

# PERP Program – Vinyl Acetate New Report Alert

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Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a new report, *Vinyl Acetate (05/06-1)*. To view the table of contents or order this report, please click on the link below:

http://www.chemsystems.com/search/docs/toc/0506\_1\_toc.pdf

### Overview

Vinyl acetate monomer (VAM) is a highly versatile and important intermediate used in the production of a variety of polymers (e.g. polyvinyl acetate, polyvinyl alcohol, polyvinyl butyral, and polyvinyl formal) that are used in many industrial and consumer products.

Global production of VAM reached almost 4.9 million metric tons in 2005. About 27 percent of VAM production is currently controlled by Celanese. Lyondell, DOW, Dairen, DuPont, and BP all fall in the 5-8 percent range. There are, however, many producers with smaller capacities. Regardless of the individual producer's capacity, approximately 80 percent of these production plants have been in operation for more than 25 years, and some continue to use older process technology that utilizes acetylene feedstock, not ethylene.

Due to inherent technological characteristics, VAM manufacturing processes utilizing fixed bed reactors have some limitations on operating reliability and expansion capability. Considering the relative old age and technology of most plants, technological innovations, which allow for improvements in operating costs and reliability and allow for expansion capability, to satisfy market demand as needed and to effect economy of scale, are no doubt critical success factors for the VAM industry.

Opportunities also exist for the participants in the industry to accomplish low-cost-base manufacturing via effective optimization of the acetyls/vinyl acetate value chain. Effective upstream integration with the production of low cost acetic acid and/or downstream integration with the manufacturing of polyvinyl acetate and polyvinyl alcohol can benefit manufacturing efficiency and enhance market leverage throughout the value chain.

The commercial vinyl acetate (VAM) manufacturing process has gone through several stages of revolutionary and evolutionary changes. The time line of commercial VAM process development is shown in Figure 1.









The industrial manufacturing of VAM was first developed by Wacker via the vapor phase reaction of acetic acid and acetylene during the early 1930s. Virtually all VAM was produced by this technology until the early 1960s when the advent of selective transition metal oxidation catalysts enabled the replacement of acetylene by ethylene as the feedstock. The ethylene based routes to VAM production moved to the forefront because of the lower raw material cost, which translated into lower cost product.

In the early 1960s, several liquid phase ethylene based production processes were developed and commercialized. Unfortunately, all of the liquid phase VAM plants were shut down between the late 1960s and the early 1970s due primarily to the unexpected chloride corrosion problems that necessitated expensive equipment modifications.

The chemistry of vapor phase ethylene acetoxylation to vinyl acetate was discovered around 1960. In less than a decade, fixed bed, vapor phase ethylene acetoxylation VAM manufacturing became the process of choice.

BP and Celanese, respectively, announced their new proprietary VAM processes, the Leap Process in late 1998 and the VAntage Process in mid 2001, to further improve the ethylene acetoxylation process.

VAM process technologies have been the subject of several previous PERP Reports: Vinyl Acetate, 00/01-3, February 2002 *Fluidized Bed Vinyl Acetate Process*, 98/99S3, February 2000; Vinyl Acetate, 96/97-5, June 1997; and Vinyl Acetate, 91-10, October 1992. In this report, both the acetylene-based and the ethylene-based commercial VAM technologies are reviewed. The latter include the Leap Process and the VAntage Process

Developing processes based on cheaper ethane, rather than ethylene, as feedstock are also discussed.

## Technology

The reaction mechanism in this process is not as simple as would be suggested by the balanced equation:

 $CH_2=CH_2 + CH_3COOH + \frac{1}{2}O_2 \longrightarrow CH_3COOCH=CH_2 + H_2O + Byproducts$ 

 $\Delta$  H = -43.33 kcal/gmol at 160°C

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but rather depends on a variety of factors including:

- The coordinating capability of Pd(II)
- The ability of acetic acid or its salts to reoxidize Pd(0) to Pd(II)

Owing to corrosion problems, both ICI and Celanese closed their liquid phase ethylene oxidation plants by 1970, and the gas phase process, which avoided corrosion problems, became the process of choice for VAM production. Stainless steel construction is adequate, and corrosion is minimized because of the absence of chloride ions (the liquid phase process used palladium chloride catalyst).



The vapor phase process can be operated anywhere in the range of 1 to 10 atmospheres and 120 to 200°C. For commercial reasons the range of 4-9 atmospheres and 150-180°C is preferred. There are economic factors behind the choice of these conditions. First, operating at higher temperatures allows the exothermic heat of reaction to be used to generate steam, subject to considerations of selectivity and life span of the catalyst employed. Next, the pressure is raised as high as possible, consistent with the reactor temperature, while maintaining a safe distance from the feed mixture dew point. Higher pressures increase the productivity of the catalyst, decrease the gas recycle energy requirements, and aid in the recovery of product from the reaction gases.

Typical gas-phase, ethylene-based VAM processes achieve an average selectivity based on ethylene of 91.5 percent across the reactor and 88 percent across the plant. The average selectivity is based on results obtained during 70 percent of the service life of a catalyst charge. The corresponding average selectivities across the plant for acetic acid and oxygen are 97 percent and 64 percent, respectively.

Optimization of the catalyst and process can produce an overall plant yield of 92 percent based on ethylene, which implies a selectivity across the reactor of 94-95 percent.

