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POLYETHYLENE BY THE ZIEGLER PROCESS

A PRELIMINARY DESIGN AND COST ESTIMATE

by

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I. Summary

A preliminary design has been developed for a plant which will be able to produce 38 million pounds of polyethylene by the Ziegler process. The Ziegler process yields a product of better quality than that made by the conventional high-pressure process, and the manufacturing costs of the former are probably lower. Also, the process is extremely flexible in that it can produce polymers in a wide range of average molecular weights, with only slight changes in the process conditions. To make an optimum use of this flexibility, the polymer is kept from dissolving during the process, thus eliminating great viscosity variations and need for large solvent circulation.

The economic evaluation of the process as described herein is quite inaccurate, but nevertheless clearly indicates that the process should be investigated. A rate of return of 70% at 100% capacity was found, and the break-even point lies at 33.5% of maximum capacity.

It is believed that at this time design and operation of a pilot plant are not feasible, since too many basic data are not known. Bench scale experiments should first be conducted to obtain the necessary minimum information.

II. Background 1)

1. General

Polyethylene has been known for a long time (1898) but it was not until 1934 that the first successful steps were made towards the development of a commercial process. This research led to a series of patents issued after 1936 to Imperial Chemical Industries, major British chemical concern. Because of the Second World War, research and development were strongly pushed, and as a result, commercial production started in the early 1940's.
Fig. 1

Million lbs/year

Polyethylene Production

Year: 1940, 1950, 1960
The process, and later-developed variants, is carried out under very high pressures (several thousand atmospheres) and elevated temperatures (up to 500°C).

The material has proved to be highly useful, so that the production and consumption rate since its introduction have increased tremendously and continue to do so (Fig. 1).

Polyethylene holds a large share of the thermoplastic resins market and continuously increases its share. It is expected to pass the billion pounds/year mark in 1960, and will be the first thermoplastic resin to be produced in such quantities.

Since 1950, three basically new processes have been announced by the Max Planck Institut fur Kohlenforschung, commonly identified with its present director, Professor Karl Ziegler, the Phillips Petroleum Company and the Standard Oil Company of Indiana. All three processes are thoroughly covered by patents, but process information is scarce, if existent at all. The former two processes have been put into commercial operation in 1956 and 1957 by several manufacturers, and more plants are under construction and in the planning stage. It seems that the Standard Oil process has been licensed, but no plans for commercial production are known. The new processes have several features in common that appear to have distinct advantages over the old process. Most important of these are relatively low operating temperatures and pressures and improved product qualities. The improved product qualities originate in the higher degree of crystallinity obtained in the polyethylene manufactured by the new processes. For further detailed information, one refers to the initial study and comparison of current polyethylene processes, which initiated underlying study and a similar one on the Phillips Process.
It should be definitely stated that at this time there is no information available on which a preference for either of the two processes could be based.

After the announcement of the low-pressure processes, a modified version of the high-pressure process was announced, which claimed improved product qualities over the old process, but gives a product inferior to the low-pressure products.

2. Ziegler Process 2)-6)

In 1949 Ziegler and co-workers discovered the addition of ethylene to Aluminum alkyl compounds, yielding compounds of the following general structure:

\[ \text{C}_2\text{H}_6\text{al} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5 - \text{CH}_2 - \text{CH}_2 \text{al} \rightarrow \cdots \]

\[ \text{C}_2\text{H}_5 (\text{CH}_2 - \text{CH}_2)_n\text{al} \]

\[(\text{al} = 1/3 \text{ Al})^*\]

This discovery opened wide perspectives for the polymerization of ethylene. However, in this way only polyolefins of relatively low molecular weight could be obtained, since a termination reaction took place: \( \text{CH}_3-(\text{CH}_2)_n\text{-al} + \text{C}_2\text{H}_4 \rightarrow \text{CH}_3(\text{CH}_2)_{n-2} \text{CH}_2=\text{CH}_2 + \text{C}_2\text{H}_5 \text{ al} \)

The frequency of this reaction apparently was too great to allow the synthesis of solid polymers.

However, it was discovered that the addition of co-catalysts not only increased the rate of the addition reaction but also diminished the ratio of termination - addition reactions. Initially, colloidal nickel was used as co-catalyst, but later metal salts were found to be even more effective. Outstanding features of the new process were the low required

* This mode of expression eliminates the difficulty of describing what happens meanwhile at the other alkyl groups of the same molecule.
pressure and temperature, the 100% yield, even if the feed contained only part ethylene, and the highly improved product properties, originating in its high degree of crystallinity and low degree of branching. Tensile strength was increased and melting point raised considerably, up to the theoretically predicted melting temperatures of alkanes of infinite molecular weight.

Experimental techniques were simple, and consequently it was expected that the process would find wide commercial application. At this time it seems that this expectation was more than justified.

III. Introduction

1. General description of process

At present it appears that the process is carried out in the following steps: Ethylene, free of non-hydrocarbon contaminants and of acetylene, is led into a solvent which contains the catalyst and co-catalyst. Solid polyethylene is formed which transforms the liquid into a slurry. After the reaction is terminated, the solvent is removed by a combination of filtration and distillation. The catalyst, which remains in the polymer, is decomposed by water and dissolved in dilute acid, which is then removed by washing. Finally, the product is dried and may then be further processed.

2. Discussion of process

The ethylene has to be entirely free of its usual inorganic contaminants such as H₂S, CO₂, H₂O and should further contain no acetylene or sulfur or oxygen compounds. All of these react with any aluminum-alkyl, as can be easily illustrated for H₂O:

\[ \text{al Alk} + \text{H}_2\text{O} \rightarrow \text{al OH} + \text{Alk H} \]

This thus deactivates the catalyst completely if sufficient of the impurities are present.
The co-catalyst, which is TiCl₄, will also be decomposed (hydrolysed by water), but only after all the organo-metallic compound has reacted. This is an unfortunate circumstance since the Al (Alk)₃ greatly exceeds the TiCl₄ in price. Since the amount of Al (Alk)₃ determines the average molecular weight of the polymer, the impurity level should be closely controlled, and because the price is high, impurity levels of lower than parts per million should be aimed at.

It appears that any al-alkyl or even any organo-aluminum compound will perform satisfactorily. However, from a manufacturing point of view it seems that the lower Al-alkyls (from Al (Eth)₃ on) are preferred, whereas for safety in handling ¹⁰) the higher Al-alkyls appear to be more attractive.

The current prices of aluminum alkyls are quite high, as high as $25/lb., but the reason for this is not the high production cost but the limited availability and the pilot-plant scale of production. Increasing application of the Ziegler process, not only for the polymerization of ethylene but also of propylene and in the future probably isoprene, are expected to bring the prices down to below a dollar a pound. The TiCl₄ is not expensive, but newest developments indicate that it may be advantageous to use TiCl₃ ¹¹),¹²) which seems to be the actual co-catalyst. If TiCl₄ is used, TiCl₃ is formed by reduction with the aluminum compound. Consequently, smaller amounts of both aluminum alkyl and Ti-salt would be required. TiCl₃ is more than ten times as expensive as TiCl₄, however.

Fortunately, only small amounts of catalyst and co-catalyst are needed for the reaction. The amount is determined from a chemical point of view by the following factors:
a) The indicated minimum amount is 0.1 gr catalyst per 1000 gr polyethylene. This would presumably be the amount that is consumed in the reaction under most ideal conditions of purity of reagents.

b) The mole ratio of aluminum alkyl to TiCl₄ is the determining factor for the average molecular weight of the polymer product. Within an approximate ratio range of 1 to 5 it is possible to obtain average molecular weights from 30,000 to 3,000,000. It may be noted that this gives the process a very great flexibility with only minor changes in catalyst quantities, and little or no changes in process conditions.

c) Within the above mentioned range of catalyst to co-catalyst ratio, and above the minimum required amount of catalyst as mentioned in a), the reaction rate is directly proportional to the concentration of co-catalyst, if the other conditions, including temperature, monomer concentration and method of catalyst and co-catalyst preparation are kept constant. 5, 12)

Summarizing, for a chosen average molecular weight of the polymer, catalyst and co-catalyst quantities are determined by desired reaction rate, minimum catalyst amounts and reaction conditions. Since it appears that the minimum catalyst amount is considerably less than that usually employed, the actual amounts will depend on desired reaction rate and operating conditions.

