A COMMERCIALLY AVAILABLE CONTINUOUS BENCH SCALE POLYOLEFINS PILOT PLANT

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ABSTRACT

New developments in Polyolefins catalyst and product technology are currently occurring the world over at a record pace. Companies are vying for technological and market positions through patent coverage, licensing activities, and business alliances. Central keys to this effort are the physical tools of technology development. With these tools, companies can create and discover new catalysts, develop new product grades, or even entirely new products, and test them in the marketplace. Traditional tools of Polyolefins R&D include Pilot Plants with capacities from 25 to more than 150 Kg/Hr, and Laboratory Batch Reactors. Batch Reactors are very suitable for catalyst screening, with advantages that they are small, inexpensive, and allow quick runs. However, they are well known to yield results and products, which are not closely relevant to commercially relevant to commercial operation. Large continuous pilot plants are used to evaluate catalyst systems and produce commercially relevant results and products. The limitations are that they are costly, labor intensive to operate, and require handling large quantities of raw materials and effluents. One more tool is needed to overcome these limitations. Xytel Corporation and Oakwood Consulting, Inc. have developed a new and unique Continuous Bench Scale Polyolefins Unit (CBSU) which promises to "bridge the R&D gap" between lab Units and large Pilot Plants. By operating in the steady-state mode at a bench scale size (2 – 5 Kg/Hr Resin), the problem of obtaining commercially relevant data and product versus the costs of time and personnel for large pilot plant operation, is effectively addressed.

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INTRODUCTION

New developments in Polyolefins catalyst and product technology are currently occurring the world over at a record pace. Companies are vying for technological and market positions through patent coverage, licensing activities, and business alliances. A central key to this effort are the physical tools of technology development.

With these tools, companies can create and discover new catalysts, develop new product grades, or even entirely new products, and test them in the marketplace. Traditional tools of Polyolefins technology development include Lab-scale Batch Reactor Units and Large Continuous Pilot Plants with capacities from 25 to more than 150 Kg/Hr. Because they are small, inexpensive, and allow quick runs, lab-Scale Batch Reactor Systems are used for initial catalyst screening in spite of recognized limitations. They are well-known to yield results and products which are not closely relevant to commercial operation. Large, Continuous Pilot Plants are used to evaluate catalyst systems and produce commercially relevant results and products. The limitations are that they are costly, labor-intensive to operate, and require handling large quantities of raw materials and effluents. One more tool is needed to overcome these limitations.

Xytel Corporation and Oakwood Consulting, Inc. have developed a new and unique Continuous Bench Scale Pilot Plant Unit (CBSU) which promises to "bridge the R&D gap" between lab-scale work and large-scale pilot plants (Figure 1). By operating in the continuous, steady-state mode at a bench-scale size (2-5 Kg/Hr of polymer), the problem of obtaining commercially relevant data and products versus the costs of time and personnel for large pilot plant operation, is effectively addressed.

DESCRIPTION OF XYTEL-OAKWOOD CONTINUOUS BENCH SCALE UNIT

The Xytel-Oakwood Continuous Bench Scale Unit (CBSU) is a computer-controlled, modular pilot plant offered as a turnkey system from Xytel Corporation in collaboration with Oakwood Consulting. The CBSU was specifically developed by Xytel and Oakwood as a means for Polyolefins researchers to obtain more timely and cost effective data and resin samples for commercial evaluation. The heart of the system is two continuously operating 10-Liter polymerization reactors in series with associated slurry and powder transfer systems. The reactors are chosen from two designs: Liquid Slurry CSTR or Continuous Stirred Gas Phase. The basic configuration with two Reactors is shown in Figure 2. Other configurations are possible.

The CBSU unit was designed in part using a detailed polymerization kinetic model contained in a custom user Fortran subroutine within the Aspen Plus^{R} process simulator. The composition and conditions of all important streams were determined at steady state. The Aspen simulation also provided an accurate heat balance for key parts of the unit. The CBSU unit is designed so that the user can obtain high-accuracy material balances during a run campaign -- and provide a comparison with the material balances from the Aspen simulations (an aid to verify catalyst consumption).

