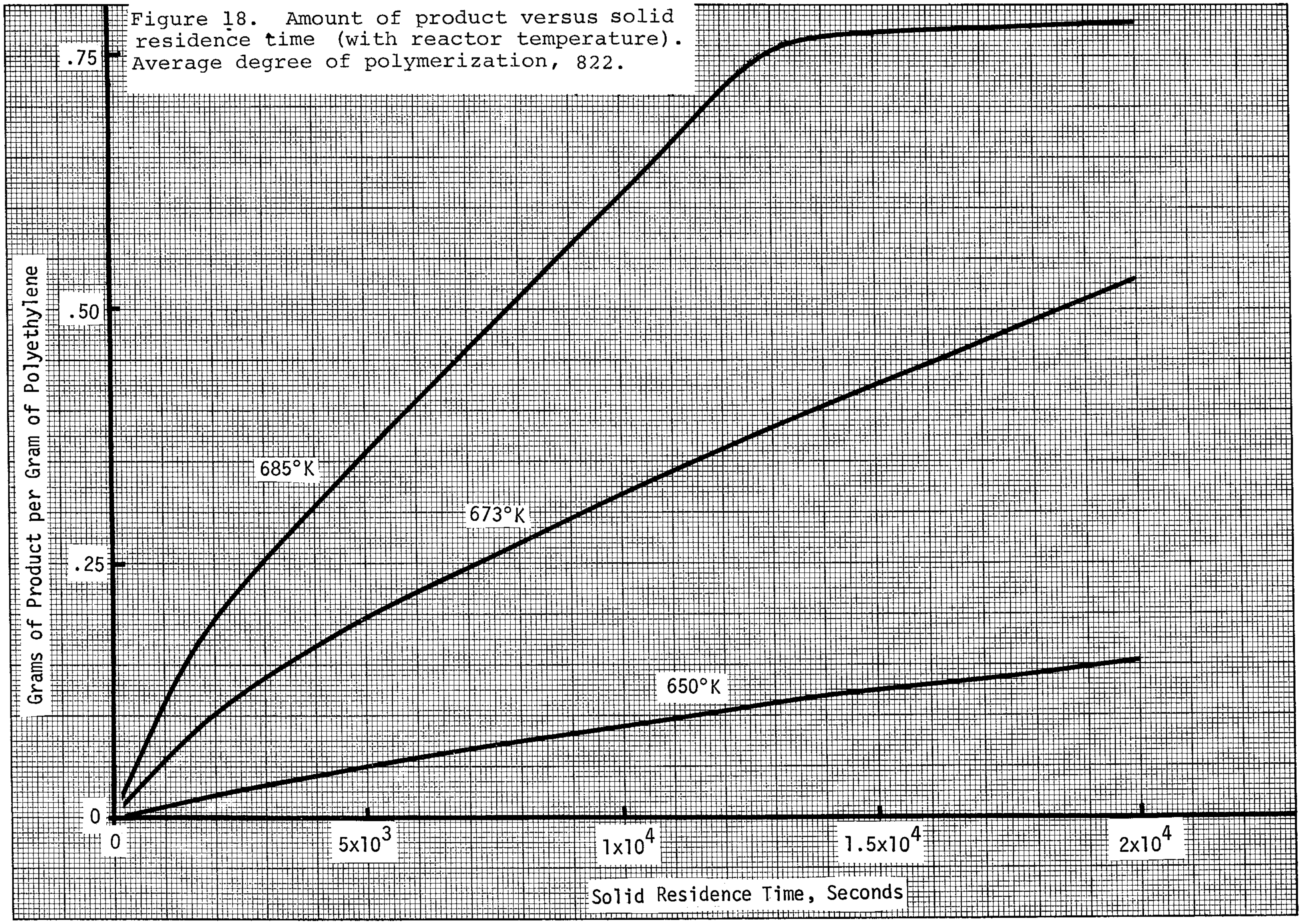


Figure 18. Amount of product versus solid residence time (with reactor temperature). Average degree of polymerization, 822.

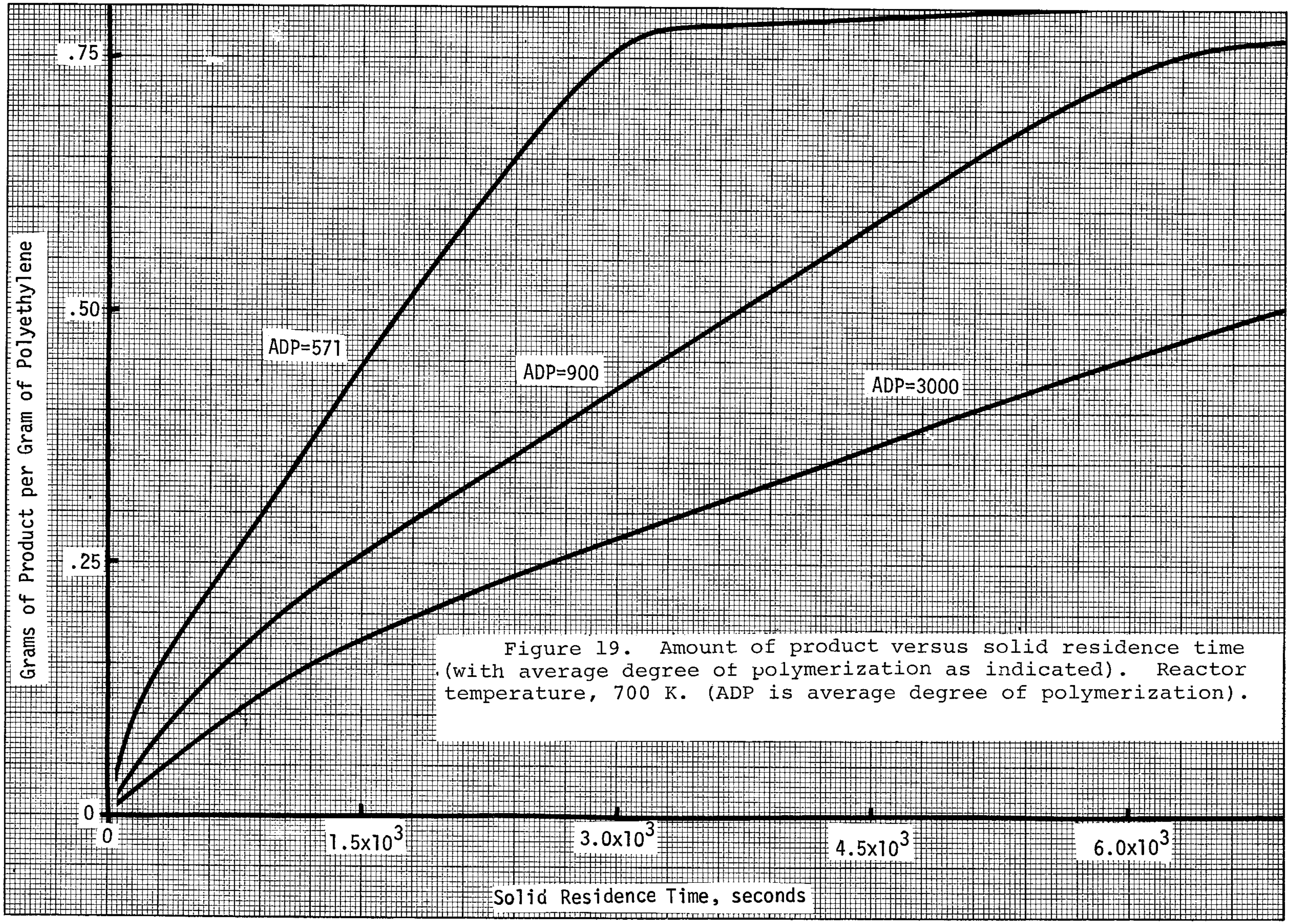


Figure 19. Amount of product versus solid residence time (with average degree of polymerization as indicated). Reactor temperature, 700 K. (ADP is average degree of polymerization).

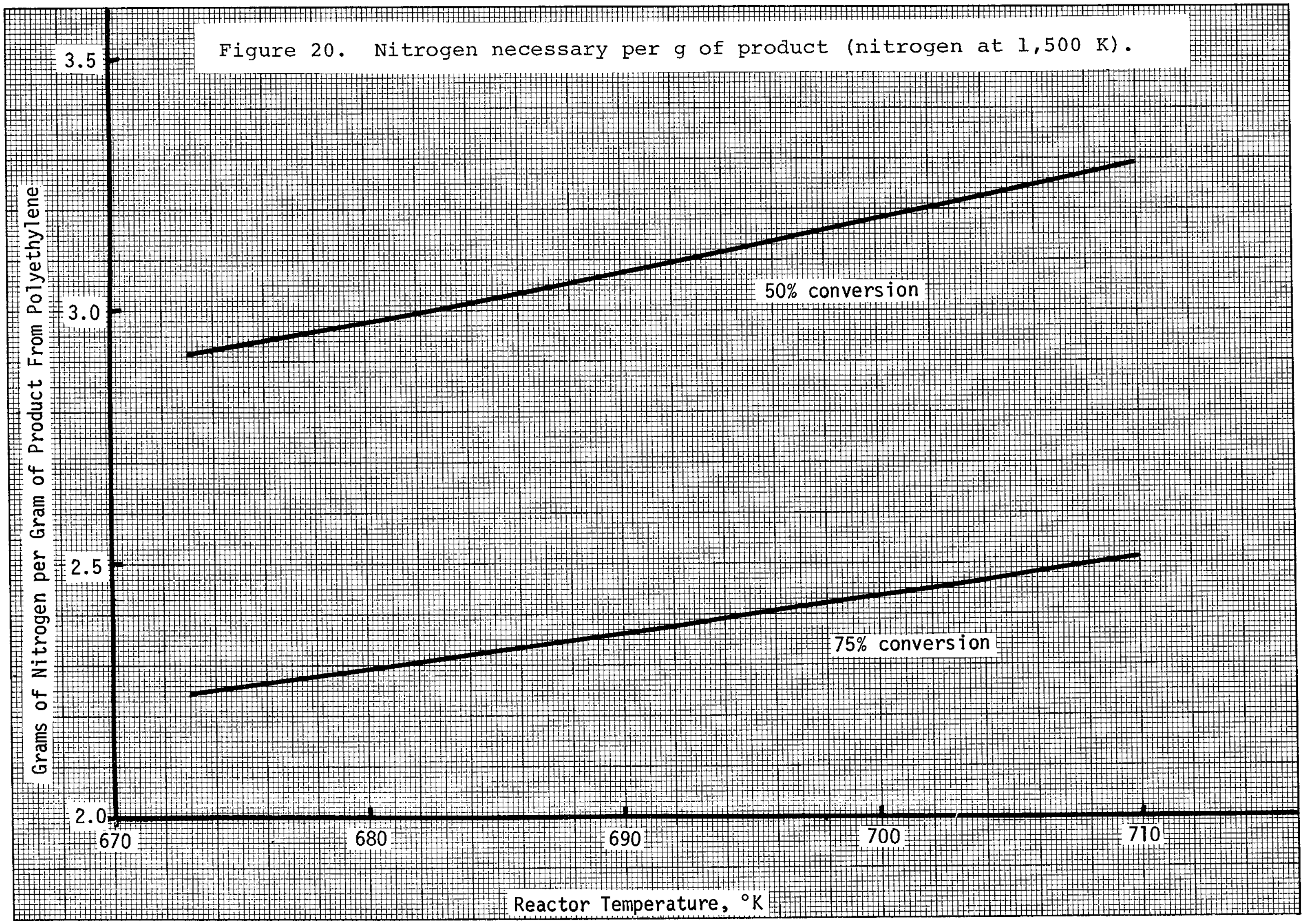


Figure 20. Nitrogen necessary per g of product (nitrogen at 1,500 K).

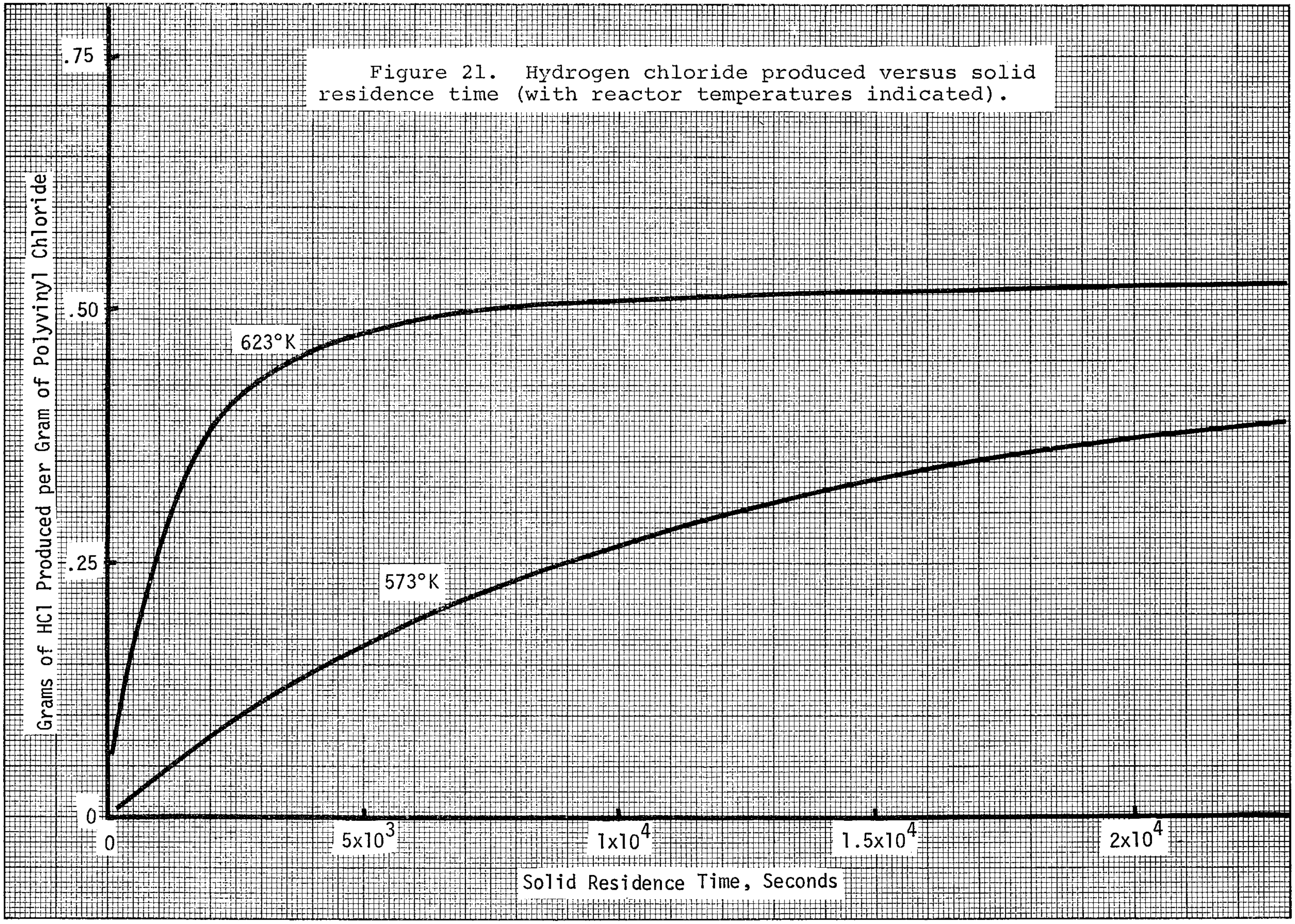


Figure 21. Hydrogen chloride produced versus solid residence time (with reactor temperatures indicated).

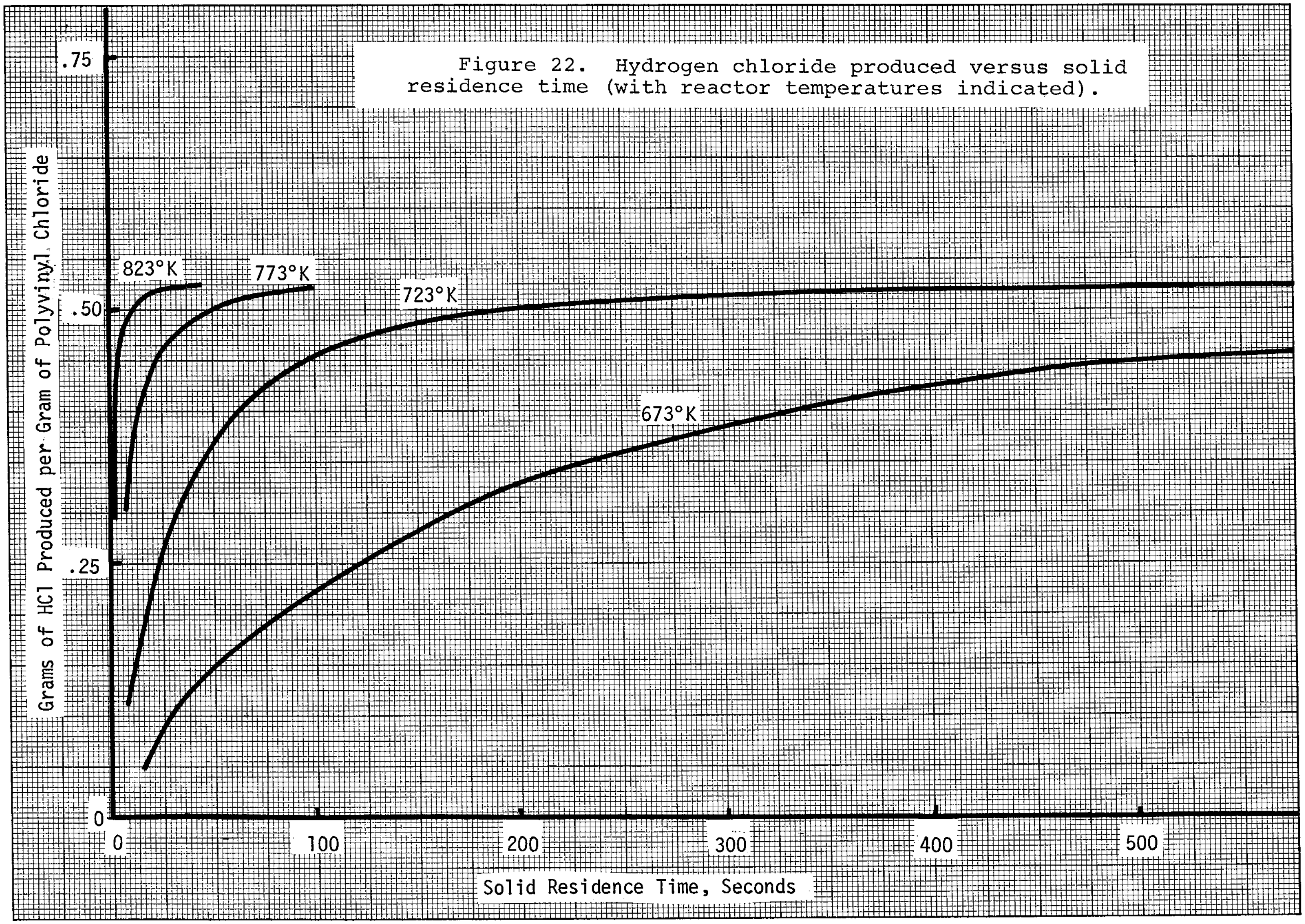


Figure 22. Hydrogen chloride produced versus solid residence time (with reactor temperatures indicated).

