

## Status of Low Pressure PE Process Licensing

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### Introduction

Not all organizations have the capabilities or want to investing in acquiring the capabilities to develop process technologies. Instead, licensing third party technology enables many organizations to utilize state-of-the-art process know-how to fulfill their resin needs or to enter a particular market, without having to invest heavily in developing proprietary process technologies.

Typically, a company desiring to produce polyethylene would acquire a license for a particular process technology, and perhaps catalyst technologies as well, from a process licensor. Currently, there are over 25 licensors offering technologies to produce linear polyethylenes. There are many factors associated with picking an appropriate technology license including, but not limited to, (1) capability of the process to produce the desired resin grades, (2) breadth of the process technology, (3) ability to produce specialty grades, (4) catalyst options, and (5) most importantly, cost. Many times, licensees overlook the importance of factors other than cost in making their discussion, which may lead to technologies that are unable to expand with the future needs of the licensee.

This article discusses the status of the most popular low-pressure process technology used to produce linear polyethylene, including a description of the process technology, process capabilities, regional

capacity breakdown, and current licensing trends.

### Types of Process Technologies

Low-pressure polyethylene processes are used in the production of linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE). Low-density polyethylenes are produced via high-pressure processes (either autoclave or tubular), and are not relevant to this discussion. There are 3 major types of low-pressure technologies, namely (1) slurry, (2) solution, and (3) gas phase.

A slurry process is conducted in an inert diluent in which the catalyst is affixed to an inert support, and the polymer formed during production remains suspended in the liquid medium, never dissolving. Slurry processes can be sub-divided into conventional slurry loops and cascade reactor, the later being capable of producing bimodal products.

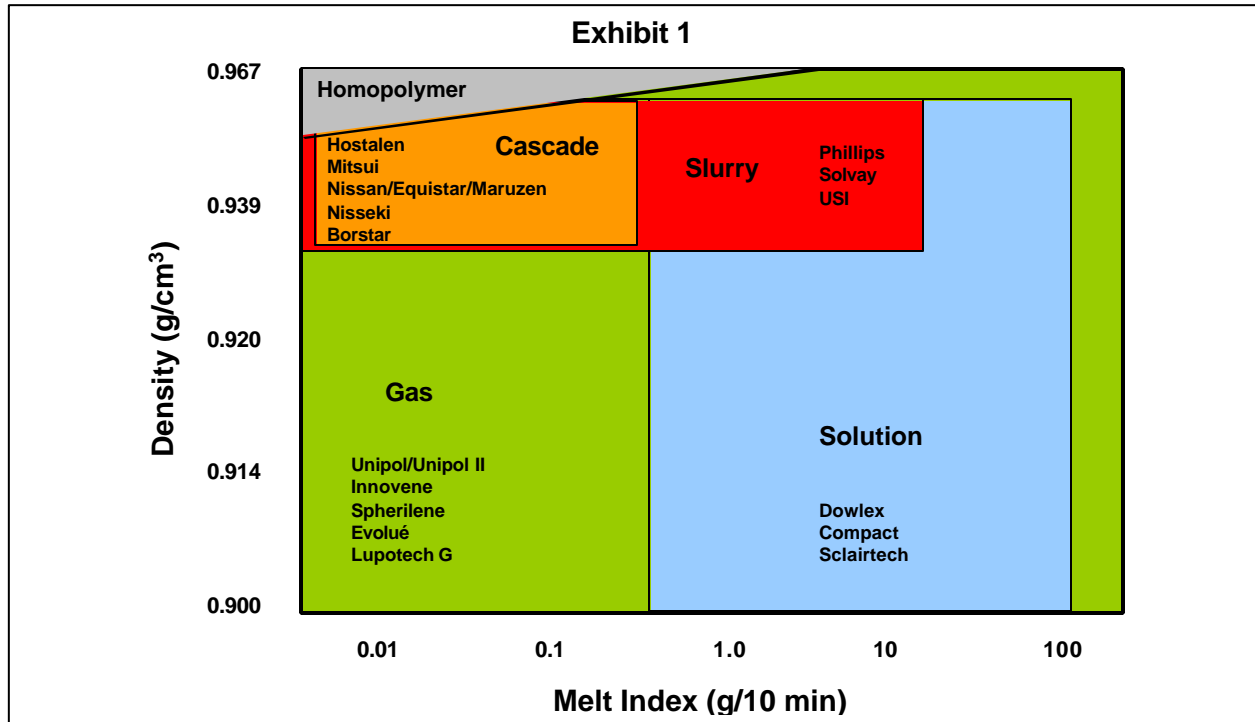
In a solution process both the catalyst and the resulting polymer remain dissolved in a solvent that must subsequently be removed to isolate the polymer.

Gas-phase processes are either of the stirred-bed type or the fluidized-bed type. Supported catalysts are the rule in gas-phase processes as well.

Each type of process has limitations on the breadth of resins its can produce. Exhibit 1 illustrates the capabilities of different processes as it pertains to density and melt index. Resins produced via the slurry process are limited to densities greater than 0.937 g/cm<sup>3</sup>, and a melt index up to 10 g/min. Solution processes have a wider window of operation in terms of densities and melt indexes. Gas-phase reactors have the widest operating window, but encounters difficulties in producing resins with very low densities due to stickiness and particle agglomeration.



