Plastic fantastic

More efficient processes and smarter catalysts are reshaping the map for polyethylene manufacture. *Jane Wiltshire* and *Terry Knott* find out more about the polyethylene business and BP's plans for its Innovene process

We are all familiar with polyethylene products, although we may not immediately realise it. Polyethylene in its many forms is used to make goods as diverse as beer crates, dustbins, food wraps, shopping bags, pipe systems for the distribution of gas and water, and a variety of drink and liquid containers. While polyethylene products are taken for granted as one of the 'plastics' of everyday life, achieving the wide range of properties needed to meet all these applications requires careful tailoring of the fundamental chemical processes employed in its manufacture. >>

KEN EWARD / SCIENCE PHOTO LIBRARY

Linear low density polyethylene (LLDPE) consists of long chains of carbon and hydrogen atoms with short side chain branches. This structure gives the material good tensile strength, making it ideal for applications including films, sheeting and bags

>> Polyethylene is derived from ethylene gas (C_2H_4). Ethylene is an olefin feedstock obtained by cracking natural gas or naphtha – a product of crude oil refining – both of which BP produces in large volumes. By joining together or 'polymerising' molecules of gaseous ethylene, polyethylene is produced as a powder or in molten form, which can be extruded into pellets, referred to as resin. The bulk resin is sold into the market supply chain where 'converter' companies transform it into a broad range of finished polyethylene products.

Polyethylene producers and process licensors, like BP, must satisfy the diverse needs of all customers if their businesses are to succeed in the long term. Recent mergers and acquisitions have placed BP's polyethylene manufacturing operations at the forefront of the group's chemicals business, positioning the company as a leading producer with access to over 2.7 million tonnes per annum of polyethylene capacity. It is also a major licenser of both polyethylene process and catalyst technologies to users around the world – BP's proprietary Innovene gas phase polyethylene manufacturing process has been licensed in 16 countries worldwide to date, with a total capacity of 4.6 million tonnes per annum.

Traditionally polyethylene has been classified by its density, which essentially defines its rigidity, or strength (see panel on page 20). Low density polyethylene (LDPE), with a highly branched molecular structure, was the first type to be developed with a plant starting up in the UK as early as 1939. Later, with the advent of suitable catalysts, high density polyethylene (HDPE) was introduced, having a linear structure with few or no side chains. As market needs changed, a linear low density variety (LLDPE) was developed in the mid-1970s, having a linear molecular structure with the important distinction of short side chain branches and narrow molecular weight distribution. LLDPE is stronger and tougher than LDPE and less expensive to make, which makes it an attractive replacement for LDPE in many applications.

Currently, BP and its licensees manufacture 150 different types of polyethylene.

Market moves

'An extremely competitive polyethylene market has recently seen significant consolidation in production and technology development,' says Colin Humpris, BP's polyethylene business manager. 'Successful mergers and recent acquisitions mean that BP is very well placed to respond to the expected market growth across North America, Europe and Asia.'

BP manufactures polyethylene at its chemical complexes at Grangemouth in Scotland, Wilton in England and Lavéra in France, in addition to joint venture plants in the expanding Asian markets – PT Peni in Indonesia, PEMSB in Malaysia and Bataan in the Philippines. BP's recent acquisition of Erdoelchemie and its petrochemical plant in Germany has also improved the company's position in Europe. Another move nearing completion is BP's proposed deal with chemical manufacturer Solvay, which will see the merging of the two companies' European HDPE businesses and will give BP a strong equity position in the North American HDPE market.

There are four distinct types of polyethylene production: a high pressure process, and three low pressure processes based upon solution, slurry and gas phase technologies.

The high pressure process, which operates at pressures around 1500-2000 bar, produces a LDPE film product with high clarity. However, the high pressure equipment involved is expensive and specialised, and consequently, with fewer new plants being built in recent years, the growth in the LDPE market has been relatively flat.

