

Polyethylene Manufacturing
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Executive Summary

This paper was written to propose solutions to many of the problems that the plastic industry is facing today. A scientific background is provided in earlier sections to familiarize the reader with the uses of this plastic, its history, chemistry, and industrial production methods. This science is carried over into application for solving to of the biggest problems in the plastic industry: energy requirements for production and containment/elimination of waste plastic. Polyethylene was selected as the plastic of choice for this study because of its mass production and the simplicity in its chemical structure. This paper should provide meaningful insight to this industry to readers of a novice background all the way to a more advanced background. This paper should demonstrate the author's skills in understanding a culmination of sciences and engineering solutions based on that knowledge.

Motivation and Materials System

2.1 Motivation

Intro

Polyethylene is the most used plastic in the world. Polyethylene is mostly used for packaging purposes within materials such as containers (bottles) and plastic bags that are used in grocery stores. PE is produced largely from natural gas and refined using a cracking method towards ethane. "Poly" stands for "many" so in this context polyethylene is a term used to denote a structure containing many bonded ethylene molecules. These ethylene molecules form hydrocarbon chains that have two noticeable behaviors that depend on its environment.

Low-density polyethylene (LDPE) is the more random orientation of PE in which hydrocarbon chains bond together in a rather unpredictable manner due to subjection of high pressures (and high temperatures. The length of these chains within these LDPE structures also varies with a mix of short chains and long chains. These characteristics result in a material that is very flexible with a typical plastic melting point of 110C (1). The LDPE version of PE is used specifically for materials such as trash/grocery bags, wire/cable insulation, flexible bottles, and agricultural mush(1).

High-Density Polyethylene (HDPE) is the second of two major strands of PE. It is manufactured at low temperatures and pressures. There is less variability in chain size especially in the realm of side chains so as a result this strand is more tightly packed hence the name. The result is a higher melting point than LDPE by 20 degrees C which translates to more durable plastics. HDPE finds its use as construction film, toys, and hard hats (1).

There are a couple of other strands that could potentially be referred to throughout this text but the aim is that focus is centered on the two mentioned strands. However, the remaining strands will be mentioned as follows: Linear Low-Density Polyethylene and Ultrahigh-Molecular-Weight Polyethylene.

History

The history of such chemical species is an important context for this text so it is important to mention that PE was first discovered accidentally by German chemist Hans Von Pechmann in 1898 in a lab experiment in which he was heating diazomethane (2). As predictably inferred from the previous reference of ethane cracking, this process of Pechmann's produced polymethylene. It was not until 35 years later when Eric Fawcett and Reginald Gibson accidentally synthesized PE at Imperial Chemical Industries in England. There were issues early on with oxygen contamination that deterred this reaction for large scale production. However, with persistence came progress and within another three decades production of PE was large-scale.

Outlook

Not only is the history of this plastic rich that resulted in worldwide industrial reliance in the matter of a half century, but the outlook of PE production is undeniably optimistic. Statista reported that production of plastics such as PE is expected to quadruple by the year 2050 (3). This trend is expected as more and more economies around the world are industrializing to newer standards with more and more access to such commodities as electricity. With an increasing demand in the sector, it is important the subject of PE and other plastics be kept under a microscope so that necessary advancements can be made that will allow more efficient production which is both economically and environmentally beneficial.

2.2 Materials System

2.21 Structures

Note: The following structures were created by author in Chemdraw application:

HDPE Structure:

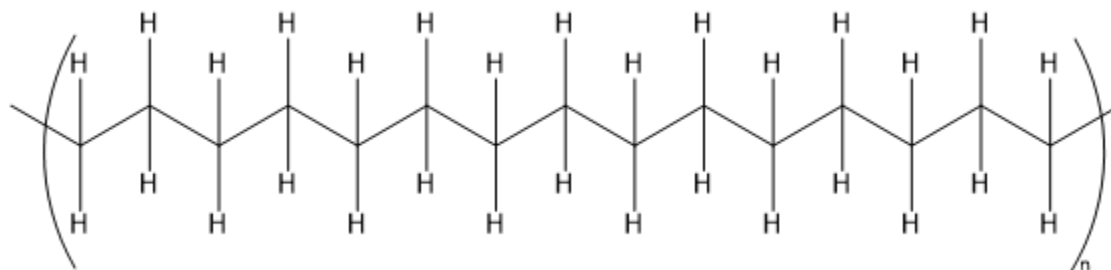


Figure 01: HDPE Structure (7)

LDPE Structure

There are many potential variations of LDPE structures as branches can differ in frequency, orientation, and length altering the properties of the composed material. Below is a typical, simple example of what would be classified as a LDPE strain.

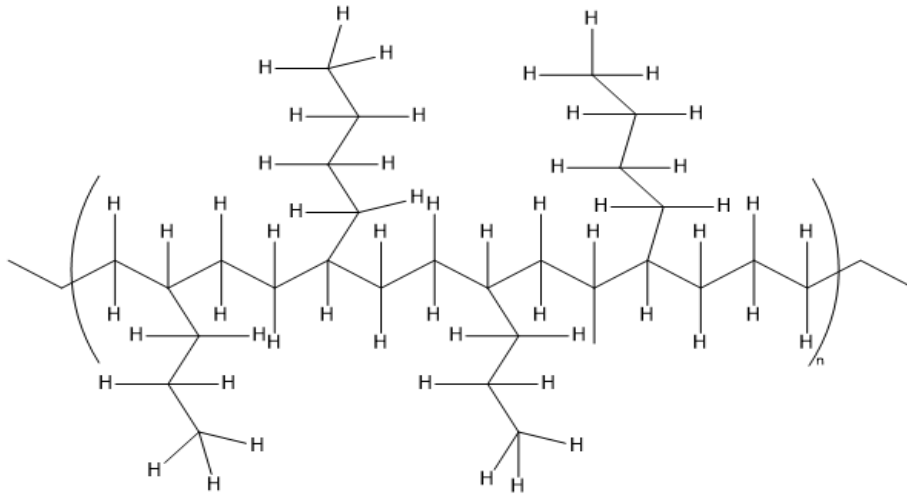


Figure 02: LDPE Structure (7)

2.22 Properties:

High Density Polyethylene (HDPE) Properties:

Property	Value	Units
Density	0.944 – 0.965	g/cm ³
Tensile Strength	0.20 - 0.40	N/mm ²
Thermal Coefficient	$(100 - 200) \times 10^{-6}$	None
Glass Transition Temperature	-100	Celsius
Melting Point	130	Celsius

Table 01: HDPE Properties (5)

Low Density Polyethylene (LDPE) Properties:

Property	Value	Units
Density	0.917 – 0.930	g/cm ³
Tensile Strength	0.20 – 0.40	N/mm ²
Thermal Coefficient	(100 – 220) * 10 ⁻⁶	none
Glass Transition Temperature	-100	Celsius
Melting Point	110	Celsius

Table 02: LDPE Properties (5)

Property Comparison:

Analyzing the two listed strains of polyethylene above, it can be observed that the two noticeable differences in the properties listed are that of the density (evidently expected) and the melting point of the compound.

2.23 Kinetics

There are two main types of polymerization techniques in which large hydrocarbon molecules are synthesized, those being addition polymerization and condensation polymerization. The former is used for products which consist of more than one molecular species, such products often include a hydroxyl group for example which acts to sway hydro properties. The latter method, additive polymerization, is the method that will be demonstrated for all catalytic methods shortly since it is most appropriate for the polymerization of polyethylene. Additive polymerization uses initiation, propagation, and termination to continuously add ethylene molecules onto a chain that is bound to a side group at the end of that chain. This chain is modified based on the catalyst used and is then terminated to extract pure product, polyethylene.

2.24 Molecular Weight Distribution

The size of finalized chain lengths within a polyethylene product batch are not constant and length and always vary with size. The size of these chains is measured through molecular weight and the length of chains is analyzed through a molecular weight distribution which is

measured illustrated through a molecular weight distribution curve. These curves illustrate the frequency of a given chain length and result in bell curve distributions. What is more interesting is that a polymer batch can have multiple distributions, that is humps, on such graph which indicates that multiple corresponding size groups exist within a batch. These distributions are referred to as modes and furthermore HDPE for example would be called bimodal HDPE if it had two modes.

2.25 Catalysts

Low Pressure Catalysts

Chromium Based

Another common catalyst for low pressure processes is a chromium-based catalyst which is often called a Phillips catalyst (6). Not too much attention will be given to these as the upcoming processes are all denoted to be using hydrogen as a cleaning agent which is not used for MW control with this catalyst. Some information regarding these types of catalysts are that they give relatively broad molecular weight distributions to their products.