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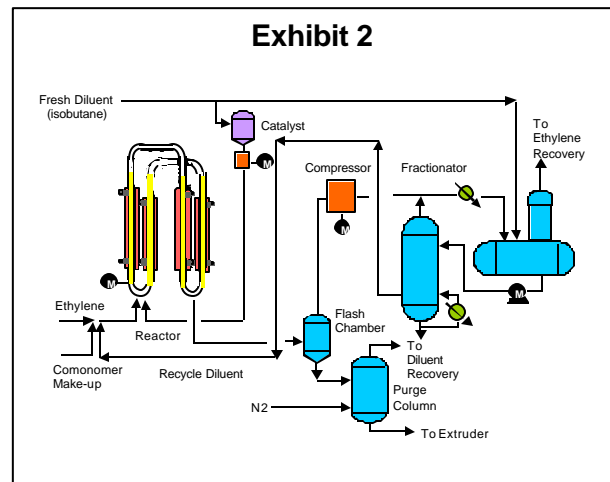
## Slurry

### Phillips Slurry Loop (Licensor: Chevron Phillips)

The Phillips slurry loop process, sometimes referred to as the loop slurry process, depicted in Exhibit 2, supported catalyst, ethylene, and comonomer, usually hexene-1, are injected into a vertical, loop-shaped reactor filled with isobutane diluent. Reactor pressure is approximately 37 bar, and reactor temperature is in the range of 85-100°C.

The mixture of catalyst particles, growing polymer particles, comonomers, and diluent is pumped around the loop, and polymer particles are harvested by directing a portion of the slurry to the settling legs, where the polymer particles settle toward the bottom, then venting the concentrated slurry to a medium-pressure separator to remove solvent and unreacted monomers then conveying the particles to an extruder where they are melted, compounded with additives, and pelletized.

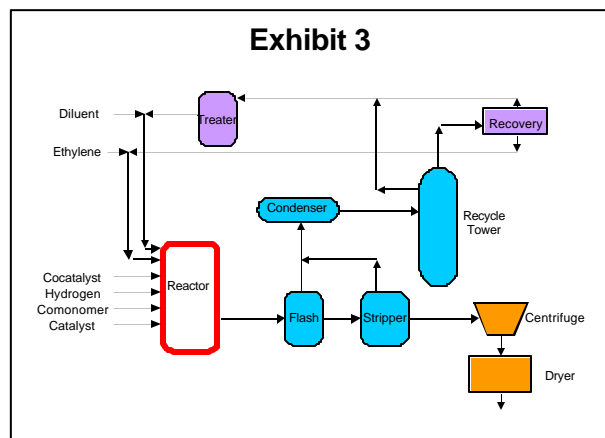
The practical lower density limit for polyethylene produced in a slurry loop slurry reactor is slightly below 0.94 g/cm<sup>3</sup>. To produce the lowest densities it is necessary to increase the level of comonomer in the reactor significantly, since conventional catalysts incorporate comonomer sluggishly. The higher concentration of comonomer makes the diluent a better solvent for the polymer, especially the lower-M<sub>w</sub> fraction, causing swelling of the particles which leads to potential reactor fouling.



Phillips developed a version of the chrome catalyst that synthesizes comonomer from ethylene *in situ*. The result is that lower-density polyethylenes can be produced since comonomer is being synthesized at the catalyst surface then is being consumed immediately. In 1993 Phillips introduced the material produced using this catalyst as LDLPE - low-density linear PE.

## Solvay Loop (Licensor: Solvay)

Catalyst, ethylene, comonomer (if desired), and hydrogen are injected into a vertical, loop-shaped reactor filled with isobutane diluent, as shown in Exhibit 3. Reactor pressure is approximately 30 bar, and reactor temperature is in the range of 75-80 °C. The mixture of catalyst particles, growing polymer particles, comonomer, hydrogen, and diluent is pumped around the loop. Polymer particles are harvested via the settling legs by venting the concentrated slurry to a medium-pressure separating vessel. The solvent and unreacted monomer are flashed, treated, and recycled back to the loop reactor. The polymer particles are further stripped, dried, and conveyed to an extruder where they are melted, compounded with additives, and pelletized.

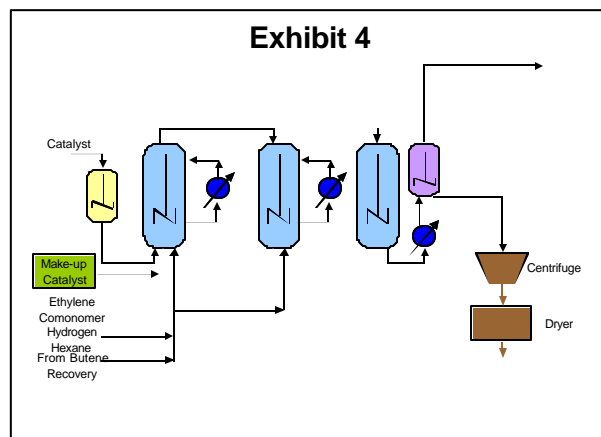


If bimodal resin is desired, the polymer particles from the first loop reactor can be transferred to another loop reactor by directing a portion of the slurry to settling legs, where the polymer particles settle

towards the bottom, then re-directed to another loop reactor. Hydrogen is flashed off prior to introduction in the second loop, and additional monomer, comonomer and hydrogen (if desired) are added, and the mixture recirculated in the second loop, before being harvested.