The system's various components of vessels, pumps, reactors, instruments, automated valves, etc. are conveniently mounted on a single painted steel frame, or "skid", with an open three-dimensional architecture for ease of operation and maintenance. The process skid occupies a footprint smaller than eleven feet in length and five feet in depth. The maximum height is eleven feet. The system's electrical design and components are installed to meet the requirements of a Class 1, Division 2, Group CD area.

The process skid contains all of the subsystems, or modules, necessary to control and feed reactants and catalysts, control the reaction parameters, and transfer and purge product. The design incorporates proprietary technologies developed by Oakwood and Xytel to allow continuous and automatic lined-out operation to produce nominally 2 to 5 Kg/Hr of resins. Some key features are highly accurate and reliable catalyst metering, choice of two reactors in series (liquid slurry and/or gas phase), reaction composition and variables control, reliable powder transfer, and fully automated operation.

The process system is automatically controlled and data logged by a Honeywell 9000 Loop and Logic Controller with SCAN 3000 software in a Windows environment. The operator interface is a Pentium-based PC with the SCAN 3000 software. Xytel configures the control system and user interface screens to provide turnkey operation.

Control of the Continuous Bench Scale Polyolefin Pilot Plant is designed for rapid start-up and line out, programmed grade transitions, and easy shutdown. Operation may be suspended at any time and resumed properly again. Within 1_-2 hours, the operation may be lined-out. Generally, for short runs, two eight hour shifts may be required. The system may be operated by one technician, although the presence of a second person in the vicinity may be advisable for safety reasons, under the "buddy" system. The unit will operate under automatic control for several hours or even days.

The system is provided with a detailed operating procedure, which identifies all existing valves and describes their sequence during operation. The operating procedure covers five main subsystems:

1. Catalyst or cocatalyst addition
2. First reactor (bulk, slurry, or gas-phase)
3. Slurry flashing and powder transfer to second reactor
4. Second reactor (bulk, slurry, or gas-phase)
5. Powder devolatilizing and purge column

The operating procedure for each section deals with start-up, operating cycle, shutdown, and other details.

Utility requirements from the users are 3-phase electric power, cooling water, and nitrogen.

IMPORTANT FEATURES OF XYTEL-OAKWOOD UNIT

Following are some of the most important features of the Xytel-Oakwood Continuous Bench Scale Unit. Due to the confidentiality of the design details, only general descriptions are presented.

Catalyst Metering and Control

One of the greatest engineering challenges for the satisfactory operation of a small pilot plant is the accurate and consistent feeding of the catalyst components. Z/N (Ziegler-Natta) or metallocene catalysts are usually fed in suspension, whereas the cocatalyst, including any modifiers are in solutions. Due to the high activity of modern catalyst systems, only minute amounts of catalyst are required for the operation of the Continuous Bench Scale Unit. For example, a catalyst yielding 50 Kg polymer/g catalyst, needs only to be fed at a maximum rate of 0.1 g per hour.

The catalyst feeding system of the Xytel-Oakwood proprietary unit is unique, and allows the automatic, microprocessor-controlled measurement, and timely addition of the catalyst components, under the high pressure and temperature of the reactors. There is no catalyst attrition or fouling attributed to the feeding. Although the catalyst injection is necessarily pulsed at this scale, the catalyst-reactor system is set up to assure a close approach to lined-out steady state conditions for excellent commercial relevance. The system can meter the slurries, solutions, and components of typical Z/N, metallocene, and single site systems. Powder transfer and/or discharge from the reactors is timely regulated with catalyst feeding.

Catalyst suspensions or solutions are usually prepared within a drybox, in containers which are part of the catalyst feeding system. These containers are then connected under nitrogen (exclusion of air) to the polymerization unit. The various steps required for a successful transfer, while maintaining the integrity of catalyst components, is described in detail in the supplied operating procedure. The amount of catalyst/cocatalyst components may usually last up to two days. New containers may replace the used ones, without interruption of the operation. Any catalyst pretreatment or prepolymerization should be carried out separately in another facility. Feeding of the prepolymerized catalyst is done similarly to the bare catalyst.