Ziegler-Natta Catalyst

The Z.N. Catalyst is the most commonly used catalyst for polymerization of ethylene into any strand of polyethylene for HDPE and LLDPE in low pressure applications. These catalysts are used in all three low pressure reactions methods that will be discussed in further sections. Some advantages of these catalysts are that they can be operated under extremely high temperatures due to their polar bonds which result in a high melting point, a necessity for the mentioned conditions of this process. The general catalyst is composed of halides and organometallic compounds. ZN catalysts result in products with broad molecular weight distributions compared to most catalysts. The formation of the catalyst is produced from the following reaction:

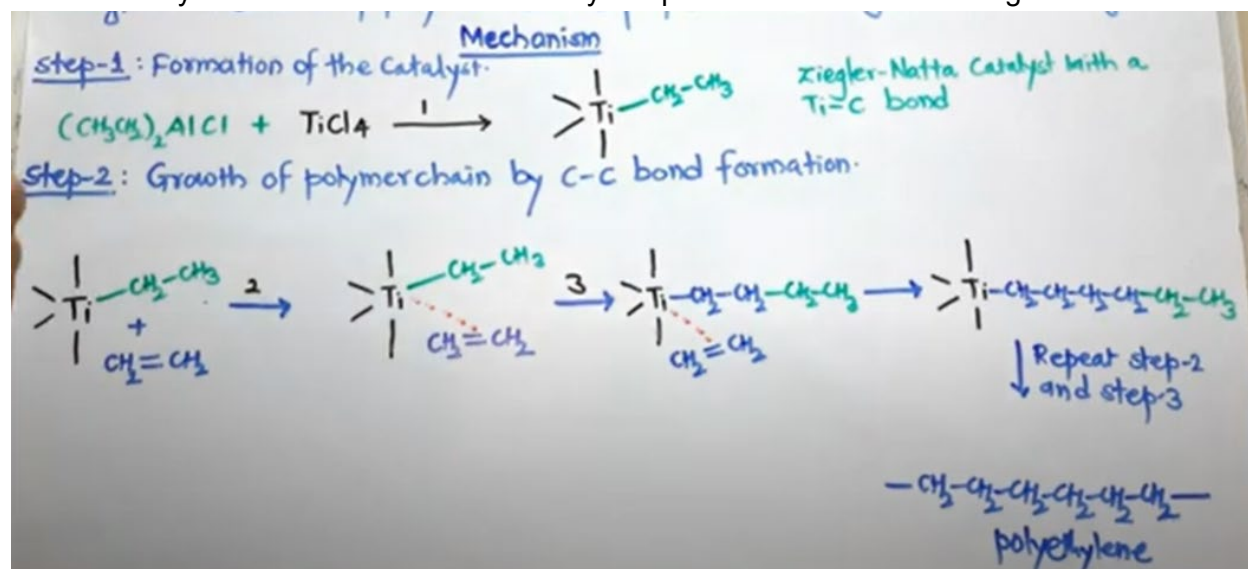


Figure 03: ZN Mechanism (8)

The figure above shows that for Step-1 titanium tetrachloride and aluminum chloride bonded with a carbon chain must be reacted together to produce an alkene-metal complex (4). These products are stored in catalyst feed tanks as shown in figure 09 for the gas-phase process flow

diagram. The catalysts are then subjected to the feed stream consisting of ethylene and other contents which will be discussed in later sections. Below are typical mechanisms for polypropylene reactions (in which only the chain differs) of the initiation, propagation and termination steps for this reaction.

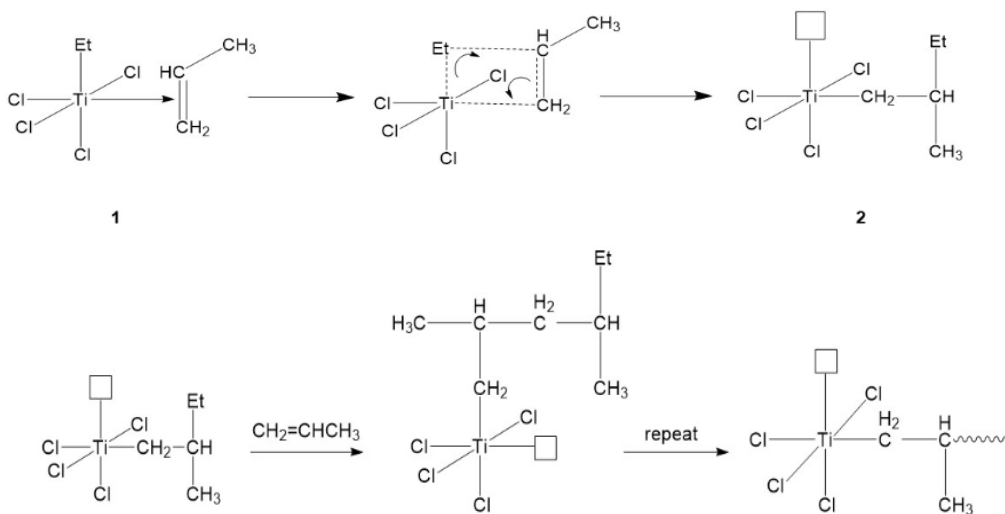
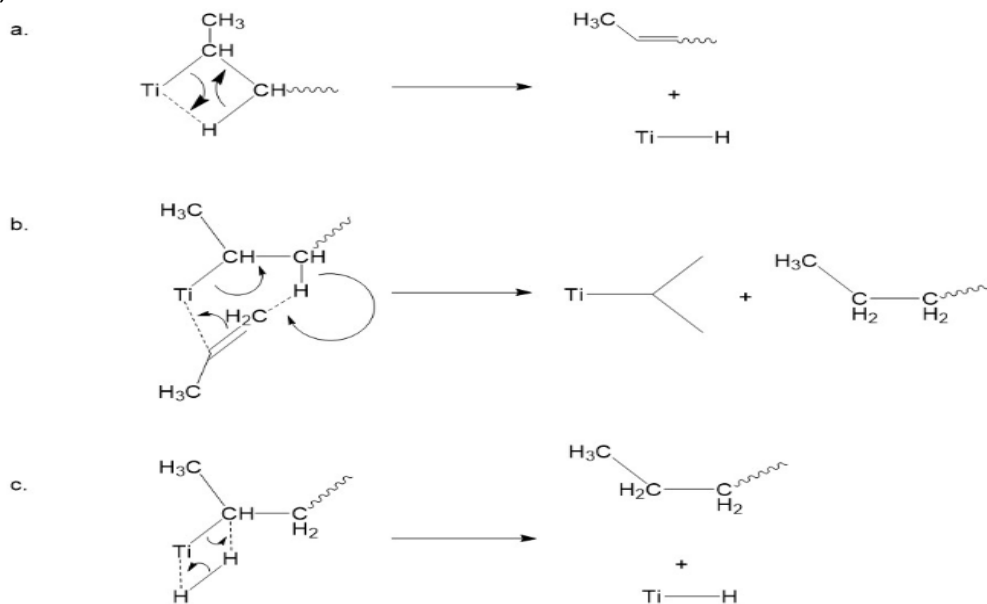


Figure 8: Propagation towards polymeric chains.

(a)
(b)



©

Figure 04: (a) initiation, (b) propagation, (c) termination of Ziegler-Natta Catalyst mechanism (4)

High Pressure Catalysts

Catalyst Reactions with polymers, regardless of the equipment used and the process executed, will have the mechanism of the traditional initiation, propagation, termination method. Below is an illustration of the mechanism in which electron transfer is highlighted. This example shows a

peroxide catalyst which is another common catalyst used in the polymerization of LDPE in high pressure methods.

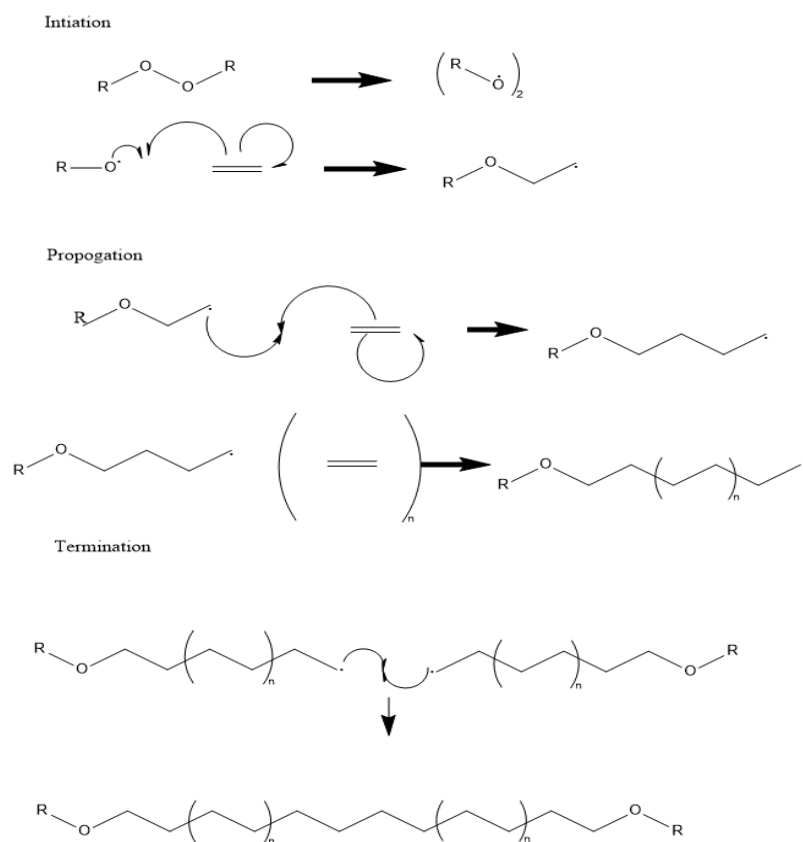


Figure 05: Peroxide Catalysis Mechanism

2.3 Theory and Design Principles

A larger portion of the scientific research for two or the improvement of the polymerization process is composed of two subjects. Organic Chemistry is an important scientific foundation of the subject because the structures of the catalysts must be understood to derive mechanisms for how different molecule types will interact with each other. It has been discussed and will be reiterated that polymers must undergo catalytic reactions to produce desired product. These catalytic reactions only need to be operated at moderately high temperatures as they are already extremely exothermic due to their increasing entropy. Catalysts are essentially impurities towards the plastic makeup of polymers but because of their radical movement they are able to assist the reactions. These catalysts must be then removed after they assist with these reactions so additional equipment is required but the cost for both installation and operation of such equations is still miles better than other alternatives. Some processes which will be discussed have very effective termination properties so catalysts are able to move from one chain to another in time before extraction of that reacted polymer species.