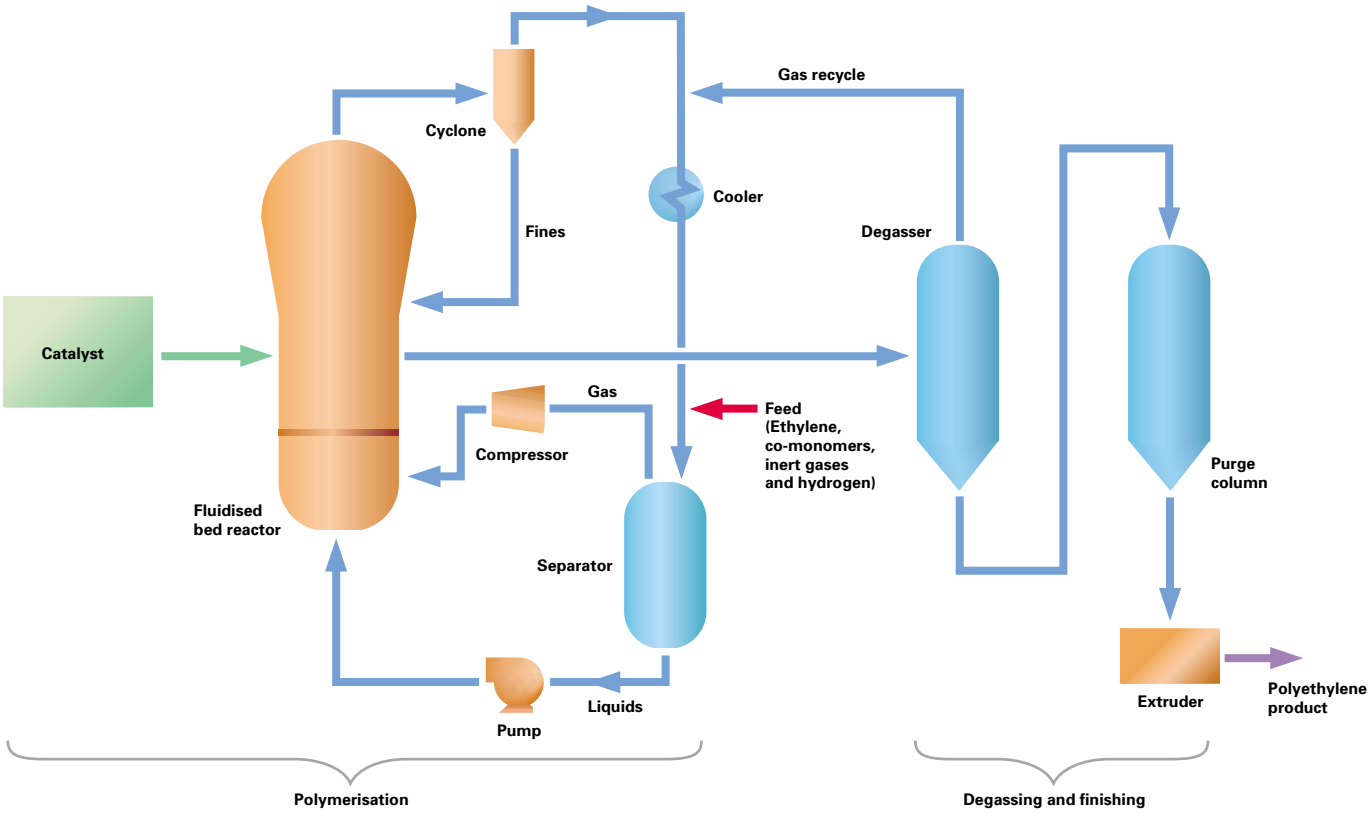
Low pressure processes, typically operating below 100 bar, are more cost effective in terms of capital expenditure but require the aid of a catalyst to obtain economical polymerisation and the required polyethylene product. The characteristics of the polymer are varied by introducing into the ethylene feed other members of the olefins family, such as butene and hexene, referred to as co-monomers.