Slurry and Gas Phase Reactor Designs

The standard configuration is based on two reactors in series, each of which can be chosen from a liquid slurry reactor design (for either bulk or hydrocarbon slurries) and an agitated gas phase reactor design. Within this configuration, most modern polyolefin processes can be simulated.

The Slurry and Gas Phase Reactors are both proven designs for the applications. Both Reactors are 10-Liter capacity, fabricated stainless steel vessels rated for 1,000 psig at 400°F with full body flange closures. The reactors both have fixed heads on a supporting stand, to which the interchangeable impellers and other internals are attached. The lower vessel body is supported on a hydraulic raising and lowering stand with a "swing out and tilt" feature for easy cleanout. The vessels' internal surfaces and attachments are polished for excellent polymer release characteristics.

Agitation is provided by custom-designed impellers driven by sufficiently powerful magnetic drives to assure the right regime of suspension, mixing, fluidization, and heat transfer. The heat transfer and mixing parameters, as well as mechanical design of the reactors and agitator systems, have been designed with proprietary software. The jackets are spiral-baffle designs.

Reactor Composition Control

Accurate monitoring and control of the monomer(s) and hydrogen composition in the reactor(s) is an important feature of the bench-scale unit. The vapor phase is sampled at a well-chosen clean location and sent to an on-line high-speed gas chromatograph (GC). The analysis is compared to a target for the selected product grade and appropriate adjustments are made to the feed rates of raw materials. Holding a target hydrogen /monomer ratio is relatively easy for a product like homopolymer. The inclusion of a second monomer makes control more challenging in the case of random copolymer.

The control methods are also able to hold a desired target composition when the unit is operated to make ethylene-propylene impact copolymer. For this product, the unit must maintain two completely different compositions in two or more reactors. Furthermore, with the periodic transfer of homopolymer precursor to the copolymer reactor, the computerized controls make adjustments to compensate for the propylene and small amount of hydrogen that are carried in the powder voids into the copolymer reactor. The successful maintenance of the target compositions provides a relevant scale-up to a commercial-size units making impact copolymer.

Full Automation for Safety, Reliability, and Data Accuracy

The standard Unit comes equipped with a fully configured Honeywell 9000/SCAN 3000 Control and Data Acquisition System. This highly reliable Control System performs all of the automated control, safety functions, start-up and shutdown, data-logging, and material balances for the Unit. The System is user-friendly and reconfigurable. The Control System and the User Interface Screens are pre-configured by Xytel to provide turnkey operation without additional configuration or programming.

In order to obtain the desired reproducible and relevant results from this pilot unit, key operating variables are controlled within narrow limits by the SCAN 3000 System. These key variables include the following: the polymerization temperature and pressure, the feed rates of catalyst components, the feed rates of raw materials, such as monomers and solvent, the reactor composition, and the mean residence time in the reactor. The result of these controls is a steady value for the polymerization rate, an important variable for design and scale-up.

Operating control by the Honeywell system assures that it is safe, easy to operate, and that the data acquired during lined-out operation are accurate for catalyst evaluation as well as being relevant for design scale-up. The controls allow essentially hands-free programmed operation and data acquisition.

APPLICATIONS TO POLYOLEFINS R&D

The Xytel-Oakwood Continuous Bench Scale Unit (CBSU) is the ideal unit for a "second stage" evaluation of polyolefin catalysts. In catalyst R&D, most of the formulations prepared in the laboratory are tested first in batch units, for a quick indication of their performance level. Some of the most attractive catalyst systems are then selected for evaluation under a continuous mode, to determine such important catalyst performance characteristics as steady-state kinetics, attrition properties, hydrogen response, suitability for the process, commercially relevant product performance, etc.

The second stage testing using the CBSU may also be regarded as necessary for tailoring the catalyst system to a company's process requirements. Part of the process scale-up effort includes the response of the catalyst system to changes of various process conditions such as pressure, temperature, residence time, residence time distribution (RTD), reactor agitation (even at idle conditions), catalyst/cocatalyst ratios, including level of modifier or a second alkyl. Although partial answers to these effects may also be obtained from multiple runs in batch units,

there are other studies such as the hydrogen response that can only be performed under a continuous mode. All these studies are performed effectively, safely, economically and in relatively short time through the use of the CBSU unit.
The CBSU may be considered as the best available platform for the initial production of commercially relevant polymers for internal evaluation. These materials are capable of establishing improvement trends in polymer product properties, which should be further verified with samples from large pilot plant and commercial plant production. Gas composition within the reactor remains constant using a high speed GC. Metering of catalyst components and feedstocks is very accurate. Exact reactor conditions are maintained through automated controls. The reproducibility of target properties of new materials produced by the CBSU is very good.