Operating variables that influence the rate of reaction, and probably to a minor extent also the average molecular weight of the product, comprise the following:

a) Preparation of the catalyst - co-catalyst slurry appears to be important. TiCl₄ and Al-Alkyl are both liquids, when pure, and are thus relatively easy to handle and to add in measured quantities. However,
the TiCl₄ transforms into a suspended material when brought in contact with the Al-alkyl. This is undoubtedly due to its reduction to TiCl₃ and possibly lower valency states. About the particular techniques to obtain the largest and most effective surface area per unit weight of co-catalyst nothing is known; this obviously belongs to the know-how of the manufacturer. Since it is known, however, that simple mixing in the presence of an organic diluent will give a satisfactory suspension, if not of optimum activity, this item certainly would not be an obstacle for successful development of the process.

b) Ziegler claims that the polymerization can be conducted at temperatures ranging from room temperature to 250°C. However, he states as most advisable the range of 50-100°C, which is confirmed by the available experimental data. Although not quantitatively illustrated, it appears true that, similar to other polymerization reactions, an increased reaction temperature will yield lower average molecular weights, under otherwise constant conditions. Also, increased temperature will cause an increase in reaction rate, which could tentatively be confirmed from available experimental data. However, not enough data were available, and the conditions of the experiments were not sufficiently defined to evaluate quantitatively the influence of temperature on reaction rate.

c) Ethylene concentration is an important factor in the reaction rate. The maximum possible ethylene concentration at a certain temperature depends on the composition of the feed gas, the nature of the solvent, and the pressure. Although only strictly true for an ideal gas, it may be said that the ethylene concentration in the solvent varies directly with pressure. Although Ziegler definitely states that increased pressure speeds up the reaction rate, the published experimental data are not sufficient to
confirm a definite relationship between pressure and reaction rate.
However, Natta, in his extensive studies on the polymerization of propylene,
found definite proof that the reaction rate of this polymerization was
proportional to the concentration of monomer in the solvent.12) The
propylene polymerization employs the same catalysts as does the Ziegler
process, and there is at present no reason to suspect any difference in
reaction mechanism between the two. Thus, it is concluded that the reaction
rate is proportional to the partial pressure of ethylene, under otherwise
constant conditions.

Although Ziegler describes a few experiments in which no solvent
was employed, the majority was conducted with solvents, and this is also
the procedure recommended by the inventor. It should be understood that
the term solvent in this case concerns only the ethylene, which is
actually dissolved before it reacts - the polyethylene is formed as a
solid, if not after the initial polymerization steps, then very quickly
afterwards. The polymer, as prepared by this process, has a negligible
solubility in any organic solvent - products with an average molecular
weight of 30,000-100,000 are not soluble at all below 100°C. Small con­
centrations of dissolved polymer give extremely viscous solutions.
Viscosity of these solutions is strongly dependent on concentration and
average molecular weight. This may explain why it is advised to keep the
reaction temperature below 100°C., avoiding a) operation with highly
viscous solutions, b) great changes in viscosity when changes in molecular
weight of the product are made, c) resulting wide range of process equip­
ment requirements, and d) high solvent-polymer ratio, which in any event
would be uneconomical. Consequently, the so-called solvent is only a
carrier for the polymer that is suspended in it, and no consideration will
be given to the possibility of actually dissolving the polymer.
The range of solvents as recommended by Ziegler is extremely wide – any saturated and well purified hydrocarbon or hydrocarbon mixture can be used, from pentane to gas oil. The selection of a suitable solvent is a complex problem which interrelates desired operating temperature, pressure and concentration of the monomer; it is thus closely related to reaction rate and required reactor volume. At a certain temperature and pressure the saturation concentration of the ethylene depends on the volatility of the solvent, its molecular weight and its density. The aforementioned factors are not solely determining, however – the choice of solvent has great influence on an important process step, namely the removal of solvent from the polymer. It should be possible to determine an optimum solvent for chosen operating temperature and pressure. This determination however is very complex, and sufficient data lack. Therefore it is impossible to make a choice now which is absolutely justified. Tentatively it may be said that the chosen solvent should be of relative low molecular weight, relative low volatility and low price if considerable losses occur and if a large hold-up proves necessary. Also, if heat removal by boiling is considered, the mol fraction ethylene in the vapor is limited, since at too high an ethylene content no complete condensation can be obtained at normal cooling water temperatures, and a low heat transfer coefficient on the vapor side of the condenser will occur. All these reasons led to the still rather arbitrary choice of a butane-pentane mixture as a solvent.

Although aliphatic impurities do not retard or impede the polymerization reaction, they will decrease the concentration of ethylene in the solvent since they add to its volatility. Obviously, while the ethylene reacts and is continuously replenished, the impurity (ethane)
accumulates and thus keeps diminishing the ethylene solubility. Thus, in a continuous reactor without gas removal, the purity of the ethylene feed has a definite influence on the reaction rate.

Cooling of the reaction is important, since the heat of polymerization of polyethylene is high as compared to other polymerization reactions, namely 1800 BTU/lb.\textsuperscript{13}) At a scheduled production of 4400 lbs/hr. of polymer, the maximum amount of evolved heat would be approximately 8 million BTU/hr., which might ideally represent a credit of $3/hour, already worth an attempt to recover it. Since the temperature at which this heat is given off is rather unfavorably low, it is believed that heat recovery should not be considered until after the optimum reaction temperature has been determined, or possibly as a part of this determination.

The amount of circulated solvent depends on the allowable solids concentration. In the experiments described by Ziegler and others \textsuperscript{6,7}, the solid concentration of the slurry at which it could no longer be stirred, is frequently indicated and falls then always in the range of 10 to 40% solids (presumably by weight), which is stated by Ziegler in his patents as to be the possible range of slurry concentrations as far as the possibility of stirring is concerned. Published values for the bulk density of polyethylene, as prepared by this process, are 200-500 g/l\textsuperscript{14}), about 20 to 50% solids, i.e. in fair agreement with the figures stated above. Two factors are important in this matter: solid polyethylene swells in an organic solvent, and a fibrous material can hold much liquid. In how far one might speak of a solid phase in this case is doubtful - it is hard to see how a fiber of molecular thickness could swell by absorption of solvent. However, it is obvious that the packed fibers, from the moment
they grow on the co-catalyst surface, will hold a large amount of solvent in their void space, which holding will probably be facilitated by the normal good solubility of the solvent in the polymer. It would seem from similar cases, that the material, in the form that it is produced in this process, will hold more organic solvent than it will hold water. When processing a slurry, it should be made certain that it always remains free-flowing, and settling should not be such that blocking of lines or equipment could occur. The first condition is controllable by the slurry concentration, and it is believed that the second one is satisfied because of the low bulk density of the polymer as it is present in the slurry. This consequently gives only a small difference in density between apparent solids (solids with solvent in voids) and solvent. An additional difficulty is the processing of slurries of thermoplastic materials like polyethylene because the temperature must not be allowed to exceed the softening point of the material. If the softening point is passed, the suspended material is liable to cover heat transfer surfaces with a very viscous film or cake, thereby greatly reducing the heat transfer coefficient.

The melting point of the highly crystalline, high-density material is in the range of 135-140°C, the softening point is stated to be above 110°C.

Since, as previously stated, impurities in the ethylene feed (ethane) tend to decrease the concentration of monomer, it is necessary to remove the dissolved impurities from the solvent before this is recirculated. In the particular case of ethane, it will be advantageous to remove this under elevated pressure so as to avoid great overhead loss of solvent material, without having to use refrigeration for the overhead condenser.
The catalyst, which forms the nucleus of the polymer particles, has to be decomposed and removed; if this is not done, the polyethylene discolors and loses in mechanical strength. Also, the presence of ionizable matter in the polymer diminishes its excellent dielectric properties. From a competitive stand-point, it is important to obtain a low ash content of the polymer, since the old process produces a material with ash content practically nil. The obvious material for the decomposing of the catalyst is water, which however hydrolyzes the aluminum compound and the titanium salt to water-insoluble hydroxides; therefore dilute acid has to be added. This again has to be removed by washing before the product can be dried. It may be that the poor wettability of the polymer will make efficient washing difficult; in this case a volatile wetting agent (such as an alcohol) might have to be added.