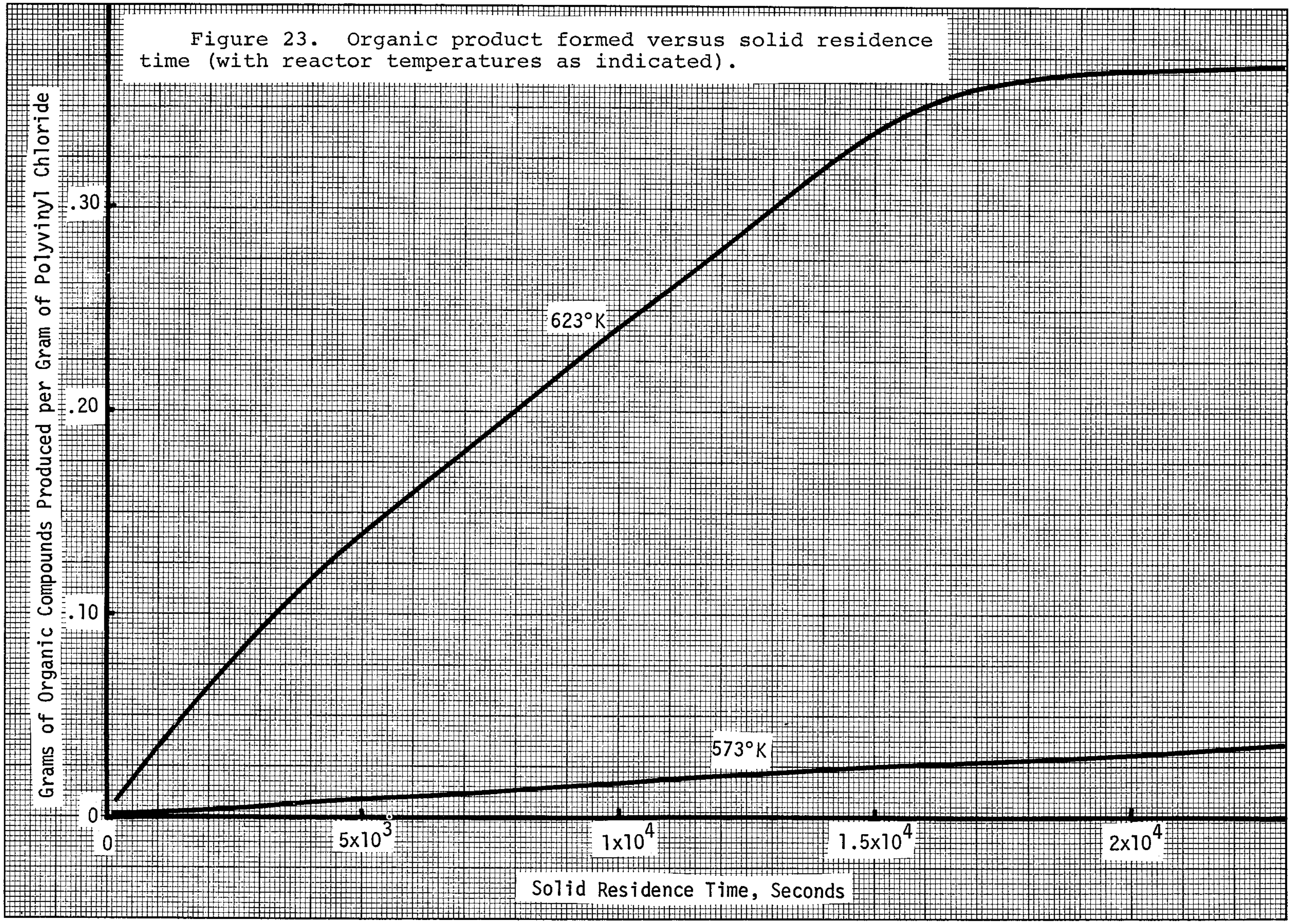


Figure 23. Organic product formed versus solid residence time (with reactor temperatures as indicated).

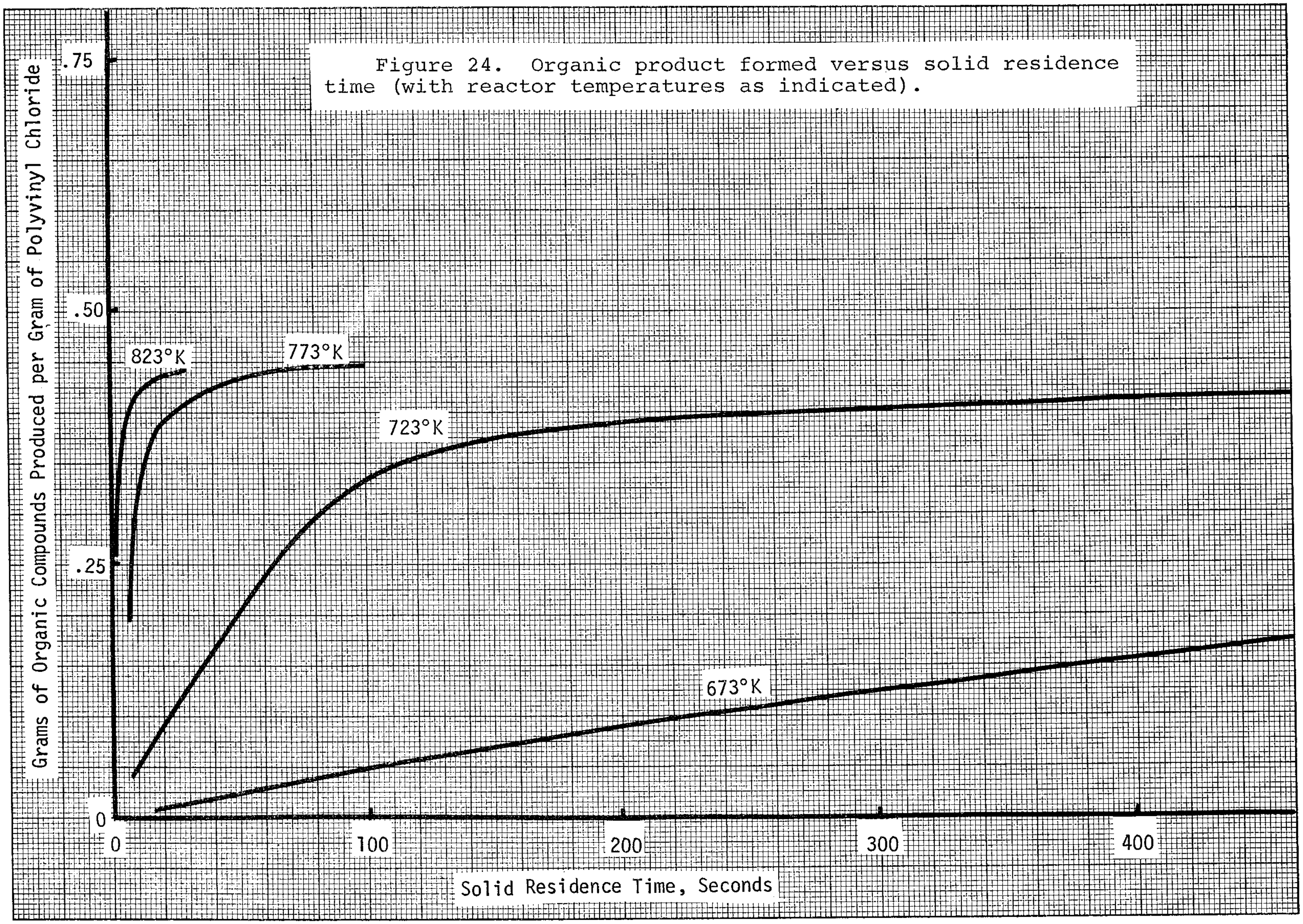


Figure 24. Organic product formed versus solid residence time (with reactor temperatures as indicated).

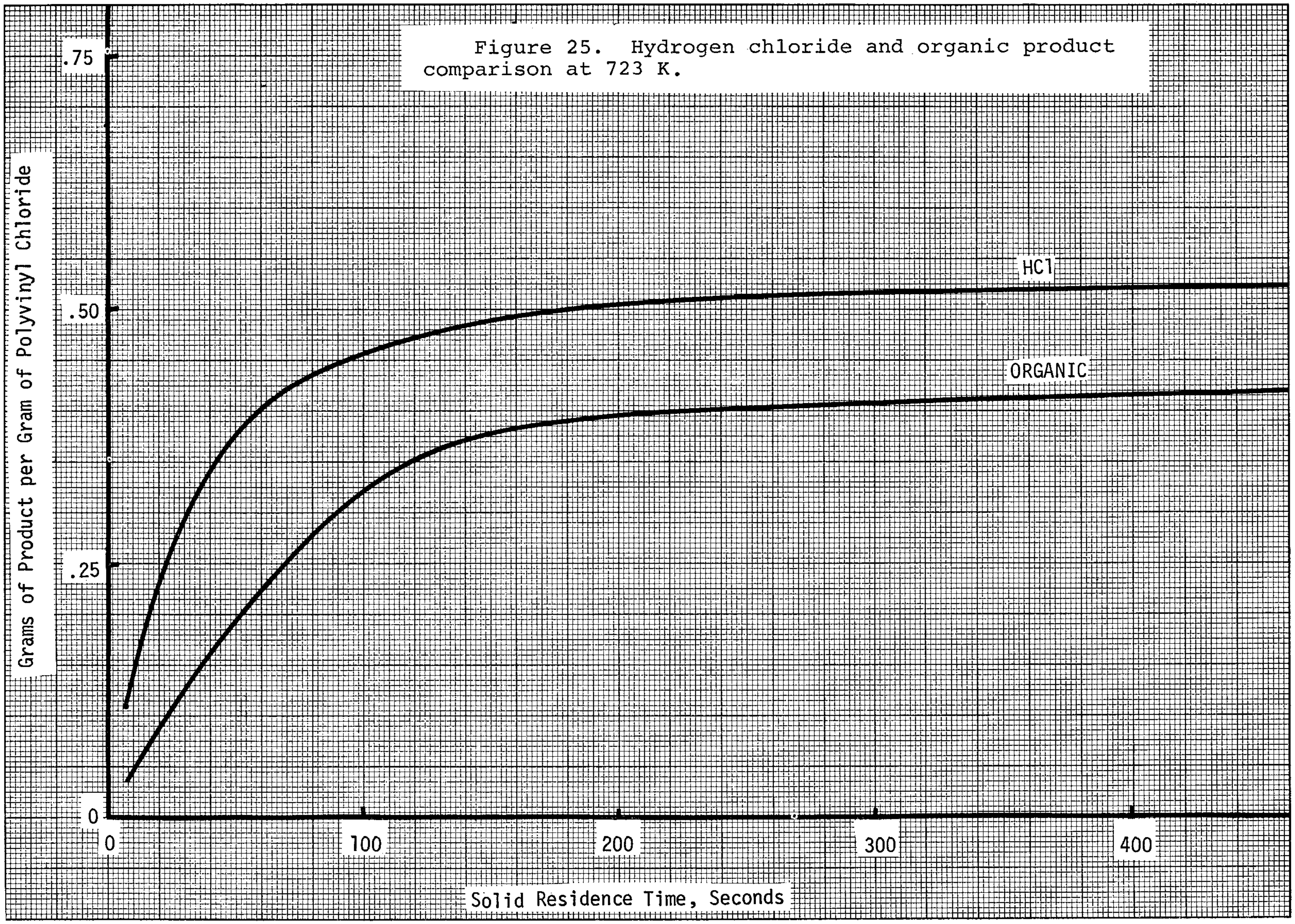


Figure 25. Hydrogen chloride and organic product comparison at 723 K.

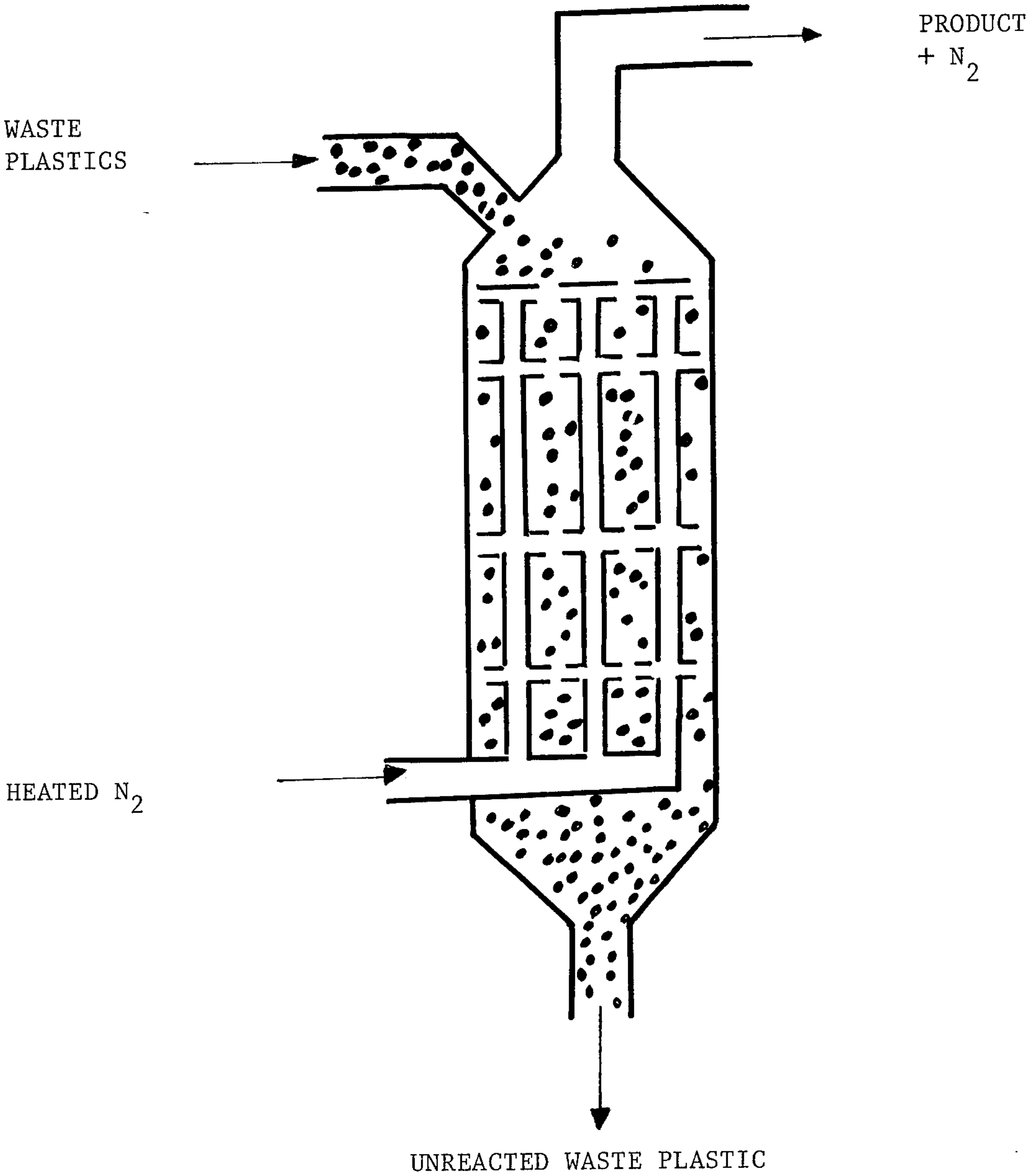


Figure 26. Semicontinuous waste plastics reactor. The dimensions specific to each of the plastic systems are given in Table 3.

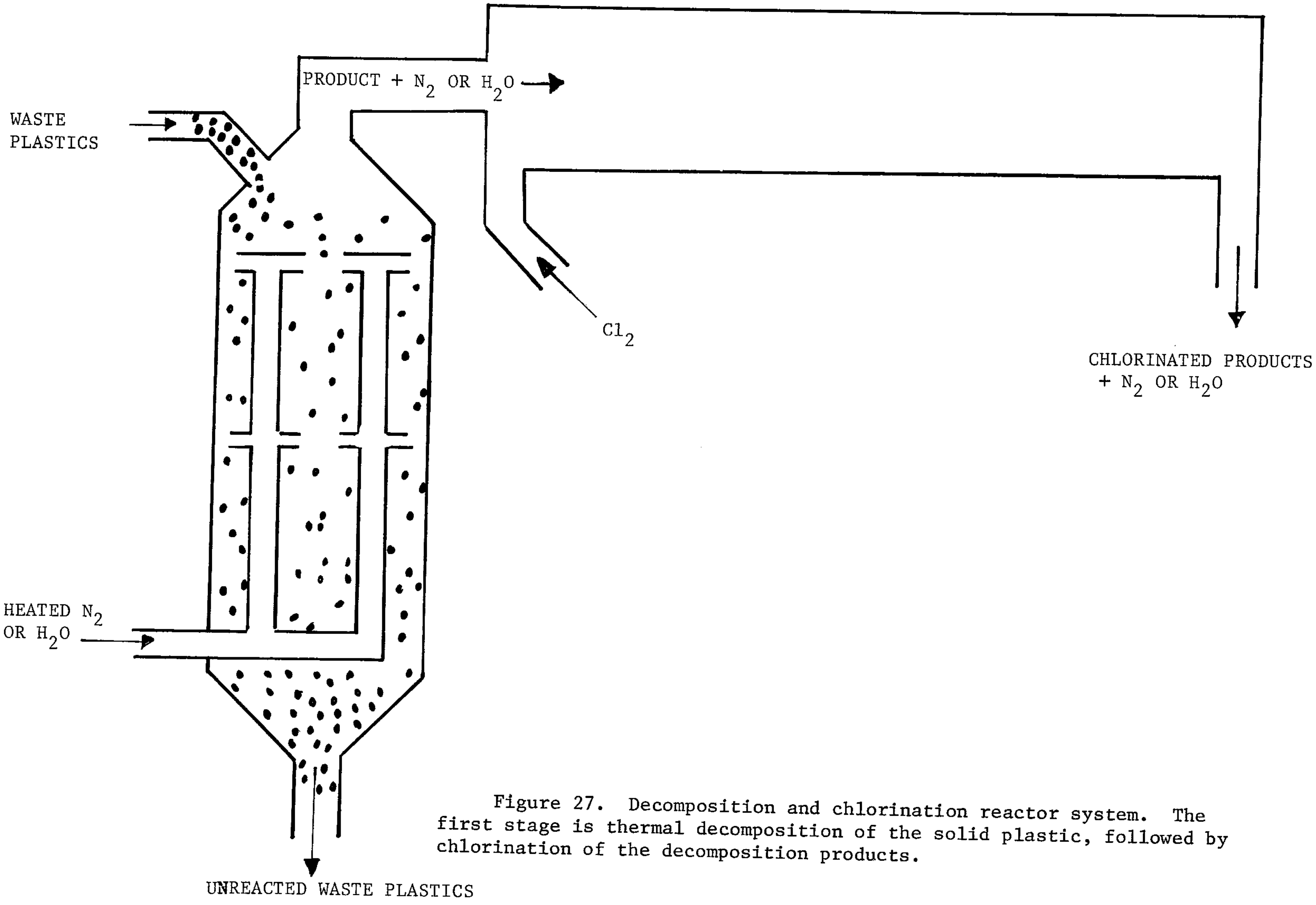


Figure 27. Decomposition and chlorination reactor system. The first stage is thermal decomposition of the solid plastic, followed by chlorination of the decomposition products.