Many polyolefins such as homopolymers and random copolymers may be produced in a single reactor system. Others, such as polypropylene impact copolymers require multiple reactors in series, the initial reactors for the homopolymer and the final reactors for the rubber components. Considerable engineering challenges affecting product properties are faced during product transfer from one reactor to another, including ethylene contamination in the first reactor and hydrogen leak in the second. The powder transfer system of CBSU is efficient and solves these problems.

Hydrogen response of the catalyst system is a very important operating parameter. Although there are differences in hydrogen response within the two main types of catalysts (Z/N or metallocenes/single site), usually metallocenes require much less hydrogen than their Z/N counterparts, for products of equal Melt Flow Index (MFI). Dilution of hydrogen as a mixture with nitrogen increases the accuracy of hydrogen addition, needed for the production of target MFI polyolefins, using either Z/N or metallocene/single site catalysts. Needles to say, such operation is not possible in batch reactors.

Catalyst Evaluation, Kinetics and Yield

Many investigators in the field of polyolefins have claimed, with good justification, that the catalyst is the process. By this claim, it is meant that all of the important phenomena of heat and mass transfer as well as polymerization kinetics that occur are essentially those that occur on a microscopic scale on or inside the supported catalyst and the associated polymer particle (20 to 300 micron diameter). The kinetic behavior of a candidate catalyst can be evaluated simply by providing a reaction environment in which the growing particles are free from hindrances to these processes of heat and mass transfer. A batch reactor is acceptable to perform this kind of kinetic evaluation. Of course, the experimental procedure for batch must be carefully planned to eliminate or at least minimize, the many artifacts that arise from the abrupt dynamics during startup and shutdown. A batch reaction is particularly well-suited to measure and characterize the profile of catalyst activity vs. time common to all polyolefin catalysts.

However, a continuous rather than a batch reaction is required to evaluate the capability of a catalyst to make a commercial grade of resin having desired physical properties. Commercial processes are nearly all continuous. It is the interaction of a catalyst's activity/time profile with the reactor's Residence Time Distribution (RTD) that can have a dominant influence on the physical properties of the resin. The batch reactor cannot duplicate the activity/RTD interaction of a continuous reactor. This interaction can significantly reduce the yield or productivity in mass of polymer made divided by catalyst fed. Catalyst productivity has a direct effect on the cost of using a candidate catalyst per mass of resin. By way of example, resins made with two reactors in series (e.g. copolymers using propylene and ethylene) have properties that are very dependent on this activity/RTD interaction.

In summary, physical properties, catalyst productivity and economics are evaluated accurately only by tests in a continuous mode. The bench-scale continuous pilot plant provides a platform in which to perform these tests in relevant, cost-effective way.

Process Scale Up

The value of a batch reactor is almost solely limited to the preliminary or screening evaluation of catalyst candidates. A batch reactor is one in which all elements of fluid have the same residence time -- a situation that differs completely from the continuous reactor RTD. Given that commercial reactors are usually continuous, the operating data critical for process design must be acquired from run campaigns in a continuous pilot plant in order to have any relevance for scale-up.

The scale-up of a design concept requires a strict correspondence between the important process operating parameters for each scale -- such items as temperature, pressure and all reactant compositions, as well as the RTD for fluid elements in the reactor. For polyolefins made with a supported catalyst, it is well-accepted that the microscopic catalyst/powder particles are the location of the important processes -- "the catalyst is the process". What this means is that heat transfer and mass transfer issues pertaining to a single growing powder particle are the ones that are crucial for design and operational relevance. The particles must be kept at the target temperature and supplied with the target monomer composition. For scale-up relevance, it is necessary only to duplicate the environment that the growing particles see. It is not necessary to duplicate the geometric factors in scale-up.