A detailed choice of dryer is not possible at this stage, since this depends very much on the particle size and particle size distribution, about which nothing is known. It is certain that the drying should be done under inert gas, since the polymer has little resistance against action of oxygen at elevated temperatures. As in case with the slurry, the drying temperature should be kept below the softening point of the polymer. At normal pressure this lies just above the boiling point of water, which would classify the operation as very low temperature drying, with consequent low heat transfer coefficient, low rate of evaporation, and low thermal efficiency. Under the given circumstances, a choice between three dryers seems to be indicated:

a) Tunnel conveyor dryer, which can not be applied if the material contains dust. This dryer has the advantage of a high thermal efficiency as compared to other dryers. Also it might be possible to
operate under vacuum in this dryer, thereby increasing speed and
efficiency. In order to use this dryer, the filter cake has to be
scored to allow gas flow through the conveyor band.

b) Indirect heated rotary dryer, which can only be applied if the
filter cake, while in the drying process, breaks up satisfactorily.
If this is the case, this dryer might be the best selection, since it
appears that vacuum could easily be applied to this dryer. This would not
be a standard design, however.

c) Spray dryer, which does outstanding service in the drying of
thermosensitive materials. The temperature of the drying gas can be
considerably higher than the highest temperature the material can stand
without damage. (Air of inlet temperature 400°F. was used to dry animal
blood.) However, the feed to a spray dryer has to be pumpable, and it is
doubtful whether the polyethylene filter cake fulfills this condition.
However, other filter cakes from rotary filters have been reported dried
in spray dryers. The possibility of adding water to make the cake
pumpable is of course on first sight not attractive. However, the
possibility should be considered.

As previously stated, the product, as manufactured by this
process, is a fine powder with low bulk density. The powder form is very
advantageous for mixing operations with other solid particles, like carbon
black 14). This is a common operation to improve on polyethylene
weathering qualities, and it is advised to look into the possibility to
produce such mixtures as part of the considered operations. Because of
the low bulk density, the optimum way of transportation would be by
railroad car loads. Hopper cars should be used. Also, it will be economical,
to keep the minimum amount of product storage. It may be economical to
use hopper cars for storage, thus having any unsold product ready for transportation.

For many uses the powdery polyethylene does not seem to be satisfactory. For this reason it might be considered to extrude and granulate part of the polyethylene production, to make sales easier by broadening the market. Since these are purely mechanical operations, not inherent to polyethylene production as such, they have not been considered in this study.

3. Economical prospects

As already stated, both production and consumption of polyethylene have risen at a great rate in the past years, and expectations are in general: - first billion pound thermoplastic material, in 1960 -. Estimates may differ by some 100 million pounds, however.

From a table by R. S. Aries\textsuperscript{38}), quote:

\begin{quote}
In 1958 it is estimated that rated capacity for all polyethylene types will be one billion pounds, of which 30\% will be the high-density types. Actual production, however, is expected to be 760,000,000 pounds, of which 18\% will be the high density types. By 1962, production is expected to climb to 1.1 billion pounds, of which 39\% will be high-density material.

The high-density types will be consumed, it is estimated, in applications such as molded articles, electrical uses, film, pipe, paper coating, bottles and tubes, and fibers in accordance with the following breakdown:
\end{quote}
Unquote. It is obvious that a prediction like the foregoing is subject to much criticism, and it should only be used as an initial, rough guide. However, it is certain that polyethylene, including its high-density variety, is here to stay and will claim an increasing share of the thermoplastics market.

The raw materials used in the process are in general readily available. The price of ethylene is rather stable around 6¢/lb. For information on the catalyst, refer to 2.

Low-density polyethylene sells, according to latest information for 35¢/lb., while the high-density material sells at 47¢/lb. It is believed that the latter will gradually drop as production capacity increases. Most people expect the price of conventional polyethylene to level off at or just below the 30-cent mark.

The major market for polyethylene is found in the northeast area of the country; it is estimated that an area stretching from 100 miles west and south of Chicago, through New England and to Washington, D. C.
oplenmv rein reactor.

A canceled trop reactor not work?

Temp ?
would include better than 75% of the market.\textsuperscript{40} Although several polyethylene plants on the Gulf Coast clearly indicate that this is not necessarily a decisive factor, it may be very significant in this case, because of the low bulk density of the product, and the consequently relatively high transportation charges.\textsuperscript{55} Thus, a plant location in the northeastern part of the U. S. should be considered.

Only one source is known to give information on the licensing costs for the Ziegler process: $1 Million and 3% royalty.\textsuperscript{43} This first number tends to agree with Ref. 40.

IV. Process Description

1. Scope

The discussions, process data and equipment specifications which follow cover the manufacture facilities for 38 Million lbs. of polyethylene per year, manufactured by the Ziegler Process.

2. Process Flow diagram

3. Description of Flow

Raw ethylene, of 97.7% purity, the balance ethane, is delivered by pipeline to the compressor. After the first stage it passes an intercooler and knock-out drum and enters the second stage. After being cooled and having passed a second knock-out drum, the compressed gas is dried and non-hydrocarbon impurities are removed in a silica gel and molecular sieve bed. It is then dissolved in the solvent, and the resulting solution is introduced in the 1st stage reactors. The liquid catalysts are also introduced into the reactors, by proportioning pumps. Heat of reaction is carried away by slurry circulation through a heat exchanger. The solvent-polymer slurry flows to the 2nd stage reactors. From here, the reaction
mixture is pumped to the light ends fractionating column where dissolved ethane and residual ethylene are removed. After heating in a steam heater, all solvent is flashed off the polymer in a flash vessel. The solvent is condensed and recirculated to the reactors. If contaminated with water, it can be dried. Solids are separated from vapors by a cyclone. The powder is then by gravity and steamflow conveyed to a treating vessel, where dilute nitric acid dissolves the inorganic catalysts at elevated temperature. Steam and traces of solvent and acid are carried overhead and are condensed and separated. Wet solvent may be dried and purified from heavier hydrocarbons and then recirculated to the reactors. Solvent make-up is added after being dried. The slurry of polyethylene in dilute acid is then filtered and the acid recirculated. The polymer is washed and conveyed to a leaching vessel. From the wash, nitric acid is regenerated and returned to circulation. To remove inorganic matter from the polymer, it is leached, filtered and washed in three subsequent stages. After the last filtration, the product is dried and polyethylene of low ash content is obtained. A part of the acid contained in the first filtercake is recovered by distillation.

V. Equipment Design

1. Compressor Section

Compressor

Feed: 4400 lbs/hr Ethylene
100 lbs/hr Ethane
14.7 psia
90°F.

Desired final conditions: 150 psia, 100°F.
Required horsepower:

\[ HP = N_s \times 0.00436 \times V_1 \times P_1 \left( \frac{n}{n-1} \right) \left[ \left( \frac{P_2}{P_1} \right)^{\frac{n-1}{n}} - 1 \right] \]

- \( N_s \) = number of stages
- \( V_1 \) = inlet flow, cu.ft/min.
- \( P_1 \) = inlet pressure
- \( P_2 \) = outlet pressure
- \( n = \frac{C_p}{C_v} = 1.23 \)

\( \frac{P_2}{P_1} = 10 \), consequently a two-stage compressor is indicated

\[ HP = 190 \]

At total compressor efficiency of 75%:

\[ HP = 253 \]

Install standard 300 HP drive.

Fuel, steam and electrical costs in the plant must be considered before a decision on the type of drive can be made. As far as size is concerned, a reciprocating steam engine, an electric motor, a gas or a diesel engine could be considered.

Since only one compressor is used, a drive of wide flexibility would be preferred from an operating point of view, which would eliminate the electric motor. An important consideration might be that because of the plant's low steam consumption additional steam consumption might be desirable (this only in case the plant has to generate its own steam). It is felt that no decision can be taken on the subject, nor has it to be taken - estimated investment and operating costs are practically the same.
Intercooler:

\[ T_2 = T_1 \left( \frac{P_2}{P_1} \right)^{\frac{n-1}{n}} \]

\[ T_1 \text{ = inlet temperature, } ^\circ\text{R} \]

\[ T_2 \text{ = outlet temperature} \]

\[ T_2 = 225^\circ F. \]

At this temperature there is no danger of polymerization of the polymer.

Heat to remove: \( H = 50 \text{ BTU/lb.} \)

Cooling water in: \( 80^\circ \text{F.} \)

out: \( 125^\circ \text{F.} \)

\[ A = \frac{Q}{U \Delta T_{e.m.}} \]

\( A \) = area exchanger \( ft^2 \)

\( Q \) = total heat to remove, BTU/hr.

\( U \) = overall heat transfer coefficient

BTU/hr. \( sq.ft. \) \( ^\circ \text{F.} \)

\( U \text{ gas-liquid} = 10 \) **

\[ A = 450 \text{ ft}^2 \]

Install 550 \( ft^2 \) exchanger

Cooling water requirements: 600 gal/hr.

Aftercooler: identical to intercooler for same duty.