## Hostalen (Licensor: Basell)

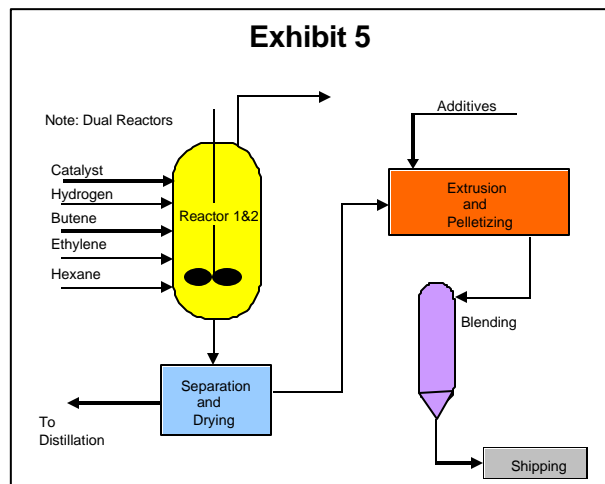
A mixture of monomer, comonomer, hydrogen and hexane (diluent) is continuously fed to the reactors operating at temperatures ranging from 75-85 °C and pressures of 5-10 bar, as depicted in Exhibit 4. The reactor conditions in each reactor may be varied independently. The polymer suspension flows from the reactors into a common post reactor where conversion rate approaches 98%. The suspension is centrifugally separated, the polymer dried, then it is sent to the extruder for pelletization. The CSTR reactors may be operated in parallel or series to produce unimodal or bimodal grades, respectively.



## Nissan (Licensor Nissan)

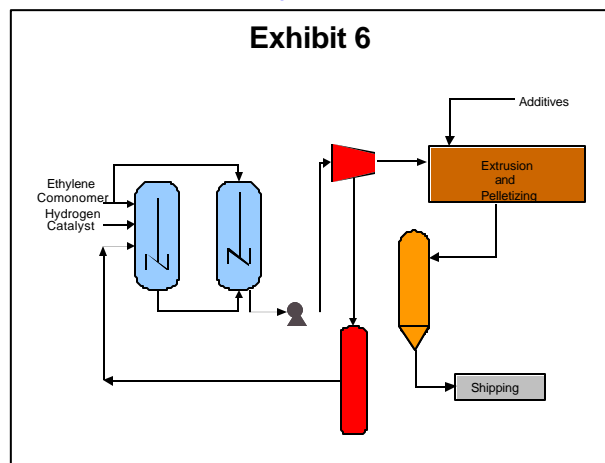
The Nissan slurry process, used to produce HDPE, is based on a stirred tank reactor as shown in Exhibit 5. Catalyst, ethylene, comonomer, and hydrogen are fed to the reactor which uses hexane diluent. The reactor is operated in a temperature range of 65-85°C at a pressure of 10-14 bar. Polymer slurry exiting the reactor is sent to a flash vessel to remove volatiles then fed

to a centrifuge where the diluent is removed. The dried powder is compounded, extruded, and pelletized. The process has been refined through the joint efforts of Nissan, Maruzen, and Equistar.



## CX Process (Licensor: Mitsui)

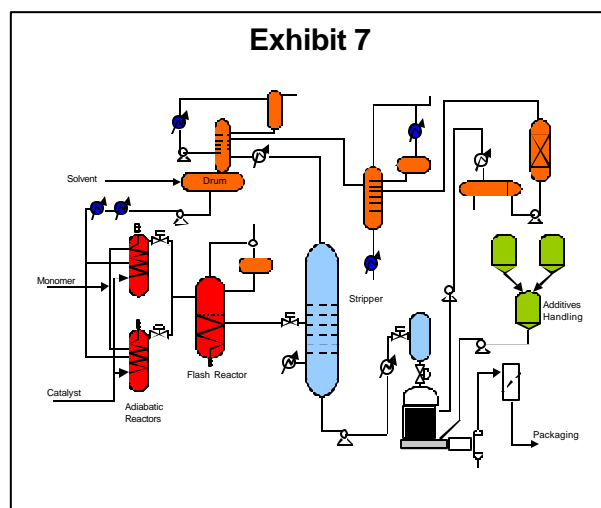
The Mitsui process comprises 2 continuous, stirred-tank reactors of identical size that are operated in series to produce film resins with bimodal MWDs (Exhibit 6). The diluent is hexane, and the usual comonomer is butene-1. Typical conditions are an operating pressure of 7.8 bar, an operating temperature of 85°C, and a 45-minute residence time per reactor. Polymer is isolated and pelletized in straightforward fashion in the Mitsui process.



