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Non-confidential status report

Novel Technology Breakthrough Process for PTA Manufacture

Reducing capital expenditure with 50% and total
production costs with 20%

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INTRODUCTION

PDC is a privately held company headquartered in Breda with additional offices in Dortmund and San Diego. The company employs professionals who are experts in physical properties, reaction kinetics, reactor selection, separation technology and energy audits. PDC is a leader in the field of conceptual process design, process optimization, energy efficiency and energy benchmarking.

In 2003 PDC started the development of new purified terephthalic acid (PTA) technology in collaboration with Reaction Design, headquartered in San Diego. Herman De Meyer, originally with Reaction Design and now a consultant to PDC, worked on the reaction chemistry and catalyst design using molecular modeling tools and is a co-inventor of the technology. Jo Sijben of PDC developed the conceptual process design based on physical property modeling and Aspen Plus process simulations and is a co-inventor of the technology. Third parties (Delft University of Technology and Bayer Technology Services) were involved in the development and testing of the catalyst.

The novel catalyst and technology have been filed in two patent applications:

1. Herman De Meyer and Johannes Sijben, Process Design Center, "Catalyst and Method for Preparing Aromatic Carboxylic Acids", WO 2006/068471 A1, December 20, 2005.
2. Johannes Sijben and Herman De Meyer, Process Design Center, "Process for Preparing Aromatic Carboxylic Acids", WO 2006/068472 A1, December 20, 2005.

In 2005, Reaction Design and PDC agreed to make PDC solely responsible for any further development and marketing of this new PTA technology. Currently, PDC owns 75% of the technology and Reaction Design owns 25%. PDC is focal point for making all decisions regarding future development and licensing of the technology.

STATE-OF-THE-ART PTA TECHNOLOGY BENCHMARK

In order to establish a benchmark for current state-of-the-art PTA technology, PDC estimated yields and energy consumptions on the basis of published reports of BP's Geel PTA process technology as well as other published literature, including IFP process publications. For a 350 kta size grassroots plant with a US Gulf coast location, the estimation yielded a total capital investment of \$161 million and a total production cost of \$680/ton PTA in 2003 dollars.

In reviewing the state-of-the-art PTA technology benchmark design, it was observed that reducing capital cost by 50% has significant impact on PTA production cost. Therefore, reducing the capital cost of a PTA unit was one of the main goals to develop improved PTA process technology. It was also recognized that a large amount of the production costs are associated with air compression, the reactor overhead system, and separating acetic acid from water. Several key problems were identified with the current PTA technology: 1.) use of acetic acid as solvent which is corrosive and expensive to separate from water; 2.) use of bromide which is highly corrosive; and 3.) precipitation of TA in the oxidation reactor, resulting in the inclusion of 4CBA in TA crystals and the need for an expensive hydrogenation process.

PROPOSED PTA TECHNOLOGY

In order to overcome the identified problems with current PTA technology, PDC developed a process design based on the use of a heterogeneous oxidation catalyst operated with all of the terephthalic acid (TA) dissolved in paraxylene. The advantages of this methodology are the avoidance of entrapment of 4CBA in the TA crystals, the relatively easy separation of water (from paraxylene), and a reduced corrosion since the technology does not rely on the use of acetic acid and inorganic bromide.

Using the same cost estimation methodology that was used for the conventional BP design benchmark, the proposed process design reduces capital cost by 50% and total production cost by 20%.

Oxidation Catalyst - The heterogeneous catalyst was designed using molecular modeling tools to develop simulations of Co/Mn complexes in zeolite structures. The proposed catalyst consists of an active μ_3 -oxo-bridged Co/Mn cluster complex encapsulated in a nanoporous zeolite with a Si/Al > 8. Coordinating ligands consisting of pyridine or pyridinic acids are employed. While the use of CoMn₂ oxo clusters were previously reported to oxidize paraxylene to TA in high yield when operated with acetic acid and HBr, these "neat" catalyst clusters are unstable when the Co changes oxidation state. By encapsulating these CoMn₂ oxo clusters inside a zeolite structure, the Mn helps the Co cycle between oxidation states while maintaining activity. Bromo anthracenes (such as 9,10 dibromo anthracene) can be used as effective

initiators (promoters) for the oxidation reaction by converting Co(III) to Co(II). From the molecular modeling results it follows that the proposed heterogeneous catalyst will have high activity (higher than the conventional homogeneous Co+Mn+Br catalyst), with high selectivity, and low production of chromophores (colored by-products) when operated with all of the TA in solution. The catalyst is designed to operate at temperatures $>200^{\circ}\text{C}$. The high temperature is required to oxidize the second methyl group of paraxylene.