Install 550 \( ft^2 \) exchanger

Cooling water requirements: 600 gal/hr

Summary of equipment requirements

Two-stage reciprocating compressor, 300 HP

2 Exchangers, E-1 and E-2, 550 \( ft^2 \)

* All enthalpies from Ref. 52

** All values of \( U \) are estimated from values in Ref. 51, 53 and 55.
2. **Ethylene Dryers** [31] [17]

Designed for maximum water content of ethylene and 8 hr. cycle. Maximum water content in ethylene is unlikely, but since process is so sensitive for traces of water, no chances should be taken at this point. Therefore, a primary bed of silica gel is used, followed by Linde's newly introduced molecular sieve. This will not only reduce the water content to <1 ppm, but also remove \( \text{CO}_2 \), \( \text{H}_2\text{S} \) and other O- and S- compounds to an extremely low level. [17]

Basis Silica gel bed design (procedure 31), p. 882)

- Vapor pressure \( \text{H}_2\text{O} \) @ 100°F.: 0.95 psia
- Feed: 5000 lbs. Ethylene/hr., 100% humidity, 100°F., 150 psia, visc. 0.0106 cp
- Maximum effluent humidity: 1%
- Cycle: 8 hours
- Silica gel: 8-10 mesh, 40 lbs/cu.ft., Sp. heat 0.2 BTU/1b. °F.
- Superficial gas velocity: approx. 1/2 ft/sec.
- Average moisture content of gel at end of cycle: 30 lbs/100 lbs dry gel
- Maximum load: 20.5 lbs \( \text{H}_2\text{O} \)/hr.

**Result:** Vessel diameter 2', length 4.5'

Contents 570 lbs Silica gel

**Basis of Molecular sieve bed design:**

- In same vessel as silica gel bed
- Capacity: 5% of total water
- \( \text{CO}_2 + \text{H}_2\text{S} \) content feed: <5 ppm
- \( \text{CO}_2 + \text{H}_2\text{S} \) content effluent: <1 ppm
- Break-through capacity: 5 lb. \( \text{H}_2\text{O} \)/lb. dry ads.
- Adsorbent: density 40 lb/cu.ft., sp. heat 0.3 BTU/1b. °F.

Resulting in bed height of 1.3 ft., containing 160 lbs. adsorbent.
Regeneration of both beds at 450°F. Required heat per cycle: 100,000 BTU under ideal conditions. Assuming 50% thermal efficiency: 200,000 BTU/cycle. Since the dryers should remain free of oxygen and carbon dioxide, the off-gas of the desorption column A-1 could be used to advantage as a purge gas.

Pressure drop through the adsorbent beds amounts to 1.5 in. H₂O, and can thus be neglected.

Summary equipment requirements drying section

2 Vessels, F-3 and F-4, 2' diam., 6' length
1200 lbs. Silica gel
320 lbs. Molecular Sieve
200,000 BTU/8 hours

3. Reactor Section

Basis for design of first stage:
Operating temperature 158°F.
Operating pressure 140 psia
Maximum volume ratio polymer-solvent: 0.15
Feed: 4400 lbs/hr. Ethylene, 107 lbs/hr. Ethane
Bulk density polymer: 300 gr/l in air
Real density polymer: 950 gr/l

Reaction rate:
\[ R = \frac{60 CC_r}{C} \]
\[ R = \text{Reaction rate, gr Ethylene/l hr} \]
\[ C = \text{Concentration Ethylene, gr/l solvent} \]
\[ C_r = \text{Concentration TiCl}_4, \text{cc/l solvent} \]
Solvent: Choice based on possibility of overhead cooling.

Arbitrarily set maximum Ethylene content of equilibrium vapor: 25 mol.%. If 150 gr Ethylene have been absorbed by the solvent, at which point it leaves the first stage reactor, it will contain $150 \times \frac{107}{4507} = 3.45$ gr Ethane/l. solvent. Using butane and pentane as solvent components, the composition of the solution in the reactor (thus excluding the polymer) is found to be by trial and error:

<table>
<thead>
<tr>
<th></th>
<th>Mol. fraction in liquid</th>
<th>Mol. fraction in vapor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>0.0327</td>
<td>0.250</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.0131</td>
<td>0.071</td>
</tr>
<tr>
<td>Butane</td>
<td>0.672</td>
<td>0.578</td>
</tr>
<tr>
<td>Pentane</td>
<td>0.282</td>
<td>0.101</td>
</tr>
<tr>
<td>Density</td>
<td>526 g/l</td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>60.8</td>
<td></td>
</tr>
<tr>
<td>Ethylene content</td>
<td>7.93 g/l. solution</td>
<td></td>
</tr>
</tbody>
</table>

Solvent composition in mol. fractions:

- Butane 0.704
- Pentane 0.296

Rate of reaction, using 0.1 cc TiCl₄/l solvent:

$R = 47.6$ gr Eth/l. solution, hour

Solvent circulation at 150 g. Polyethylene/l. solvent:

$$\frac{4400 \times 454}{150 \times 3.785} = 3520 \text{ gal/hr.}$$

Volume of solution in reactors:

Polymerized in 1st stage reactor, allowing for 7.93 gr ethylene/l. leaving 1st stage reactor:

4170 lbs/hr. Thus, at reaction rate 47.6 gr/l. hr:

Volume of solution: 1395 cu. ft.
Add to this the volume of suspended polymer:

Total Volume of contents: 1600

Heat balance:

Heat of reaction $1800 \text{ BTU/lb.}$

Heat contents of catalyst have been neglected.

<table>
<thead>
<tr>
<th>In</th>
<th>BTU/lb</th>
<th>BTU/hr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4400 lbs/hr. Ethylene, 100°F</td>
<td>309</td>
<td>1,360,000</td>
</tr>
<tr>
<td>107 lbs/hr. Ethane, &quot;</td>
<td>328</td>
<td>35,000</td>
</tr>
<tr>
<td>10,130 lbs/hr. Butane, &quot;</td>
<td>160</td>
<td>1,621,000</td>
</tr>
<tr>
<td>5,290 lbs/hr. Pentane, &quot;</td>
<td>152</td>
<td>804,000</td>
</tr>
<tr>
<td>Heat of polym, $4170 \times 1800$</td>
<td></td>
<td>$7,560,000$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10,300,000</td>
</tr>
</tbody>
</table>

Out: (158°F.)

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>235 lbs/hr. Ethylene</td>
<td>246</td>
<td>58,000</td>
</tr>
<tr>
<td>107 lbs/hr. Ethane</td>
<td>265</td>
<td>28,000</td>
</tr>
<tr>
<td>10,130 lbs/hr. Butane</td>
<td>198</td>
<td>2,020,000</td>
</tr>
<tr>
<td>5,290 lbs/hr. Pentane</td>
<td>188</td>
<td>994,000</td>
</tr>
<tr>
<td>4170 lbs/hr. Polyethylene</td>
<td>150</td>
<td>625,000</td>
</tr>
</tbody>
</table>

Thus, 6,655,000 BTU/hr. has to be removed.

Surface of heat exchangers

Cooling water: inlet 80°

         outlet 90°

$U = 125 \text{ BTU/hr. ft}^2 \circ{\text F}$

Slurry: exit 100°

$A = 1370 \text{ ft}^2$

Install 1600 ft$^2$
Cooling water:
\[
\frac{6,655,000}{(10)(8.35)} = 80,000 \text{ gal/hr.}
\]

Quantity of circulated slurry
\[
158^\circ: \quad H = 187 \text{ BTU/lb.}
\]
\[
90^\circ: \quad H = 142 \text{ BTU/lb.}
\]

Circulate \( \frac{6,655,000}{45} = 148,000 \text{ lbs/hr.} \)

Pumps
Assume a differential head of 100 ft. Total pump - efficiency 0.7
\[
\text{HP} = \frac{148,000 \times 100}{3600 \times 0.7 \times 550} = 10.7 \text{ HP}
\]
Install 15 HP

Alternate for heat removal

Forced circulation of vapor for better heat transfer coefficient.

Cool vapor to 90°F.

By trial and error, when \( L + V = 1 \)
\[ \text{at } 90^\circ: \quad L = 0.697 \]

Composition of liquid

<table>
<thead>
<tr>
<th></th>
<th>Mol. fraction</th>
<th>vapor Mol. fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>0.1094</td>
<td>0.575</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.0403</td>
<td>0.1415</td>
</tr>
<tr>
<td>Butane</td>
<td>0.714</td>
<td>0.2626</td>
</tr>
<tr>
<td>Pentane</td>
<td>0.1364</td>
<td>0.0201</td>
</tr>
</tbody>
</table>
Heat removed per lb. hot vapor: 140.5 BTU
Thus, circulate 47,500 lbs. hot vapor/hr.