## Solution

### Dowlex (Proprietary: Dow)

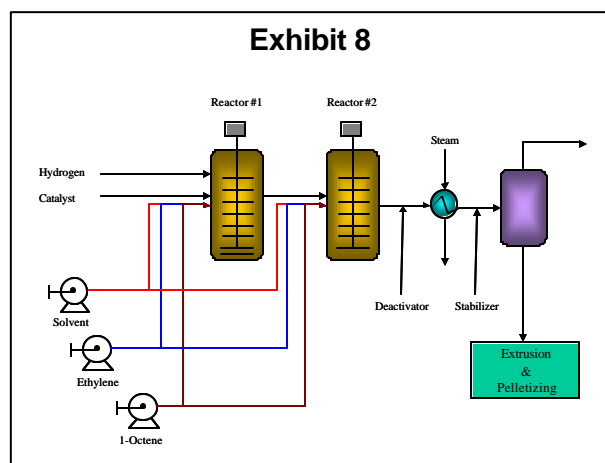
Dow developed the Dowlex process to produce linear polyethylenes comprising octene-1 comonomer. As shown in a schematic representation in Exhibit 7, the principle hardware consists of 2 stirred tank reactors in series filled with an isoparaffin solvent (a mixture of C<sub>8</sub> and C<sub>9</sub> isoparaffins). Ethylene, octene-1, and catalyst are introduced into the reactors, where they remain in solution. The reactors are run at approximately 160°C and 27 bar, and total residence time in the reactors is ca. 30 minutes. When the solution exits the second reactor it is flashed to remove ethylene monomer. Solvent and residual octene-1 are removed in a 2-stage flash unit, and the remaining polymer melt is compounded with additives, extruded, and pelletized. Dow has not made the process available for license.



### Sclairtech/AST (Licensor: NOVA)

NOVA acquired the rights to SCLAIRTECH technology, the SCLAIR<sup>®</sup> trademark, and the worldwide SCLAIRTECH licensing business when it acquired DuPont Canada's polyethylene business in 1994.

SCLAIRTECH operates at temperatures up to 300°C in cyclohexane solution. Polymerization is very rapid, requiring less than 2 minutes, so small reactors can turn out relatively large volumes of polymer. The extrusion and stripping sections of a SCLAIRTECH plant are also designed to facilitate very quick transitions between products, on the order of 30 minutes. The SCLAIRTECH process produces polymers from the LLDPE to the HDPE range using butene-1 or octene-1 comonomers.



Advanced SCLAIRTECH technology, or AST, is a significantly updated version of SCLAIRTECH technology based on a number of modifications and centered on a set of 2 sequential autoclave reactors, each fitted with independent monomer, comonomer, and catalyst feed systems plus high-intensity mixing technology. Discrete polymers can be produced in each reactor under a different set of tightly controlled conditions, enabling production of novel polyethylenes with bimodal MWDs having specific end-use properties. The short residence times that figure heavily in SCLAIRTECH technology are retained in AST. Densities ranging from 0.905 to 0.967 g/cm<sup>3</sup> with melt indices ranging from 0.2 to 150 dg/10 min can be produced in the AST process. Exhibit 8 is a schematic of the AST reactor system.

AST differs in several ways from its predecessor, including (1) use of a

proprietary solvent lighter than cyclohexane; (2) introduction of ethylene and comonomer into the reactor directly rather than their being introduced predissolved; (3) maximum reactor temperature of less than 200°C, (4) a stripper section that can accommodate lower-density polyethylenes, and (5) no deashing is required. AST is said to be significantly more economical to build and operate than SCLAIRTECH, and it is claimed to take advantage of synergies when an AST-based plant is built in conjunction with an ethylene cracker.

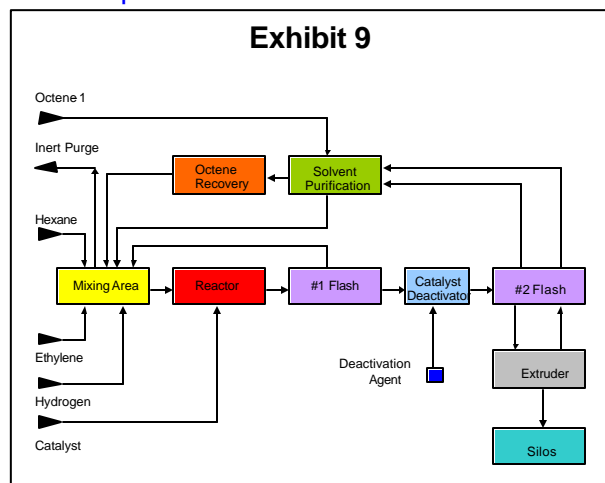
### Compact (Licensor: Stamicarbon-SABIC)

The Compact solution process was originally developed by DSM in the 1970s to produce HDPE. It was adapted in the 1980s to produce linear medium- and low-density polyethylenes based on butene-1 or octene-1 comonomers using proprietary Ziegler catalysts. The Compact solution process is capable of producing polyethylenes across a density range of 0.900 to 0.967 g/cm<sup>3</sup> and a melt-index range of 0.8 to 100 using propylene, butene-1, or octene-1 comonomers.