The determination of the catalysts is guided by the principles of organic chemistry. As discussed in the last section, a catalyst must be used that essentially combines the structures of ethylene in a chain-growth polymerization reaction. The mechanistic objective of the reaction is to build long polymers chains by combining smaller molecular components, those being ethylene molecules. Chemists have performed research (and still are) towards what type of molecule will best sort this purpose. Since chemicals are not infinite in supply, the cost/availability of such catalysts is also taken into consideration especially in a process where catalysts need to be replaced.

Reaction Kinetics are a vital science that must be considered for effective completion of this process. The biggest component of the design of this process is the reactor type. Different reactor configurations will be discussed in the next section so this section aims to primarily discuss the considerations that contribute to reactor design for the mentioned purposes. Reactors are either a modification of a plug flow reactor or a constant-stirred tank reactor. A fluidized bed reactor is also used which incorporates principles of both reactor types with stirring and in a mechanical gradient. Plug flow reactors such as slurry and tubular processes are optimal for conditions where a temperature change is desired as heat transfer is more feasible due to more relative surface area. This degree of temperature control is not possible with a CSTR because reactions happen in one volumetric container with less surface area to apply or retract heat through.

CSTRs such as autoclave and Solution reactors are used when the catalytic reaction conversion is more dependent on mass transfer than it is heat transfer, such as the case when a heavy amount of solvent is used. A CSTR best ability is molding the reagents together using some sort of stirring technology to assure that the reaction takes place.

2.4 Assumptions

Basic assumptions that will be stated are in the realms of the conditions that will be established for each reactor type and/or pressure process. The biggest assumption that needs to be made is one in regards to safety and that is that exothermic reactions have the potential for hazardous conditions. All reactions under any sort of reactor type must not, for a constant amount of heat maintained (adiabatic conditions), exceed a certain threshold. There is also the assumption that has already been referred to but will be reiterated for clarity and that is that energy is not infinite and must be considered when designing a reactor. Polyethylene is produced on an industrial scale by a given producer and the aim of the producer is to accumulate profit from the PE plastics that are produced large-scale must be done so in an efficient manner. The equipment required to polymerize a plastic such as PE requires a heavy financial investment and so a non-profit organization scenario can be ignored; every company that produces PE aims to stay in business. This means that processes will be designed with respect to money so constant optimization between quality, quantity and price will always take place throughout the design process.

Current State of the Art

3.1 Pre-Polymerization

Ethane is first derived from a distillation column in which crude oil is inserted into and then sent to an ethylene cracker. A cracker in this context is a piece that breaks hydrogen bonds to alter the molecular structure. Once ethylene is cracked from ethane using high heat to increase the temperature significantly, the product stream is then purified to 99.99 + percent ethylene.

3.2 Polymerization

Production of polyethylene is done through three main methods dependent on pressure including low, medium and high-pressure production. As mentioned in the previous section, high pressure results in LDPE and low pressure typically results in HDPE. The low-pressure method has been given more industrial attention with technological and catalyst advancements. An important note is that the majority of this research will be centered around the production process of getting ethylene into polyethylene while the former process of natural gas and oil to ethylene will only be mentioned for contextual purposes.

3.3 High Pressure Method:

Beginning with the high-pressure method to produce LDPE, literature refers to methods that use oxygen and peroxide as initiators to polymerize ethylene. Pictured below is process flow diagram of a high-pressure LDPE production process in which peroxide is used:

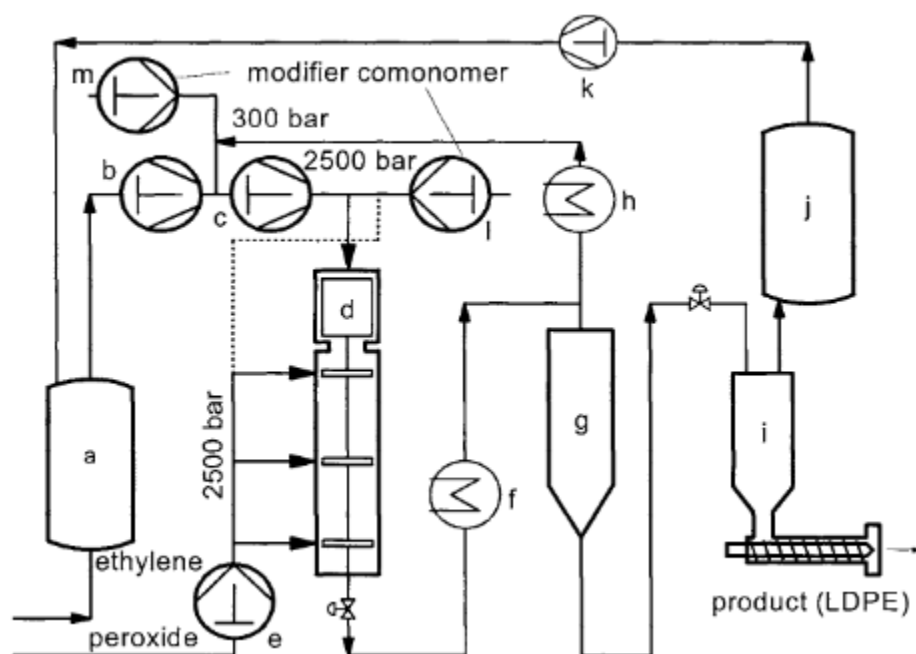


Figure 06: LDPE Polymerization PFD (11)

The ethylene is sent from the storage tank (a) to a series of compressors (b,c) and then subjected to a stirred-vessel reactor (d) in which the initiator solvent peroxide is gradually mixed. The product is sent to a heat exchanger (g) and a depositor(i) for product extraction. Side streams in this diagram include a recycle stream for copolymers(h) and a recycle stream for undesired product(j) which is reinstated to another cycle.

Reactor:

It should be noted that the reactor (d) pictured above can be designed with two different types of reactors: autoclave or tubular (Otherwise known as CSTR and PFR respectively). The stirred-vessel reactor pictured above is classified as an autoclave reactor. Literature suggests that the industrial process mostly consists of autoclave processes for mixing process purposes as demonstrated by the following figure of industrial processes in Western Europe:

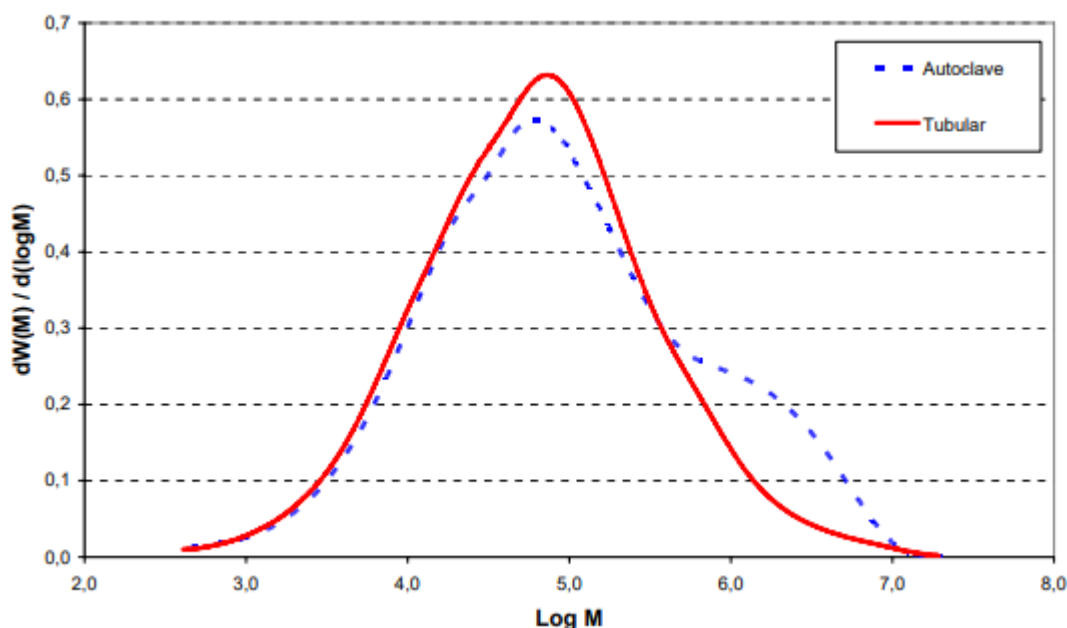


Figure 07: MW Distribution Tubular vs Autoclave LDPE Reactors (10)

The molecular mass distribution illustrated above correlates to the amount of entropy in the mixture, in simple terms it is a measure of how well the reagents react under similar conditions (10).

Compressors:

LDPE is ideally produced at high flow rates but because the relationship between pressure applied and resultant density tails off from linear there is an optimal number of cylinders that must be used to pressurize the substance. Given the flowchart in Figure 08, the compressors are a vital part of the polymerization process as they are the basis for the reactor's performance,

it is pivotal that the compressors are effective to get a desired product. The figure below shows the mentioned relationship between pressure, mass flow, and power consumed.

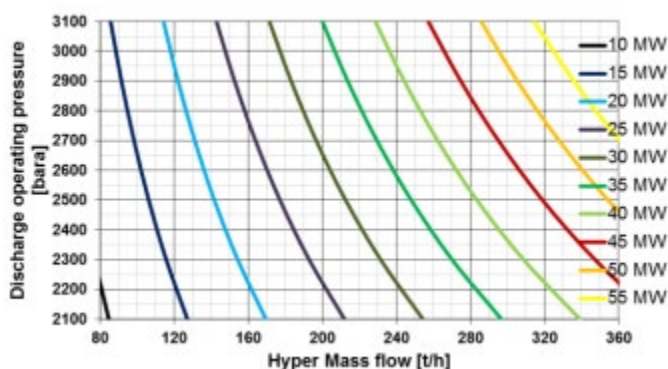


Figure 08: LDPE Compressor Analysis (9)

3.4 Low Pressure Method

As mentioned, the low-pressure method used to produce High Density Polyethylene is the most common in industrial practices as linear, as opposed to LDPE's cluttered structure, orientations are found in most container plastics such as jugs, bins, etc. As mentioned in previous text, a byproduct of this process is Linear Low-Density Polyethylene (LLDPE). Parallel to the LDPE section above, the overall process(es) will be discussed first.