Blowers for cool vapor
Assume maximum pressure drop 5 lbs. Use 2-impeller blower.
\[ W = V (P_2 - P_1) \]
Circulate 10,700 lbs/hr. cool vapor, \( MW = 37.1 \)
\[ HP = 5 \]

Condenser
\[ U = 175 \text{ BTU/ft}^2 \text{ hr. oF.} \]
Cooling water 80 → 90°F.
\[ A = 1270 \text{ ft}^2 \]

Basis for design of 2nd stage
Exit concentration ethylene: 1 gr/l solution
Temperature: 5° below bubble point
Reaction rate: assumed equal to rate at 158°, although in reality higher
\[ R = 6 \text{ g/l. hr.} \]
Consequently, residence time:
\[ t = \frac{7.93 - 1}{6} = 1.16 \text{ hrs.} \]
Volume of contents:
\[ 1.16 \times \frac{(1.15)(3520)}{7.48} = 630 \text{ cu. ft.} \]

Operating temperature
Bubble point for solution is found by trial and error to be 178°F.
Since no boiling is desired, the operating temperature will be 173°F.

Heat balance
\[
\begin{align*}
\text{In} & & \text{BTU/hr} \\
\text{From 1st stage reactor} & & 3,725,000 \\
\text{Heat of polym.} & 206 \times 1,800 & 374,000 \\
\end{align*}
\]
\[ 4,099,000 \]
<table>
<thead>
<tr>
<th></th>
<th>BTU/lb.</th>
<th>BTU/hr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>29 lbs/hr.</td>
<td>253</td>
</tr>
<tr>
<td>Ethane</td>
<td>107 lbs/hr.</td>
<td>271</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>4371 lbs/hr.</td>
<td>163</td>
</tr>
<tr>
<td>Butane</td>
<td>10,130 lbs/hr.</td>
<td>207</td>
</tr>
<tr>
<td>Pentane</td>
<td>5,290 lbs/hr.</td>
<td>198</td>
</tr>
</tbody>
</table>

To remove by cooling: 204,000 BTU/hr.

Surface of cooling coil

Cooling water 80°F → 90°F.

\[ U = 125 \text{ BTU/hr. ft}^2 \text{°F.} \]

\[ A = 18.6 \text{ ft}^2 \]

Install 25 ft²

Cooling water: 2440 gal/hr.

**Size Reactor Vessels**

For flexibility of plant operation, and because of reactor diameter, it is probably preferable to use two reactor vessels.

For smooth pressure control, a vapor space above the slurry in the 1st stage reactor is required.

1st and 2nd stage reactors are in the same vessel, separated by a horizontal baffle. The same opening in this baffle is used for slurry flow and transmission of the stirrer shaft.

Required volume for each reactor vessel:

1st stage reactor: 800 cu ft.

Vapor space: 300 cu ft.

2nd stage reactor: 315 cu ft.

Total: 1415 cu ft.
From this, approximate dimensions of reactor vessels: Diameter 10 ft.
Length 18 ft.

**Stirrers**

To avoid a vortex, stirrers have to be installed off-center, or the vessel has to contain baffles. Flat-blade turbines will be used.

Diameter turbines: 3 ft.
Other dimensions: standard
Shaft: off-center
Speed: 90 RPM

Maximum slurry concentration: 150 gr polymer/l. solution, resulting in 131 gr polymer/l. slurry.
300 gr polymer absorbs 700 ml solvent.

Specifications slurry:

- Volume fraction apparent solids: 0.437
- Volume fraction total solvent: 0.869
- Bulk density: 38.2 lb/cu. ft.
- Bulk viscosity: $9.1 \times 10^{-4}$ lb/ft. sec.

$$N_{Re} = \frac{D^2 N_p}{\nu}$$

$D =$ diameter turbine
$N =$ Revolutions per second
$p =$ density fluid
$\nu =$ viscosity fluid

$$N_{Re} = 5.7 \times 10^5$$
In this range the power number $N_p$ is independent of $N_{Re}$

$$N_p = \frac{P}{\rho g h} = 6$$

$P$ = required power, ft. lb/sec.
$g$ = gravity constant, 32.2 ft/sec$^2$
$\rho = 5840$
$HP = 10.6$

One turbine is required for both 1st stage and 2nd stage reactor.
Installed HP per stirrer: 25

**Catalyst handling**

A thorough study should be made of the handling of $\text{Al (Et)}_3$ and $\text{TiCl}_4$. Both are dangerous and poisonous. Locations where leakage is liable to occur should be well vented with a dry inert gas.

**Pumps P-3 and P-4**

These are proportioning pumps. Approximate maximum capacity 2 gal/hr each.

**Summarized equipment requirements for reactor section**

2 Reactor vessels F-5 and F-6, Diam. 10 ft.
Length 18 ft.

2 Pumps P-15 and P-16, each 7.5 HP
240 gal/min.

2 Heat exchangers E-3 and E-4, 800 ft$^2$ each

2 Cooling coils, 13 ft$^2$ each

2 Stirrers, 25 HP each

2 Proportioning pumps, P-3 and P-4, 2 gal/hr.

4. **Ethane and Ethylene Removal**

Pumps from reactors to tower:
Assume 100 ft head
Duty: 20,000 lb/hour, density 38.2 lb/cu ft.

Total pump efficiency 0.4

\[
\text{HP} = \frac{20,000 \times 100}{3600 \times 0.4 \times 550} = 2.53
\]

Installed Horse power: 4

Operating specifications tower

Pressure: 147 psia
Top temperature: 95°F.
Mol. fraction Ethane in bottoms: 0.0001
Feed: 173°F.

Assuming that no ethylene reacts after leaving 2nd stage reactor, the composition of the liquid phase of the slurry is:

<table>
<thead>
<tr>
<th>Mol. fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
</tr>
<tr>
<td>Ethane</td>
</tr>
<tr>
<td>Butane</td>
</tr>
<tr>
<td>Pentane</td>
</tr>
</tbody>
</table>

From preliminary rough calculation, approximate composition of bottoms:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane</td>
<td>0.702</td>
</tr>
<tr>
<td>Pentane</td>
<td>0.298</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

The bubble point of this mixture is calculated by trial and error: 199°F. at 147 psia.

The same calculation, starting with overhead composition

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>0.1</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.3</td>
</tr>
<tr>
<td>Butane</td>
<td>0.6</td>
</tr>
</tbody>
</table>
gave as tentative overhead composition

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>0.160</td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>0.526</td>
<td></td>
</tr>
<tr>
<td>Butane</td>
<td>0.313</td>
<td></td>
</tr>
<tr>
<td>Pentane</td>
<td>0.0014</td>
<td></td>
</tr>
</tbody>
</table>

Minimum theoretical stages to separate Ethane from Butane in desired degree:

\[
S_M = \log \left( \frac{X_{LKD}}{X_{LKW}} \right) \left( \frac{X_{HKW}}{X_{HKD}} \right) \frac{\log \alpha_{LK}}{\log \alpha_{LK}}
\]

LKD : Light Key in distillate
HKD : Heavy " "
LKW : Light Key in bottoms
HKW : Heavy " "
\( X \) : Mol fraction
\( \alpha \) : Relative volatility

\[
S_M = 4.65
\]

If \( D + W = F \)

\[
D = 0.0255 F \text{ moles}
\]

\[
W = 0.9745 F \text{ moles}
\]

<table>
<thead>
<tr>
<th></th>
<th>Comp. overhead</th>
<th>reflux</th>
<th>bottoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>0.160</td>
<td>0.0314</td>
<td>0.000008</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.525</td>
<td>0.1439</td>
<td>0.0001</td>
</tr>
<tr>
<td>Butane</td>
<td>0.315</td>
<td>0.818</td>
<td>0.702</td>
</tr>
<tr>
<td>Pentane</td>
<td>0.001</td>
<td>0.0075</td>
<td>0.298</td>
</tr>
</tbody>
</table>

Minimum Reflux Ratio

Detailed method outlined in Ref. 52, p. 231.

It is a modification of the Gilliland method.
### Mol. % of feed vaporized

<table>
<thead>
<tr>
<th></th>
<th>(O/D) M:</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>3.9</td>
</tr>
<tr>
<td>71.0</td>
<td>30.9</td>
</tr>
<tr>
<td>Thus:</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>3.9</td>
</tr>
</tbody>
</table>

Column will have reboiler and partial condenser, each counting as one stage.