In the Compact solution process, depicted in Exhibit 9, ethylene and comonomer, usually octene-1, are dissolved in hexane, cooled, and fed to a stirred, liquid-filled reactor. The reactor is operated adiabatically, so it is necessary to precool the reactor feed to control temperature. The enthalpy of polymerization raises the reactor to its normal operating temperature, ca. 200°C. Molecular weight is controlled by hydrogen. Ethylene conversion of at least 95% is achieved during a short reactor residence time.

The hot solution exits the reactor into vessels where volatiles plus the major portion of the hexane are flashed off, and catalyst residues are deactivated. The polymer concentrate is fed to a degassing extruder where the residual hexane and octene-1 are flashed, the appropriate

additives are compounded, and the polyethylene is pelletized and transported to silos for pack out.



## Gas-Phase

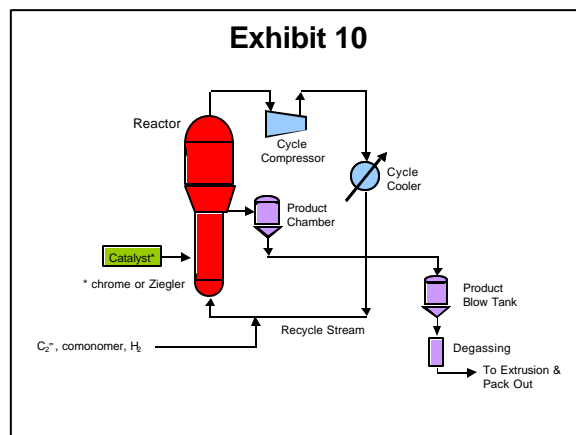
### Unipol (Licensor: Univation)

The Unipol process was developed by Union Carbide during the late 1960s and early 1970s in an effort to enable production of HDPE and LLDPE in a low-pressure, fluidized bed reactor significantly cheaper to build and operate than conventional high-pressure or solution processes. Unipol was first applied to HDPE production in 1968 and to LLDPE production in 1975. Exhibit 10 depicts a schematic of the Unipol process. Supported catalyst is fed into a reactor where it is fluidized in a stream of ethylene, comonomer, and hydrogen. Polyethylene forms on the fluidized catalyst particles. Unreacted gases are continually withdrawn from the reactor, compressed, cooled, and recycled. Polymer particles are removed from the reactor through a differential valve, conveyed to an extruder, compounded with the appropriate additive formulations, and pelletized.

Unipol II, which comprises not one but 2 reactors, appeared on the scene in 1992 with the intent to provide Union Carbide (and potential licensees) with the ability to produce polyethylenes having a bimodal

MWD. There are only 2 Unipol II lines in the world, a Union Carbide plant in Taft, Louisiana, and one belonging to EQUATE Petrochemical Company K.S.C., a Union Carbide joint venture with Petrochemical Industries Company and Boubyan Petrochemical Company in Shuaiba, Kuwait.

The production rate of a Unipol reactor is determined by the amount of heat that can be removed. To increase the heat-removal capacity of the fluidized bed Union Carbide developed what it called condensed-mode operation. The recycle stream is partially condensed, and some liquid is re-injected into the system. The enthalpy of vaporization absorbs extra heat, enabling higher production rates. In the mid 1990s Exxon developed and patented what it refers to as Super Condensed Mode Technology that enables even higher production rates. SCMT is one of the technical cornerstones of Univation Technologies.

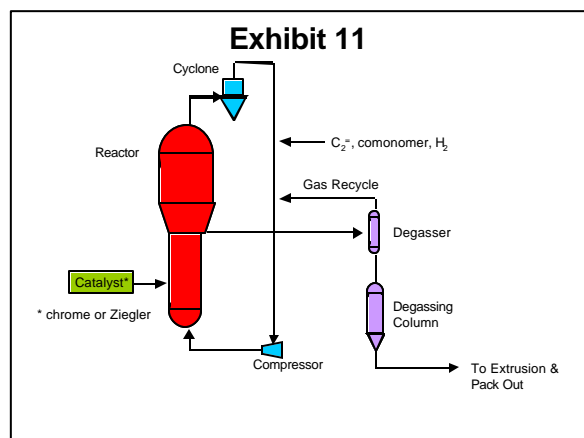


### Innovene (Licensor: BP Amoco)

The other major fluidized-bed production technology for polyethylene production is BP Amoco's Innovene process. A block diagram of the Innovene process is shown in Exhibit 11. Though Innovene is very similar to Unipol, there are a few differences. In Innovene the recycle stream is passed through a cyclone to capture solids in the gas stream in order to eliminate

fouling of the compressor and the heat exchangers and minimize cross contamination during product transitions. The Innovene design features 2 heat exchangers in the recycle loop whereas the Unipol design has only one heat exchanger.

In 1995 BP introduced its version of condensed-mode operation that it called "High Productivity" technology. Univation and BP ended up in court over the rights to condensed-mode operation, and Univation prevailed.