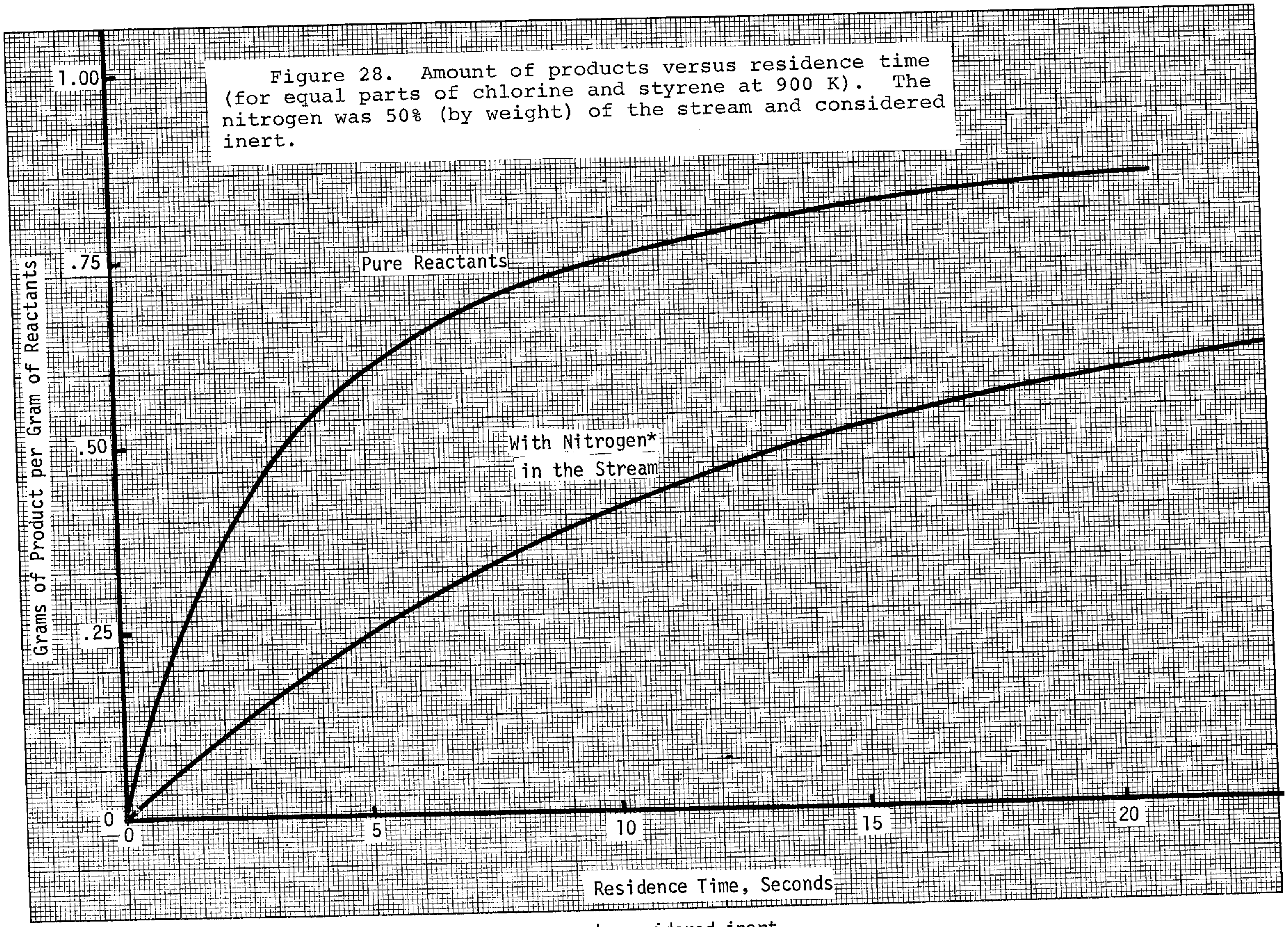


Figure 28. Amount of products versus residence time (for equal parts of chlorine and styrene at 900 K). The nitrogen was 50% (by weight) of the stream and considered inert.

*The Nitrogen was 50% (by weight) of the stream and considered inert.

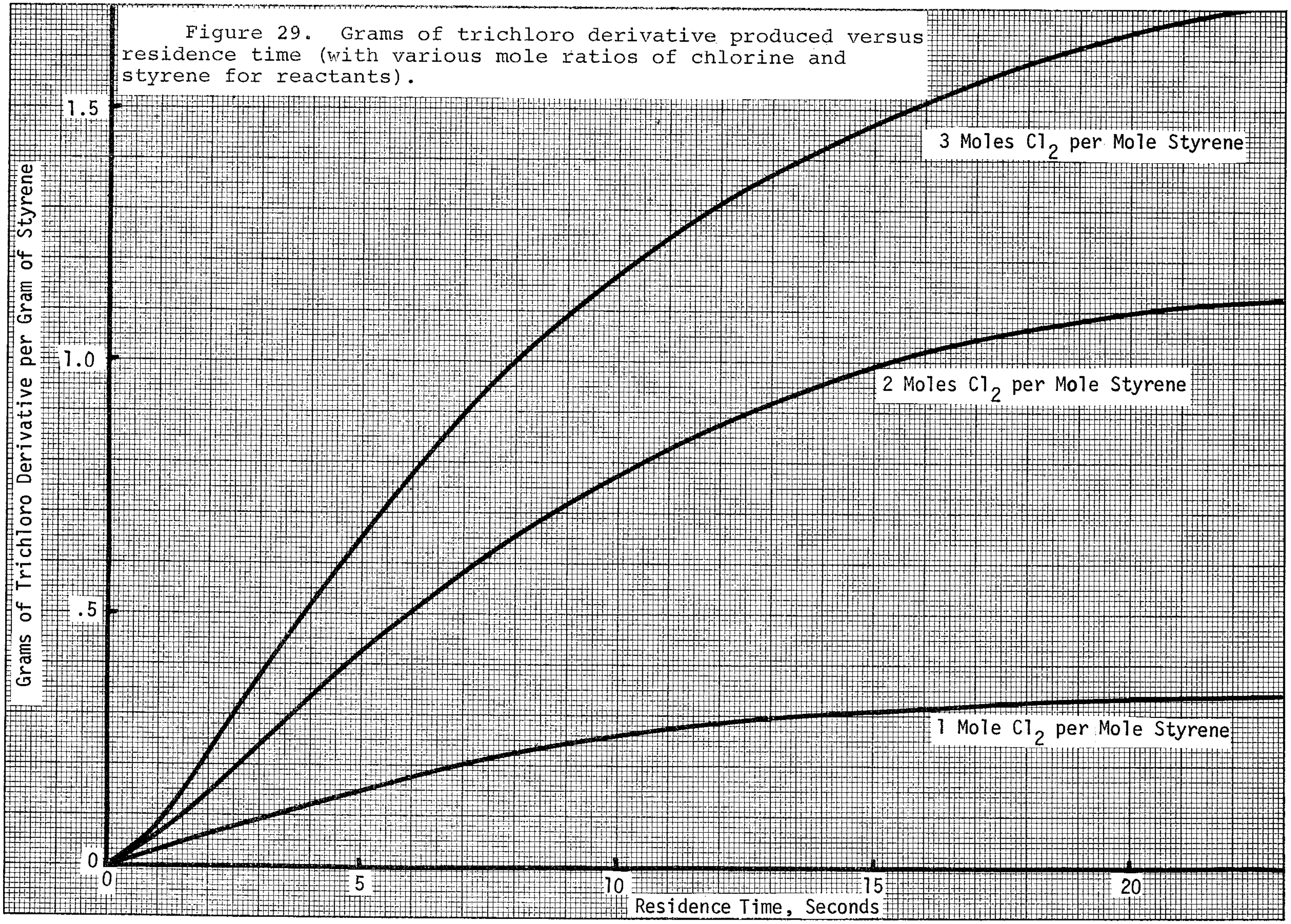


Figure 29. Grams of trichloro derivative produced versus residence time (with various mole ratios of chlorine and styrene for reactants).

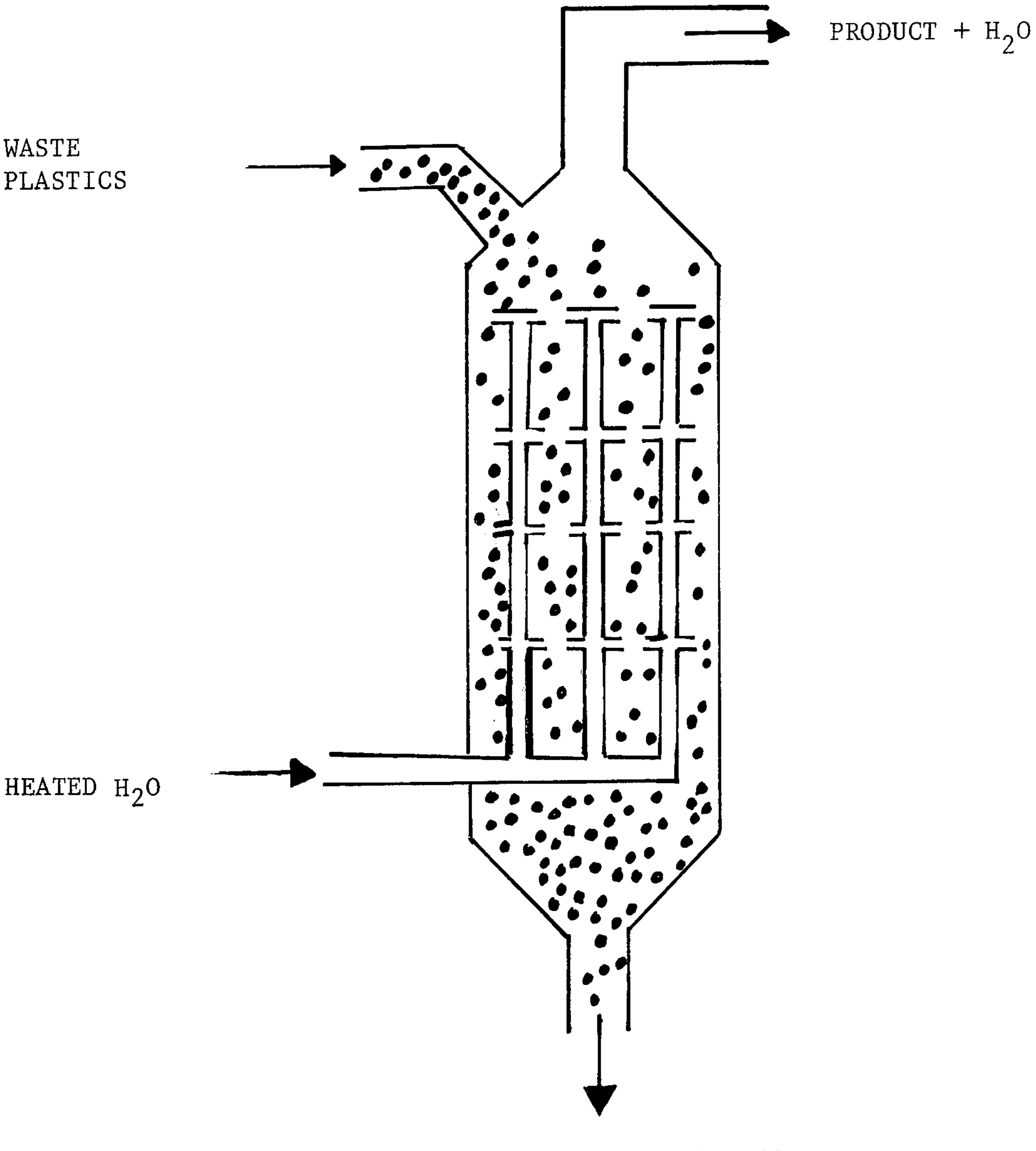


Figure 30. Semicontinuous waste plastics reactor. Thermal decomposition of mixed plastics system.

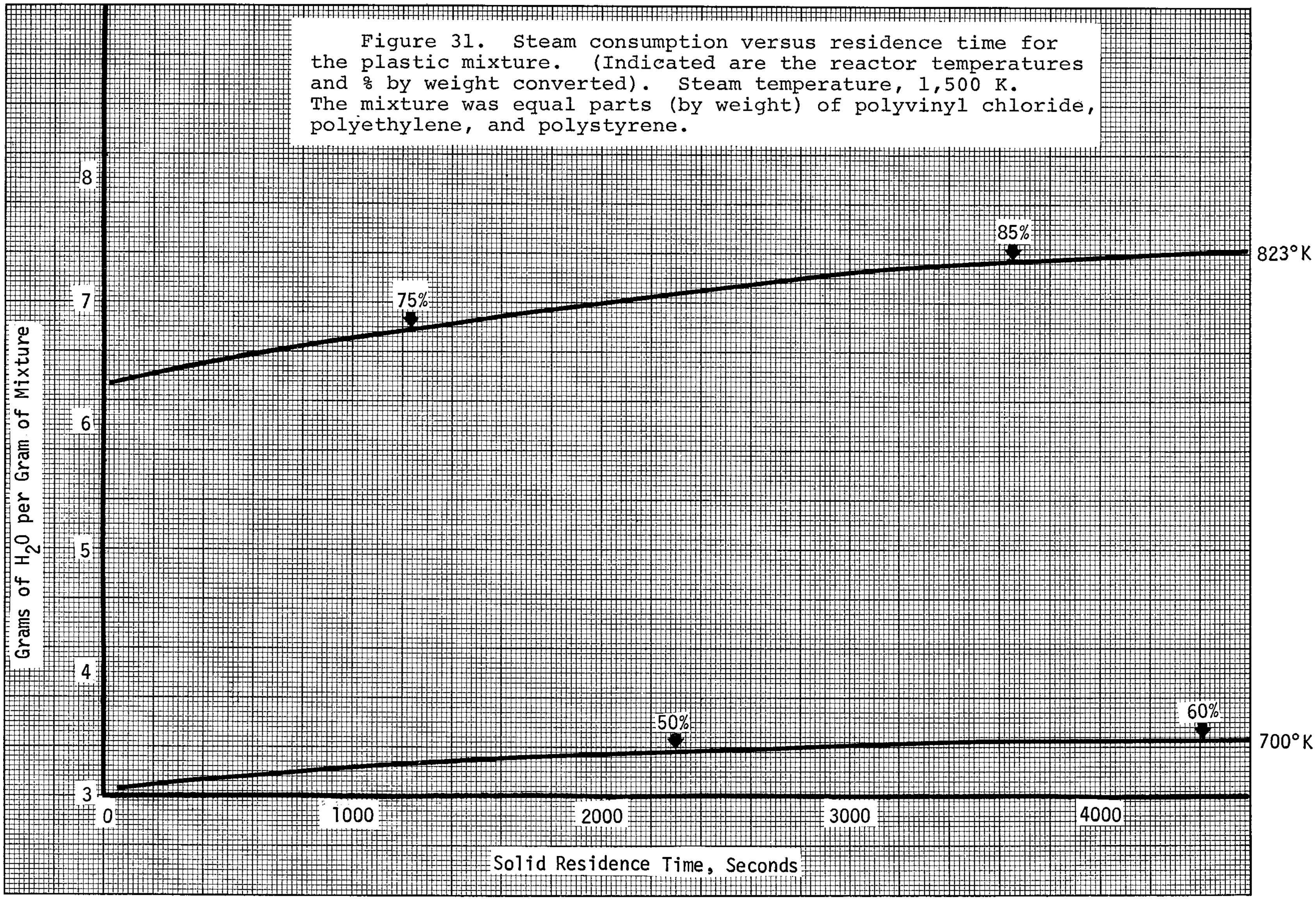


Figure 31. Steam consumption versus residence time for the plastic mixture. (Indicated are the reactor temperatures and % by weight converted). Steam temperature, 1,500 K. The mixture was equal parts (by weight) of polyvinyl chloride, polyethylene, and polystyrene.

*Equal Parts (by Weight) of Polyvinyl Chloride, Polyethylene and Polystyrene.

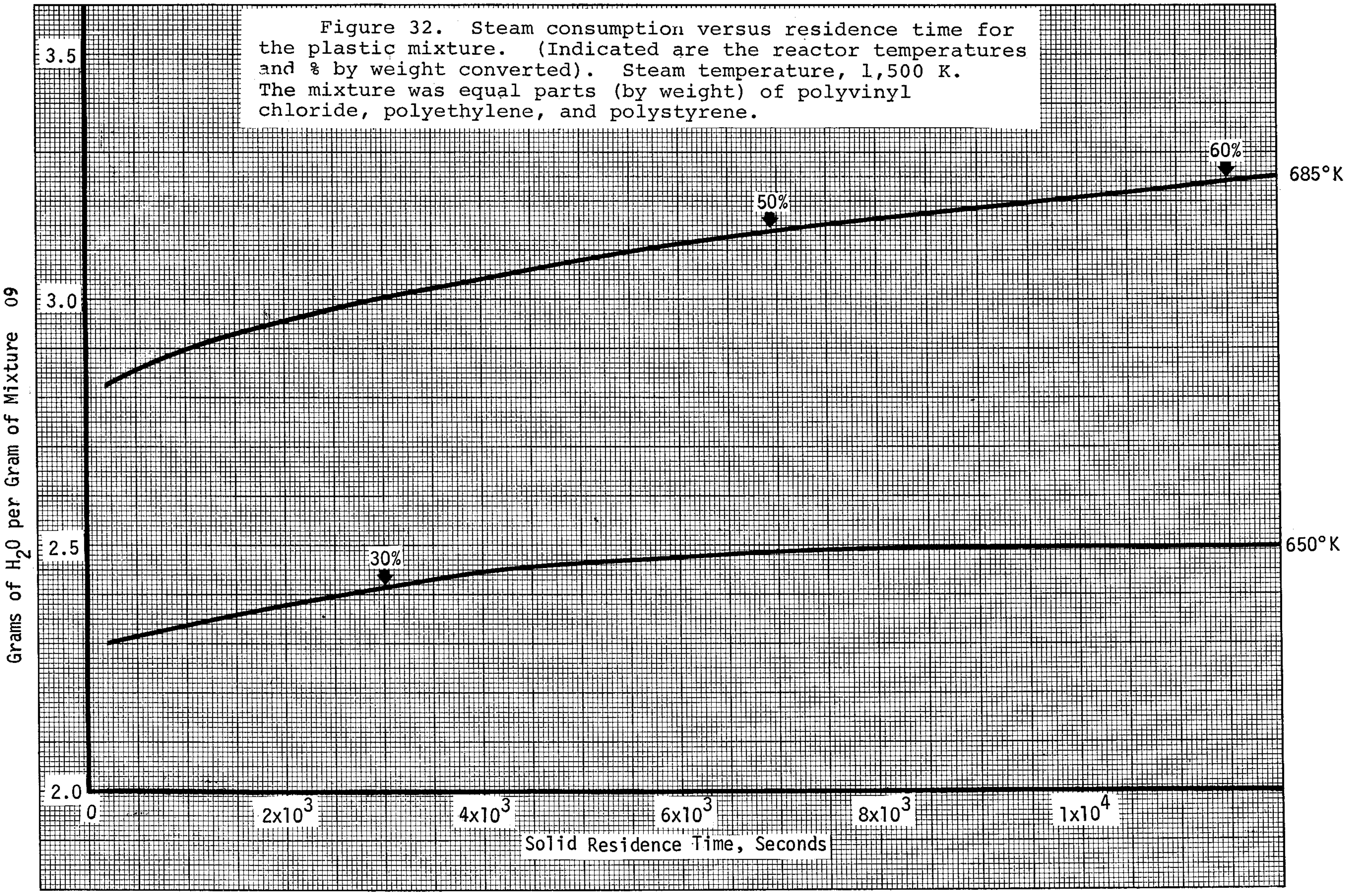


Figure 32. Steam consumption versus residence time for the plastic mixture. (Indicated are the reactor temperatures and % by weight converted). Steam temperature, 1,500 K. The mixture was equal parts (by weight) of polyvinyl chloride, polyethylene, and polystyrene.

*Equal Parts (by Weight) of Polyvinyl Chloride, Polyethylene and Polystyrene.