HDPE is typically produced from 3 different low-pressure methods including Gas Phase processes, slurry processes and solution processes (15). The Gas Phase processes typically use PFR reactors while the Slurry (unless it is a loop) (17). Solution processes use CSTRs most often (17). Notably, the Gas Phase and Slurry processes operate at temperatures around 80-100 C (13). These temperatures are designed around the melting point of the polymers being polymerized in which HDPE is under and LDPE is over the boundary.

All of the low-pressure processes that will be shown incorporate similar feed systems. There is expectedly the ethylene stream that comes from a cracking process but also combined with this stream is the comonomer feed. The comonomer feed is the supply of hydrocarbons that bond to the ethylene molecules during reaction which determine, to an extent, the density. Popular comonomers include butene, hexene, and octene. There are also hydrogen and nitrogen feeds. The hydrogen is used for the purpose of limiting side chain concentrations as they use mechanical force to break the forming side chains. The greater the hydrogen steam, the more the products are as fewer side chains will be prevalent (20). Referring back to the section describing the reaction science, side chains decrease the density of a polymer because they interfere with feasible coexistence between chains, essentially making the structure less linear with more molecular void space. The last-mentioned component is the nitrogen stream which is often (and will be discussed) induced directly into the reactor. The purpose of the nitrogen stream is to decrease the amount of moisture in the reaction chamber (20).

Gas Phase Process

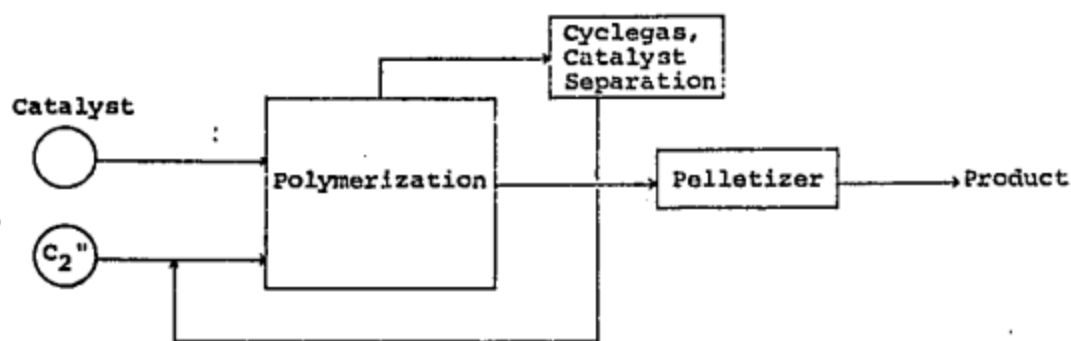
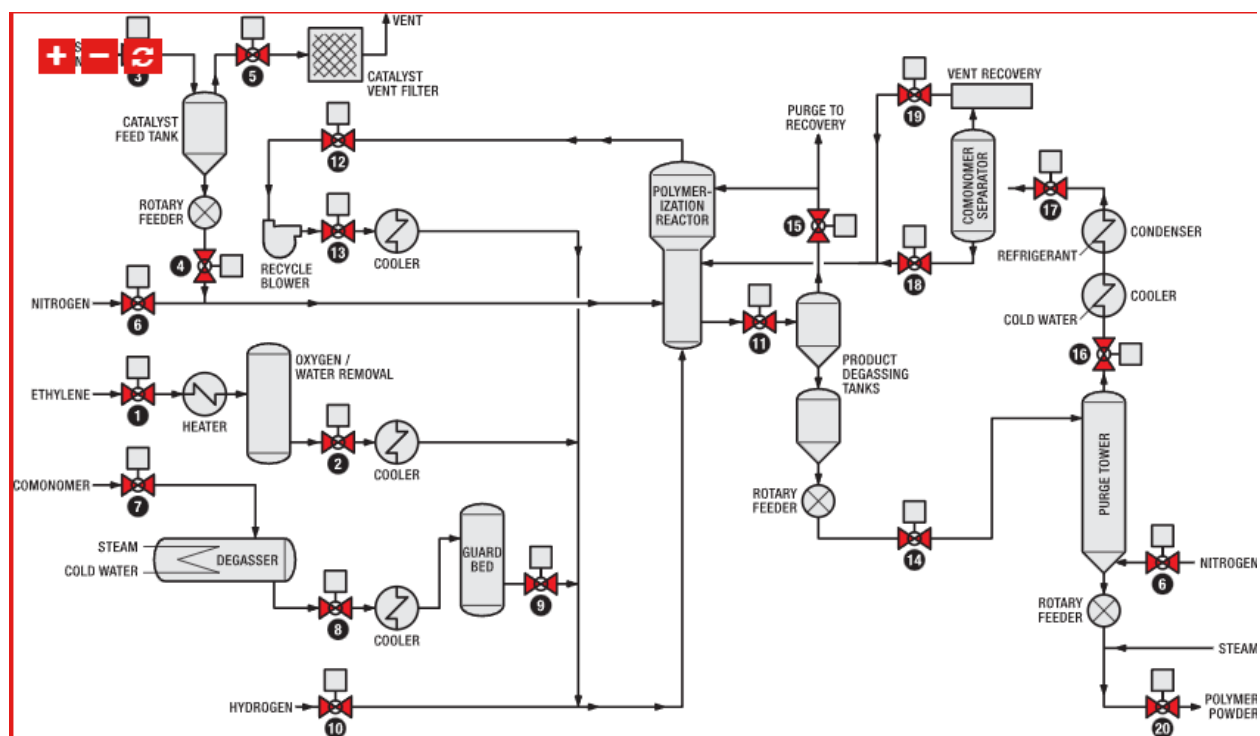


Fig. 4-5 HDPE Vapor Phase Process

(a)



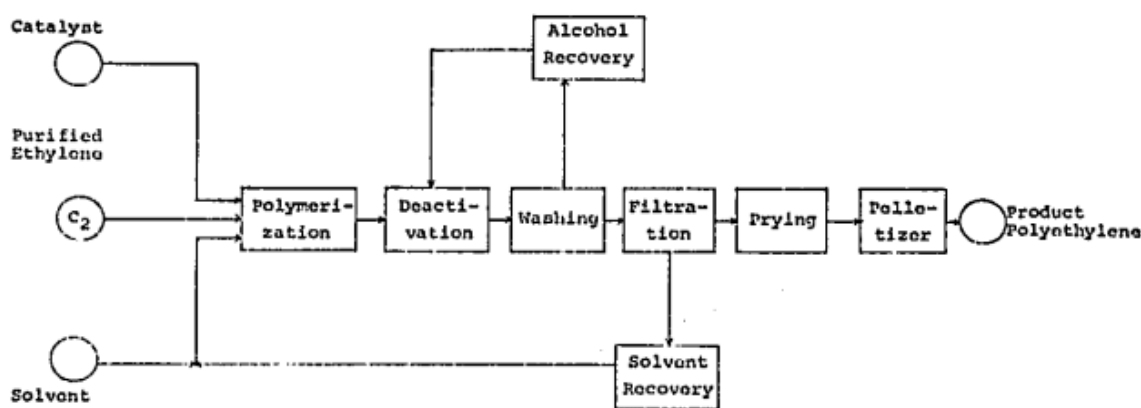
(b)

Figure 09: (a) general PFD and (b) Equipment Specific PFD of Gas-Phase (Suspension) Process (15)(14)

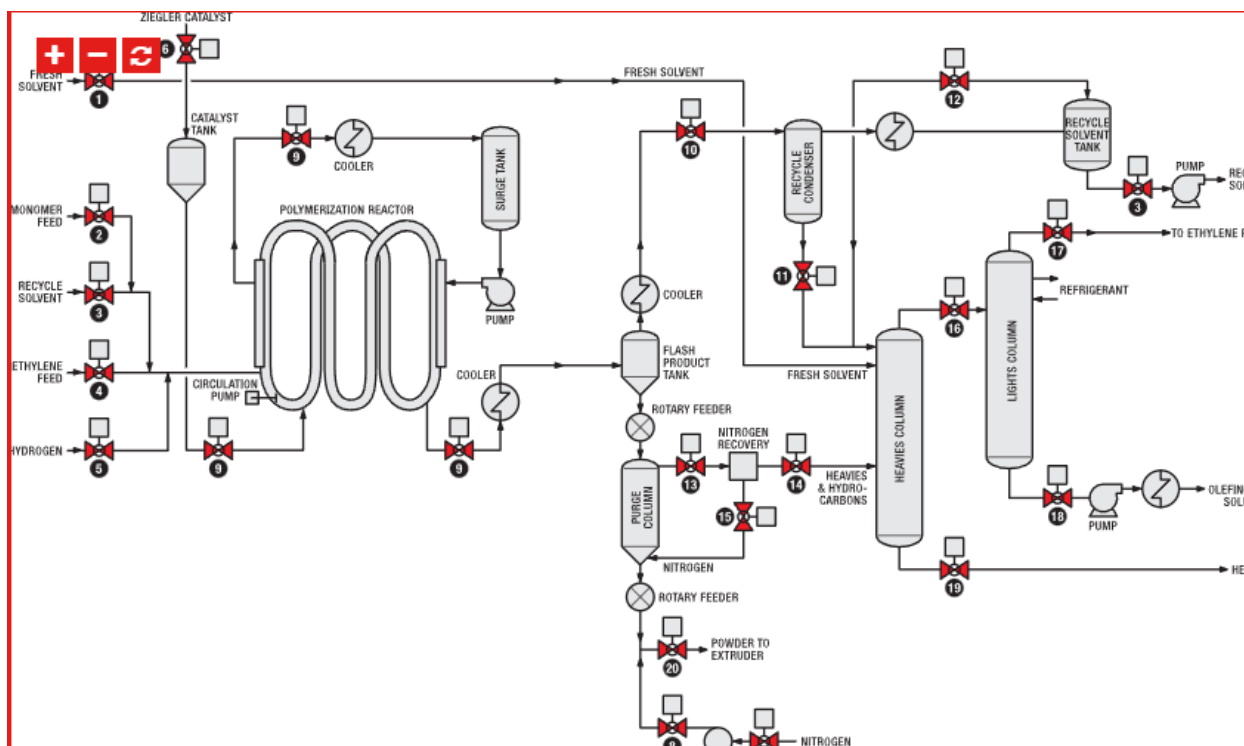
A fluidized bed is used for this design as or in which polymers (ethylene) are fed through the bottom in the gas phases while catalysts are combined with nitrogen and fed through the top of the reactor so that they fall down and react. Polymerization reactions are highly exothermic and