In slurry phase processes, mainly used for the production of HDPE, monomers and catalyst are suspended in a liquid, isobutane for example. The polyethylene product is not soluble and forms a slurry of suspended solid particles. The solution phase processes, primarily aimed at the LLDPE market, are similar except that the polyethylene is dissolved in a solvent, for example cyclohexane, requiring an added process step to recover the polyethylene.

Gas phase grows

While such processes are employed at some of BP's manufacturing sites, the cornerstone of the company's polyethylene production technology is its proprietary Innovene gas

BP's Innovene process for polyethylene manufacture



phase process. Significantly, Innovene allows both HDPE and LLDPE to be generated from a single reactor in a swing production process, allowing broad market coverage of product applications. All three Asian plants use Innovene technology as do the Grangemouth, Lavéra and Erdoelchemie sites. In the highly competitive world of polyethylene manufacture, Innovene is regarded as a market leader in gas phase technology, and is already being used by 25 licensees around the world. The advantages of Innovene and rival gas phase technologies have meant a rapid increase in gas phase polyethylene capacity in recent years compared with slurry and solution processes. World output of polyethylene is expected to grow by about 20% over the next few years, reaching 60 million tonnes per annum by 2005, some 50% of which is expected to be produced in the gas phase.

The Innovene process (see diagram above) operates at relatively low temperatures between 80-100°C and low pressures of 20-24 bar. Ethylene, along with co-monomers, inert gas carriers, and hydrogen – which helps terminate the long chain polymers thereby controlling some key physical properties – are fed as gases into a bed of catalyst particles, injected as powder. The gases create a fluidised bed reactor, with polyethylene forming around the catalyst particles and growing into a solid, which is taken off as product.

The fluidisation gas leaves the vessel and is cooled in a circulation loop to remove the heat of reaction, compressed and returned to the reactor to maintain the fluidised bed of polymer. A key feature is the use of cyclones at the beginning of the loop, which remove any fines carried from the reactor to prevent fouling of downstream equipment, and to avoid potential cross-contamination of the different polymer grades which are to be made subsequently in the same process plant.

> World output of polyethylene is expected to grow by 20% over the next four years

Among other innovative technology developments associated with the process is BP's proprietary 'High Productivity' system. In this unique system the cooling stage in the loop also condenses liquid hydrocarbons, which are separated from the gas. The liquid is then injected back into the reactor using specially developed nozzles, achieving the optimum removal of heat, with significant operating cost benefits and debottlenecking capability.

'The Innovene process is simple, flexible and enables a wide range of products to be manufactured,' observes Brian Turtle, BP's polyethylene business technology manager. 'It allows true swing production between HDPE and LLDPE combined with attractive operating and capital costs. There are big safety and environmental advantages too, arising from the low design temperature and pressure, and minimal waste streams.'

Catalyst collaboration

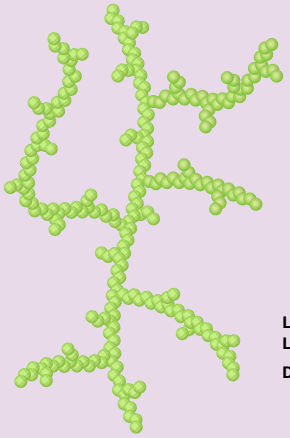
In low pressure polyethylene manufacturing processes, the choice of catalyst is critical since it directly influences the physical properties and characteristics of the polyethylene produced, as well as affecting the economics of production. The number of 'active sites' on the catalyst material where chemical reactions may take place has a direct bearing on the control of the product's characteristics. For example, one key property of the produced polymer is its molecular weight – some catalysts produce polyethylene with a broad band of molecular weights, while others can restrict this to a narrow band, giving a more tailored product for specific practical applications.