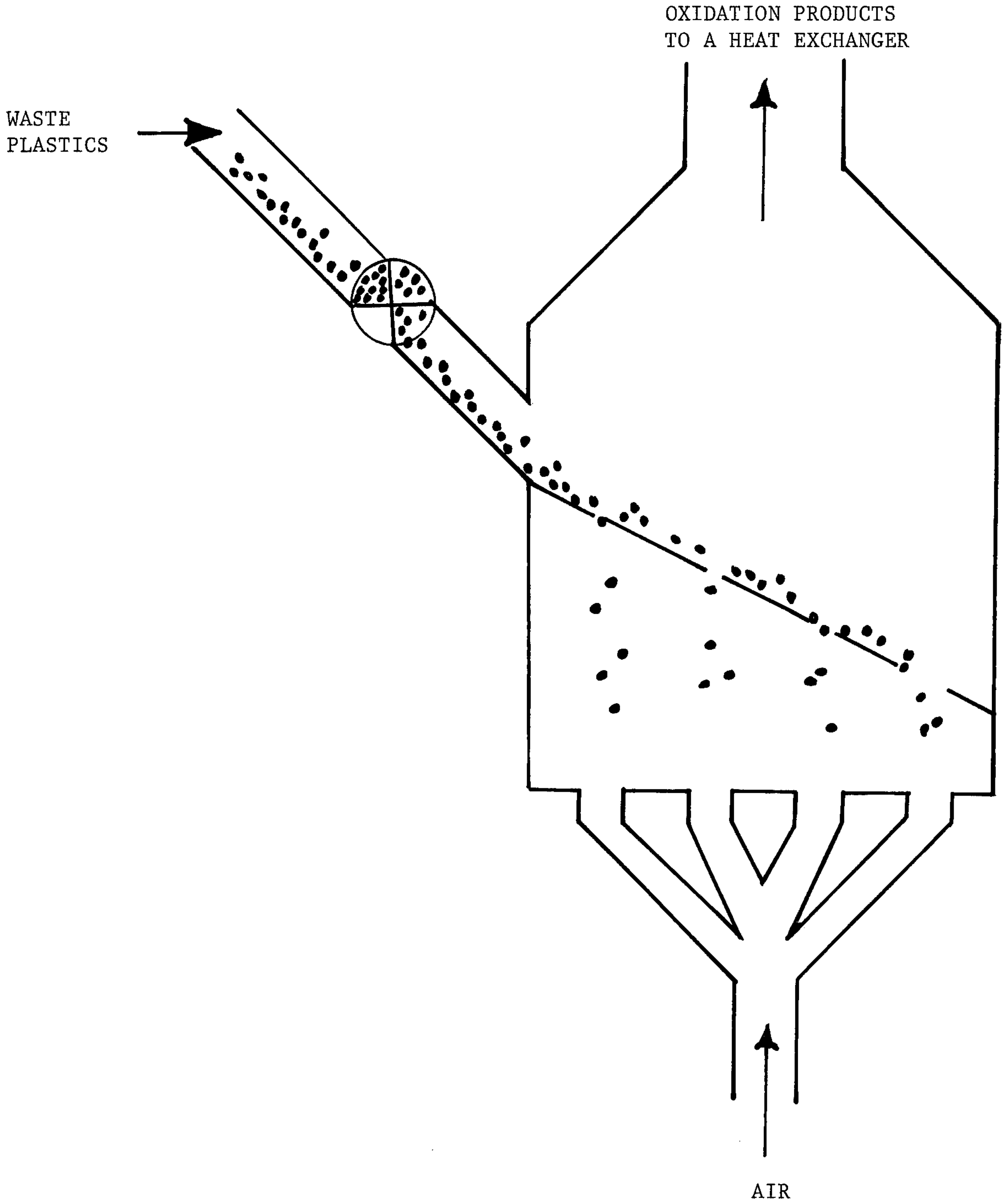


Figure 33. Waste plastic combustion reactor. Solid plastics are burned with air for the production of heat energy.

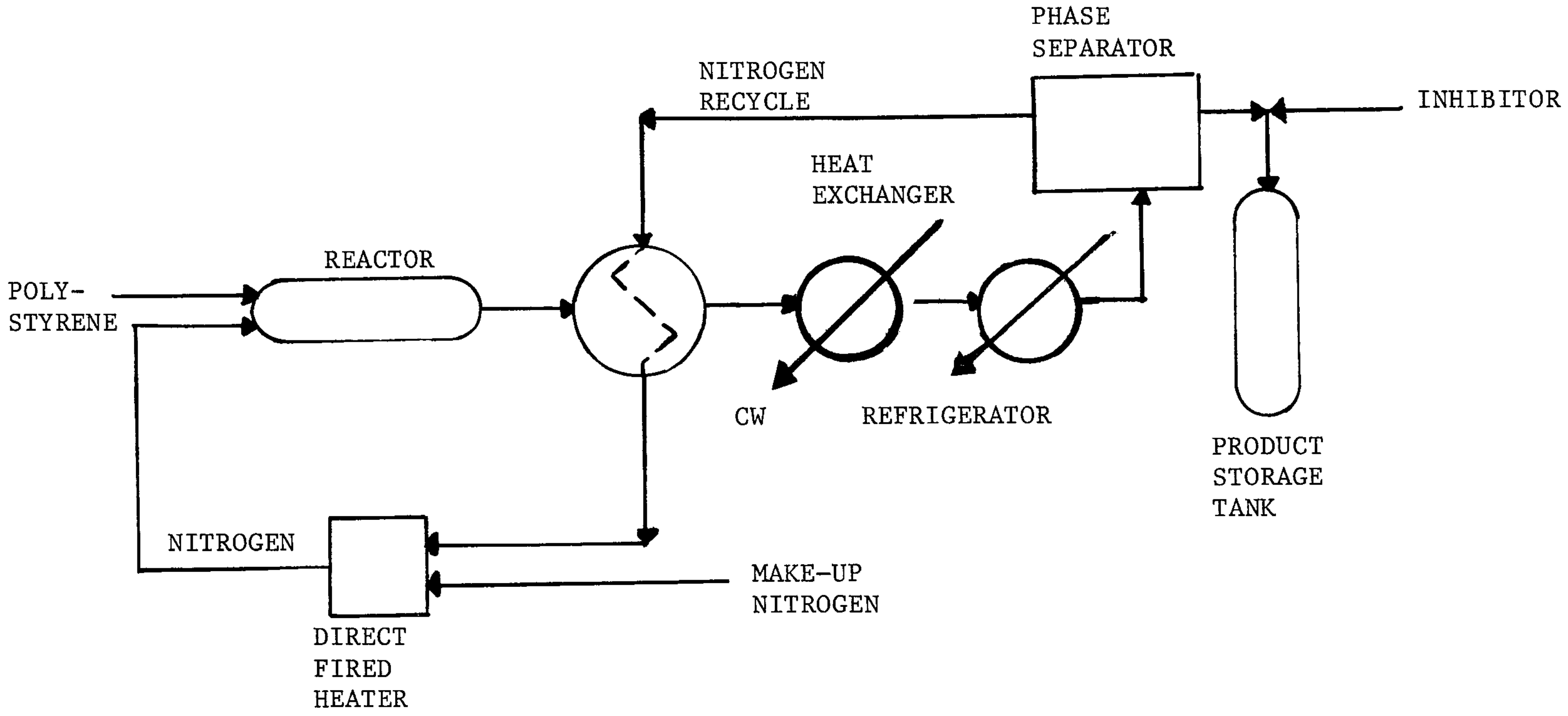


Figure 34. Proposed process for the decomposition of polystyrene with nitrogen as a heat carrier.

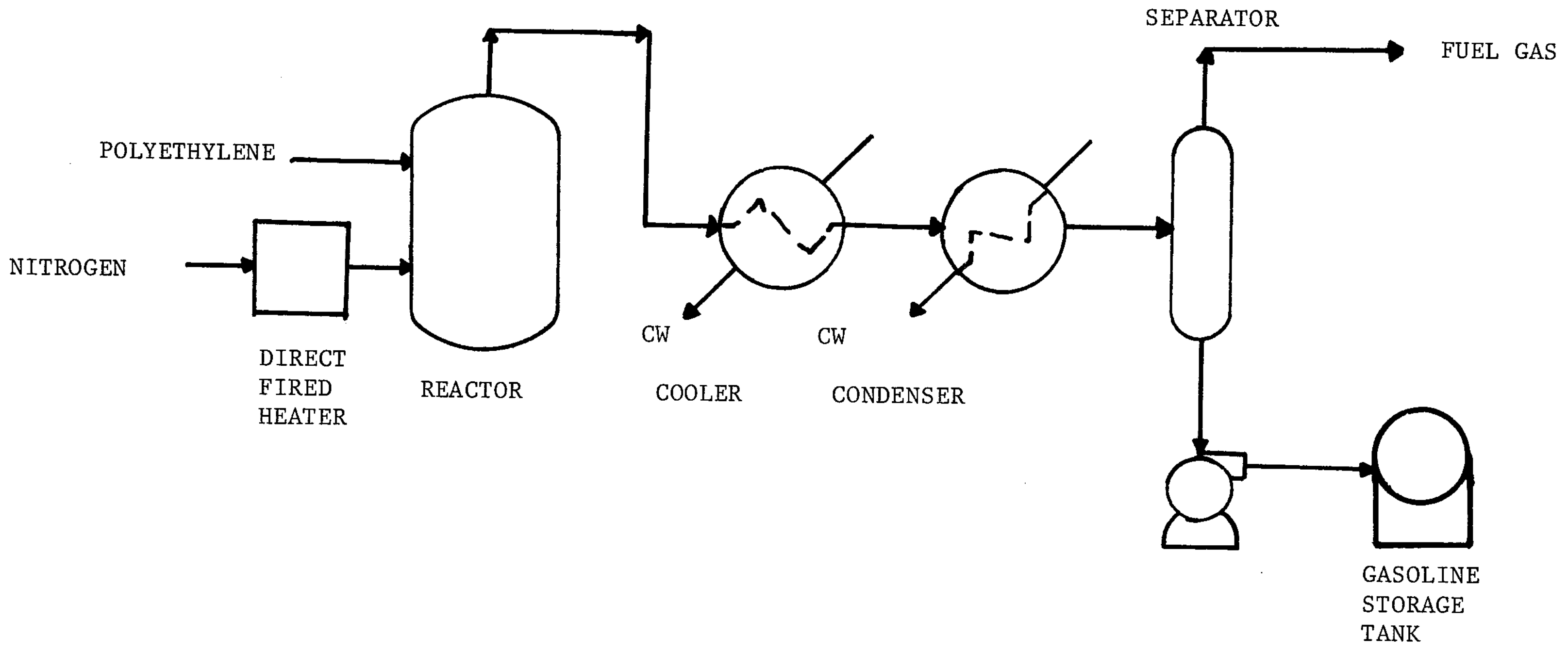


Figure 35. Proposed process for the decomposition of polyethylene with nitrogen as a heat carrier.

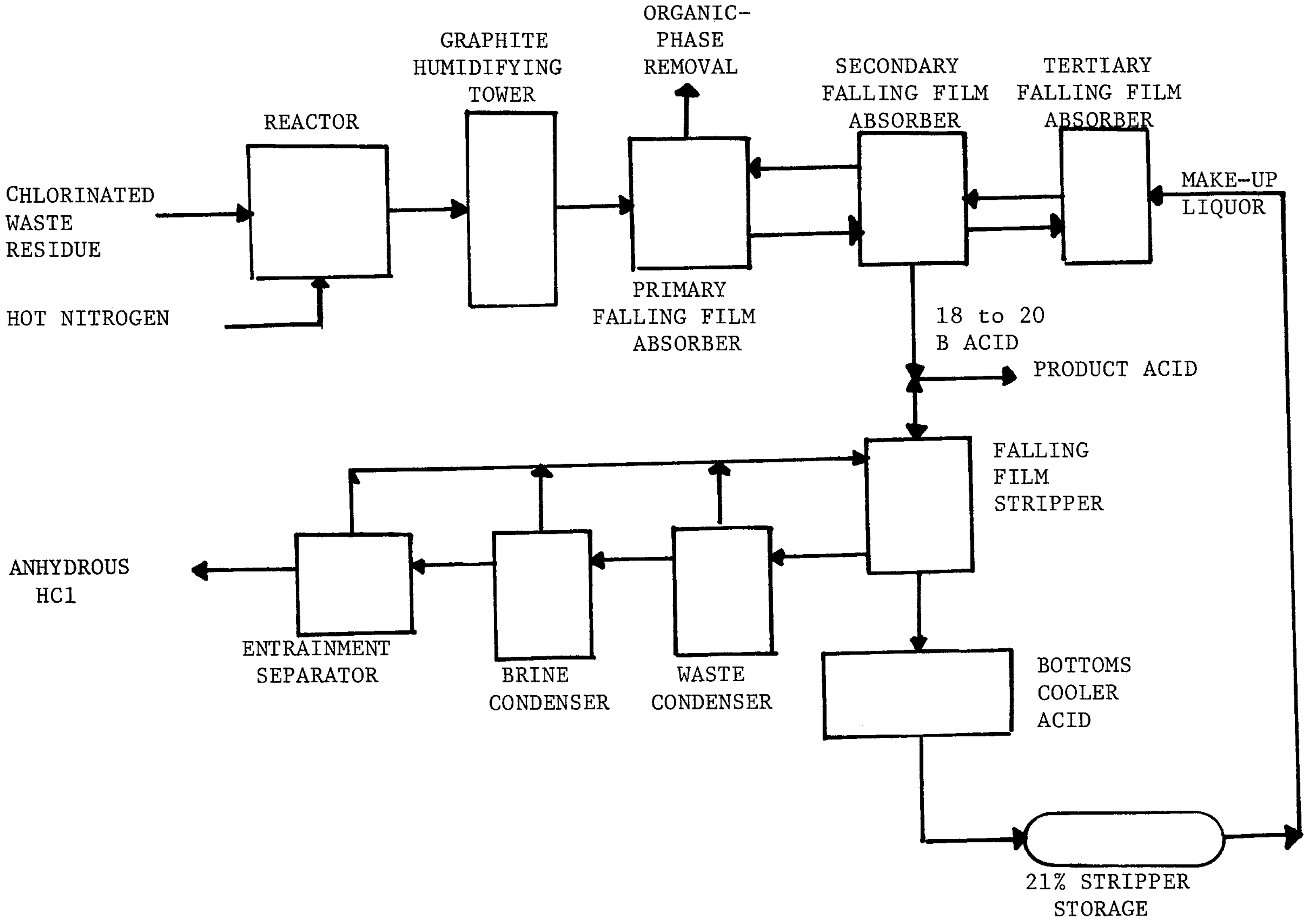


Figure 36. Proposed process for the decomposition of polyvinyl chloride with nitrogen as a heat carrier.

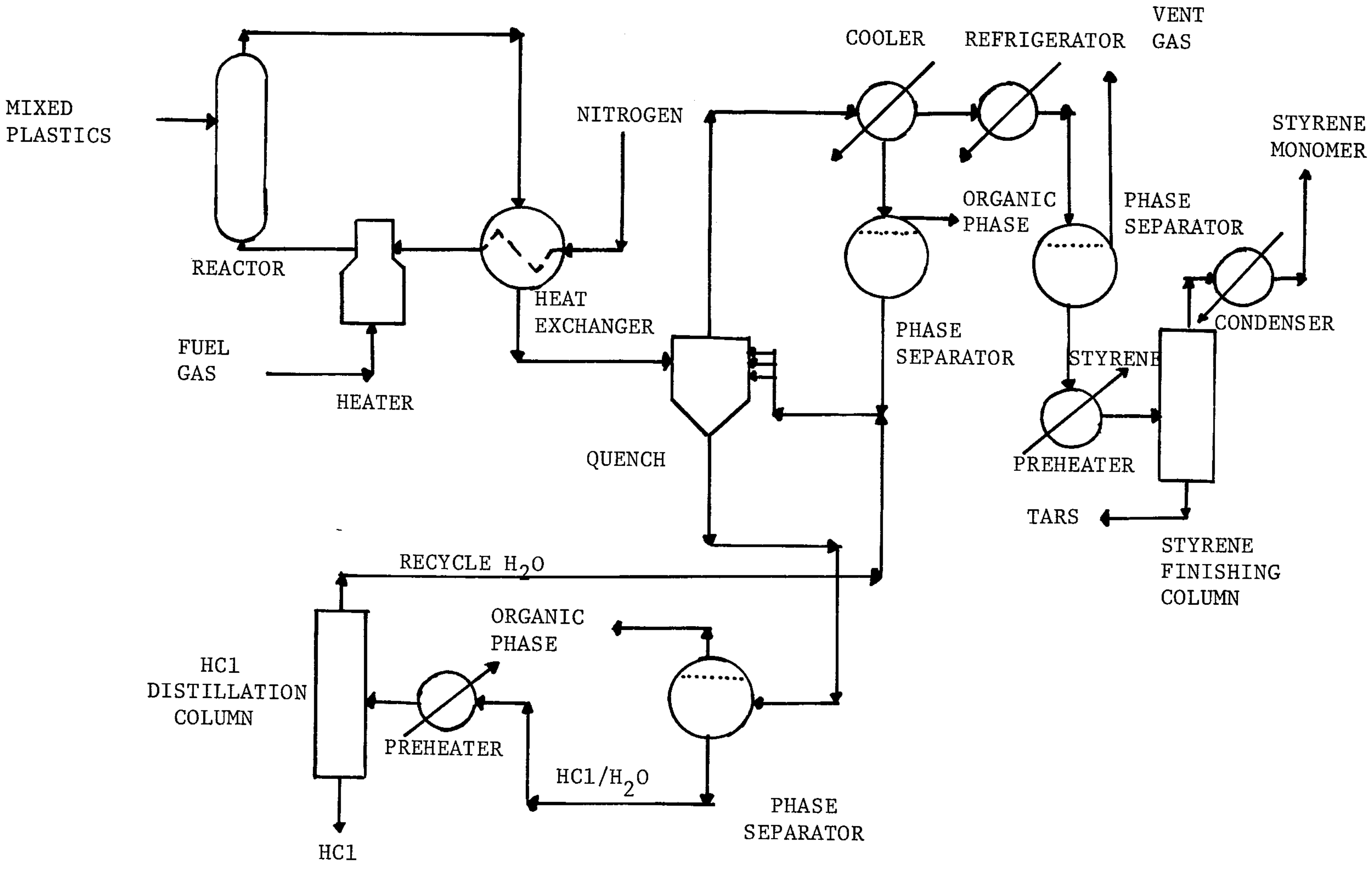


Figure 37. Proposed process for the decomposition of a mixture of three waste plastics with nitrogen as a heat carrier.

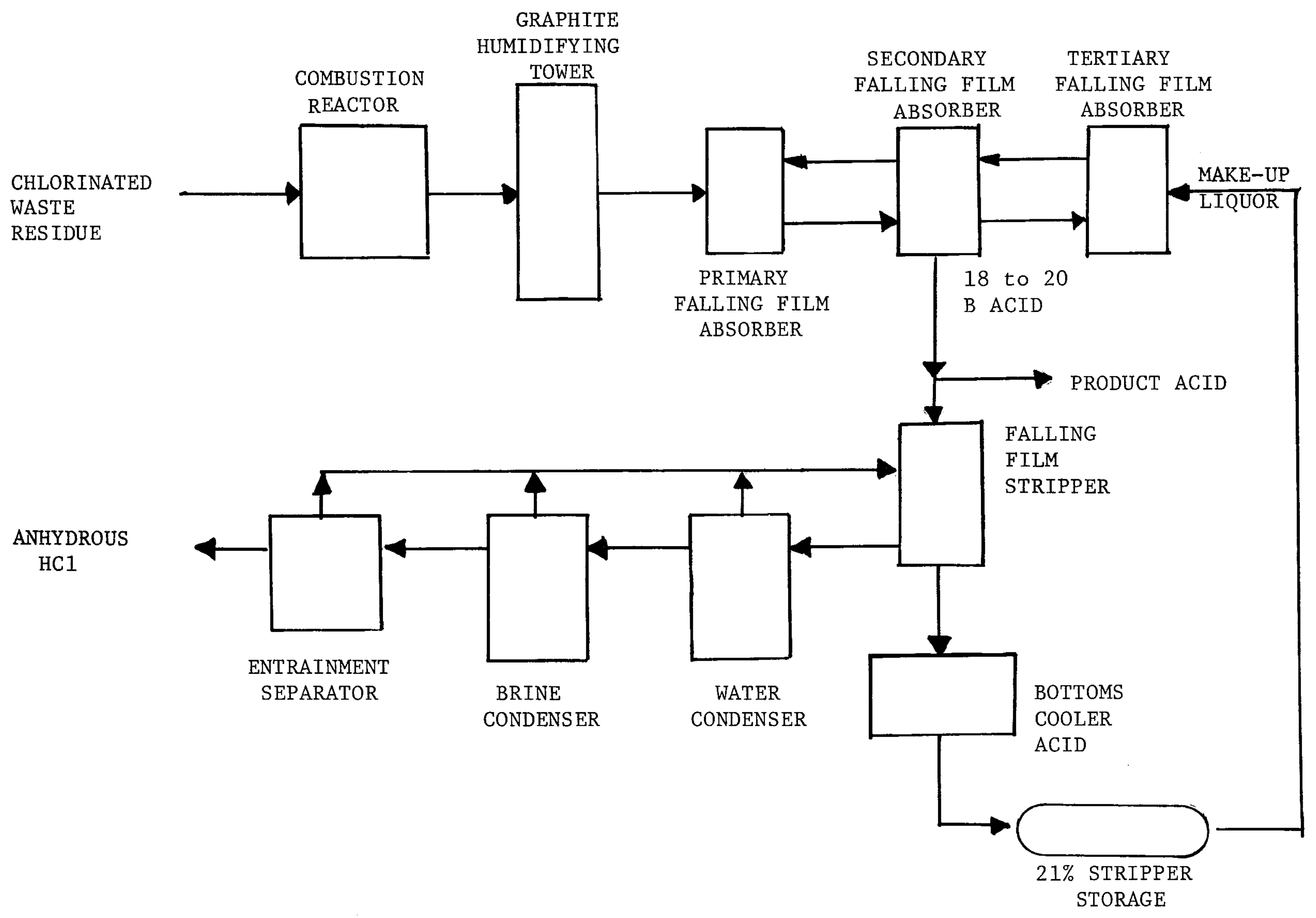


Figure 38. Proposed process to react polyvinyl chloride or a mixture of waste plastics with air.