this is why the bulb shape reactor is shown. This extra space at the top allows room for heated gas (N_2/H_2) to lose its energy before being recycled (12). One notable problem with this reactor design is that it is prone to buildup and clogging of the gas stream due to particle erosion (12). Heat-exchanger-integrated variations of these reactors have been used to prevent this problem although this is notably more expensive due to the energy costs (19). This recycled gas is combined with the feed and is fed at a very high rate for maximum conversion. In the recycle stream, heat is removed and the gas is further compressed before it is combined with the feed gas. This type of reactor design does not have mass transfer issues pertaining to viscosity as material moves rather easily throughout the material. Polymerization reactions have high usage of heat transfer as there is much gaseous movement throughout and so temperature provided from the bottom of the reactor must travel feasibly throughout for optimal mixing. The biggest difference between this process and the other two processes is that there is no solvent used. As will be shown, much equipment is devoted towards separation of solvents and so this process saves a considerable amount of space in that regard. It is notable that this reactor type is the largest of the 3 that is mentioned for fixed production as gas is more volumetric than liquid. Shown to the right of the reactor are degassing tanks which are used to separate unreacted monomers from the product (19).

Slurry Process



(a)

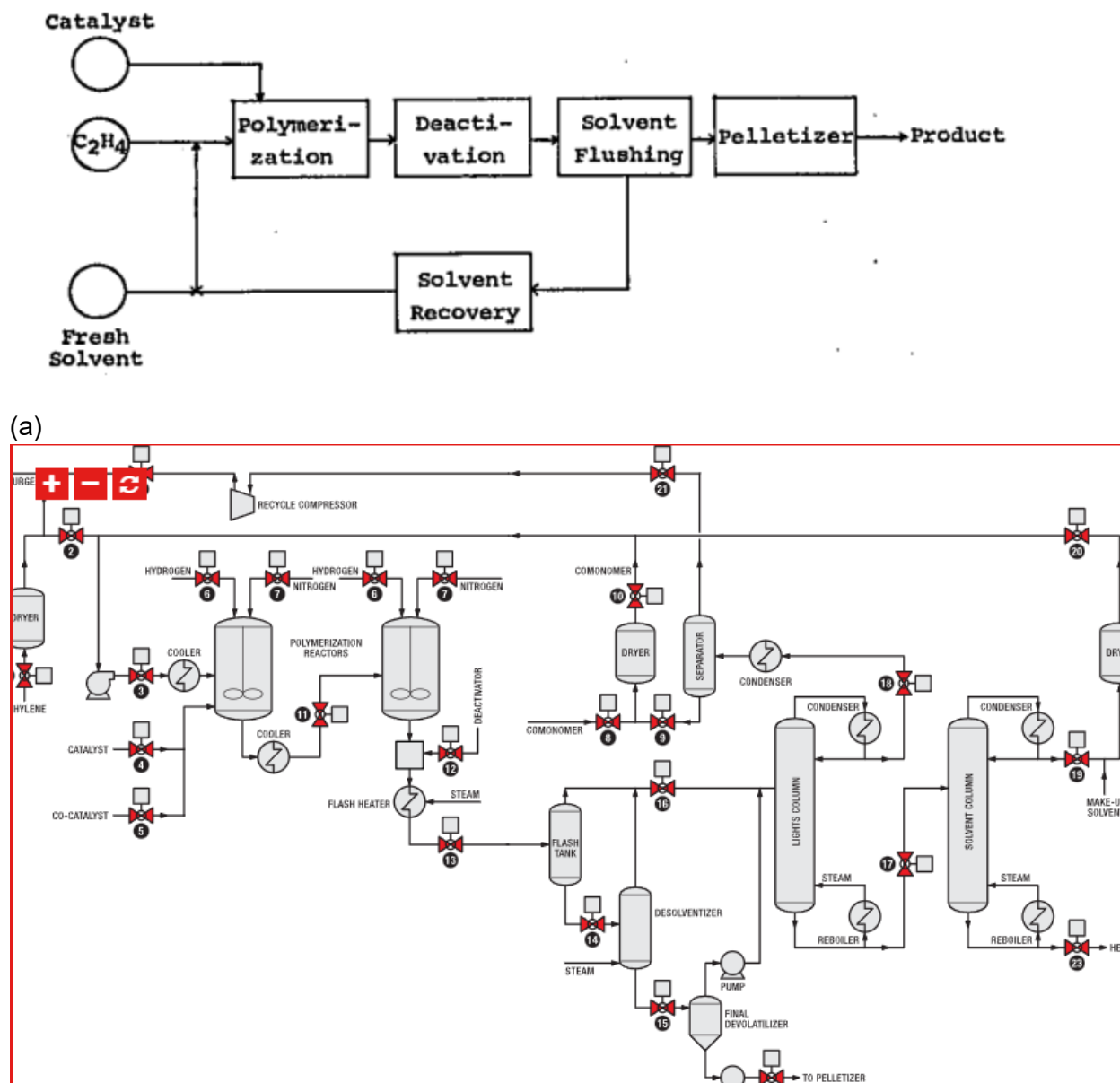


(b)

Figure 10: (a) general PFD and (b) equipment specific PFD of Slurry Process (15)(14)

A slurry process is another method used to produce HDPE and LLDPE at low pressures and it is very similar to a solution Process which will also be discussed. This process is used with either a CSTR or a loop reactor shown in Figure 10 but is mostly used with loop processes since a CSTR for these conditions is very prone to buildup. In this process the catalyst is diluted before it is subjected to the reactor (20). This fluid that dilutes the catalyst also acts as the carrier for the reaction in which the catalyst and reagents (ethylene) are reacted (18). The catalysts are then removed by evaporating the carrier and subjecting it to nitrogen to eliminate catalyst activity (16). Slurry processes are performed at lower temperatures than solution processes because more reactants are in contact with the surface area of the reactor and so less heat needs to be applied (13). The slurry process is the most prominent of any HDPE production process (57 percent of market) and since, as mentioned, HDPE is the most prominently produced strand of polyethylene this is therefore the most common process in the industry (16).

Solution Processes



(b)
Figure 11: (a) General PFD and (b) equipment specific PFD of Solution Process (15)(14)

Solution Processes are the last and least common method for HDPE production of the three major methods mentioned (15). Despite this, they are the most emerging technology among the three as recent improvements have bolstered their MW distribution to be narrower. Solution processes take place in CSTRs as shown above and are notorious for having high operating costs and investments (14). The reactors are a lot more durable and so operating temperatures are a lot higher than slurry processes. These higher operating temperatures products can be produced at a higher rate. Problems do arise with this reactor type in terms of maintenance as the CSTR rotor blades are subjected to extreme torque as solute is used in the greatest concentration of the 3 methods and buildup plausible (15). The upside of these systems is that

the process is the fastest of the three and has the highest yield on top of that which gives more controlled products in terms of density. Products of such processes are therefore characterized by narrow molecular weight ranges (15).

Analysis and Potential Innovation

4.1 Nuclear Energy

There is always a major block that interferes with optimal production. These processes, high or low pressure, require a heavy and continuous input of energy. For specifics, current processes require 5 MJ per kg of HDPE produced and 8 MJ for LDPE (23). To put this into perspective, the United States itself consumed 2.26×10^7 kg of polyethylene in 2019 alone (25). The vast majority of energy is used from fossil fuels and so according to Stanford research CO₂ is produced at a 1:1 mass ratio to polyethylene (24). The math will confirm that this is a very problematic scenario especially considering the state of the atmosphere and predictive trends. Plastics are an essential component to many economic functions but are not a necessity to survival and so if things do not change then plastics production will for the most part come to a halt.

This literature will suggest popular methods that can resolve this problem. The current laws of thermodynamics and material science suggest that the amount of required energy for PE production will only slightly decrease over upcoming years due to research efforts. What is the aim for adjustment in this process is the energy source. Industrial processes such as PE production not only need mass amounts of energy but they need it on a reliable, consistent basis. Currently energy transport methods allow for multiple sources of energy to contribute to a destination but there must be a primary source of energy that is the most dependable and powerful. Fossil fuels are very energy dense which has allowed for such supply but due to currently inevitable emissions, other methods must be suggested. What needs to be additionally considered for this proposal is the energy transport required. A source could have all of the attributes necessary to apply energy to a process in its own self but if that source is on the other side of the country then costs will be noticeably higher to obtain such energy. So, while this subject is present, it is relevant to bring up locations of polyethylene plants in the United States. This analysis will be scaled to a national level so that concepts can be demonstrated that apply to an international scale and are simplistic in terms of quantity.