From correlation of theoretical stages with actual and minimum reflux ratio:

<table>
<thead>
<tr>
<th>O/D</th>
<th>Stages</th>
<th>Theoretical Plates</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.9</td>
<td>00</td>
<td>00</td>
</tr>
<tr>
<td>4.9</td>
<td>10.7</td>
<td>8.7</td>
</tr>
<tr>
<td>5.9</td>
<td>9.2</td>
<td>7.2</td>
</tr>
<tr>
<td>6.9</td>
<td>8.2</td>
<td>6.2</td>
</tr>
<tr>
<td>7.9</td>
<td>7.8</td>
<td>5.8</td>
</tr>
<tr>
<td>9.9</td>
<td>7.5</td>
<td>5.5</td>
</tr>
<tr>
<td>13.9</td>
<td>6.7</td>
<td>4.7</td>
</tr>
</tbody>
</table>

Employ O/D = 10

Add 3 theoretical phases as safety measure.

Total theoretical plates: 9.5

Plate efficiency

Average viscosity on plates: 0.14 cp

Fluidity \( \frac{1}{\text{visc}} = 7.1 \)

Overall plate efficiency \(52^\circ\): 90%

Therefore, use 10 plates.

However, according to Ref. 20:

Since \( \alpha K^* = 1.33 \)

Efficiency = 45%
Since a generous allowance already was made by adding 3 theoretical plates, it is felt that 15 plates will be adequate.

Tray spacing above feed plate: 1½'
Feed tray spacing: 3'
Tray spacing below feed plate (greater vapor load): 2'

Location of feed plate.

Assume that fraction of actual plates above the feed will be the same as that required to effect the same separation of the key components at total reflux. For feed plate to top:

$$S_M = 2.21$$

Thus the number of plates above the feed plate:

$$\frac{2.21}{4.65} \times 17 = 8.1$$

Feed is introduced on plate 8, counted from the bottom.

Heat balance around tower

<table>
<thead>
<tr>
<th>In</th>
<th>Out</th>
<th>lbs/hr</th>
<th>BTU/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge</td>
<td></td>
<td></td>
<td>3,900,000</td>
</tr>
<tr>
<td>X lbs steam @ 17.5 psia, ΔH=970</td>
<td></td>
<td></td>
<td>970 X</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3,900,000 + 970 X</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>H</th>
<th>11'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overhead: Ethylene, 29</td>
<td>307</td>
<td>9,000</td>
<td></td>
</tr>
<tr>
<td>Ethane, 107</td>
<td>325</td>
<td>35,000</td>
<td></td>
</tr>
<tr>
<td>Butane, 119</td>
<td>305</td>
<td>36,000</td>
<td></td>
</tr>
<tr>
<td>Bottoms: Butane, 10,011</td>
<td>225</td>
<td>2,248,000</td>
<td></td>
</tr>
<tr>
<td>Pentane, 5,290</td>
<td>215</td>
<td>1,360,000</td>
<td></td>
</tr>
<tr>
<td>Polyethylene, 4,371</td>
<td>185</td>
<td>809,000</td>
<td></td>
</tr>
</tbody>
</table>
Reflux: Ethylene, Ethane, Butane, Pentane,

<table>
<thead>
<tr>
<th></th>
<th>lbs/hr.</th>
<th>(\Delta H)</th>
<th>BTU/hr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>565</td>
<td>85</td>
<td>5,000</td>
</tr>
<tr>
<td>Ethane</td>
<td>251</td>
<td>88</td>
<td>25,000</td>
</tr>
<tr>
<td>Butane</td>
<td>3090</td>
<td>149</td>
<td>460,000</td>
</tr>
<tr>
<td>Pentane</td>
<td>33</td>
<td>156</td>
<td>5,000</td>
</tr>
</tbody>
</table>

Heat duty (reboiler)

Steam: 1130 lbs/hr.

Reboiler surface

\[ U = 200 \text{ BTU/ft}^2 \text{ hr. } ^\circ\text{F.} \]

Steam temperature: 220\(^\circ\)F.

\[ A = 260 \text{ ft}^2 \]

Install 300 ft\(^2\) surface area

**Tower diameter**

Vapor load under top tray = reflux + overhead

Volume: 7.94 cu ft/sec.

Density: 0.129 lb/cu ft.

Reflux density: 29.0 lb/cu ft.

Allowable vapor velocity at \(1\frac{1}{2}\) ft. tray spacing and \(1\frac{1}{8}\) in. liquid seal:

\[ V_{\text{All.}} = 1.94 \text{ ft/sec.} \]

Required tower diameter: 2.3 ft.

Vapor load under bottom tray = \(\frac{\text{Reboiler duty}}{\text{Heat of vap. bottoms}}\)

Volume: 18.3 cu ft/sec.

Density: 0.130 lb/cu ft.

Bottoms density: 31.3 lb/cu ft.

Allowable vapor velocity at 2 ft. tray spacing and 1 in. liquid seal:

\[ V_{\text{All.}} = 2.64 \text{ ft/sec.} \]
Minimum tower diameter: 2.98 ft.
Use 3 ft. tower diameter.

**Partial condenser**

Duty: 500,000 BTU/hr.

\[ U = 150 \text{ BTU/ft}^2 \text{ hr. } ^\circ\text{F}. \]

Cooling water: 80 — 85°F.

\[ A = 271 \text{ ft}^2 \]

Install 350 ft² surface area.

Cooling water requirements: 12,000 gal/hr.

**Summary of equipment requirements for ethane-ethylene removal section**

Distillation column A-1: 15 bubble cap plates

Diameter 3 ft.

Length approximately 35 ft.

Reboiler H-1, surface area 300 ft².

Condenser E-7, surface area 350 ft².

2 Pumps P-1 and P-2, each 2 HP

each 33 gal/min.

5. **Flash Chamber**

All solvent has to be flashed off the polymer. The pressure in the vessel should be such that the vapors can be totally condensed at 100°F. (cooling water). Thus, this is the pressure at which the bubble point of the mixture is 100°F. By trial and error:

\[ P = 43.5 \text{ psia} \]

At this pressure, the dew point of the mixture is found to be by trial and error:

\[ T_D = 120^\circ\text{F}. \]
To make sure that all solvent has flashed, the solid polymer should leave the vessel at 125°F.

The average vapor temperature is estimated to be 130°F.

Heat balance, including heater.

<table>
<thead>
<tr>
<th>In</th>
<th>BTU/hr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane tower bottoms</td>
<td>4,417,000</td>
</tr>
<tr>
<td>Heater Duty</td>
<td>R</td>
</tr>
<tr>
<td></td>
<td>4,417,000 + R</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Out</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene, 4371 lbs/hr.</td>
<td>128</td>
</tr>
<tr>
<td>Butane, 10,000 lbs/hr.</td>
<td>325</td>
</tr>
<tr>
<td>Pentane, 5,280 lbs/hr.</td>
<td>326</td>
</tr>
<tr>
<td></td>
<td>5,539,000</td>
</tr>
<tr>
<td></td>
<td>4,417,000</td>
</tr>
<tr>
<td></td>
<td>1,122,000</td>
</tr>
</tbody>
</table>

Heater duty

Steam, [17.5 psia, 220°F], ΔH = 970

Required: 1160 lbs/hr.

U = 200 BTU/ft² hr. °F.

Est. slurry temp.: 200°F.

A = 281 ft²

Install 350 ft²

A U-tube exchanger would seem advisable for this type of duty since it offers the least resistance and has the least obstacles.

Condenser

<table>
<thead>
<tr>
<th>In</th>
<th>BTU/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flashed vapor</td>
<td>4,970,000</td>
</tr>
</tbody>
</table>
Butane, 10,000 lbs/hr. 160 1,600,000
Pentane, 5,280 lbs/hr. 152 800,000
Condenser duty

Condenser duty: 2,570,000 BTU/hr.

\[ U = 150 \text{ BTU/ft}^2 \text{ hr. } \circF. \]

Cooling water: 80 \( \rightarrow \) 90\( ^\circ F. \)

\[ A = 700 \text{ ft}^2 \]

Install 800 ft\(^2\) surface area

Cooling water: 512 gal/min.

**Vessel**

Size of vessel hard to predict. Minimum will be governed by size of cyclone. Cyclone is not used by itself only, because

1) Additional pressure vessel is probably cheaper than pressure resisting cyclone.

2) Residence time of solids is greater, which gives more complete vaporization of the solvent.

**Cyclone**

Design inlet velocity: 50 ft/sec.

Volume: 9.83 cu ft/sec.

Inlet opening: 0.2 ft\(^2\)

Basic dimensions of cyclone (Ref. 51, p. 1024):

Diameter: 1.3 ft

Length of cylinder and cone: 5.2 ft.

From this, estimated size of vessel:

Diameter 2.5 ft.

Length 8 ft.
Figure 2
Solvent surge drum F8
Half hour solvent circulation capacity.
Volume: 215 cu ft.
Diameter: 5 ft.
Length: 10 ft.