TABLE 1

POLYETHYLENE THERMAL DECOMPOSITION (710 K REACTOR TEMPERATURE, 3,000-sec RESIDENCE TIME, 1.0 g/sec POLYETHYLENE FEED)

COMPONENT	(10^{+2}) g/sec
C_2H_4	1.8
C_2H_6	5.5
C_3H_4	0.15
C_3H_6	3.25
C_3H_8	9.60
C_4H_8	19.90
C_4H_{10}	15.85
C_5H_8	0.35
C_5H_{10}	7.65
C_5H_{12}	6.40
C_6H_{10}	0.40
C_6H_{12}	3.95
C_6H_{14}	1.65
C_7H_{14}	0.30
C_7H_{16}	0.60
N_2 $\left\{ T_{N_2} = 1{,}500 \text{ K} \right.$	191.00
 $\left\{ T_{N_2} = 1{,}000 \text{ K} \right.$	520.40
Unreacted polyethylene	22.65

TABLE 2

POLYVINYL CHLORIDE THERMAL DECOMPOSITION (723 K REACTOR TEMPERATURE, 255-sec RESIDENCE TIME, 1 g/sec POLYVINYL CHLORIDE)

COMPONENT		(10^{+2}) g/sec
HCl		51.00
C_2H_4		7.18
C_2H_6		3.71
C_3H_6		1.28
C_3H_8		1.97
C_4H_8		4.16
C_4H_{10}		2.12
C_5H_{10}		3.63
C_5H_{12}		1.13
C_6H_6		5.67
C_6H_{12}		0.83
C_6H_{14}		0.91
C_7H_8		3.02
C_8H_8		1.29
$C_2H_4Cl_2$		1.44
H_2		0.23
CH_4		1.44
N_2	T_{N_2} = 1,500 K	127.62
	T_{N_2} = 1,000 K	344.90
Unreacted polyvinyl chloride		9.00

TABLE 3

REACTOR GEOMETRY FOR A WASTE PLASTIC/NITROGEN DECOMPOSITION REACTOR*

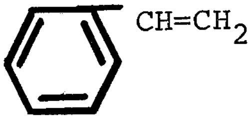
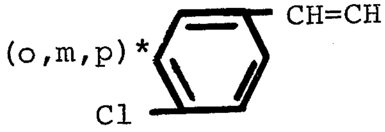
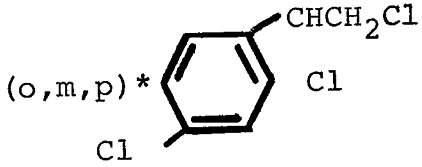
Reactant	Temperature (K)	Converted (%)	Radius (cm)	Length (cm)	Volume (cu)
Polyvinyl chloride	723	85	10	95	2.99×10^4
Polystyrene	873	90	30	115	3.25×10^5
Polyethylene ADP = 822	710	75	30	190	5.37×10^5
Polyethylene ADP = 571	700	75	30	230	6.51×10^5
ADP = 900		75	30	500	1.41×10^6
ADP = 3,000		50	30	565	1.60×10^6

* All data are based on 1.25 million lbs of plastic annually. "ADP" signifies average degree of polymerization. The nitrogen input was held at 1,500 K.

TABLE 4

NITROGEN EFFECT ON STYRENE-CHLORINE

REACTION-SECOND REACTOR (900 K REACTOR TEMPERATURE, 1.25 atme, 0.68 g/sec CHLORINE FEED, 1.00 g/sec STYRENE FEED, 25 sec RESIDENCE TIME)

Species	0 g/sec N_2 (g/sec)	1.66 g/sec N_2 (g/sec)
Cl_2	0.023	0.211
HCl	0.098	0.073
	0.207	0.397
	0.866	0.664
	0.140	0.159
	0.348	0.178

*(ortho, meta, para).

TABLE 5

AMOUNT OF INDICATED HEAT SOURCE*

NECESSARY FOR THE SPECIFIED CONVERSION

		Nitrogen	Steam
Polystyrene, 823 K		(g)	(g)
Converted (%)	55	9.35	4.47
	50	9.13	4.38
	25	7.96	3.82
Polyvinyl Chloride, 673 K			
Converted (%)	90	1.14	0.58
	75	1.04	0.55
	50	1.00	0.53
Polyethylene, 685 K ADP 822			
Converted (%)	75	1.75	0.86
	50	1.51	0.74

* 1,500 K heat source temperature, 1 g plastic.

TABLE 6

MIXTURE REACTION PRODUCTS AT 700 K AND 4,400 sec SOLID RESIDENCE TIME. BASIS: 1 g OF MIXTURE, WITH EQUAL PARTS (BY WEIGHT) OF POLYVINYL CHLORIDE, POLYETHYLENE, AND POLYSTYRENE.

Product	g $(x10^3)$	Product	g $(x10^3)$
CH_4	1.00	C_6H_6	21.40
C_2H_4	32.73	C_6H_{10}	1.23
C_2H_6	31.35	C_6H_{12}	15.64
C_3H_4	0.49	C_6H_{14}	8.71
C_3H_6	14.99	C_7H_8	11.42
C_3H_8	37.79	C_7H_{14}	0.98
C_4H_8	78.68	C_7H_{16}	1.96
C_4H_{10}	58.39	C_8H_8	39.47
C_5H_8	1.22	C_2HCl_2	5.52
C_5H_{10}	37.96	H_2	0.99
C_5H_{12}	24.77	HCl	175.92
Polyvinyl chloride	14.56		
Polystyrene	298.52	Steam (1,500 K) Required	1045.30
Polyethylene	88.17		

TABLE 7

REACTOR GEOMETRY FOR A WASTE PLASTIC/WATER DECOMPOSITION REACTOR*

Reactant	Temperature (K)	Converted (%)	Radius (cm)	Length (cm)	Volume (cm^3)
Polyvinyl Chloride	700	85	30	24	$6.79 x 10^4$
Polystyrene	823	55	20	555	$6.98 x 10^5$
Polyethylene ADP = 822	700	75	30	375	$1.06 x 10^6$
Mixture of these three (1/3 each by weight)	823	85	20	550	$6.91 x 10^5$

* All data are based on 1.25 million lbs of plastic annually. "ADP" signifies average degree of polymerization. The steam input was held at 1,500 K.

TABLE 8

WASTE PLASTICS/AIR ADIABATIC REACTOR*

Products (g)	Polyvinyl Chloride	Polyethylene	Polystyrene	Mixture (Equal Parts by Weight of the three)
CO_2	1.41	3.06	3.19	2.69
CO	traces	0.06	0.08	< 0.01
H_2O	0.30	1.27	0.66	0.77
N_2	12.00	13.19	11.74	12.85
NO	traces	0.06	0.06	0.05
O_2	2.12	0.34	0.34	0.01
HCl	0.55	--	--	0.18
Cl_2	0.04	--	--	traces
Others	traces	0.02	0.02	0.01
Temperature out of reactor	1,200 K	2,130 K	2,200 K	1,870 K
Weight of Air input	15.40	16.99	15.10	16.55

* All data based on 1 g of plastic.

TABLE 9

PROCESS COST SUMMARY. POLYSTYRENE DECOMPOSITION WITH NITROGEN AS A HEAT CARRIER. INSTALLED UNIT COST: $219,000

Summary	$/hr	
Utilities	0.90	
Raw materials	1.40	
Labor with 100% overhead	9.50	
Depreciation, maintenance, taxes, etc. (20% of capital annually)	5.50	
Total	17.30	
Waste polystyrene-processing cost	1.1	¢/lb feed
Product credit: styrene	7.2	¢/lb feed
Net credit	6.1	¢/lb feed

TABLE 10

PROCESS COST SUMMARY: POLYETHYLENE DECOMPOSITION WITH NITROGEN AS A HEAT CARRIER. INSTALLED UNIT COST: $199,000

Summary	$/hr	
Utilities	1.50	
Raw materials	5.30	
Labor with 100% overhead	9.50	
Depreciation, maintenance, taxes, etc. (20% of capital annually)	5.05	
Total	21.35	
Waste polyethylene-processing cost	1.8	¢/lb feed
Product credits: Gasoline stream and fuel gas	0.5	¢/lb feed
Net expense	1.3	¢/lb feed

TABLE 11

PROCESS COST SUMMARY: POLYVINYL CHLORIDE DECOMPOSITION WITH NITROGEN AS A HEAT SOURCE. INSTALLATION UNIT COST: $464,000.

Summary	$/hr	
Utilities	7.80	
Raw materials	19.70	
Labor with 100% overhead	9.50	
Depreciation, maintenance, taxes, etc. (20% of capital annually)	11 70	
Total	48.70	
Waste polyvinyl chloride-processing cost	3.1	¢/lb feed
Product credits: organic stream and HCl acid	3.1	¢/lb feed
Net expense	0	¢/lb feed

TABLE 12

PROCESS COST SUMMARY: MIXED PLASTICS DECOMPOSITION WITH NITROGEN AS A HEAT CARRIER. INSTALLED UNIT COST: $307,000

Summary	$/hr
Utilities	3.35
Raw materials	7.90
Labor with 100% overhead	9.50
Depreciation, maintenance, taxes, etc. (20% of capital annually)	7.75
Total	28.50
Waste mixed plastics-processing cost	1.8 ¢/lb feed
Product credits: styrene, HCl acid, gasoline stream	1.7 ¢/lb feed
New expense	0.1 ¢/lb feed

TABLE 13

PROCESS COST SUMMARY: COMBUSTION WITH AIR OF POLYSTYRENE OR POLYETHYLENE WASTE. INSTALLED BOILER UNIT: $13,000

Summary	$/hr
Utilities*	(0.40)
Labor with 100% overhead	9.50
Depreciation, maintenance, taxes, etc. (20% of capital annually)	0.35
Total	9.45
Waste polystyrene or polyethylene disposal cost	0.6 ¢/lb feed

*Includes credit for process heat generated.

TABLE 14

PROCESS COST SUMMARY: COMBUSTION WITH AIR OF POLYVINYL CHLORIDE OR MIXED PLASTICS SYSTEM. INSTALLED PLANT COST: $395,000.

Summary	$/hr	
Utilities and raw materials	18.00	
Labor with 100% overhead	9.50	
Depreciation, maintenance, taxes, etc. (20% of capital annually)	9.85	
Total	37.35	
Chlorinated plastic-processing cost	2.4	¢/lb feed
Product credit: hydrochloric acid	3.1	¢/lb PVC feed
Net credit	0.7	¢/lb feed*

*Calculated on the basis of pure PVC feed.

TABLE 15

PROCESS COST SUMMARY: POLYSTYRENE DECOMPOSITION WITH STEAM AS A HEAT CARRIER. INSTALLED UNIT COST $183,000.

Summary	$/hr	
Utilities	2.20	
Raw materials	1.40	
Labor with 100% overhead	9.50	
Depreciation, maintenance, taxes, etc. (20% of capital annually)	4.60	
Total	17.70	
Waste polystyrene-processing cost	1.1	¢/lb feed
Product credit: styrene	7.2	¢/lb feed
Net credit	6.1	¢/lb feed

TABLE 16

PROCESS COST SUMMARY: POLYETHYLENE DECOMPOSITION WITH STEAM AS A HEAT CARRIER. INSTALLED UNIT COST $151,000.

Summary	$/hr	
Utilities	2.50	
Labor with 100% overhead	9.50	
Depreciation, maintenance, taxes, etc. (20% of capital annually)	3.80	
Total	15.80	
Waste polyethylene-processing cost	1.0	¢/lb feed
Product credits: gasoline stream and fuel gas	0.4	¢/lb feed
Net expense	0.6	¢/lb feed

TABLE 17

PROCESS COST SUMMARY: POLYVINYL CHLORIDE DECOMPOSITION WITH STEAM AS A HEAT CARRIER. INSTALLED UNIT COST: $436,000.

Summary	$/hr	
Utilities	7.80	
Raw materials	7.20	
Labor with 100% overhead	9.50	
Depreciation, maintenance, taxes, etc. (20% of capital annually)	11.00	
Total	35.50	
Waste polyvinyl chloride-processing cost	2.3	¢/lb feed
Product credits: organic stream and HCl acid	3.1	¢/lb feed
Net credit	0.8	¢/lb feed

TABLE 18

PROCESS COST SUMMARY: MIXED PLASTICS DECOMPOSITION WITH STEAM AS A HEAT CARRIER. INSTALLED UNIT COST: $282,000.

Summary	$/hr	
Utilities	3.65	
Raw materials	1.40	
Labor with 100% overhead	9.50	
Depreciation, maintenance, taxes, etc. (20% of capital annually)	7.15	
Total	21.70	
Waste plastic disposal cost	1.4	¢/lb
Product credits:		
styrene	0.3	
HCl (18 B)	1.0	
gasoline stream	0.4	
Total	1.7	¢/lb feed
Waste plastic-processing cost	1.4	¢/lb feed
Product credits: styrene, HCl acid, gasoline stream	1.7	¢/lb feed
Net credit	0.3	¢/lb feed

APPENDIX A

EQUILIBRIUM PRODUCT DISTRIBUTION

The quantities presented in this appendix represent the results of the equilibrium product distributions and analyses described in chapter 3. The values tabulated are the moles of each particular product per unit monomer of plastic. The values are presented as a function of temperature, pressure, and initial composition (weight percent polymer in the reacting system).

The tabular form used is convenient for the preparation of plots, as is illustrated in Figure 39, where methane production is presented as a function of temperature for the polyethylene decomposition. The data format used in the tables is an exponential form, i.e., X.XX-Y is equivalent to X.XXX * 10^{-Y}. Zero indicates a number of moles less than 1 * 10^{-5}. A complete list of the species considered in the equilibrium analysis is included in this appendix.

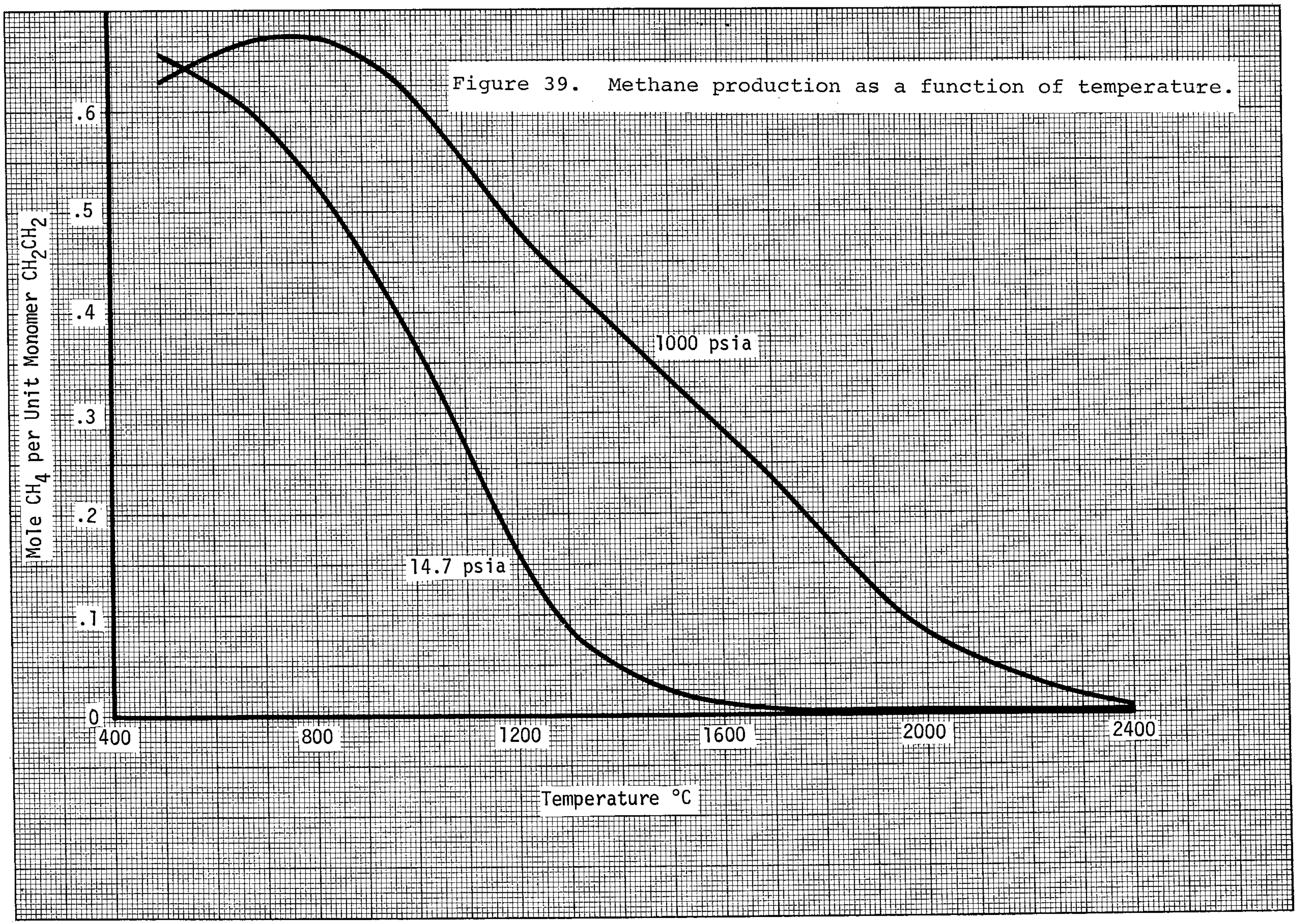


Figure 39. Methane production as a function of temperature.