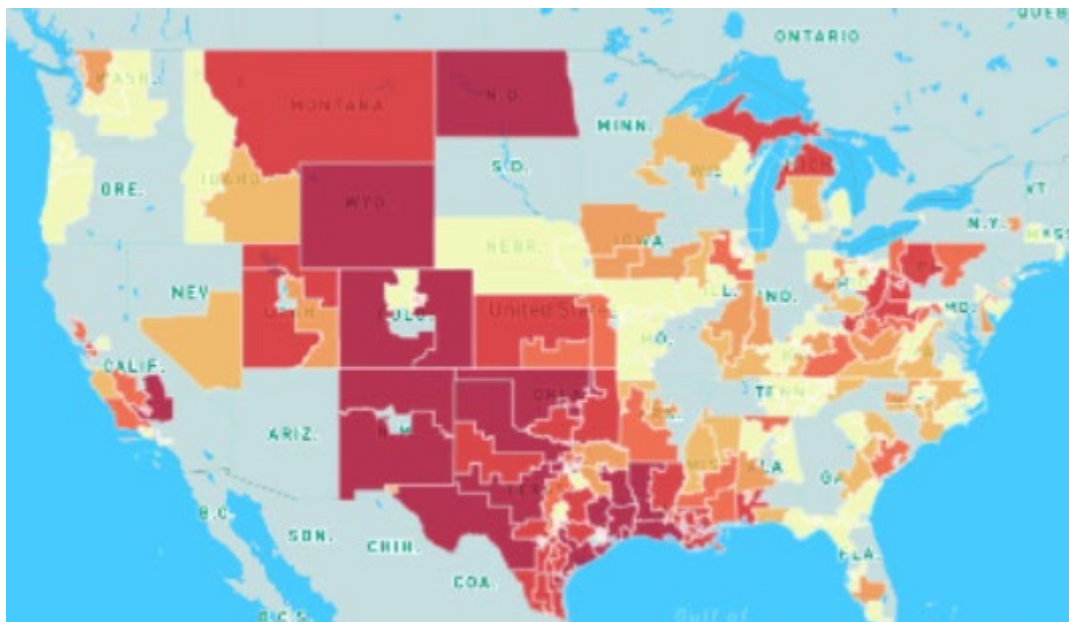


Figure 12: Plastic Manufacturing Map – United States (26)

Shown above in Figure 12 is a map of the plastic manufacturing centers around the United States. The majority of plants reside in states with lower-than-average population density for US standards. Considering potential candidates for primary sources of energy for PE processes amongst the available, non-emitting technologies, Nuclear seems to be the clear answer. Reasoning will be shown soon but first an explanation must be given for the deferral of other potential options. Solar panels are not reliable for industry standards and are not able to produce the amount of energy required for these processes. Wind energy is a favorable candidate especially considering that the Gulf of Mexico is an optimal place to put wind turbines since offshore wind collects more than onshore wind sources. What discounts wind sources for these purposes is that they are not able to produce nearly enough energy to power these intensive processes. The remaining option is Nuclear energy and it is favorable for such processes for many different reasons.

Nuclear energy saw falls in production in the 1990s largely due to the Chernobyl incident in 1986 and has since received much criticism on an international scale over fear of another incident of the same magnitude (22). Nuclear energy if handled incorrectly can have devastating results not only for the people on sight but the residents in nearby communities as was the case in 1986. Safety processes have been developed and more research has been executed that is giving this energy source more legroom for future manufacturing and production. It was evidently unfortunate what happened at Chernobyl but it is important to note that many things went wrong in terms of controllable execution as many procedures were ignored. What helps the case for nuclear energy, especially in the United States, is that most energy-intensive plants follow similar trends as shown in Figure 12 in terms of surrounding population density. Nuclear plants could be optimally manufactured in states such as Texas because populations are a lot scarcer and so there is a lot less of casualty risk than building a nuclear plant in the middle of a metropolitan area for example. The potential for catastrophe in terms of impact is prevalent and should not be ignored, but the average likelihood of any sort of incident that is measured to a

single casualty, is much lower than the general public believes. Nuclear energy has been reported to be the safest source of energy production on the planet.

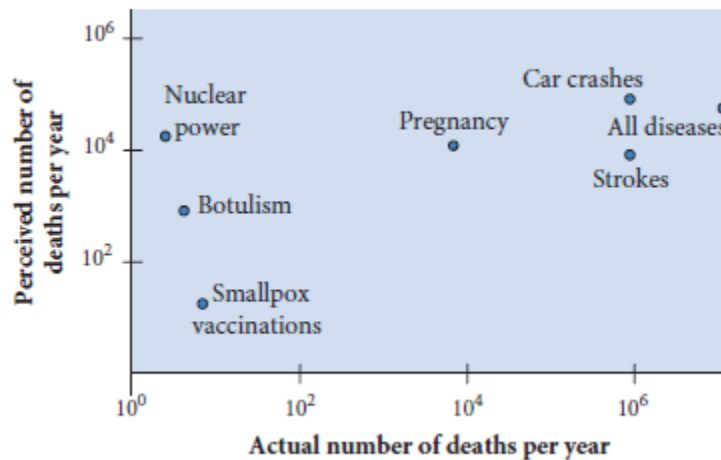


Figure 13: Nuclear Power Fear Diagram (22)

Past the questionable safety concerns, Nuclear energy is second to none in terms of efficiency. This energy is extracted through nuclear reactors in which heavy water is flown through uranium rods to initiate fission. Nuclear fission is the process in which an atom is moved to its unstable state upon receiving a neutron (from heavy water in this case) and therefore decomposing into smaller atoms with additional neutrons (usually 3 released per 1 received). Breaking an atom not only results in a energy dense process (highly exothermic) but the addition of neutrons freely present before and after the reaction means that runaway reactions can be performed. These reactions are obviously controlled in industrial settings and the result is a process that produces about 25,000 times more energy per mass than coal processes (22). Coal was the go-to source for industrial processes such as PE production before discovery of natural gas so this confirms that the nuclear energy sources are plenty intensive. Reliability for nuclear energy is dependent upon supply and current projections suggest that there is known to be 90 years worth of uranium left on earth accounting for potential (projected) consumption (21). Additionally, plutonium can be used for such processes as it is already used to power NASA's rocket ships into space. Nuclear energy production is indeed a limited process but will not be limited in the near future.

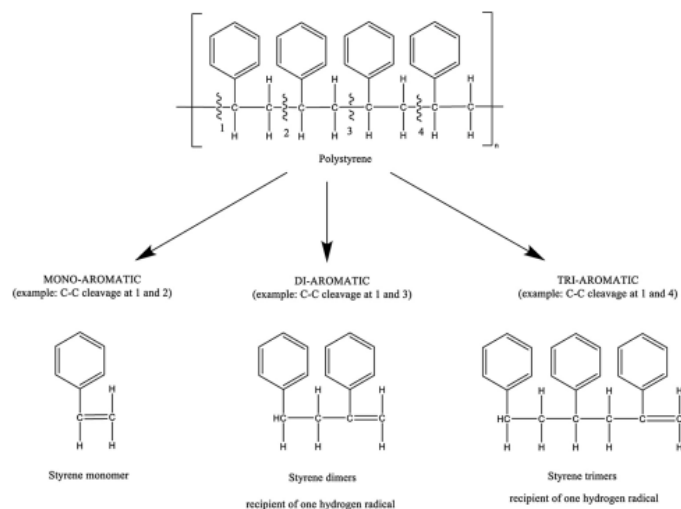
While safety is a notable concern of this technology, costs are as well. The startup investment costs of a nuclear plant are extremely high at about 6 to 9 billion (22). This kind of money is not going to show up on the US's doorstep especially considering the national debt just surpassed 30 trillion dollars, but there are methods and changes that can and should be implemented so that sufficient funding is available. First, it should be noted that the United States already invests in heavy subsidies for wind and solar energy. These technologies are intriguing but their capacity in current production and future innovation is extremely limited. To power the economy of tomorrow requires an energy source such as nuclear that can be scaled to meet these industrial demands. Funding can be accumulated over time as many people, even those who are skeptical about nuclear energy, would be willing to accumulate a fund for nuclear plants. The skepticism from these taxpayers comes from allocating money towards renewable energy research because this money is being, in their eyes, gambled. Investing

money in a reliable energy source under the assumption that it will be used for that energy source will provide a more unified foundation. There is large skepticism about nuclear technology and while it is improving for the better this is still something that needs to be considered. Another potential source of funding is imported foreign aid. Currently the United States has a significant surplus in terms of how much they give to other countries in comparison to how much they receive from other countries. Countries will be willing to devote foreign aid to the United States for nuclear development for several reasons with the most notable being that it benefits themselves. Nuclear technology is optimal for larger scale purposes and so it is most beneficial for the most developed countries, that is the second biggest exporter in the world for this case. Helping the United States shift towards reliable renewable sources will allow developing countries (which have been on the rise of late) an opportunity to rely on non-renewable sources of energy such as crude oil. This will mitigate the climate issue and allow economies across the world to develop in the meanwhile. It is also notable that majority of crude oil comes from the middle east which is the most sustainable source of oil looking ahead and this location is a lot closer to most developing countries than say the United States. This is worth mentioning because transportation costs of energy sources like crude oil are actually a major downside of such a source.

