Design of a production plant of LDPE in Colombia

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Abstract
The present article is a study on the production of polyethylene as a product of the polymerization reaction of ethylene monomer, a thorough analysis of its production, raw materials and catalyst required to carry out this reaction. The study begins by inquiring about generalities on the compound, physical and chemical properties, and current industrial applications.

Key words: Polyethylene, ethylene, polymerization, monomer, tubular reactor.

1. Introduction

Polyethylene is made from a raw material derived from petroleum: Ethane, and subsequently by reacting, ethylene monomer catalytic cracking is obtained.

The reaction for obtaining ethylene cracking is carried out at high temperatures and special conditions of pressure.

Once the ethylene is obtained through a reaction of appropriate ethylene polymerization, several chains of ethylene are formed. This polymer has properties and diversity of changes in pressure and temperature used in the processes.

Polyethylene is an olefin, a member of the family of thermoplastics. The raw material for the manufacture is high purity ethylene produced from ethane flows, from the gas oil cracking process, which in the Colombian context is currently produced by the Ecopetrol industry (Martin, 2005).

The high purity ethylene is subjected to high pressure and temperature for polymerization in the presence of a reaction initiator and thus produces tubular reactors polyethylene, low density.

Production and Characterization

The polyethylene in the market is produced at a cost of between US $1200/t and US $1800/t, the average annual world production is 80 million tons, which are directed to various processing industries where polyethylene is used for molding processes such as blow types, compression transfer, among others, for various applications where the polyethylene is marketed.

The production plant of LDPE, was modeled for the production of about 12 t/h, from a feedstock flow of 65 t/h of ethylene entering a compressor in order to rapidly increase the pressure before entering the reaction zone.

The main physical characteristics that contain the main information of each compound, including the principal raw material and product characterization that will be obtained, were found in Malppas (2012).
Location

Currently the only producer of LDPE in Colombia is the Ecopetrol business group, which has two production plants, one in Cartagena and the other in Barrancabermeja. Ecopetrol Business Group is the greatest supplier of raw material, and has high levels of production of this requirement, the plant plans to build and operate in the municipality Puerto Colombia located in the Atlantico department due to this town is near to the plant ecopetrol and it is a strategic site given its port as an enabler to export polyethylene in the form of raw material (APCA, 2013).

The location of the plant is chosen by the ease and efficiency improvement in the processes of internal and external logistics regarding acquisition of raw materials and distribution of products and in terms of transportation costs, distribution and cellar times of both raw materials and products.

Industrial Impact

One of the beneficiaries of this project are the petroleum businesses, since they would have a large customer demand for its products as raw material, produced as a product of petroleum. Also, there are industries getting benefits from the prosecution of plastic to finished products requiring the LDPE as raw material, not only in the national context, just as Riduco in the city of Manizales, but in the international context as well. All of this due to LDPE is the most widely used polymer in the thermoplastic industry worldwide for various applications.

The following companies are currently the largest producers of plastic in the global market based on sales of chemicals: BASF, Germany Dow Chemical, USA INEOS Group, LyondellBasell England, and Netherlands ExxonMobil, USA SABIC, Saudi Arabia DuPont, USA Total, France Formosa Plastics Group, Taiwan Bayer and Germany (C&EN, 2014).

Given that the plant that uses different resources derived from petroleum, this production would increase the commercialization of these derivatives for various applications which would increase the development, and the economy of the country.

2. Methods and Structure of process

Process Basic Structure

Polyethylene is produced from the polymerization of ethylene. The polymerization reaction is sensitive to a very large number of catalysts and it is initiated particularly easy by compounds that produce free radicals, for our process, benzoyl peroxide and Di tert butyl peroxide were used as substances for the initiation of the reaction. Polyethylene production requires a source of pure ethylene, suitable compression equipment to operate at about 2000 bar, and a high pressure reactor to perform quick and high exothermic polymerization control. The process takes place in continuous operation.