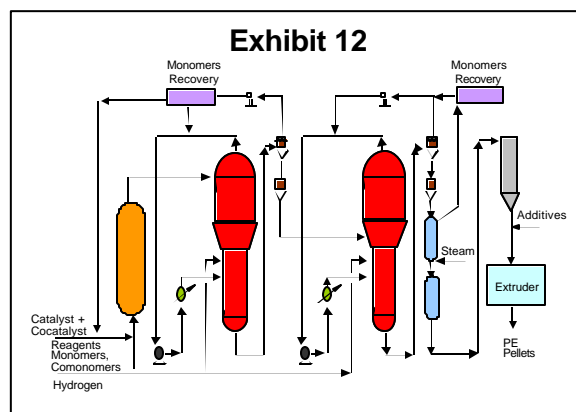
## Spherilene (Licensor: Basell)

Long the major player in polypropylene production technology, Basell has a polyethylene production process as well. In 1990 Himont embarked on an effort to design a polyethylene process based on the extensive experience it had garnered during development of the very popular Spheripol<sup>®</sup> polypropylene process, and it announced it had perfected the process in 1993, calling it Spherilene. Taking another cue from its polypropylene technology, Himont designed a catalyst for the process based on its Reactor Granule Technology that gives the final product a spherical morphology.

A schematic of the Spherilene process is shown in Exhibit 12. Catalyst is fed initially to a prepolymerization reactor, actually a small slurry loop, where it is pre-coated with polyethylene then injected into the first reactor. Spherilene is a multireactor,

fluidized-bed process. Residence time in the process is ca. 2.5 hours. Basell says the advantages of Spherilene over competitive gas-phase processes include (1) the reactor can be started up empty, (2) fouling is minimal, (3) grade transitions are rapid, and (4) steam stripping of the powder prior to compounding minimized hydrocarbon contaminants.

Basell has not had much success in licensing the Spherilene process. Due to over capacity issues in North America, Basell recently closed down the Spherilene plant in Lake Charles, LA. It is anticipated that Basell will slowly phase-out this technology platform.

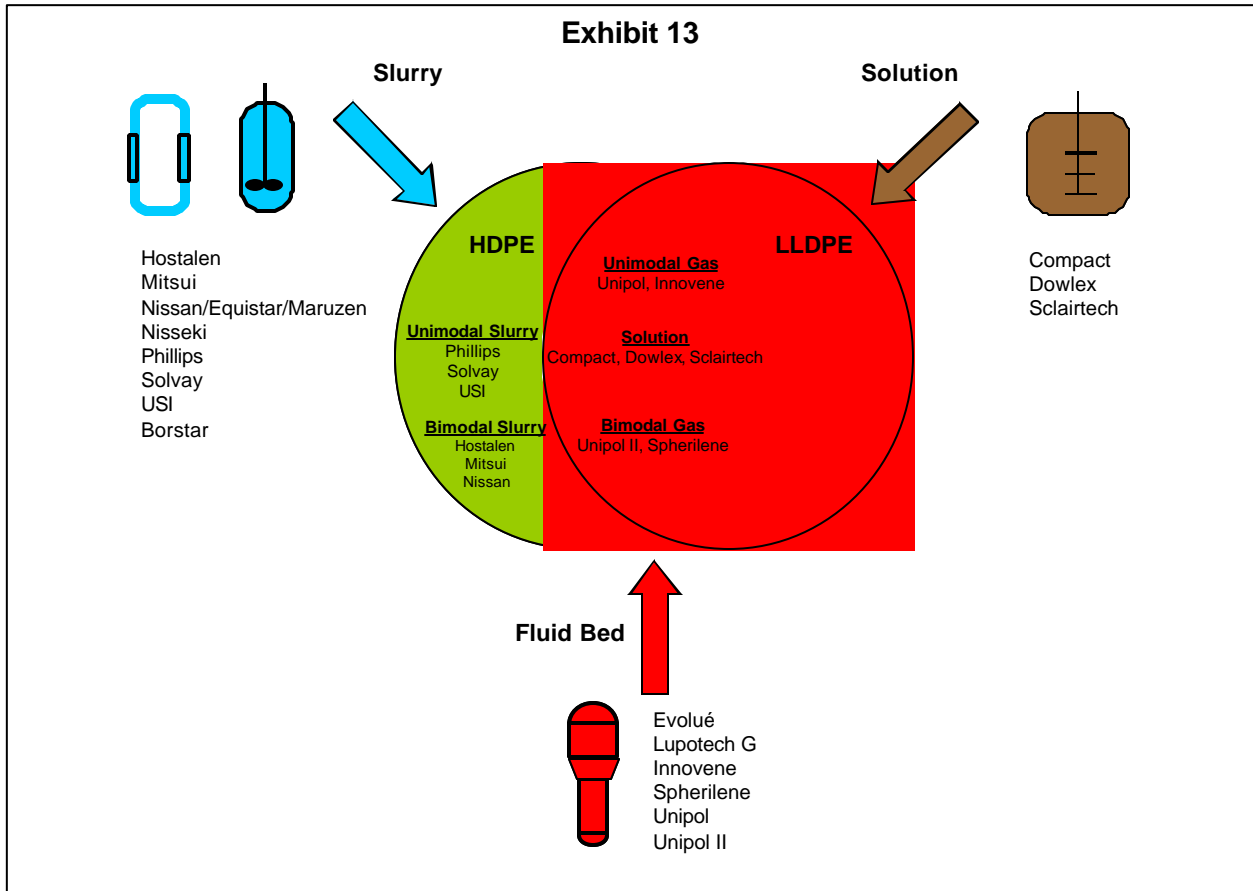


## Inter-Process Competition

The processes described above, along with others, compete with one another for the production of linear polyethylenes. Some are optimized for the production of either HDPE or LLDPE, and others are efficient at swing operation. Exhibit 13 shows the overlap between the different processes in the realm of linear polyethylenes.