Ziegler-Natta (Z-N) catalysts, a long-established category of catalysts based >>

Varieties of polyethylene

HDPE
High density polyethylene
Density 935-965mg/cm^3

LLDPE
Linear low density polyethylene
Density 915-930mg/cm^3



LDPE
Low density polyethylene
Density 910-925mg/cm^3

HDPE is a rigid plastic product, manufactured in many grades to match its physical properties with a diverse range of applications. For example, HDPE for milk bottles needs to be extremely pure for food contact, whereas for underground pipes, reliable performance over 50-year lifespans is a key feature.

Both LDPE and LLDPE are mainly used in the packaging film market. LLDPE is stronger than ordinary LDPE and although it is less clear, the film produced is thinner due to its strength properties. The ability to manufacture the film at reduced thickness means that less polymer is required per unit of product, saving feedstock costs. It also leads to reduced tonnage of packaging waste. For these reasons, BP believes that the LLDPE sector has considerable potential for expansion.

Currently the total global market for polyethylene is around 50 million tonnes per annum. HDPE commands the greatest share at 45%, followed by LLDPE at 30% and LDPE at 25%. The highest growth rates are in the LLDPE sector, which is expanding at a global average of around 9% per annum.

>> mainly on titanium with an organo-aluminium activator, and chromium-based catalysts, have traditionally been used for low pressure processes, and are widely used for Innovene polyethylene manufacture. However, BP is also actively pursuing other more advanced catalysts to improve performance still further for its customers. The recently launched collaboration with NOVA Chemicals Corporation (RE*view*, April 2001) to develop and commercialise advanced Z-N catalysts for use in the gas phase process is just one example. Trials of advanced high activity Z-N catalysts have already demonstrated that polyethylene resins with improved performance can be manufactured commercially.

Another avenue is being followed with Eastman Chemical Company, under an agreement reached in April this year, in which BP will market and license Eastman's Energx polyethylene technology worldwide to existing gas phase polyethylene producers.

But alongside these ventures, what seems to have really captured the imagination of BP and its competitors – including the giants of the marketplace, Dow Chemical Company and ExxonMobil – is the use of metallocene catalysts. Metallocenes are a class of organo-metallic complexes, attracting significant research and development spending in recent years to understand their sensitivities and find ways to best exploit the manufacturing precision offered by their single activity sites. The ability of metallocenes to control the molecular structure of the polyethylene resin results in products exhibiting superior strength compared with traditional Z-N and chromium-based products, more closely matching customers' product demands.

A commercial scale test of Innovene polyethylene production, using new catalysts developed by BP and Dow Chemical Company – based on Dow's proprietary Insite metallocene catalyst technology – was completed at BP's joint venture PT Peni site at Merak in Indonesia in 1999. The trials successfully demonstrated that high performance tailor-made products can be delivered economically, representing a breakthrough in polyethylene manufacture, with Chevron Phillips Chemical Company becoming the first licensee of the combined technologies to produce 'metallocene polyethylene'.

Following Dow's recent merger with Union Carbide, BP has acquired Dow's interest in the jointly developed technology, giving the company the right to develop and license 'constrained geometry' metallocene catalysts for gas phase polyethylene processes. Competition already exists in the market, principally coming from Univation Technologies – a joint venture originally established between Union Carbide and Exxon Chemicals – which offers the proprietary Unipol gas phase polyethylene process and Exxpol metallocene catalyst technology.

Colin Humphris views the metallocene breakthrough, which is currently targeted at the high performance film markets, to be a key factor in the future of polyethylene production.

'Metallocenes will enable gas phase polyethylene manufacturers to access a broader range of products with easier processing, greater strength and superior optical properties compared with existing polymer resins,' he explains. 'Due to more efficient co-monomer incorporation and reduced co-monomer consumption, the metallocene product will give better end-use performance than traditional LLDPE, and use less material in manufacture.'

BP will take advantage of this growth area through its now wholly owned Innovene metallocene technology, not only by granting licences but also for its own manufacturing sites – metallocene polyethylene production is planned to start in 2002 at the company's flagship Innovene plant at Grangemouth under the polyethylene expansion project already under way. ■

Metallocenes are a key factor for future production