One specific, and common, example of this scale-up relevance is the dilemma posed by a large-scale fluidized bed reactor. How are the scale-up data to be acquired on a bench scale? It is very costly to duplicate the gas-circulation blower and peripherals on a bench-scale. In fact, the investigator is forced to use a blower that may be an order of magnitude too large a capacity. However, this sort of geometric duplication is simply not necessary to obtain scale-up data from a very small lab unit. The key to this dilemma is to duplicate only the parameters that are critical: T, P, composition, RTD *and* another one -- the "mixedness" of the fluids in the reactor. The materials in a large fluid bed are typically very well-mixed. A small gas-solid reactor can use a mechanical agitator to achieve the desired mixedness without the cost and complexity of a gas-fluidized reactor bed. The bench-scale pilot plant relies on exactly this kind of agitation to be well-mixed.

Producing Commercially Relevant Resins

The Continuous Bench Scale Polyolefins Unit is designed to operate in a dependable, reproducible continuous mode. It is believed to be the smallest-capacity commercially available continuous polyolefin pilot plant. Multiple product grade transitions may be scheduled during a single run campaign. Figure 2 shows a simplified block flow diagram of the pilot unit configured to make ethylene-propylene (EP) impact copolymer using two reactors in series: the first one liquid pool slurry, the second one gas-phase.

The reproducible production of a resin having an accurate composition and melt flow rate is an important feature of the Unit. In contrast to a batch polymerizer, this continuous unit produces a resin that has the same residence time distribution (RTD) in each reactor that is typical of the corresponding full-scale commercial reactors. Thus, the physical properties of the polyolefin are expected to be essentially the same as the properties that would be achieved in a full-scale plant.

Polyolefin catalysts, whether Z/N or single-site, typically experience a decay in polymerization activity with time. Given the relevance of the RTD in the CBSU unit vs. a plant, catalyst evaluation is expected to be reliable -- such features as the activity, productivity, and comonomer incorporation. Both the catalyst and cocatalyst are metered under exacting conditions by a proprietary system. The result is a very smoothly lined-out reaction at a narrowly controlled temperature. This also provides relevant operating data for scale-up. The smooth operation makes it possible to use feedforward control of the hydrogen used to maintain a target resin melt flow rate.

Testing Melt Flow Index Response

Control of Polymer MFI (Melt Flow Index), or for polypropylene MFR (Melt Flow Rate), is among the most important parameters of any polyolefins process. MFI, a measure of polymer rheology, is a defining commercial product property relating to the molecular weight. MFI is affected by the partial hydrogen pressure in the process and by the type of catalyst and/or modifiers used. Even within the same family of catalyst (Z/N or metallocenes/single site-SS) there may be significant differences in hydrogen response. Usually Z/N types require higher hydrogen concentrations, whereas the hydrogen level needed with metallocenes and other SS's to produce similar MFI products to those from Z/N may be minuscule. This fact is generally regarded as an advantage of metallocene and SS catalysts, because it allows greater monomer and coolant concentrations, with ramifications in overall process efficiency and productivity.

Needless to say, the effects of catalyst hydrogen response on polymer product properties and process efficiencies could only be studied in a continuous system such as the CBSU, where the hydrogen level in the reactor(s) is automatically monitored and controlled. Further, grade transition is usually production of a higher or lower MFI product. As indicated elsewhere in this report, product transition constitutes one more application of the CBSU.

SUMMARY

The Xytel-Oakwood Continuous Bench Scale Polyolefins Unit effectively bridges the gap that exists between the commonly used Lab-scale Batch Units and large-scale Pilot Plants. It provides the type of commercially relevant information and products which cannot be obtained in a Batch Unit, and are expensive to obtain in a large-scale Pilot Plant. Many specific features contribute to this capability, including a highly accurate means of catalyst addition under pressure, proven liquid slurry and gas phase reactor designs, powder transfer between reactors and to the purge column, carefully designed reactor composition and variables control, and full automation. These features, and others not covered here, allow the Unit to very effectively deal with the applications in polyolefins R&D of catalyst evaluation, kinetics, and yield; process scale-up data; the production of commercially relevant resins; and testing melt flow index response.