Process Technology - PDC designed the TA process technology on the basis of full-liquid operation of the reactors, keeping all components (including TA) dissolved in the paraxylene solvent. The solubility of water in paraxylene and of TA in paraxylene/water mixtures was estimated using a modified Redlich-Kwong-Soave equation of state with a fitted γ -model to extrapolate known experimental data to the higher temperature and pressure conditions. Cloud point measurements of water in paraxylene have been performed by a German company, which confirmed the solubility estimates up to 180°C . It is not believed that TA and CO_2 will influence the solubility of water in paraxylene very much. Because water will associate with TA more than paraxylene, it may influence the local composition and lead to a TA solubility, which is actually higher than predicted. All of the oxygen will be soluble in the solvent at the proposed operating conditions in the oxidation reactors.

Based on the solubility estimates, a first liquid-phase oxidation process was designed with four adiabatic fixed-bed reactors in series. The inlet to the first reactor is at 240°C while the outlet of the final reactor is 300°C , resulting in a 60°C adiabatic temperature rise. The reactors are operated at 50 bar to prevent the formation of a separate vapor phase. Since the process doesn't use inorganic bromide or acetic acid, 316SS clad was selected as the construction material for the reactors.

The oxygen feed (95% O_2 + 5% N_2) could be added through any suitable device, which allows dissolving the oxygen into the solvent without formation of a vapor phase or without formation of a vapor phase with a composition within the explosion limits. For example, the oxygen could be introduced by some type of suitable membrane that would allow the oxygen to diffuse and dissolve into the solvent.

The reactors operate with a low per-pass conversion of ca. 1.5% (0.4% per reactor), resulting in a 15°C temperature rise per reactor. The molecular modeling results show that paraxylene will fully react in the zeolite cage to form TA before diffusing back into the bulk liquid phase.

The patent applications provide graphs of TA concentrations and TA solubilities plotted against temperature and water concentration, which show how the process is designed to keep all of the TA dissolved in the solvent while flowing through the oxidation reactors. After leaving the reactors, the pressure is reduced in a flash drum, allowing the TA to form solids which are then separated and dried. Most of the recovered mother liquid is then recycled back to the first oxidation reactor, less whatever purge is required to maintain product quality. Water formed during the oxidation reaction is removed as vapor from the flash drum, condensed and decanted from the paraxylene solvent. Some of the water is returned to the oxidation reactor to maintain the desired water concentration in the reactor feed stream. Energy recovered from the overhead condenser above the flash drum can be used to reheat the recycled solvent, thereby minimizing the need to supply additional energy to the process.

For the proposed process, PDC estimates a total capital investment of \$79m (51% reduction) and a total production cost of \$531/ton PTA (22% reduction). This assumes the overall yield of paraxylene to TA and selectivity of paraxylene to CO_2 are the same as for a conventional PTA process and no additional product purification is required. In preparing these estimates, it is assumed that the amount of paraxylene conversion to CO_2 and water is the same as that estimated for the conventional process.

CURRENT STATUS OF TECHNOLOGY DEMONSTRATION

PDC worked with Koos Jansen (retired) and Paolo Pescarmona (post doc) at Delft University to prepare and initially test the catalyst. Although the researchers at Delft successfully prepared the heterogeneous catalyst as designed, they were unable to conduct suitable experiments to test the catalyst at the desired reaction conditions. Rather, they were limited to operating at 190°C using air instead of pure oxygen for safety reasons and an autoclave that operated with a separate gas phase above the reaction liquid.

Also other research facilities have not been able to test the catalyst at the desired reaction conditions. So far, experimental work neither proved nor disproved the effectiveness of the catalyst for the proposed oxidation process.