Solvent circulation pump P-5
Approximate pressure head: 120 psi ~ 480 ft. head
Duty: 15,280 lbs/hr., density 36 lbs/cu. ft.
Efficiency: 0.4

Install 11 HP

Summary of equipment requirements for flash section
Vessel F-7: Diam. 2.5 ft.
Length 8 ft.
Cyclone: 10 cu ft/sec.
Heater H-2: 350 ft²
Condenser E-5: 800 ft²
Condensate drum F-8, Diam. 5 ft.
Length 10 ft.
Pump P-5 11 HP
53 gal/min.

6. Catalyst removal section
Catalyst is decomposed by and dissolved in a hot 10% nitric acid solution.
Catalyst consumption: 5.1 lbs/hr. TiCl₄
4.6 lbs/hr. Al (Et)₃
For their decomposition is required 14.3 lbs/hr HNO₃.
Generated are then 16.4 lbs/hr dissolved nitrates and 3.9 lbs/hr. HCl.

Schematic balance of acid and water in filtration section

The polymer travels in a straight line. Its quantity does not change during the operations, and is therefore not shown. Also, the salt content is not shown, although the prime objective is the removal of catalyst. The reason is that it is easier to picture the dilute acid flow. The ratio solids: HNO₃ is everywhere equal, except for the fresh supply of HNO₃. Since 16.4 lbs solids leave the system with 109.3 lbs HNO₃, this ratio prevails in the entire system.

The mass balance is based on the following assumptions:

a) Perfect mixing in the mixing vessels.

b) Washing on filter reduces HNO₃ content of filter cake by 50%, except in the 1st wash.

c) The filter cake contains equal amounts of polymer and aqueous solution.

Vessel F-9

Operating temperature : 220°F.

Pressure : 17.5 psia

To bring polyethylene and dilute acid up to 220°F., 700 lbs/hr steam are required. In addition, 500 lbs/hr. steam are used to strip the polymer of remaining solvent, thus giving total requirement of 1200 lbs/hr. steam (< 20 psia).

Residence time : 1 hour, 70% filled

Volume : 530 cu ft.

Diameter : 7 ft.

Height : 14 ft.

Vessel has to be glass-lined because of HNO₃ + HCl.
Stirrer: 2 propellers

At common \( N_{Re} \):

\[
N_p = 1 \quad \text{(Stirrer shaft off center or vessel baffled)}
\]

\[
N = 120 \ \text{rev/min.}
\]

Diam. propeller: 2 ft.

For 2 propellers required 2 HP.

Install 2.5 HP

Heat exchanger E-6

Because of highly corrosive nature of slurry and of filtrate, Karbate has to be used.

1st section: heat exchange

Slurry: 2202 \( \rightarrow \) 135°F.

Filtrate: 100 \( \rightarrow \) 200°F.

\[
U = 100 \ \text{BTU/ft}^2 \ \text{hr. °F.}
\]

Heat duty: 1,690,000 BTU/hr.

\[
A = 625 \ \text{ft}^2
\]

2nd section: cooler

Slurry: 135 \( \rightarrow \) 100°F.

Cooling water: 80 \( \rightarrow \) 90°F.

Take \( U = 100 \ \text{BTU/ft}^2 \ \text{hr. °F.} \)

Heat duty: 700,000 BTU/hr.

\[
A = 226 \ \text{ft}^2
\]

Install 1000 ft\(^2\) for both sections.

Cooling water: 8400 gal/hr.

Pump P-7

Assume head: 100 ft.

Load: 17,000 lbs/hr.

Efficiency: 0.5

\[
\text{HP} = 2
\]

Install 2.5 HP: Haveg or equal.
Vessel F-10

Operating temperature: 100°F.
Plastic lined or Haveg.
Residence time: approx. 1 hour
Diameter: 6 ft.
Height: 12 ft.

Stirrer: identical to stirrer in F-9
Required 2 HP
Install 2.5 HP

Vessel F-11

Operating temperature: 100°F.
Plastic lined or Haveg
Residence time: approx. 1 hour
Diameter: 8 ft.
Height: 16 ft.

Stirrer: Diameter propeller 2.5 ft.
2 propellers on shaft
N = 100 rev./min.

Required HP = 3.15
Install 4 HP

Vessel F-12

Entirely identical to F-11
Stirrers also identical

Filters V-1 to V-4
Nothing is known about the filterability of the product, except the statement 7): - the material filters extraordinarily quickly-.
Because of the quite possible resemblance between paper pulp and the polyethylene slurry, a low filtration rate of the former is used to estimate the size of the required filters.

- Filtration rate: 500 lbs/ft² day
- Total polymer: 105,000 lbs/day

Required filter area: 200 sq. ft.

Install 200 sq. ft. continuous rotary vacuum filters (Oliver), having facilities for separate collection of filtrate and wash.

The filters should be covered so the filtration can take place under inert gas.

Because of the corrosive nature of filtrate and wash, all metal parts of the filters should be plastic coated.

Pumps P-8 and P-14
- Assume head: 50 ft.
- Load: 8800 lbs/hr.
- Efficiency: 0.4

Required HP: 0.55
Install 0.75 HP
Haveeg or plastic coated.

Pumps P-9 to P-13
- Assume head: 50 ft.
- Load: 40,000 lbs/hr.
- Efficiency: 0.6

Required HP: 1.32
Install 1.5 HP
Haveeg or plastic coated.
Screw conveyors from filters

The length of the conveyors will depend on the lay-out of the plant. It is obvious that they should be kept as short as possible, since both investment and operating cost are approximately proportional to the length. The conveyors should be plastic coated, which is possible since the wet polyethylene is probably not abrasive (waxy).

Estimate for 5 screw conveyors:

- Av. length: 20 ft.
- Scope: 25°
- Capacity: 10,000 lbs/hr.

Total required HP: 5

Summary of equipment requirements of catalyst removal section

- Vessel F-9: Diam. 7 ft. Glass-lined
  
  Height: 14 ft.

- Stirrer: 2.5 HP

- Exchanger E-6, Karbate, 1000 ft²

- Pump P-7, Haveg, 2 HP, 33 gal/min.

- Vessel F-10, plastic lined
  
  Diam.: 6 ft.

  Height: 12 ft.

- Stirrer: 2.5 HP

- 2 Vessels F-11 and F-12, plastic lined
  
  Diam.: 8 ft.

  Height: 16 ft.

- 2 Stirrers: 4 HP
4 Rotary vacuum filters, 200 sq. ft. per filter

Metal parts plastic coated

2 Pumps P-8 and P-14: 0.75 HP, 18 gal/min.

Haveg or coated.

4 Pumps, P-9 to P-13: 1.5 HP, 80 gal/min.

Haveg or coated

7. Additional equipment

Dryer

Choice of dryer is not possible at the moment (see introduction).

Load: 4400 lbs H₂O/hr.

Estimated thermal efficiency: 50%

Heat input: 8,600,000 BTU/hr.

If indirect dryer is used with steam:

Steam: 8,600 lbs/hr.

Power: estimated 10 HP

Vibrating conveyor

From dryer to storage and loading hoppers.

For vertical displacement a spiral conveyor.

This could be equipped for final drying and cooling of the product.

Size depends on outlay of plant and on material handling properties; none of this information is available.

Estimate for required power: 10 HP

Storage and loading hoppers

Because of the low bulk density of the material, it will be advantageous to maintain only a minimum of storage space and ship the material as soon as possible. If this is done, as suggested, by railroad cars, a factor of uncertainty of car supply is introduced. Therefore, it may be advisable to
have some trucks available for bulk transport.

When products are made of several specifications, the minimum number of hoppers is three.

The storage space cannot be cut down indefinitely, since the running of the plant at low capacity increases the cost of the product. The maximum size of a hopper is dictated by product properties, which are not known at the present. It certainly would be advisable to look into the possibility of using railroad hopper cars for storage.

If all product is shipped in bulk by hopper car, approximately 2½ cars of 2,100 cu ft. each are loaded per day.

It is estimated that 7 days storage should be provided, mostly to buffer fluctuations in sales. This would then amount to approximately 40,000 cu ft storage space.

8. Nitric acid recovery section

No information is available which allows the evaluation of a tower design for this purpose, because of the very great relative volatility of water. However, the most recent information indicates that 2 theoretical stages will result in a practically HNO₃-free overhead.

Because of the corrosive nature of the fluid (dilute HNO₃ with HCl, at boiling point), a stoneware flanged packed tower should be used.

Feed : 8411 lbs/hr. H₂O
            328 lbs/hr. HNO₃
            100°F.