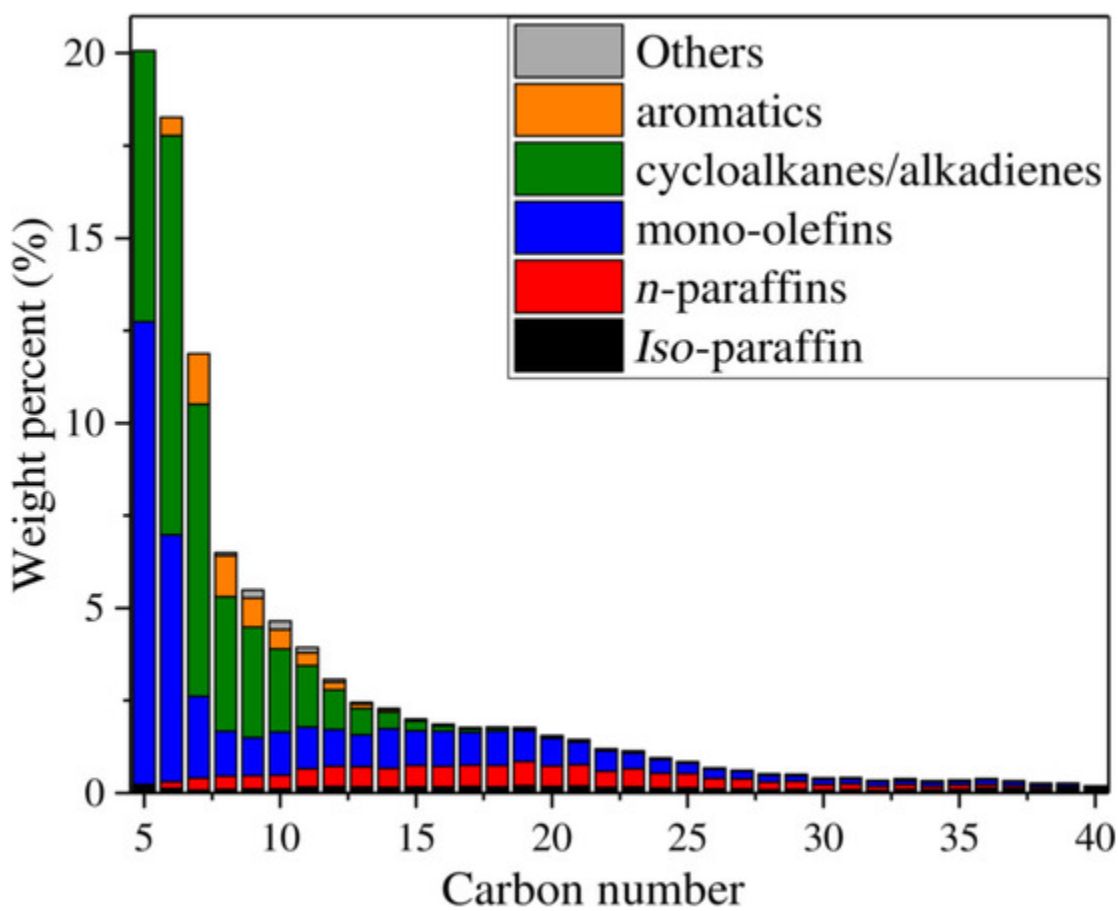
4.2 Suggestions for New Materials Designs – Pyrolysis

Distillation is a very energy intensive process that is used to separate carbon. While supplying this energy is a problem presented by this industry, successfully disposing of materials is just as prominent. Current rates of plastic deposition into oceans is so high that there are landfills of plastic being formulated by currents and millions of marines' lives dying each year. One emerging technique that is being implemented to recycle plastics is pyrolysis. A quick synopsis of this process is that plastic material is heated without the presence of oxygen, resulting in decomposition of the deposited material (31). In this case, PE is decomposed into its original hydrocarbon chains. These hydrocarbon chains can be modified back into liquid fuel which can be used for energy consumption. Considering how much plastic is circulating the earth right now, this process has a lot of potential. What is even more exciting is that of all of the major plastic forms which is about 12, HDPE and LDPE are two of the top three most favorable for this process in terms of liquid yield (29).

What should be considered for the purpose of this research is the mechanist step of pyrolysis on PE strains. Knowing this will determine the general shift in terms of polyethylene properties that must be implemented to better accommodate this emerging industry. The general mechanism, as shown through polystyrene's pyrolysis (a plastic very similar in properties to PE and currently the most optimized plastic for pyrolysis), a random scissor cutting is implemented towards the subjected polymers (29). That is, the polymer chains are broken into smaller chains. What chains exactly are dependent on the subjected polymer but all polymers follow a similar distribution to that shown in Figure 14. It should be noted that higher chain lengths convert to greater energies for hydrocarbons.



(a)



(b)

Figure 14: (a) Polystyrene Pyrolysis Mechanism (General) (b) Product Chain Carbon Distribution (29)

It was revealed through SABIC's information that there are hundreds, even thousands of polyethylene variations that can be produced. This paper aims not to suggest which exact strains should be produced, but what properties of different strains should be aimed for. The best pyrolysis process for the decomposition of polymers on a large scale is the fast method for several reasons. The method has short residence times which allows the method to be run in a continuous manner so that polymers such as PE can be continuously fed and extracted, requirements for a large-scale industrial process. Additionally, the process is shown to produce relatively high concentrations of wax, that is high-carbon chains that are most suitable for energy generation purposes.

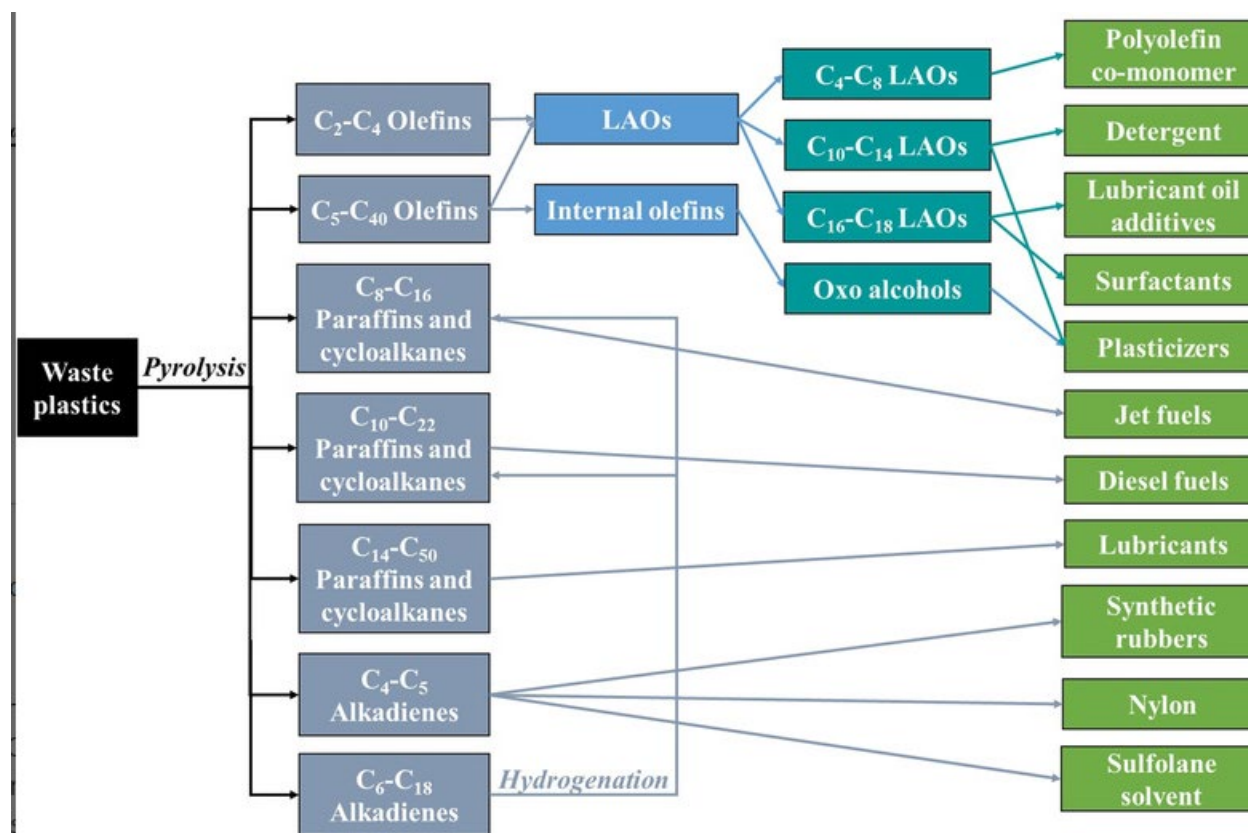


Figure 15: Plastic Pyrolysis Products and their Uses (29)

With this information in mind, it is evident that the properties that influence the conversion of products are highly dependent on the molecular structures of the polymers that are being inserted into the system. Polystyrene is able to be converted to liquid oil at a higher rate than any other plastic and this is largely due to its properties (29). Having benzyl side groups gives much more available sites for breakage to occur. These sites are characterized by relatively high carbon proportions. This can be simply analyzed by how amorphous a material is. Styrene is considered an amorphous polymer and so it is very susceptible to pyrolysis processes. But why are other amorphous polymers such as PVC not subjected to this process. The answer for this exception and others such as PMMA and PC is that the presence of impurities is more of an influential property than crystallinity (29). The most used plastics for pyrolysis practices are PS, LDPE, HDPE, and PP, all consisting of hydrocarbon chains that are devoid of impurities such as oxygen or sulfur. Impurities significantly impede pyrolysis process for a material because it

strengthens the intra and inner-molecular forces of the structure. While the applied temperature gradient is not known, it can be assumed from the provided information that the greater variation in direction, that is the greater entropy with respect to chains, is directly proportional to a hydrocarbon-based material to decompose in these conditions.

Accommodations (Solution)

Based on the properties described above, it is desirable to create a PE product that makes pyrolysis processes more feasible. Different MW distributions will directly contribute to this design facet such that narrower molecular weight distributions are more favorable. The reason is that residence times are very fast and to ensure the most ideal conditions in designing an optimal process and therefore creating profit (and incentive) for pyrolysis production, mitigations need to be minimized. Higher MW distributions among a PE substance decrease heat transfer because different molecule sizes (larger) are less prone to immediate breakage which affects yield and presents complications in terms of varying temperatures. Large-scale production of processes relies on efficiency which in most cases is determined by simplicity. To accommodate this, industries should shift towards usage of solution processes for HDPE production. The biggest reason for this is that solution processes produce the narrowest molecular range which, while already an important property of the product, has gained that much more relevance due to the growing demand to recycle this material through a pyrolysis process. Solution processes require heavier investments by firms as they use the most material, most equipment, and highest temperatures out of the three listed processes.