The catalysts used in this process are manufactured rather simply, but their performance has undergone dramatic improvement during the commercial life of the process. The quoted productivity of the catalyst has increased from 150 to 250 grams of VAM per liter of catalyst per hour to 700-1,200 grams. The essential catalyst ingredient is palladium, but cocatalysts such as gold are also employed.

Many companies and research institutes have been working to improve the conventional vapor phase ethylene acetoxylation VAM process. Two companies, BP and Celanese Chemicals, have succeeded in the development of VAM technologies that overcome some of the inherent disadvantages of the conventional fixed bed process.

BP's proprietary VAM technology, the Leap Process, utilizes a fluid bed reactor system to overcome some of the disadvantages inherently associated with the fixed bed operation mentioned above.

#### **Economics**

Stand-alone and integrated production economics for vinyl acetate manufacture are presented in the report for a conventional VAM process, BP LEAP process and Celanese's Vantage process. Both the BP and Celanese process technologies show a modest improvement over conventional technology. Cost of production assessments for acetic acid using conventional methanol carbonylation and state-of-the-art BP Cativa and Celanese Acid Optimization processes are also presented.

Owing to the rapidly growing use of acetylene in China to produce vinyl chloride monomer, we have explored the use of coal-based acetylene to make vinyl acetate in China. Economics of a notional 450 million pound per year acetylene-based VAM plant in China shows that Chinese VAM based on acetylene can be competitive in some world markets, even after allowing for shipping and tariffs.



The following cost of production analyses are given in this report:

- Acetic acid via conventional methanol carbonylation (200,000 metric tons/yr)
- Acetic acid via BP Cativa process (500,000 metric tons/yr)
- Acetic acid via Celanese AO Plus process (500,000 metric tons/yr)
- Vinyl acetate via conventional fixed bed vapor-phase ethylene acetoxylation (200,000 metric ton/yr) with acetic acid at market price
- Vinyl acetate via conventional fixed bed process (200,000 metric tons/yr) with acetic acid at cost plus 10% ROI
- Vinyl acetate via conventional fixed bed process (200,000 metric tons/yr) integrated with a proportionately-sized methanol carbonylation plant
- Vinyl acetate via BP Leap process (250,000 metric tons/yr) with acetic acid at market price
- Vinyl acetate via BP Leap process (250,000 metric tons/yr) integrated with BP Cativa acetic acid process
- Vinyl acetate via BP Leap process (385,000 metric tons/yr) integrated with BP Cativa acetic acid process
- Vinyl acetate via Celanese Vantage process (228,000 metric tons/yr) with acetic acid at market price
- Vinyl acetate via Celanese Vantage process (228,000 metric tons/yr) integrated with Celanese AO acetic acid process
- Acetylene via calcium carbide process (68,000 metric tons/yr), Chinese location
- Vinyl acetate via acetylene/acetic acid addition (200,000 metric tons/yr), Chinese location

## **Commercial Analysis**

Vinyl acetate monomer is a key intermediate in a wide range of end products. Polyvinyl acetate (PVAc), used mainly for adhesives, accounts for about half of VAM use. Polyvinyl alcohol (PVOH), which is used for textiles, films, adhesives, and photosensitive coatings, consumes about 28 percent of VAM produced. PVAc and PVOH together consume more than three quarters of VAM produced.

Other uses of VAM include ethylene vinyl acetate (EVA), vinyl acetate ethylene (VAE), polyvinyl butyral (PVB), ethylene vinyl alcohol (EVOH), polyvinyl formal (PVF), and vinyl chloride-vinyl acetate copolymer. EVA, which has less than 50 percent vinyl acetate in content, is mainly used for films and wire and cable insulation, accounting for about 7 percent of VAM use. Major applications for vinyl chloride-vinyl acetate copolymer include coatings, paints, and adhesives, representing



about 5 percent of VAM. VAE, which contains more than 50 percent vinyl acetate, is primarily used as cement additives, paints, and adhesives. PVB is mainly used for interlayer in laminated safety glass, coatings, and inks. EVOH is used for barrier films and engineering polymers. PVF is used for wire enamel and magnetic tape.

Regional distribution of VAM capacity is illustrated in Figure 2. About 60 percent of VAM capacity is currently located in developed regions, with 30 percent in the United States, 17 percent in Western Europe, and 12 percent in Japan. Other Asia, excluding Japan but including China, Taiwan, and South Korea, accounts for 34 percent of capacity. All world VAM capacity presently utilizes oxygen-based acetoxylation of propylene, with the exception of the Celanese unit in France and eleven in China that use acetylene as feedstock. Nexant forecasts that the Middle East, specifically Saudi Arabia, will develop a VAM supply position by 2010.



Figure 2 VAM Capacity by Region, 2005

In Figure 3, global VAM capacity is parsed by facility ownership. Celanese is the leading VAM producer, with 27 percent of capacity, following its acquisition of Acetex. Lyondell, which acquired Millennium Chemical in late 2004, is presently a distant second at 8 percent of capacity. Dairen has a 350 KMTA unit under construction in Mailiao, Taiwan for start-up in 2007. At that time, its





global capacity share will jump from 6 percent to 11 percent. Dow, DuPont, and BP are all in the 5 to 6 percent range of global capacity.

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