Exhibit 14 shows the breakdown on linear polyethylene capacity by type and process. The current global capacity of linear polyethylene processes is in excess of 96 billion pounds. Approximately, 63% of linear polyethylenes are HDPE resins, of which 67% are unimodal and 23% bimodal resins.

# NEW GENERATION POLYOLEFINS



Sixty-five percent of HDPE resins are produced via slurry processes, 25% using gas-phase processes, and 10% with solution processes.

Linear low-density polyethylenes account for 37% of all linear polyethylenes. Compared to HDPE, only 4% of LLDPE resins are produced via slurry processes, 75% using gas-phase processes (the dominant process type for LLDPE), and 21% using solution processes.

Exhibit 15 shows the regional differences/similarities in the type of process utilized to produce linear polyethylene. Gas and slurry processes hold an equal share of the linear polyethylene market accounting for 85% of the total capacity, the remainder being solution processes.

North America holds the largest share of gas-phase processes (33%), followed by Rest of the World and Other Asia categories

(26% each). North America also holds the largest share for slurry processes (31%), followed by Other Asia (29%), and Western Europe (19%). Largest producers of solution processes are located in North America (34%) and Western Europe (24%).

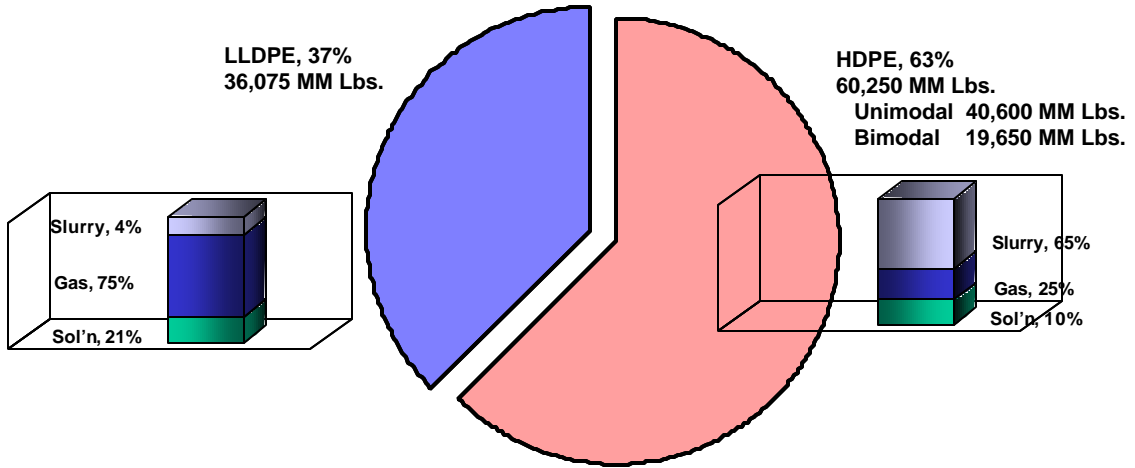
The linear polyethylene capacities are divided by licensor in Exhibit 16. The top five largest licensors, in terms of capacity licensed, in descending order are (1) Univation Technologies, (2) Chevron Phillips, (3) BP, (4) Mitsui, and (5) Dow.

Univation is the largest licensor, accounting for 29% or 28 billion pounds with their gas-phase Unipol process. The second largest licensor is Chevron Phillips with 15% or 14.5 billion pounds. BP and Mitsui each have approximately 10% or 9.6 billion pounds. Dow accounts for 7% or 6.9 billion pounds, however the Dowlex process is currently unavailable for third party licensing.