TABLE 19

POLYETHYLENE DECOMPOSITION. COMPOSITION AS A FUNCTION OF TEMPERATURE, PRESSURE, AND INITIAL COMPOSITION

Percent polymer W/W	T (C)	psia	C_6H_6	C_2H_4	CH_4	CH_2CH C_6H_5
100	2,400	1,000	0	1.19-2	1.95-2	9.53-1
		14.7	0	1.64-4	2.86-4	1.01
	2,000	1,000	0	4.44-2	8.01-2	8.29-1
		14.7	0	7.88-4	1.50-3	9.97-1
	1,600	1,000	0	1.62-1	2.86-1	4.06-1
		14.7	0	6.32-3	1.45-2	9.70-1
	1,200	1.000	1.90-1	2.08-2	4.84-1	9.70-1
		14.7	2.62-1	1.73-2	1.56-1	7.44-1
	800	1,000	1.66-1	1.83-2	6.72-1	3.22-2
		14.7	2.32-1	2.88-3	5.32-1	1.92-1
	500	1,000	1.29-1	0	6.27-1	1.85-3
		14.7	2.04-1	0	6.51-1	1.20-2

TABLE 20

POLYETHYLENE/NH_3 COMPOSITION AS A FUNCTION OF TEMPERATURE, PRESSURE, AND INITIAL COMPOSITION

Percent polymer W/W	T (C)	psia	CH_4	C_6H_6	H_2
70	1,200	1,000	9.81-1	1.23-1	5.05-1
		14.696	2.90-1	2.08-1	1.59
	800	1,000	1.30	8.65-2	7.91-2
		14.696	1.07	1.46-1	4.45-1
	500	1,000	1.34	6.53-2	4.65-3
		14.696	1.35	9.95-2	2.92-2
50	1,200	1,000	1.57	3.93-2	1.03
		14.696	4.42-1	1.56-1	2.75
	800	1,000	1.98	0	4.69-1
		14.696	1.71	4.29-2	8.87-1
	500	1,000	1.99	0	4.36-1
		14.696	1.99	0	4.69-1
20	1,200	1,000	1,99	0	7.93
		14.696	9.63-1	2.58-2	9.44
	800	1,000	2.01	0	7.80
		14.696	2.01	0	7.91
	500	1,000	2.01	0	6.90
		14.696	2.01	0	7.90

TABLE 21

POLYETHYLENE/H_2O COMPOSITION AS A FUNCTION OF TEMPERATURE, PRESSURE, AND INITIAL COMPOSITION

Percent polymer W/W	T (C)	psia	CH_4	CO	CO_2	H_2
	1,200	1,000	9.16-1	6.64-1	3.61-4	5.76-1
		14.7	2.57-1	6.65-1	0	1.59-1
70	800	1,000	1.24-1	6.18-1	2.25-2	8.43-2
		14.7	9.95-1	6.65-1	0	4.96-1
	500	1,000	1.22	1.33-1	2.66-1	4.50-3
		14.7	1.29-1	5.70-1	4.80-2	3.63-2
	1,200	1,000	5.09	1.46	2.46-2	2.46
		14.7	2.63-1	1.55	0	2.91
	800	1,000	1.19	4.82	3.15-1	7.25-1
50		14.7	4.69-1	1.51	1.03-2	2.59
	500	1,000	1.47	1.62-2	5.07-1	8.62-2
		14.7	1.30	1.72-1	5.18-1	5.91-1
	1,200	1,000	9.63-3	1.50	5.06-1	4.49
		14.7	0	1.50	5.05-1	4.52
	800	1,000	7.32-1	4.67-1	8.09-1	2.62
20		14.7	2.24-3	1.14	8.64-1	4.88
	500	1,000	1.40	9.95-3	6.02-1	4.31-1
		14.7	8.24	1.31-1	1.05	2.59

TABLE 22

POLYETHYLENE/AIR COMPOSITION AS A FUNCTION OF TEMPERATURE, PRESSURE, AND INITIAL COMPOSITION

Percent polymer W/W	T (C)	psia	CH_4	CO	CO_2	H_2	HCN
70	1,200	1,000	5.04-1	1.75-1	0	2.83-1	1.93-2
		14.696	1.43-1	1.74-1	0	8.51-1	8.36-2
	800	1,000	6.74-1	1.72-1	1.24-3	4.28-2	5.07-4
		14.696	5.55-1	1.74-1	0	2.44-1	2.24-3
	500	1,000	6.75	6.61-2	5.41-2	2.37-3	0
		14.696	7.07-1	1.69-1	2.84-3	1.59-2	0
50	1,200	1,000	5.33-1	4.06-1	0	3.58-1	3.24
		14.696	1.34-1	4.06-1	0	9.83-1	1.40-1
	800	1,000	7.45-1	3.97-1	4.62-3	5.66-2	8.47-4
		14.696	5.89-1	4.08-1	0	3.11-1	3.74-3
	500	1,000	7.28-1	1.27-1	1.39-1	3.00-3	0
		14.696	7.79-1	3.85-1	1.05-2	2.09-2	0
20	1,200	1,000	3.54-1	1.62	3.43-3	6.62-3	1.83-2
		14.696	7.64-2	1.64	0	0	1.79-1
	800	1,000	7.32-1	1.01	2.61-1	1.04-1	0
		14.696	3.70-1	1.64	1.90-3	1.35-3	1.62-3
	500	1,000	9.89-1	3.21-1	6.59-1	3.14-3	0
		14.696	8.78-1	6.53-1	4.77-1	3.17-2	0

TABLE 23

POLYETHYLENE/Cl_2 COMPOSITION AS A FUNCTION OF TEMPERATURE, PRESSURE, AND INITIAL COMPOSITION

Percent polymer W/W	T (C)	psia	CH_4	C_6H_6	HCl
70	1,200	1,000	3.84-1	2.09-1	3.37-1
		14.696	1.14-1	2.67-1	3.38-1
	800	1,000	5.08-1	1.87-1	3.37-1
		14.696	4.26-1	2.50-1	3.38-1
	500	1,000	5.16-1	1.50-1	3.37-1
		14.696	4.77-1	2.23-1	3.38-1
50	1,200	1,000	2.61-1	2.34-1	7.86-1
		14.696	6.76-2	2.72-1	7.88-1
	800	1,000	3.63-1	2.16-1	7.86-1
		14.696	2.93-1	2.72-1	7.87-1
	500	1,000	3.69-1	1.80-1	7.86-1
		14.696	3.89-1	2.50-1	7.89-1
			C_2H_6	CCl_2 CCl_2	HCl
20	1,200	1,000	2.77-1	0	2.21
		14.696	1.14-1	0	3.06
	800	1,000	2.64-1	1.87-1	2.39
		14.696	2.68-1	1.90-1	2.39
	500	1,000	2.69-1	1.82-1	2.39
		14.696	2.69-1	1.90-1	2.39

TABLE 24

POLYSTYRENE DECOMPOSITION, COMPOSITION AS A FUNCTION OF TEMPERATURE, PRESSURE, AND INITIAL COMPOSITION

Percent polymer W/W	T(C)	psia	C_2H_2	C_6H_6	$C_2H_2CHC_6H_5$
100	1,200	1,000	8.98-3	1.19	1.03-1
		14.7	1.62-1	1.25	2.59-2
	800	1,000	0	1.29	3.10-2
		14.7	3.36-4	1.32	7.81-3
	500	1,000	0	1.33	5.18-3

TABLE 25

POLYSTYRENE/NH_3 COMPOSITION AS A FUNCTION OF TEMPERATURE, PRESSURE, AND INITIAL COMPOSITION

Percent polymer W/W	T (C)	psia	CH_4	C_6H_6	H_2
	1,200	1,000	1.85	7.88-1	9.82-1
		14.7	5.43-1	1.00-1	3.05
70	800	1,000	2.44	7.02	1.46-1
		14.7	2.04	9.48-1	8.49-1
	500	1,000	2.49	5.58-1	8.44-3
		14.7	2.57	8.37-1	5.46-2
	1,200	1,000	4.27	4.41-1	2.51
		14.7	1.19	7.68-1	7.25
50	800	1,000	5.78	2.79-1	3.92-1
		14.7	4.67	5.26-1	2.14
	500	1,000	6.03	2.06-1	2.32-2
		14.7	6.01	3.07-1	1.45-1
	1,200	1,000	7.96	0	2.50+1
		14.7	3.48	1.59-1	3.17+1
20	800	1,000	8.08	0	2.46+1
		14.7	8.08	0	2.50+1
	500	1,000	8.09	0	2.18+1
		14.7	8.08	0	2.49+1

TABLE 26

POLYSTYRENE/H_2O COMPOSITION AS A FUNCTION OF TEMPERATURE, PRESSURE, AND INITIAL COMPOSITION

Percent polymer W/W	T (C)	psia	CH_4	CO	CO_2	H_2
	1,200	1,000	1.70	2.48	1.25-3	1.03
		14.7	4.67-1	2.49	0	2.97
70	800	1,000	2.30	2.36	6.18	1.57-1
		14.7	1.87	2.48	0	8.92-1
	500	1,000	2.05	5.21-1	9.82-1	7.25-3
	1,200	1,000	2.27	5.68	2.48-2	5.16
		14.7	8.25-1	5.78	0	7.38
50	800	1,000	3.94-1	2.85	1.20	1.36
		14.7	2.24	5.74	1.53-2	5.28
	500	1,000	4.84	5.20-1	2.62	3.45-2
		14.7	4.43	1.54	2.02	7.34-1
	1,200	1,000	2.88-2	5.87	2.20	1.42+1
		14.7	0	5.89	2.19	1.43+1
20	800	1,000	2.47	1.98	3.64	8.38
		14.7	7.13-3	4.46	3.61	1.57+1
	500	1,000	4.71	4.97-2	3.32	1.29
		14.7	2.84	5.39-1	4.68	8.28

TABLE 27

POLYSTYRENE/AIR COMPOSITION AS A FUNCTION OF TEMPERATURE, PRESSURE, AND INITIAL COMPOSITION

Percent polymer W/W	T (C)	psia	CH_4	CO	CO_2	C_6H_6	H_2	HCN
70	1,200	1,000	1.07-1	6.52-1	0	1.03	1.17-1	6.56-2
		14.7	2.27-2	6.53-1	0	1.05	2.82-1	2.66-1
	800	1,000	1.59-1	6.45-1	2.78-3	1.03	1.90-2	1.79-3
		14.7	1.36-1	6.52-1	0	1.17	1.12-1	7.52-3
	500	1,000	8.82-2	3.21-1	1.64-1	9.93-1	6.99-4	0
		14.7	1.96-1	6.41-1	6.83-3	1.15	7.94-3	0
50	1,200	1,000	2.75-1	1.52	2.20-4	8.73-1	2.90-1	1.19-1
		14.7	5.37-2	1.51	0	8.36-1	6.65-1	4.80-1
	800	1,000	4.29-1	1.49	1.12-2	8.69-1	4.89-2	3.23-3
		14.7	3.24-1	1.51	0	9.98-1	2.63-1	1.36-2
	500	1,000	2.79-1	6.01-1	4.60-1	8.70-1	1.97-3	0
		14.7	4.74-1	1.46	2.62-2	9.62-1	1.89-2	0
20	1,200	1,000	1.00	6.12	2.35-3	8.93-2	1.52	2.48-1
		14.7	1.33-1	6.12	0	4.27-2	2.86	8.93-1
	800	1,000	1.79	5.85	1.38-1	4.43-2	3.03-1	5.94-3
		14.7	1.16	6.14	9.26-4	1.25-1	1.34	2.91-2
	500	1,000	1.29	1.78	2.18	3.80-1	1.01-2	0
		14.7	1.88	5.55	2.91-1	5.98-2	1.10-1	1.45-4

TABLE 28

POLYSTYRENE/Cl_2 COMPOSITION AS A FUNCTION OF TEMPERATURE, PRESSURE, AND INITIAL COMPOSITION

Percent polymer W/W	T (C)	psia	CCl_4	C_6H_6	CCl_2CCl_2	HCl
	1,200	1,000	2.18-1	1.16	0	3.20-1
		14.7	1.34-4	1.25	0	1.25
70	800	1,000	2.75-4	1.24	2.07-1	4.19-1
		14.7	0	1.26	2.07-1	4.19-1
	500	1,000	2.56-3	1.26	2.05-1	4.17-1
		14.7	4.42-4	1.26	2.07-1	4.19-1
	1,200	1,000	5.46-1	1.12	0	5.94-1
		14.7	2.13-3	7.45-1	0	2.88
50	800	1,000	8.61-4	1.14	4.78-1	9.69-1
		14.7	1.69-4	1.17	4.84-1	9.79-1
	500	1,000	7.04-3	1.16	4.72-1	9.63-1
		14.7	1.40-3	1.17	4.84-1	9.79
	1,200	1,000	2.25-1	8.81-1	0	2.26
		14.7	6.94-1	2.82-3	0	7.87
20	800	1,000	5.22-3	6.70-1	1.94	3.94
		14.7	1.02-3	6.83-1	1.96	3.95
	500	1,000	4.22-2	6.84-1	1.90	3.89
		14.7	8.42-3	6.83-1	1.96	3.94

TABLE 29

SYSTEM: POLYVINYL CHLORIDE DECOMPOSITION, COMPOSITION AS A FUNCTION OF TEMPERATURE, PRESSURE, AND INITIAL COMPOSITION

Percent polymer W/W	T (C)	psia	C_2H_2	C_2H_6	CH_2CHCH_5	HCl
	1,200	1,000	5.82-3	3.08-1	1.69-2	9.98-1
		14.7	9.88-2	2.95-1	3.84-3	1.00
100	800	1,000	0	3.25-1	4.90-3	1.00-0
		14.7	2.12-4	3.31-1	1.23-3	9.98-1
	500	1,000	0	3.31-1	8.13-4	9.98-1
		14.7	0	3.33-1	2.01-4	9.98-1

TABLE 30

SYSTEM: POLYVINYL CHLORIDE/NH_3. EQUILIBRIUM COMPOSITION AS A FUNCTION OF TEMPERATURE, PRESSURE, AND INITIAL COMPOSITION (moles products/unit monomer)

Percent polymer W/W	T (C)	psia	CH_4	H_2	HCl
70	1,200	1,000	1.052	7.207-1	9.983-1
		14.696	2.691-1	1.929	9.996-1
	800	1,000	1.443	1.974-1	9.989-1
		14.696	1.154	6.201-1	9.999-1
	500	1,000	1.553-1	7.002-3	9.995-1
		14.696	1.541	4.378-2	9.997-1
50	1,200	1,000	1.911	2.602	9.995-1
		14.696	5.735-1	4.600	9.998-1
	800	1,000	1.999	2.478	1.000
		14.696	1.985	2.507	9.964-1
	500	1,000	2.000	2.251	1.000
		14.696	2.000	2.500	9.999-1
20	1,200	1,000	1.982	1.899+1	9.997-1
		14.696	1.172	2.023+1	1.000
	800	1,000	2.000	1.874+1	9.999-1
		14.696	1.999	1.902+1	9.999-1
	500	1,000	2.000	1.650+1	9.998-1
		14.696	2.000	1.897+1	1.000

TABLE 31

POLYVINYL CHLORIDE/H_2O COMPOSITION AS A FUNCTION OF TEMPERATURE, PRESSURE, AND INITIAL COMPOSITION

Percent polymer W/W	T (C)	psia	CH_4	CO	H_2	H_2O	HCl
70	1,200	1,000	5.211-1	1.465	1.424	1.158-2	9.996
		14.696	1.80-1	1.486	1.946	0	9.998-1
	800	1,000	9.469-1	7.60-1	4.404-1	1.502-1	9.996-1
		14.696	5.179-1	1.478-1	1.447	2.643-3	9.997-1
	500	1,000	1.219	9.448-2	1.834-2	2.563-2	9.996-1
		14.696	1.084	4.702-1	2.569-1	6.206-2	1.000
50	1,200	1,000	2.317-2	1.710	3.197	1.226	9.998-1
		14.696	0	1.738	3.262	1.208	1.000
	800	1,000	7.630-1	5.569-1	1.389	1.553	1.000
		14.696	6.826-3	1.516	3.457	9.982-1	9.997-1
	500	1,000	1.197	1.576-2	1.949-1	1.879	1.000
		14.696	8.820-1	1.701-1	1.302	1.403	1.000
20	1,200	1,000	0	9.569-1	4.042	1.083+1	9.999-1
		14.696	0	9.574-1	4.042	1.083+1	9.999-1
	800	1,000	1.998-1	4.382-1	3.763	1.072+1	1.000
		14.696	0	5.606-1	4.438-1	1.044+1	9.999-1
	500	1,000	1.046	1.218-2	8.020-1	1.198+1	9.999-1
		14.696	2.409-1	1.185-1	3.917	1.048+1	1.000

TABLE 32

POLYVINYL CHLORIDE/AIR COMPOSITION AS A FUNCTION OF TEMPERATURE, PRESSURE, AND INITIAL COMPOSITION

Percent polymer W/W	T (C)	psia	CH_4	CO	CO_2	C_6H_6	H_2	HCl	HCN
70	1,200	1,000	6.37-2	3.898-1	0	2.211-1	8.686-2	9.991-1	3.592-2
		14.696	1.042-2	3.897-1	0	1.939-1	1.769-1	9.996-1	1.410-1
	800	1,000	1.108-1	3.866-1	1.657-3	2.206-1	1.581-2	9.995-1	9.825-4
		14.696	7.586-2	3.899-1	0	2.500-1	7.958-2	9.998-1	4.115-3
	500	1,000	8.145-2	1.893-1	1.002-1	2.217-1	7.056-4	9.995-1	0
		14.696	1.227	3.819-1	3.987-3	2.399-1	6.135-3	9.999-1	0
50	1,200	1,000	1.551-1	9.092-1	0	1.262-1	2.083-1	9.991-1	5.910-2
		14.696	2.392-2	9.088-1	0	8.943-2	4.165-1	9.997-1	2.264-1
	800	1,000	2.703-1	8.936-1	7.926-3	1.215-1	3.801-2	9.996-1	1.599-3
		14.696	1.791-1	9.097-1	0	1.464-1	1.858-1	1.000	6.782-3
	500	1,000	1.969-1	3.410-1	2.843-1	1.586-1	1.613-3	9.986-1	0
		14.696	2.876-1	8.726-1	1.849-2	1.321-1	1.433-2	9.998-1	0
20	1,200	1,000	0	1.059	9.431-1	0	3.166-3	9.998-1	0
		14.696	0	1.060	9.434-1	0	3.169-1	9.998-1	0
	800	1,000	2.879-2	8.356-1	1.138	0	4.230-1	9.999-1	0
		14.696	0	9.000-1	1.103	0	4.763-1	1,000	0
	500	1,000	3.099-1	6.660-2		0	6.806-2	9.999-1	0
		14.696	1.247-1	4.211-1	1.456	0	4.559-1	9.999-1	0

TABLE 33

POLYVINYL CHLORIDE/Cl_2 COMPOSITION AS A FUNCTION OF TEMPERATURE, PRESSURE, AND INITIAL COMPOSITION

Percent polymer W/W	T (C)	psia	CCl_4	C_6H_6	CCl_2CCl_2	HCl
	1,200	1,000	1.31-1	2.86-1	0	1.13
		14.696	2.02-3	1.75-1	0	1.71
70	800					
		14.696	0	2.90-1	1.23-1	1.25
	500	1,000	3.50-3	2.90-1	1.18-1	1.25
		14.696	7.34-4	2.91-1	1.25-1	1.25
	1,200	1,000	3.18-1	2.56-1	0	1.32
		14.696	1.81-2	4.13-2	0	2.57
50	800	1,000	1.01-3	2.30-1	2.84-1	1.58
		14.696	0	2.34-1	2.88-1	1.58
	500	1,000	8.18-3	2.34-1	2.78-1	1.58
		14.696	1.63-3	2.35-1	2.88-1	1.58
	1,200	1,000	1.32	9.13-2	0	2.32
		14.696	1.01	0	0	2.97
20	800	1,000	4.32-1	0	7.83-1	3.00
		14.696	1.95-1	0	9.02-1	3.00
	500	1,000	5.24-1	0	7.33-1	2.99
		14.696	5.18-1	0	7.40-1	3.00

SPECIES CONSIDERED IN EQUILIBRIUM ANALYSIS

carbon
graphite
carbon charged +1
carbon charged +2
carbon charged -1
diatomic carbon charged +1
diatomic carbon charged -1
methyl ion +1
carbon monoxide charged +1
carbon dioxide charged +1
carbon dioxide charged -1
cyanide ion -1
carbon hydroxide ion +1
diatomic carbon
(C_3) carbon, trimeric
(C_4) carbon, tetratomic
(C_5) carbon pentatomic
CCH radical
methylidyne
methylene
methyl
ethylene
acetylene
methane
ethylene oxide
carbon monoxide
carbon dioxide
CCO radical
carbon suboxide
cyano (CN)
CNN radical
NCN radical
cyanogen
carbon subnitride
carbon monochloride
carbon dichloride
carbon trichloride
carbon tetrachloride
$CHCl_3$
CH_2Cl_2
CH_3Cl
carbonyl monochloride
carbonyl chloride
ethane
propane
N-butane
N-pentane
N-heyane
iso-butane
isopentane
neo-pentane

2-methyl-pentane
3-methyl-pentane
2,2-dimethyl butane
2,3-dimethyl butane
cyclo pentane
methyl cyclopentane
ethyl cyclopentane
cyclohexane
methyl cyclohexane
ethyl cyclohexane
propylene
1-butene
2-butene (cis)
2-butene (trans)
1-pentane
2-penene (cis)
2-pentene (trans)
2-methyl, 1-butene
3-methyl, 1-butene
2-methyl, 2-butene
propadiene
1, 2-butadiene
1, 3-butadiene
cyclopentane
cyclohexene
propyne
1-butyne
2-butyne
1-pentyne
2-pentyne
3-methyl, 1-butene
benzene
methyl benzene
ethyl benzene
1, 2-dimethyl benzene
1, 3-dimethyl benzene
1, 4-dimethyl benzene
phenyl ethene
cis-1-phenyl, 1-propene
trans-1-phenyl, 1-propene
(2-methyl phenyl) ethene
(3-methyl phenyl) ethene
(4-methyl phenyl) ethene
1-chloro ethene
dichloro ethene
1,2,2 trichloro ethene
tetrachloro ethene
1-chloro propane
1, 2-dichloro propane
chloro ethane
1, 2dichloro ethane
1-propanol
1-butanol
ethanol
methanol

2-butanol
2-methyl, 1-propanol
1-pentanol
1-hexanol
3-hydroxy, 1-propene
1, 2-epoxy butane
1, 2-epoxy propane propylene oxide
3-chloro, 1,2 epoxy propane
1, 2 ethandiol
2 (2 hydroxy ethoxy) ethanol
1, 2 propandiol
2, 3-dihydroxy propanol
3-(3-hydroxy propoxy) propanol
trans-1, 2-dichlora ethene
cis-1, 2-dichloro ethene
1,1,1-trichloroethane
1,1,2,2-tetrachloroethane
butanal
propanal
ethanal
methoxymethane
ethoxyethane
propoxypropane
methoxyethane
methoxypropane
ethoxypropane
2-methoxypropane
2-ethoxypropane
2-(2-propoxy) propane
2-propanone
3-pentanone
4-heptanone
2-butanone
3,3-dimethyl, 2-butanone
1-chlorohexane
1 chloropentane
1 chlorobutane
2-chlorohexane
2-chloropentane
2-chlorobutane
2, chloropropane
3-chlorohexane
3-chloropentane
aminomethane
aminoethane
1-aminopropane
1-aminobutane
1-aminopentane
1-aminohexane
2-aminopropane
2-aminobutane
2-aminopentane
chlorine, monotomic
chlorine, monotomic charged + (unipositive ion)
chlorine, monotomic charged - (uninegative ion)

chlorine
chlorine monoxide
chlorine dioxide
dichlorine monoxide
cyanogen chloride
hydrogen monatomic
proton (H+)
hydrogen uninegative ion
hydronium unipositive ion
hydrogen
hydroperoxyl
water
hydrogen peroxide
hydrogen chloride
hydrogen oxychloride
formyl
formaldehyde
hydrogen cyanide
nitroxyl
nitrous acid cis & trans
nitric acid
hydrogen isocyanate
nitrogen monotomic
" " unipositive ion
" " dipositive ion
" " tripositive ion
nitrogen diatomic unipositive ion
uninegative ion
nitric oxide unipositive ion
nitrogen diatomic
imidogen (NH)
amidogen (NH_2)
ammonia
hydrazine gas, liquid, solid
nitrogen tetraoxide gas, liquid solid
nitric oxide
nitrogen dioxide uninegative ion
nitrogen trioxide
dinitrogen monoxide
dinitrogen trioxide
dinitrogen pentoxide
nitrosyl chloride
nitryl chloride
ammonium chloride crystal
ammonium perchlorate crystal
oxygen monatomic
oxygen unipositive ion
oxygen uninegative ion
oxygen diatomic uninegative
hydroxyl unipositive ion
hydroxyl uninegative ion
oxygen monatomic 2+
" " 3+
oxygen diatomic
oxygen triatomic
hydroxyl

APPENDIX B

KINETIC MODELS AND PARAMETERS

Presented in this section is a brief description of the mathematical models, computer models, and estimated rate data employed in the waste plastics kinetic analysis.