The process of production of LDPE, basically has three key stages (see Figure 1) which are: Pretreatment, an essential step to adapt the conditions of pressure and temperature of the stream prior to entering the reaction zone commodities, this stage consists of equipment such as compressors and heat exchangers, which ensure that the flow of the ethylene and the initiators being introduced in the reactor of polymerization are at least 2000 bar and about 150 degrees centigrade. The second key step is the reaction zone, this process is modelled in high pressure tubular reactors, which has a water vapor stream to ensure the temperature conditions in the reactor, the plant as a reaction zone is subdivided into four subzones, since injection points are the initiators for the start of reaction mechanism. The final part is the area of separation, consisting of a Flash equipment, which evaporates the amount of ethylene that do not react and then it is used in recirculation but also in the current obtained from the product (Textos Científicos, 2005).

Reactor Operation

For this part of the process, an exhaustive review of the literature was carried out, from which the following conclusions were addressed: The polymerization reaction occurs by a kinetic chain reaction mechanism by free radicals, consisting of 10 semi-reactions (Odian, 2004).

· The tubular reactor is a PFR in countercurrent, countercurrent PFR, divided into 4 sections due to the injection of the initiators of the reaction mechanism.
· The reactor operating temperature is between 150-300 °C.
· The reaction works at high pressures in a range of 2000-3000 bars.
· The length of the reactor is about 1000 m.
· The internal diameter of the tubular reactor is in a range of 25-50 mm.
· Conversion reactor is quite low for the process, about 20 % (Cuevas, 2012).
Kinetic Model

The reaction zone is conducted by a mechanism of reaction of 10 reactions (Kienle et al., 2005).

The reaction rate constants (k) are represented by modified Arrhenius equations (Kienle et al., 2005); including the effects of temperature (T), change of pressure and Activation Energy:

\[ k = k_0 \exp \left( \frac{-E_a + (\rho - \rho_0)dV}{RT} \right) \]  \hspace{1cm} (1)

Here \( k_0 \) is the frequency factor specified for each reaction, the term \( -dE \) is the activating energy, \( IR \) is the gas constant and \( T \) is the temperature. The kinetics for the reactions is of first order, the kinetics parameters were found in (Brandup, 1989).

The reactor is the central body in the production process, this works continuously, therefore the injection of the initiators should always be listed in each section of the reactor, and the tubular reactor shall keep its conditions of temperature, pressure and condition of phase to the reactive mixture, so that the kinetic rate laws and reaction mechanisms are not affected (Dong and Piet, 2004).

Different points in the reactor have steam inlets in order to maintain an appropriate temperature and pressure conditions; this steam is supplied by a boiler producing it at medium pressure.

3. Process Description

Ethylene Pre-treatment

The ethylene required as input into this process is transported in tankers to withstand high pressure liquid inflammable from the supplier company, Ecopetrol. This is acquired and deposited in a storage tank at atmospheric conditions before entering to the process (Ecopetrol, 2014).

After it enters the process, it is initiated in the conditions of pretreatment to have the raw material prepared before being in the reaction zone.

The ethylene stream is required to be pressurized thus it enters a compressor prior the reaction zone.

After the content of ethylene stream is pressurized, it is split into two streams: The first one is going to react to the first two reaction zones with injection of the initiators, and this must react at a higher temperature.

The second stream enters another heat exchanger that should be operated at a lower temperature and also enters the mixer with the injection of new initiators in addition to the current coming from the reaction zone 2. The mixture has to be carried out before entering the reaction zone 3 and 4.

Reaction

The reaction process is carried out in PFR tubular reactors, where a reaction mechanism of PCR is performed; this is subdivided into 10 reactions or...
steps in the various stages of the mechanism, such as initiation, which generates free radicals that will link with different chains of ethylene, forming a vinyl polymer. Then at the stage of propagation different transfers of radical and monomer occur in order to gradually increase the number of chains formed. Finally, the polymerization process is completed by temperature conditions that disrupt the chemical bond formed, producing low density polyethylene in the temperature range established for the reaction (Idarraga, 2010).