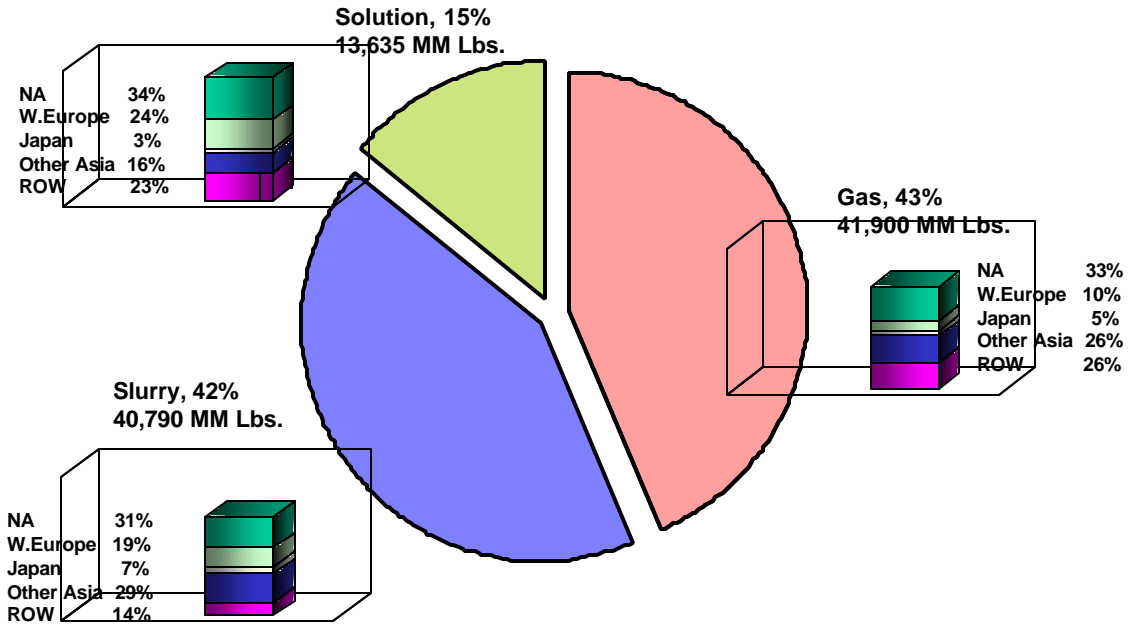
# NEW GENERATION POLYOLEFINS

Exhibit 14 – Linear PE Capacity by Type and Process



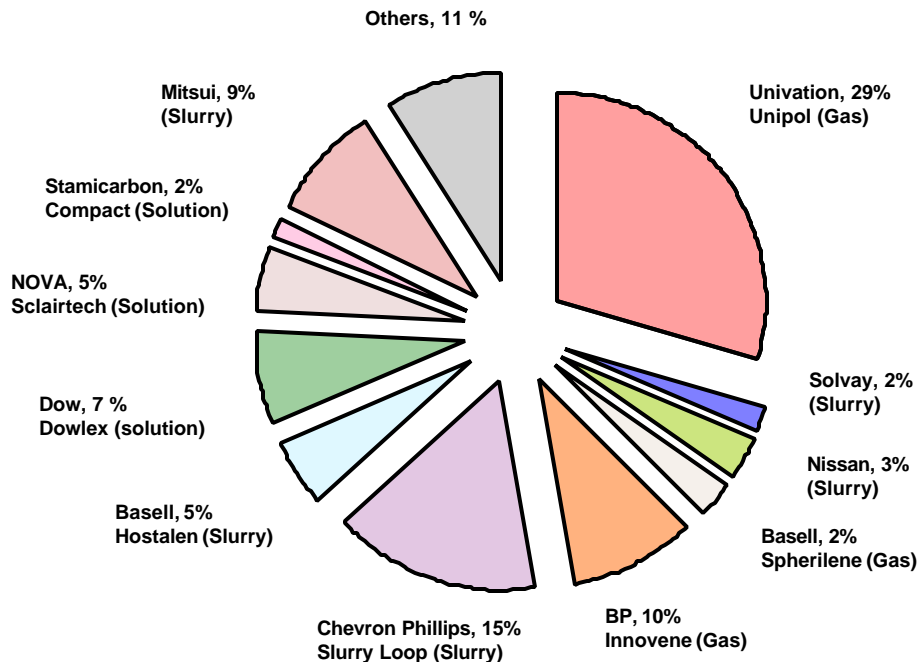
Source: Chemical Market Resources, Inc.

Exhibit 15 – Linear PE Capacity by Type and Region



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**Exhibit 17 – Linear PE Capacity Breakdown By Licensor**



## Future Trends

Gas-phase capacity has experienced a healthy growth rate over the past ten years growing at an average rate of 6.1%. Gas-phase processes are very economical at producing commodity grade resins, and thus are popular with resin producers in China and other Asian countries.

Slurry capacity has grown at an average rate of 5.1%, although bimodal slurry processes have seen growth rates in excess of 7% in the past five years, mainly due to bimodal pipe resin markets in Western Europe, and bimodal films in Asia. Bimodal resins are being driven by the film, blow molding, and pipe markets, where the bimodality provides enhanced processing and performance characteristics.

Solution processes have experienced the lowest growth rates mainly due to lack of third-party licensing activity, and perhaps the level of difficulty involved with operating

such process. Solution processes are well suited for higher-value added products such as octene-1 based resins. Nova Chemicals has recently brought online its 850 million pound Advanced Sclairtech plant at the Joffre, Calgary site. Although, only about 180 million pounds of resin was produced last year, the company plans to ramp up production to keep pace with demand.

An addition 12.1 billion pounds of linear polyethylene capacity is expected to come on stream by 2007. Approximately 50% of the capacity addition will be based on gas-phase technologies, 48% on slurry, and 2% on solution.

*To learn more about these and other polyolefins technologies, please attend the **2002 Polyolefins & Elastomers Licensing Fair** scheduled for September 17, 2002 at the Hilton NASA Clear Lake, Houston, TX. Please review program on the next page.*