Distillate : 5506 lbs/hr. H₂O

Reflux : 1100 lbs/hr. H₂O

Operating pressure : 20 psia
Based on liquid load in bottom of 11240 lbs/hr., and vapor load of 7680 lbs/hr., the velocity at which flooding occurs is determined to be for 2 in. packing: \( V_F = 10.1 \text{ ft/sec.} \)

If operating at \( V = 7.0 \text{ ft/sec.}, \) and 45 cu ft/sec. vapor,

\[ \text{H.E.T.P.} \approx 3 \text{ ft.} \]

Diameter tower : 3 ft.

Height tower : 8 ft.

Reboiler

Heat load : Feed, 8740 lbs/hr., 100 \( \rightarrow \) 225° \(1,100,000\)

Overh'd + Reflux, 6600 lbs/hr. \(6,460,000\)

\[ \text{Total} = 7,560,000 \]

Use Karbate reboiler tubes

Steam, 75 psia : 8400 lbs/hr.

\[ U = 150 \text{ BTU ft}^{-2} \text{ hr.} \cdot \text{°F.} \]

\[ A = 625 \text{ ft}^2 \]

Install 750 ft\(^2\)

The overhead vapors are slightly acid. It is proposed that they be given an ammonia injection, consequently be washed free of salts, and then used in the dryer, together with other low-pressure steam.

Summary of required equipment

1 Stoneware tower A-2, flanged, packed with 2 in. rings

Diam. : 3 ft.

Height : 8 ft.

Reboiler H-3, Karbate, 750 ft\(^2\)
## Economics

1. **Capital requirements**

   **Equipment cost, purchased**

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Cost</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressor</td>
<td>$29,000</td>
<td>32</td>
</tr>
<tr>
<td>Vessel F-3</td>
<td>800</td>
<td>32, 34</td>
</tr>
<tr>
<td>F-4</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>F-5</td>
<td>15,000</td>
<td></td>
</tr>
<tr>
<td>F-6</td>
<td>15,000</td>
<td></td>
</tr>
<tr>
<td>F-7</td>
<td>900</td>
<td></td>
</tr>
<tr>
<td>F-8</td>
<td>2,000</td>
<td></td>
</tr>
<tr>
<td>F-9</td>
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<tr>
<td>F-10</td>
<td>2,900</td>
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</tr>
<tr>
<td>F-11</td>
<td>6,100</td>
<td></td>
</tr>
<tr>
<td>F-12</td>
<td>6,100</td>
<td></td>
</tr>
<tr>
<td>Heat Exchanger E-3</td>
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<td>32, 34</td>
</tr>
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<td>E-4</td>
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<td>Condenser E-5</td>
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<td>Condenser E-7</td>
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<td>Reboiler H-1</td>
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<td>Heater H-2</td>
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<td>Reboiler H-3</td>
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<td>Vibrating conveyor</td>
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<td>Total purchasing cost equipment</td>
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<td>Write</td>
<td>$460,000</td>
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</table>

* Very rough estimate, because of incomplete specifications.
Capital Requirements

Total plant investment

\[ \times 4.5 \times \text{Purchased Cost} \]

- Total capital investment: $2,100,000
- 50% contingency: $1,000,000
- Process license: $1,000,000
- Estimated own preliminary process research: $300,000
- Working capital, 1½ months product: $1,900,000

Total capital requirements: $6,300,000

2. Annual Operating Costs

Variable costs, based on 360 days operation per year.

**Raw materials**
- 39,000,000 lbs. Ethylene @ 6¢/lb.
- 43,000 lbs. TiCl₄ @ 30¢/lb.
- 40,000 lbs. Al(Et)₃ @ $5/lb.
- 1,120,000 lbs. Butane @ 1¢/lb.
- 86,000 lbs. Pentane @ 3¢/lb.
- 1,100,000 lbs. HNO₃ @ 4¢/lb.

**Process services**
- 155,000,000 lbs. @ 60¢/1000 lbs.
- 4,200,000 KWh @ 1.5¢/KWh
- 1,150,000,000 gal. cooling water @ 4¢/1000 gal
- 50,000,000 Demineralized water @ 50¢/1000 gal.

**Maintenance**
- 5% of plant investment: $105,000

**Miscellaneous supplies**
- $10,000

**Laboratory charges**
- $55,000
Fig. 3  Break-even Chart

Sales Income

Total Costs

Fixed Costs

% of capacity
Royalty
3% of sales 400,000

Credit
2,200,000 lbs. gas @ $1/lb. -22,000

Overhead deethanizer - to use as fuel gas

Total variable cost at 100% of capacity $3,346,000

Fixed costs

Direct labor
17,000 man-hours @ $2.30 + 15% $105,000

Direct supervision
10% of direct labor 19,000

Depreciation plant investment - 10 yrs. 310,000

Depreciation license and research - 5 yrs. 260,000

3% of plant investment 90,000

Overhead
~10% of annual operating cost 600,000

Management expense
~5% of annual operating cost 300,000

Selling and distributing expense
~15% of annual operating cost 900,000

Total fixed costs $2,664,000

3. Rate of return
At 100% capacity:

Sales income, 38,000,000 lbs. Polyethylene
@ 30¢/lb. $11,400,000

Total costs 6,010,000

Net Gross profit 4,390,000

Rate of return: 70%
Break-even point

Graphically determined to be at 33.5% of maximum capacity.

4. Discussion on economics

The capital estimate is quite inaccurate for the following reason:

The major pieces of equipment, filters and dryer, could not be specified with any precision because of the lack of data for polyethylene. This and the general uncertainty of equipment requirements explain the excessive contingency.

The price of the process license is probably in the right order of magnitude. When observing the total purchased equipment cost, it seems rather low as compared to the annual sales volume.

Total plant investment was calculated by using Lang's 36 factor 4.5 for an almost entirely fluid process. Purchased equipment cost is multiplied by this factor to obtain the total investment. It is obvious that a greater precision is not at all justified.

Because only the most basic facts are known about this process and the license appears to give only the right to use this commercially, quite an extensive research will have to be conducted to gather the required know-how. The mentioned capitalized research is a mere estimate. Costs have been calculated according to process requirements, and to custom.36 One change has been made: labor expenses are considered as fixed costs, since operating at below maximum capacity will give little or no reduction in the required manpower.

Although capital and cost estimates have great shortcomings, it is felt that rate of return and break-even point strongly indicate that this process is worth looking into.
Appendix

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Ziegler-proces.

Het betreft beurzen tussen hoog- en laagdruk procesen, ontbreken een juiste opsomming van de gevolgen van deze beurzen op de dichtkheid ½ polytheen, de eigenschappen (mook dielectrische) van het product, de spreiding in mol. gew. enz.

De reactie.

Het verhaal over de katalysator is van redeneringen vang, enkele dat is temp. en dink. Het ongetwijfeld vast echte argumentloop een mengsel van pap betreft en part, als „oplosmiddel“ gekozen, bij 10 atm., in twee compartimenten van resp. 15 en 173°F. De reactiemoeweil is (letken van het 2e compartiment) constaart met de tijd veranderend, mutterande vic. tonene en steds verder oploemings (p. 22 en 25)

De keren van een „twee-trops-proces“ in één reactie is bedacht en zeker of kantsebekeheid bij gelijke roemelheid of voedselstructuur groter.

Voor procesbesluit vindt zui p. 16 en 17. Veel te

De berekeningen die de eet ½ verder verbeenen (p. 17 en)

Bedoelde drogers (p. 20) tot nu bekend.

Voldoend uiterlijk is het neger bij 10 atm.

Dat is nodig bij kernen oplosmiddel, maar die is alleen maar licht. Gedeel is 2-trops compresor met twee hodjes en die 7% naar de inwevering opweekt (p. 46 en 47)

Turbinevicede in reacties loopt niet goed bij go fip en heeft veel hogere snelheids modi, en dat zijn niet. (p. 27)
Bij behoede benaming van een Re-gezel
is ongepast (p. 27-28)
De bov. van de destillatiekolom p.31.
"from correlation of theor. stages with actual
and min. reflux ratio" met 50% extra theor.
schotels + 50% voor schotelrendement, dat
mijkbaar tussen 45 en 90% ligt, is wat wild.

Flash chamber: argumentatie aangep. (p.34)

Gebruik schroeftransporteur had bester niet
wordt toen gedane word

Concl.
Wild verhaal, zorgeloos opgeget. Bedoeling is een
willekeurige een stille vaart te krijgen op en
economische vondsten aan het proce zitten. De
mogelijkheden zijn hierdoor anders dat
Voldoet niet aan ene wiser,
ook de tekening niet.