LDPE is polymerized forming large chains and generating enough entropy in the order of their bonds between monomers, causing a reduction of their density given that the internal structure has different types of defects (Donald et al., 2004).

Specifying the fluid service

In order to preserve the conditions of the reaction, specify and justify the operating conditions, reactors should have a thermal fluid service, which for our case is water.

Separation Zone

In the design of the production plant of LDPE, there are two separators: Flash isothermal type, located at the exit of the reaction zone 4, which is used to reduce the pressure to an intermediate value at the atmospheric pressure, in order to carried out Flash separation is required:

- A total mass balance.
- A mass per component balance.
- A total energy balance.

The first Flash separator works at high pressures; the second Flash separator works at lower pressures (Lipatov and Nesterov, 1998).

In the Flash 1, the liquid phase contains the monomer and polymer, whereas the gas phase is a recycle stream since it is not a product. Ethylene by itself does not react.

The Flash 2 is assumed as an ideal separator for polymer-monomer mixture, the monomer is recycled to the process and the polymer is removed from the plant.

Treatment of ethylene recirculation

Due to the low conversion in the polymerization reaction that produces polyethylene, the large amount of ethylene that does not react and is evaporated in the Flash separator. The reagent that does not react is carried out to some storage tanks, which have to enter a purification process before returning to the starting point.

The storage tank must have hermetic conditions to maintain the pressure and temperature for the ethylene stream.

4. Results

Simulation Process

The project was carried out using a process of simulation tools. The objective of this procedure was to generate the mass and energy balances from which raw materials were required. The utilities and energy needs are calculated.

The main simulation tool used was the commercial package Aspen Plus V8.0.

The method of calculation of the properties for the polymerization process is known as the Sanchez-Lacombe equation, also known as the basis Polysil method in the Aspen Plus software.

Sanchez-Lacombe equations are few models used to calculate thermodynamic properties of liquid solutions for polymers (Dimitrios et al., 2011).

Sanchez-Lacombe Equation State

The equation of state of Sanchez and Lacombe (1976), is based on the theory of crosslinked flow, assuming that the polymer has a liquid structure flexible. This limits the use of this equation a non-crystalline polymer. This equation is also used to model the solubility of supercritical CO₂ in solid and amorphous and molten polymers. It also describes the subsequent swelling of the polymer when the FSC in the polymer dissolves. Three considerations are necessary when Sanchez-Lacombe equation is used:
1. The solubility of gas in the polymer represents a balance data,
2. the solubility of the polymer in the stage of high pressure gas is essentially zero and
3. Amorphous polymer about its glass transition temperature can be modeled as a liquid (Rozzi and Singh, 2006).

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<th>Table 1. Simulation results.</th>
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<td>Product</td>
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<td>Ethylene For Recirculation</td>
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<tr>
<td>Polyethylene (LDPE)</td>
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Environmental analysis of the production of LDPE

The environmental analysis was performed with the help of software WAR-GUI, which is an algorithm that analyzes the conditions and environmental impacts of the project from 8 different categories (EPA, 2011).

The environmental potential impact was defined as the effect that could have on the environment emissions of gases such as ethylene and others that are part of this project.

The environmental analysis developed in WAR-GUI required:

- Flow rate and composition of each in and out stream of the process.
- Rate of energy consumption.
As noted in Figure 3, the environmental impact is largely marked by the formation of smog, aquatic and terrestrial toxicity.

It must be taken into account that a process that uses raw materials derived from petroleum has high emissions of carbonic gas into the atmosphere. Caution is required given the output currents of the process and especially those that are gases.

5. Conclusions

Through the simulation of processes that lack the recycle of ethylene, it was concluded that the amount of ethylene that does not react is considerable, which affects largely the efficiency of the process, reaching only a 30%. It should be recycled before a purification stage in order to increase the rate of the operative profitability of the production process of LDPE.

References