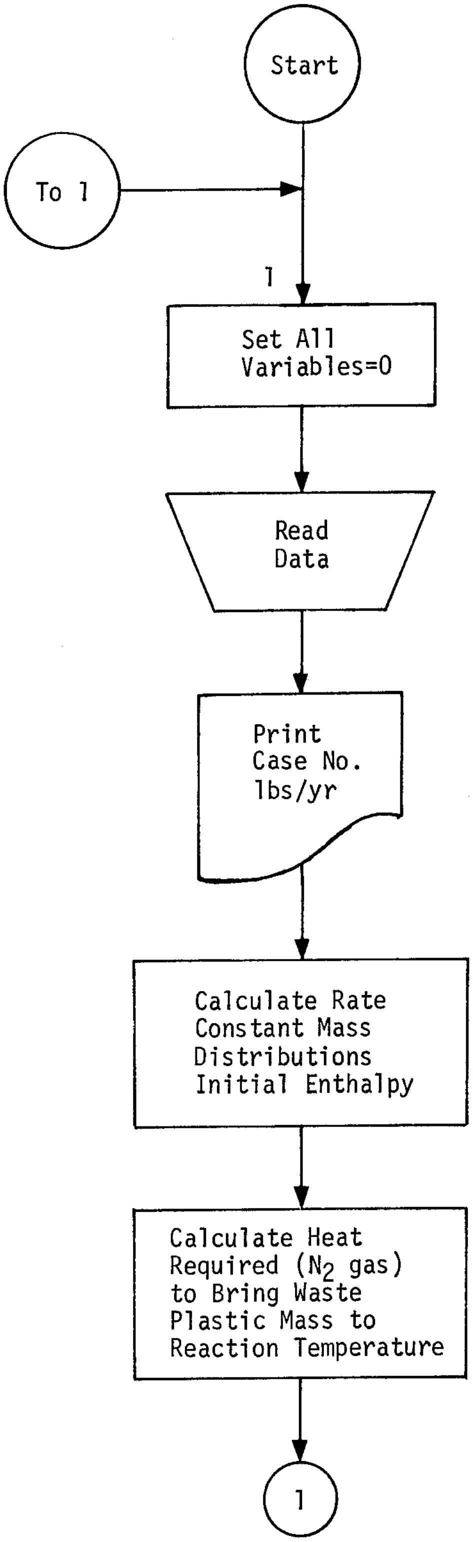


Figure 40. Computer program flow diagram.

Figure 40. Computer program flow diagram (continued).

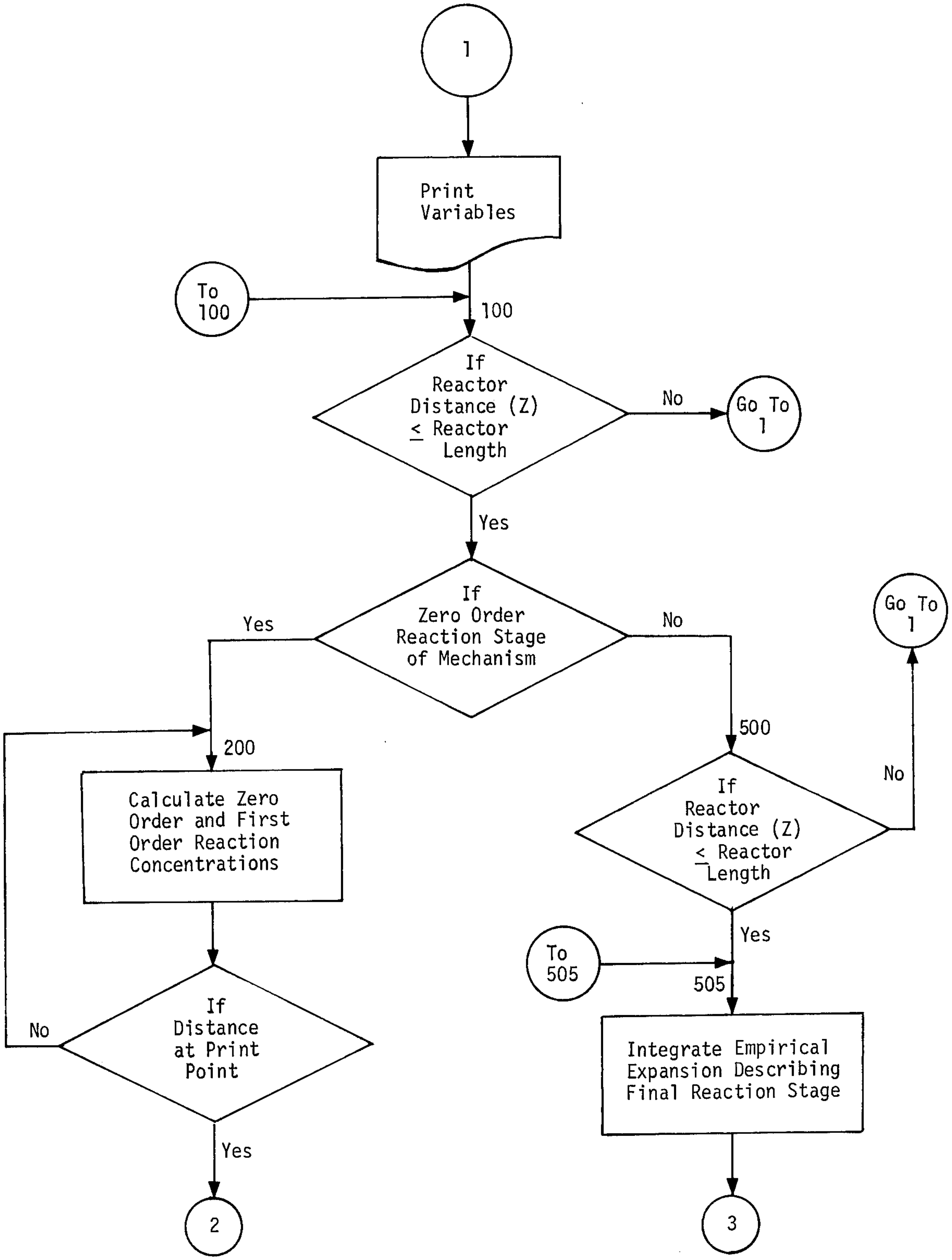


Figure 40. Computer program flow diagram (continued).

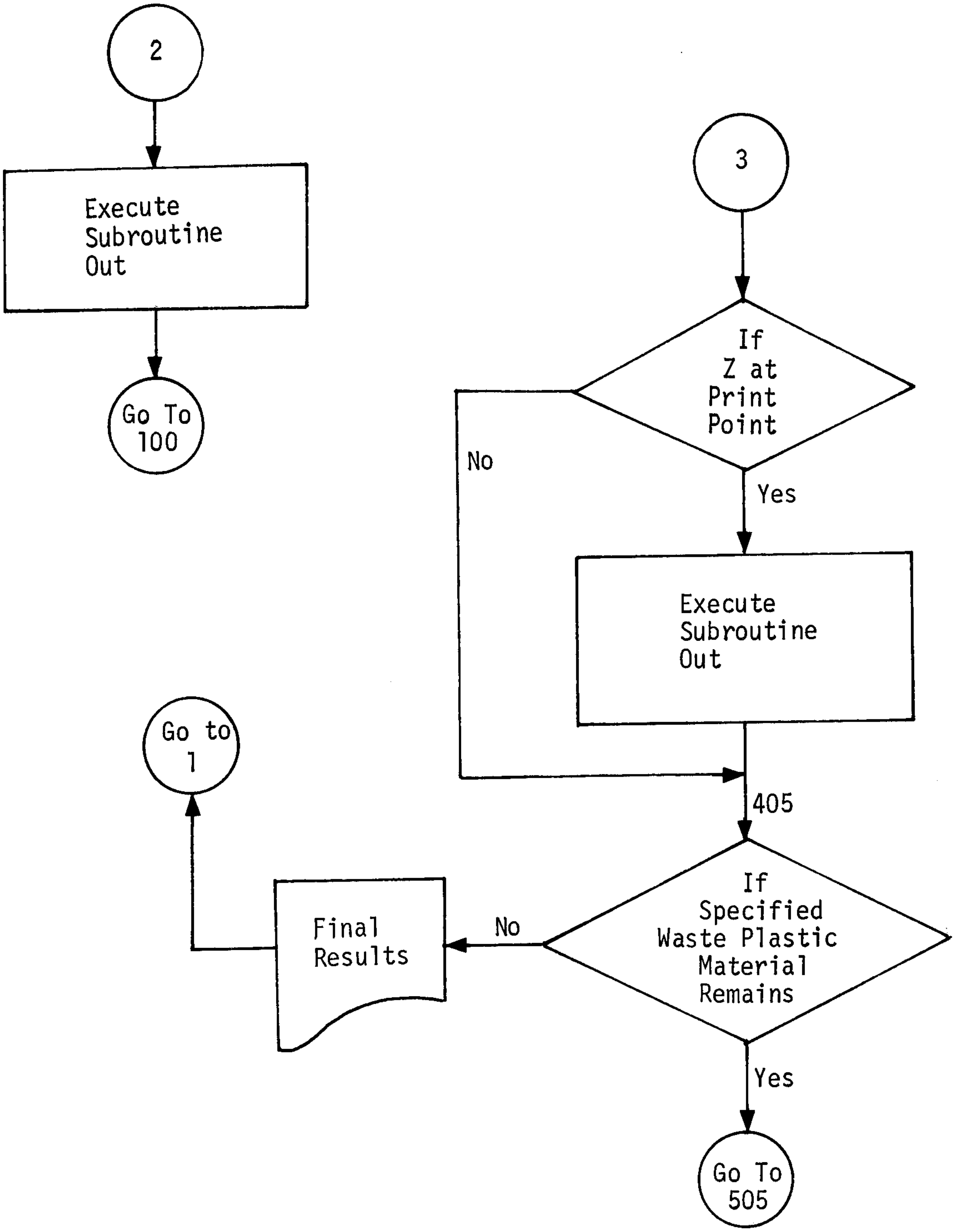


Figure 40. Computer program flow diagram (continued).

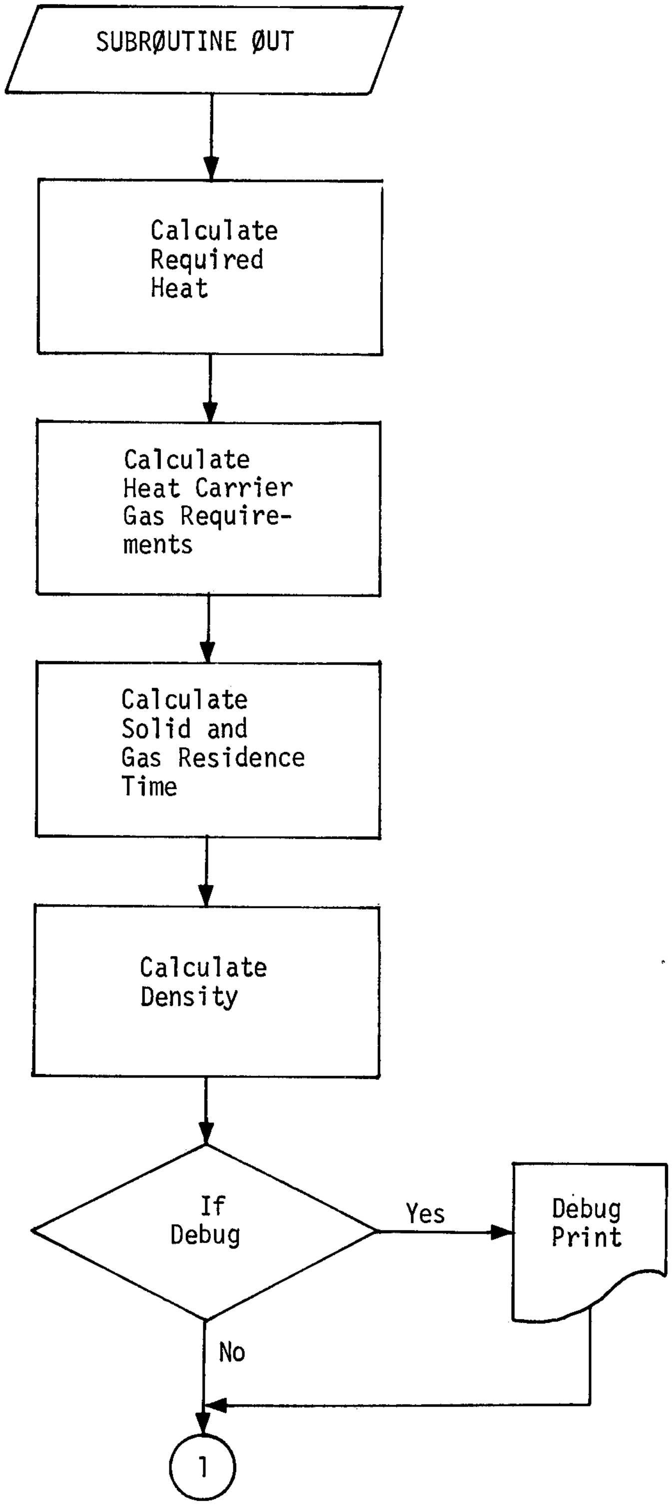


Figure 40. Computer program flow diagram (continued).

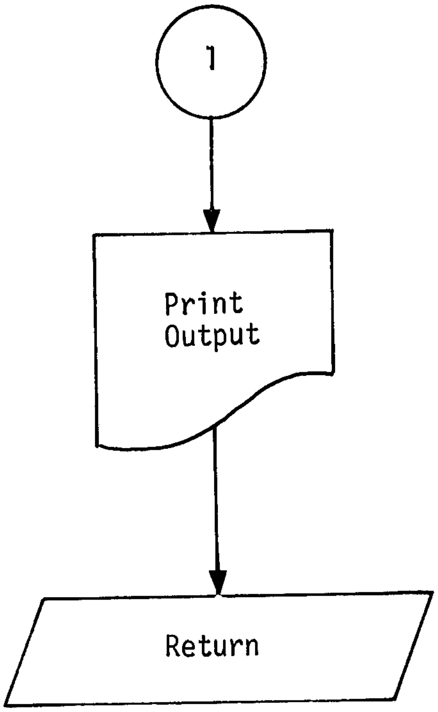


TABLE 34

VARIABLES USED IN MATHEMATICAL MODEL

M = original polymer feed (gr sec^{-1})

M_{HCl} = original HCl feed (gr sec^{-1})

M_r = original polymer involved in random degradation (gr.sec^{-1})

M_z = original polymer involved in zero order degradation (gr.sec^{-1})

M_ℓ = original polymer involved in final stage of degradation (gr.sec^{-1})

N = total mass of gas product (gr.sec^{-1})

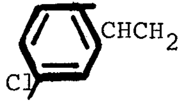
n_r = mass of gas product due to random reaction (gr.sec^{-1})

n_z = mass of gas product due to zero order reaction (gr.sec^{-1})

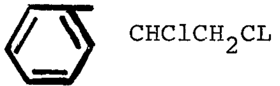
n_ℓ = mass of gas product due to final stages of reaction (gr.sec^{-1})

n_{HCl} = mass of HCl product (gr.sec^{-1})

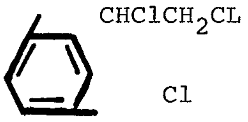
n_0 = moles of styrene product (moles.sec^{-1})

n_1 = moles of (ortho,meta,para) 

(moles.sec^{-1})

n_2 = moles of 

(moles.sec-1)

n_3 = moles of (ortho,meta,para) 

(moles.sec^{-1})

n_{Cl_2} = moles of Cl_2 (moles.sec^{-1})

n_{R-H} = moles aliphatic material (moles.sec^{-1})

Z = distance along reactor (cm)

ADP = average degree of polymerization

k_r = random rate constant (related to sec^{-1})

TABLE 34 (continued)

k_z = zero order rate constant (related to sec^{-1})
ρ = density of waste plastic at z (gr . cm^{-3})
ρ_O = density of unreacted waste plastic (gr . cm^{-3})
V = void space of reactor (cm^2)
t = time (sec)
MW = molecular weight (gr . gr-$mole^{-1}$)
A = cross sectional area of reactor (cm^2)
T = Temperature (K)

TABLE 35

THERMAL DECOMPOSITION DIFFERENTIAL RATE EQUATIONS*

$$(1)\quad \frac{dN}{dt} = \left[\frac{dn_r}{dt} + \frac{dn_z}{dt} + \frac{dn}{dt}\right] \cdot \left(\frac{M}{ADP \cdot MW}\right)$$

$$(2)\quad \frac{dn_r}{dt} = k_r \cdot M_r$$

$$(3)\quad \frac{dn_z}{dt} = k_z$$

$$(4)\quad \frac{dn_\ell}{dt} = k_z \quad \cos\left(\frac{\pi \cdot n_\ell}{z \cdot M_\ell}\right)$$

$$(5)\quad \frac{dz}{dt} = \left(\frac{M}{A \cdot (1-V)}\right) \cdot \frac{d\rho}{dt}$$

$$(6)\quad \frac{dn_j}{dz} = \frac{dn_j}{dt} \cdot \frac{dt}{dz} \quad \text{where } j=r \text{ or } z \text{ or } \ell$$

$$(7)^{+}\quad \frac{dn_{HCl}}{dz} = \left(\frac{dt}{dz}\right) \cdot M_{HCl} \cdot k_{HCl} \cdot \left(1 - \frac{n_{HCl}}{M_{HCl}}\right)\ 3/2$$

---

* It was assumed that the three plastics underwent thermal decomposition by a three-stage mechanism as follows: (1) an initial random degradation reaction (2) a zero order reaction, and (3) a final stage characterized by an empirical expression.