Plastic Pyrolysis Market

The plastic pyrolysis market is projected to more than double within the next 6 years (28). The process is currently economically viable and has increasing profits for large scale investments (33). What is also contributing to this projected market growth is the fact that investment costs will go down due to s-curve behavior of emerging technologies such as this one (30). Plastic producers are expected to modify production in a favorable way and these shifts will be aided by government subsidies in the future as research develops and environmental urgency increases.

4.3 Uncertainty and Error Analysis

The uncertainty analysis in these pyrolysis assertions mainly consist around the thousands of possible variations in polyethylene types. Such properties have been assigned under two main groups, HDPE and LDPE, for simplicity of this research but in reality, there are many micro-variations that need to be considered when assessing the potential of liquid fuel extraction from a polyethylene-based plastic feed. Additionally, composite material needs to be considered. There are many applications in which PE is only part of the material and a theoretically difficult process must be implemented to separate such materials.

Perhaps the biggest source of error throughout this research is the generalization of equipment, whether that be the polymerization processes or the pyrolysis processes mentioned. Companies implement different modifications or different equipment in all sorts of manners and these variations could not be discussed in detail in this paper not only because of confidentiality but

because the variations are so individualized. A general synopsis of each process was given to identify the sole purpose of that process and the different impediments/advantages of that given process. There are variations that prioritize one particular optimization over the other for different reasons and so those complexities could not be discussed in a paper scaled to this size. Rather, an interaction of the variables at hand had to be established so that the reader has a clear understanding and is taken into consideration when designing such processes.

Discussion

5.1 Inlet Energy

Polyethylene production is the cornerstone of today's economy and will be for some time. It has developed into one of the largest shares of the total plastic industry of today. There is no erasing this industry that has already immersed itself as far as it has but only embracing and improving it. Every process is down to cost/money and this is directly correlated with the amount of energy required to run that process. There were three major components of this process discussed consisting of the energy input, the energy efficiency, and the product return, which is ultimately a different form of energy input. These processes are very costly in regards to energy and so a method had to be proposed for fulfilling such demand. The urgency of change was brought to the author of this paper by a current high-ranking engineer at one of the world's leading plastic producers. This information was delivered through a conversation in which guidelines were established that suggested the plastics industry is facing a great challenge of reducing emissions and if those emissions are not met, catastrophic action will be taken against the plastic industry and the economy will take a huge blow. This insight prompted brainstorming and solutions as to what can be done and for reasons discussed in previous sections, nuclear appears to be the eminent answer.

5.2 Process Energy

When a PE process gets its energy from whatever source is being used, the process must use that energy in the most efficient way possible in terms of production amount. Research needs to continue in the realm of polymerization catalysts. The last notable breakthrough in this regard was Carl Ziegler who was largely responsible for the Ziegler-Natta catalysts which are used in every low-pressure process. This breakthrough won a noble prize but the research in this area should never be stalled as this is the one step that would result in major improvements in the process. The thermodynamics and mass transfer of the available reactor systems are not going to be optimized that much more but improvement of the residence times will prove vitally important especially for the upcoming solution processes.

5.3 Recycled Energy

The standard of that product which is measured through molecular weight distribution among other things will need to be improved because an additional process will be dependent on the quality. It will be necessary going forwards that plastic producers are in coordination with pyrolysis industrial leaders to ensure an optimized cycle. Lack of communication between these industries will result in accumulation of waste plastic as the pyrolysis leaders will be behind in terms of collecting and reducing that waste. Communication will need to be centered around changes in product compositions along with a geographical distribution of these products. The

more these industries are in sync, the more waste plastic will be off the street and the more energy will be collected for usage through liquid fuel.

Homework and Problem Solution

6.1 Problem Statement

Consider a PE plant that produces 510 kg of 0.94 g/cm^3 Polyethylene per day. To surpass initial investments for the plant, 2000 tons of this PE strain must be produced. The problem is that the plant is not sure which energy source to use for powering this plant. There are two potential options, one being a nuclear energy plant and the other being a natural gas refinery. The Nuclear plant is projected to collect 80 kg of U-235 uranium over this timespan while the refinery is projected to collect 400 tons of natural gas. Take the uranium energy content for this process to be $2 \times 10^{10} \text{ kJ/kg}$ and for natural gas $4.6 \times 10^4 \text{ kJ/kg}$. Transportation must be considered. Since the PE plant is next to a refinery there is no energy lost due to transmission. However, the nuclear plant has to be installed 130 miles away from the PE plant. Energy losses can be calculated by using the following data:

Distance(Miles)	Percentage Lost
1000	8.71
2000	17.4
3000	26.1
4000	34.8

What must also be considered is the reliability of each facility. Considering production consistencies and facility inspections, nuclear power can be assumed to have a 99.8 percent efficiency while the natural gas method is 84.6 percent efficient. Furthermore, the energy required to produce two different polyethylene densities is shown below:

PE Density (g/cm^3)	Energy Required(MJ/kg)
0.98	5
0.91	8

Finally, take the production cost of nuclear energy to be $\$0.093/\text{kW-hr}$ and $\$0.043/\text{kW-hr}$ for natural gas.

- Using the information required, determine the best energy source for the required production of polyethylene.

6.2 Solution

Solution

First Determine if Both Source has enough Supply to power the plant throughout timeline:

To find required Total PE:

$$\text{Interpolate} \rightarrow @ 0.94 \frac{\text{g}}{\text{cm}^3} \rightarrow 6.71 \frac{\text{MJ}}{\text{kg}} \times \frac{1000 \text{ KJ}}{\text{MJ}} = 6714 \frac{\text{KJ}}{\text{kg}}$$

PE Plant Required Production

$$2000 \text{ hrs} \times \frac{907 \text{ kg}}{1 \text{ ton}} \times 6714 \frac{\text{KJ}}{\text{kg}} = 1.22 \cdot 10^{10} \text{ KJ} \leftarrow \text{Energy required}$$

Consider Travel Deduction

Interpolate from Table $\rightarrow @ 130 \text{ miles} \rightarrow 1.14\% \text{ energy lost } (0.988)$

Find Available Energy from each source:

$$\text{Uranium: } 80 \text{ kg} \times 2 \cdot 10^{10} \frac{\text{KJ}}{\text{kg}} \times (0.988) = 1.58 \cdot 10^{12} \text{ KJ}$$

$$\text{Natural Gas: } 400 \text{ ton} \times \frac{907 \text{ kg}}{1 \text{ ton}} \times 4.6 \cdot 10^4 \frac{\text{KJ}}{\text{kg}} = 1.64 \cdot 10^{10} \text{ KJ}$$

These values are both bigger than required Supply:

$$\text{Uranium: } 1.58 \cdot 10^{12} \text{ KJ} - 1.22 \cdot 10^{10} \text{ KJ} = 1.57 \cdot 10^{12} \text{ KJ} \leftarrow \text{unused energy}$$

$$\text{Natural Gas: } 1.64 \cdot 10^{10} - 1.22 \cdot 10^{10} \text{ KJ} = 4.21 \cdot 10^9 \text{ KJ}$$

Consider Costs of Each method

$$\text{Uranium: } \$0.093 \frac{\text{\$}}{\text{KW-h}} \cdot 3600 \left(\frac{\text{s}}{\text{hr}} \right) \cdot 1.22 \cdot 10^{10} \text{ KJ} = 4.08 \cdot 10^{12} \$ \leftarrow \text{Cost}$$

$$\text{Natural Gas: } \$0.046 \frac{\text{\$}}{\text{KW-h}} \cdot 3600 \left(\frac{\text{s}}{\text{hr}} \right) \cdot 1.22 \cdot 10^{10} \text{ KJ} = 1.89 \cdot 10^{12} \$$$

Efficiency Comparison

Uranium: 0.998 $\rightarrow$ For every 1 Uranium Failures there are 34 Natural Gas Failures.

Natural Gas: 0.846

Conclusion: The Comparing the costs, reliabilities, and extra energy; it is clear which energy source is The better option. Nuclear, while twice the price, is 34 x more reliable. Taking into account Polyethylene production and how it is scaled, it is pivotal that production is not stalled. Much more money would be lost if production stopped for even a day (510 kg) than the cost difference.

Conclusion and Recommendations

Plastics, and in this scope Polyethylene, have detrimental consequences in terms of energy and waste that are produced but will continue to be prominent for industries across the world. This is something that needs to be considered and recognized on a larger scale because with such realization will come more brilliant minds devoted towards improving and even solving such problems. The difficult thing for even the most brilliant minds is recognizing what will be the technologies of the future. This requires higher wisdom and enlightenment that most individuals regardless of intelligence are just not blessed with. It is however vitally important for those gifted with true insight to spread this knowledge with communities so that research is devoted towards appropriate causes. A big mistake in the scientific community is the invention of other technologies because these technologies diverge people from focusing on the actual technologies of tomorrow. The scientific community is a technical Las Vegas in the sense that many brilliant minds devote their time and efforts towards dead-end technologies in hope that these technologies will be the future. This is where higher wisdom comes into play and must be utilized. There must be fair consideration but additionally appropriate optimism to each technology. In the case of plastics, a recycling method such as pyrolysis would have never been developed if scientists and engineers simply looked down upon the plastic industry as something of the past. PVC and other plastics give very low yield for this process due to their impurities but it is up to the scientific community to address this issue and innovate. If scientists falsely anticipate this material's extinction then a solution will never get proposed and the world will be stuck running in place.

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