+ Applicable to polyvinyl chloride system.

TABLE 36

WASTE PLASTIC(S)/Cl_2 DIFFERENTIAL RATE EQUATIONS

$$(1) \quad \frac{dN}{dt} = \left(\frac{dn_r}{dt} + \frac{dn_\ell}{dt}\right) \cdot \left(\frac{M}{ADP \cdot MW}\right)$$

$$(2) \quad \frac{dn_r}{dt} = M_r \cdot k_r$$

$$(3) \quad \frac{dn_\ell}{dt} = k_r \cos\left(\frac{\pi}{2} \cdot \frac{n_\ell}{M_\ell}\right)$$

$$(4) \quad \frac{dz}{dt} = \left(\frac{M}{A \cdot (1-V)}\right) \cdot \frac{d\rho}{dt}$$

$$(5) \quad \frac{dn_j}{dz} = \frac{dn_j}{dt} \cdot \frac{dt}{dz} \quad \text{where } j=r \text{ or } \ell$$

$$(6)^{*} \quad \frac{dn_{HCl}}{dz} = \frac{dt}{dz} \cdot M_{HCl} \cdot k_{HCl} \left(1 - \frac{n_{HCl}}{M_{HCl}}\right)^{3/2}$$

* Applicable to polyvinyl chloride system.

TABLE 37

DECOMPOSITION PRODUCTS/Cl_2 DIFFERENTIAL RATE EQUATIONS*

$$(1)\quad \frac{dn_O}{dt} = -n_{Cl_2}\; n_O\; (k_A + k_C)$$

$$(2)\quad \frac{dn_1}{dt} = n_{Cl_2}\; [n_O k_C - n_1 k_B]$$

$$(3)\quad \frac{dn_z}{dt} = n_{Cl_2}\; [n_O k_A - n_2 k_D]$$

$$(4)\quad \frac{dn_3}{dt} = n_{Cl_2}\; [n_1 k_B + n_2 k_D]$$

$$(5)\quad \frac{dn_{Cl_2}}{dt} = n_{Cl}\; [n_O k_A + n_1 k_B + n_O k_C + n_2 k_D = n_{R-H} k_E]$$

$$(6)\quad \frac{dn_{HCl}}{dt} = n_1 Cl_2\; [n_O k_C + n_2 k_D + n_{RH} \cdot k_E]$$

$$(7)\quad \frac{dn_{RH}}{dt} = n_{RH}\; n_{Cl_2} \cdot k_E$$

---

*Reactions

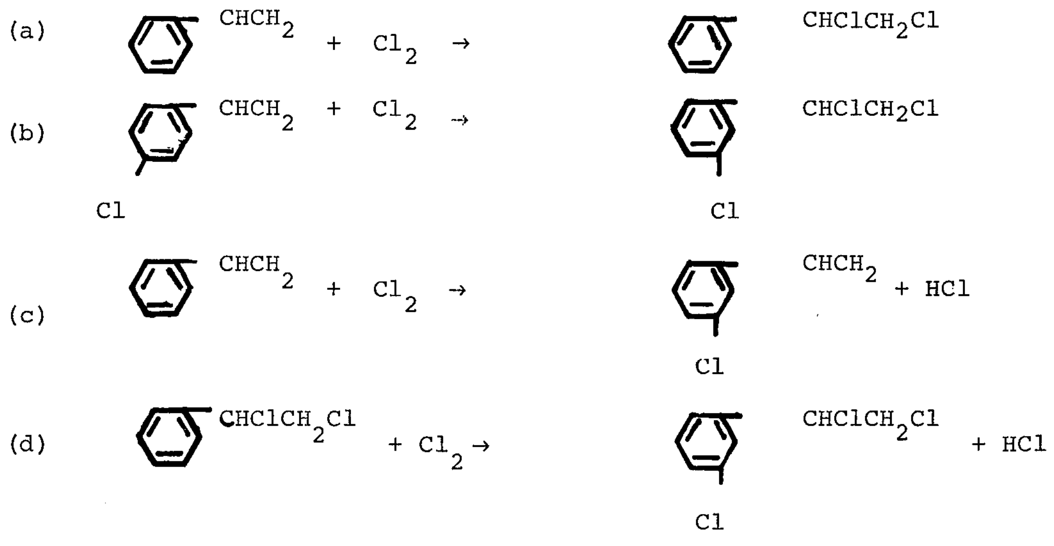


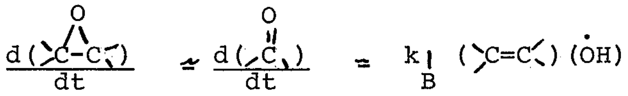
TABLE 37 (continued)

(e) R-H + Cl_2 → R-Cl + HCl where R equals various saturated and unsaturated hydrocarbons with various degrees of Cl substituting.

TABLE 38

THERMAL DECOMPOSITION PRODUCTS/AIR DIFFERENTIAL RATE EXPRESSIONS*

(1)+ $$\frac{d(\gt C=C\lt)}{dt} \simeq k'_A\,(R\text{-}H)(O_2)$$

(2)+ 

$$\frac{d(\gt C\overset{O}{-}C\lt)}{dt} \simeq \frac{d(\gt\overset{O}{\overset{\|}{C}}\lt)}{dt} \simeq k'_B\,(\gt C=C\lt)(\dot{O}H)$$

(3)+ $$\frac{d(CO_2)}{dt} \simeq \frac{d(H_2O)}{dt} \simeq k'_C\,(O_2)(\gt C-C\lt)$$

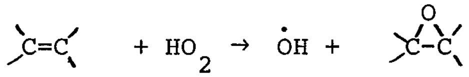
* The differential rate expressions were not programmed into equivalent computer programs. As such, these above rate expressions were used to characterize the systems.

\+ The preliminary kinetic analysis equations are (see reference 1) the following:

(A) $\dot{R} + O_2 \rightleftarrows H\dot{O}_2 + \gt C=C\lt$

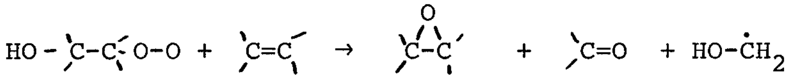
(B) $HO_2 + RH \rightarrow HO_2H + \dot{R}$

(C) $M + H_2O_2 \rightarrow 2OH + M$

(D) 

$\gt C=C\lt + HO_2 \rightarrow \dot{O}H + \gt C\overset{O}{-}C\lt$

(E) $\gt C=C\lt + \dot{O}H + O_2 \rightarrow HO - \gt C-C\lt - O\text{-}O$

(F) 

$HO - \gt C-C\lt O\text{-}O + \gt C=C\lt \rightarrow \gt C\overset{O}{-}C\lt + \gt C=O + HO\text{-}\dot{C}H_2$

(G) $RH_3 + 2O_2 \rightarrow \underline{R} + 2H_2O + CO_2$

TABLE 39

WASTE PLASTICS (SOLID)/AIR DIFFERENTIAL RATE EXPRESSIONS

---

(1)* $$\frac{dN}{dt} = K \cdot M$$

(2)+ $$\frac{d(\rangle C{=}C\langle)}{dt} \simeq k'_A\,(R\text{-}H)(O_2)$$

(3)+ $$\frac{d(\rangle \overset{O}{C\text{-}C} \langle)}{dt} \simeq \frac{d(\overset{\overset{O}{\|}}{\diagup C \diagdown})}{dt} \simeq k'_B\,(\rangle C{=}C\langle)(\dot{O}H)$$

(4)+ $$\frac{d(CO_2)}{dt} \simeq \frac{d(H_2O)}{dt} \simeq k'_C\,(O_2)(\rangle C\text{-}C\langle)$$

---

* Oxidation occurs in a random reaction to yield intermediate gas products from the solid waste material.

\+ See note 2 on Table 38.

TABLE 40

PREDICTED RESULTS COMPARED WITH EXPERIMENTAL RESULTS

STYRENE

Based on 1. gr/sec polystyrene feed

	Calculated	Experimental(17)
	970 K @ 2.5 min	898 K
Styrene	0.81 g	0.74 g
Toluene and ethylbenzene	----	Trace "
Residue	0.19 g	0.26 "

POLYETHYLENE

Based on 1 gr/sec polyethylene feed

	Calculated		Experimental(18)	
	710 K @ 50 min		702 K @ 30 min	
C_2H_4	0.018	g	0.016	g
C_2H_6	0.055	g	0.048	g
C_3H_4	0.0015	g	--	
C_3H_6	0.0325	g	0.028	g
C_3H_8	0.0960	g	0.085	g
C_4H_8	0.1990	g	0.177	g
C_4H_{10}	0.1585	g	0.144	g
C_5H_8	0.0035	g	0.003	g
C_5H_{10}	0.0765	g	0.068	g
C_5H_{12}	0.0640	g	0.057	g
C_6H_{10}	0.0040	g	0.003	g
C_6H_{12}	0.0395	g	0.035	g
C_6H_{14}	0.0165	g	0.014	g
C_7H_{14}	0.0030	g	0.002	g
C_7H_{16}	0.0060	g	0.005	g
Unreacted	0.2265	g	0.373	g

TABLE 40 (continued)

POLYVINYL CHLORIDE

Based on 1 gr/cc polyvinyl

	Calculated 723 K @ 4.25 min		Experimental(19) 873 K with H_e	
HCl	0.510	g	0.555	g
H2	0.0023	g	0.0006	g
CH4	0.0144	g	0.0100	g
C_2H_6	0.0371	g	0.0069	g
C_2H_4	0.0718	g	0.0052	g
C_6H_6	0.0567	g	0.0560	g
C_7H_8	0.0302	g	0.0067	g
Other	0.1875	g	--	g
Residue	0.0900	g	0.0630	g

TABLE 41

WASTE PLASTICS KINETICS COMPUTER PROGRAM

```
$SLANG MIST3,LIST                                                                   101
/WASTE PLASTICS POLYSTYRENE KINETICS MODEL                                          102
/13MARCH 1969 WALTER LUSK                                                           103
    1 SET C8H8Z=C8H8R=C8H8L=C8H8=N2=Z=DENKCL=T=0.                                   104
      SET ENHKCL=VOL=ENHBTU=N2IN=SPCVEL=RESTIM=FC8H8=FN2=DEN=GRMSEC=0.              104A
      READ DATA                                                                     105
      DEN=DENSI                                                                     105A
      LBSYRP=POLYIN*36.*24.*330./4.563                                              106
      PRINT VARIABLES CASE,LBSYRP                                                   107
      AREA=3.1416*RAD**2                                                            108
      VOLMOL=(82.06*TMPR)/PRS                                                       109
      RATEZ=2.0E+11*EXP(-44700./(TMPR*1.98726))                                     110
      RATER=4.5E+14*EXP(-44700./(TMPR*1.98726))                                     201
      POLSTY=POLYIN                                                                 202
      MASSRO=GAMMA*POLYIN                                                           203
      MASSZO=(1.-GAMMA)*POLYIN*.7222222                                             204
      MASSLO=POLYIN-MASSRO-MASSZO                                                   205
      TIME=(1.-VOID)*AREA*DENSI/POLYIN                                              206
      ENGPST=0.001*(1.849*(TMPR-300.)+.5*(-.01084*(TMPR**2-9.E+4))+.3333            207
*     *(1.8745E-5*(TMPR**3-2.7E+6)))+19.0/104.14                                    208
      ENMSTY=30.24+6.3E-4*TMPR+5.623E-5*TMPR**2-1.5066E-8*TMPR**3                   209
      ENMN2R=0.001*(-60023.+7.084*TMPR+.001337*TMPR**2)                             210
      ENMN2N=0.001*(-60023.+7.084*TMPN+.001337*TMPN**2)                             301
      ZPT=ZPRNT                                                                     302
      N2=POLYIN*(ENGPST-.182)/(ENMN2N-ENMN2R)                                       302A
      H2O=N2                                                                        302B
      PRINT VARIABLES                                                               303
      BLOCK OUT                                                                     304
      DENKCL=ENHKCL                                                                 305
      ENHKCL=C8H8*(104.14*ENGPST-ENMSTY)
      VOL=AREA*Z*VOID
      ENHBTU=ENHKCL/.25198                                                          307
      DENKCL=ENHKCL-DENKCL                                                          308
      N2IN=DENKCL/(ENMN2N-ENMN2R)                                                   309
      N2=N2+N2IN                                                                    310
      H2O=N2                                                                        310A
      SPCVEL=(C8H8+N2)*VOLMOL/(VOL*Z)                                               401
      RESTIM=1./SPCVEL                                                              402
      POLSTY=POLYIN-104.14*C8H8                                                     403
      FC8H8=C8H8/(N2+C8H8)                                                          404
      FN2=N2/(N2+C8H8)                                                              405
```

```
      DEN=POLSTY*DENSI/POLYIN
      GRMSEC=C8H8*104.14
      IF BUG EQ 1 THEN PRINT VARIABLES
     PRINT VARIABLES Z,RESTIM,POLSTY,C8H8,H2O,ENHKCL,ENHBTU,DENKCL,N2IN,
*C8H8Z,C8H8R,C8H8L,DEN,GRMSEC
      END BLOCK
  100 IF Z LT ZMAX
         THEN IF C8H8*104.14 LT MASSRO+MASSZO-POLYIN*0.1
             THEN GO TO 200
             ELSE GO TO 500
             REJOIN
         ELSE GO TO 999
         REJOIN
  200 Z=Z+DELZ
      C8H8Z=RATEZ*TIME*Z*POLYIN/(ADPZ*104.14)
      C8H8R=MASSRO/104.14*(1.-EXP(-Z*RATEZ*TIME*POLYIN))
      C8H8=C8H8R+C8H8Z
      IF Z-ZPT+.5*DELZ GE 0
         THEN ZPT=ZPRNT+ZPT
             EXECUTE OUT
         ELSE GO TO 200
         REJOIN
      GO TO 100
  500 IF Z LT ZMAX
         THEN Z=Z+DELZ
              GO TO 501
         ELSE GO TO 999
         REJOIN
  501 BLOCK DERS
         DC8H8L=TIME*RATEZ*COS(3.14159/2.*104.14*C8H8L/MASSLO)*POLYIN/(A
*     DPZ*104.14)
      END BLOCK
      INTEGRATION DERS,Z,DELZ,C8H8L,DC8H8L
  505 INTEGRATE DERS
      T=POLSTY
      C8H8=C8H8+C8H8L
      IF Z-ZPT+.5*DELZ GE 0
         THEN ZPT=ZPRNT+ZPT
              EXECUTE OUT
         ELSE GO TO 504
         REJOIN
```

TABLE 41 (continued)

```
 504 C8H8=C8H8-C8H8L                                                    710
     POLSTY=T                                                           710A
     CHECK=104.14*(C8H8+C8H8L)-POLYIN*.925                              801
     IF CHECK GE 0                                                      802
        THEN PRINT VARIABLES CHECK                                      803
             GO TO 1                                                    804
        ELSE GO TO 510                                                  807
        REJOIN                                                          806
 510 IF Z LT ZMAX THEN GO TO 505                                        807
 999 GO TO 1                                                            808
     END                                                                809
DATA                                                                    810
```

TABLE 42

KINETIC RATE PARAMETERS

	$A(\frac{g}{\text{base mole}\cdot\text{sec}})$	E (Kcal/mole)
• Thermal decomposition		
Polystyrene		
Random RXN	1.92×10^{12}	44.7
Zero order RXN	4.33×10^{9}	44.7
Polyethylene		
Random RXN	†	*
Zero order RXN	‡	*
Polyvinyl chloride		
Random RXN	4.8×10^{10}	44.2
Zero order RXN	1.9×10^{9}	44.2
HCl RXN	§ 1.9×10^{9}	33.0
• Plastic (solid)/Cl_2		
Polystyrene	3.4×10^{8}	32.2
Polyethylene	1.9×10^{8}	31.0
Polyvinyl chloride	5.0×10^{8}	30.0
• Decomposition (g)/Cl_2		
RXN A	§ 3.2×10^{5}	17.0
RXN B	§ 2.1×10^{5}	17.0
RXN C	§ 4.0×10^{6}	23.5
RXN D	§ 4.0×10^{6}	23.5
RXN E	§ 1.0×10^{6}	1.0
• Decomposition (g)/air		
RXN 1	§ 2×10^{8}	10.00
RXN 2	§ 1×10^{15}	43.0
RXN 3	§ 3.2×10^{9}	9.0
• Waste plastic (solid)/air		
Polystyrene	§ 2×10^{9}	40.7
Polyethylene	§ 1×10^{9}	44.7
Polyvinyl chloride	§ 2×10^{7}	44.7

* $E = 27586. + 46.853 \times ADP.$

† $A = EXP\ (42.4 + 0.1445 \times \sqrt{E}).$

‡ $A' = 4 \times 10^{2} \times A.$

§ Units in sec^{-1} (pressure units).

APPENDIX C

ECONOMIC MODELS

This appendix contains brief descriptions of some of the computer models (subroutines) used in the economic analyses of chemical systems for waste plastic utilization. These subroutines are called by the main program when needed and were written to calculate the capital and operating costs associated with that specific piece of equipment.

Subroutine COMPRS

Subroutine COMPRS calculates the actual brake horsepower required to drive a compressor. A mechanical efficiency of 94 percent and a compression efficiency of 83.5 percent were assumed. The intake and exit volumes are calculated based on stream composition, entrance and exit temperatures, and the input-output pressure ratio. Subroutine ECON is then called to determine the more economical type of compressor, the installed cost of the compressor, and the operating cost in dollars per hour.

Subroutine ECON

Subroutine ECON determines which type of compressor is more economical, centrifugal or reciprocating. The subroutine calculates the capital cost of each type of compressor for the brake horsepower required and the operating cost per hour based on which source of power is chosen, steam or electricity. The resultant costs for each type of compressor are compared and the smaller of the two is chosen.

Subroutine SEPAR

Subroutine SEPAR calculates the minimum required volume of a vapor-liquid gravity settling tank. As the vapor passes upward through the tank, particles with terminal velocities equal to or greater than the vertical velocity of the vapor stream will be removed. A particle terminal velocity of 1 ft/sec was assumed to exist in the settler, and a tank height of 10 ft was assigned. The subroutine then calculates the area required to decrease the vapor velocity to 1 ft/sec. The installed cost of the vessel is determined as a function of vessel capacity.

Subroutine REF

Subroutine REF calculates the brake horsepower required to refrigerate the product to the desired temperature. Based on the change in enthalpy, the type of power specified for driving the refrigerator, and the materials involved, the installed cost is determined.

Subroutine EXCH

Subroutine EXCH calculates the square feet of heat exchanger required based on the heat load in Btu per hour, and the inlet and exit temperatures. The capital cost is then calculated from the area required and the operating pressure.

Subroutine PUMP

Subroutine PUMP calculates the gallons of liquid per minute that must be moved by a process pump. The capital cost is then calculated as a function of flow (gal/min).

Subroutine BCCOL

Subroutine BCCOL calculates the minimum allowable diameter of a bubble-cap distillation column. A column must have sufficient cross sectional area to handle the rising gases without excessive carryover of liquid from one tray to another. The vapor velocity

$$V_m = 0.12 \; \frac{\rho_L - \rho_G}{\rho_G}$$

where: ρ_L, ρ_G = density of liquid and vapor, respectively.

APPENDIX D

ASSUMPTIONS MADE IN ECONOMIC ANALYSES

Utilities

Cooling water	2¢/1,000 gal
Electrical power	0.7 ¢/kw-hr
Fuel Gas	25 ¢/million Btu
Boiler water	20¢/1,000 gal
Steam	50¢/1,000 lb

Operating Costs

Operating labor	$75,000 per position/yr*
Depreciation Maintenance Taxes Insurance	20% of capital/year

330 operating days/year

Product Values

Styrene	8 ¢/lb
HCl acid (18 b)	32 $/ton
Fuel gas	25 ¢/million Btu
Gasoline steam	10.5 ¢/gal

Raw Materials Costs

Nitrogen	8 $/ton
Air	Free

*Based on one operator position: 3 shifts per day, 7 days per week, including overhead.

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