

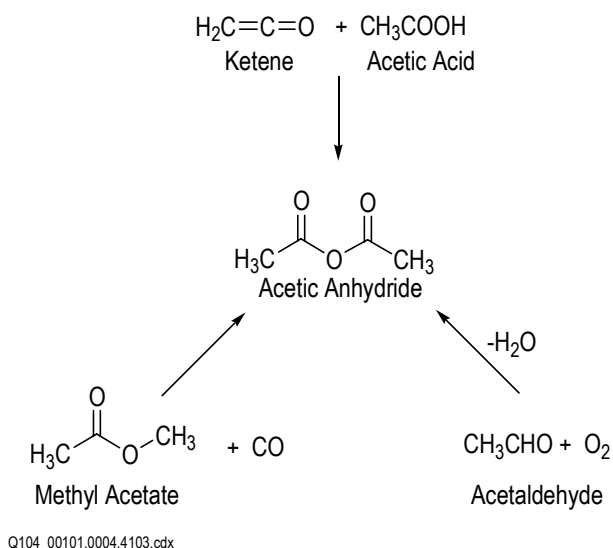
## PERP Program – New Report Alert

June 2004

Nexant's *ChemSystems* Process Evaluation/Research Planning (PERP) Program has published a new report, *Acetic Anhydride/Cellulose Acetate (03/04S1)*.

### Processing Routes to Acetic Anhydride

There are three commercial routes to acetic anhydride. Two routes, the ketene-based process and the methyl acetate carbonylation route, have emerged as the major economic processes. An earlier commercial technology, the liquid phase oxidation of acetaldehyde, has been replaced with the above mentioned two other processes (one major plant known to be operating using acetaldehyde technology recently shut down). Today, virtually all new commercial plants utilize the low-pressure methyl acetate carbonylation technology.



The ketene route is based on the catalyzed thermal dehydration of acetic acid to ketene, and the subsequent reaction of the ketene with more acetic acid to form acetic anhydride. The ketene process is characterized by high selectivity in the conversion of acetic acid to ketene (90 percent) and in the conversion of ketene to acetic anhydride (100 percent).

Methyl acetate carbonylation involves the reaction of methyl acetate with carbon monoxide. The former is made in an esterification reaction using methanol and recycled acetic acid. As with methanol carbonylation, a number of metal catalysts are active for catalyzing the carbonylation of methyl acetate to acetic anhydride. The key difference between methanol and methyl acetate carbonylation is that in the latter case, the reactor operates under anhydrous condition. The rhodium catalyst system operates with a large molar excess of methyl iodide as a co-promoter and an ionic

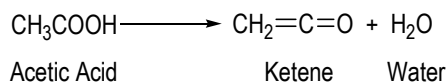
iodide salt such as a quaternary ammonium, quaternary phosphonium, or alkali metal iodide. Another difference between methanol and methyl acetate carbonylation is that in the latter case, a relatively high concentration of hydrogen is co-fed with the carbon monoxide. In the absence of hydrogen, increased levels of the inactive complex  $[\text{RhI}_4(\text{CO})_2]^-$  are observed and the carbonylation rate decreases. Introduction of hydrogen reduces the inactive complex back to the active rhodium (I) catalyst.

Plants utilizing the carbonylation technology are generally “swing” plants that can produce both acetic acid and acetic anhydride. BP Chemicals currently operates such a plant in Hull, United Kingdom. Eastman uses a similar process to produce acetic acid and acetic anhydride, based entirely on coal feedstock.

The third commercial route to acetic anhydride is the acetaldehyde oxidation process. This is conducted in the liquid phase, and can be directed by appropriate catalysts such as transition metal salts of cobalt or manganese to produce acetic anhydride.

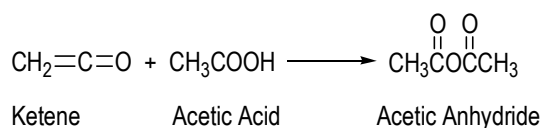
#### *Ketene Route*

In the acetic anhydride manufacturing process involving the dehydration of acetic acid via ketene, acetic acid is first dissociated into ketene and water.



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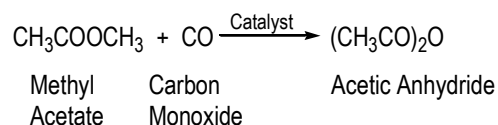
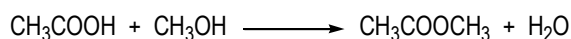
The heat of reaction is approximately 35.1 kcal/mole, and the optimum reaction temperature is in the range of 730°C to 750°C for maximum ketene yield. The reaction proceeds in the vapor phase in the presence of 0.2 to 0.3 percent triethyl phosphate. Equilibrium conversion is closely approached (85-90 percent on acetic acid). Ammonia is then injected to destroy the catalyst and to freeze the equilibrium. Selectivity to ketene is typically 90 to 95 mole percent. The gaseous ketene is removed from the heavier boiling acetic anhydride, acetic acid, and water in a system of graduated coolers. Ketene is then reacted with fresh and recycled acetic acid and converted to acetic anhydride. In this stage selectivity approaches 100 percent.



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### *Methyl Acetate Carbonylation Route*

The process technology for acetic anhydride production via methyl acetate involves the carbonylation of methyl acetate (derived from the esterification of acetic acid and methanol) with carbon monoxide. The reactions are:



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### *Rhodium Catalyzed Process*

A major development was the introduction of hydrogen with the carbon monoxide feed to reduce  $\text{Rh}^{\text{III}}$  to the activated  $\text{Rh}^{\text{I}}$  carbonylation complex. This reduction reaction minimizes the formation of unreactive  $\text{Rh}^{\text{III}}$  species that form insoluble compounds such as rhodium triiodide.

The carbonylation is accomplished in the liquid phase with a rhodium/iodide catalyst system promoted with ligands such as lithium, phosphines, or picolines. Reaction of an acyl iodide intermediate with acetate ions yields the desired acetic anhydride product.

Ethylidene diacetate is formed as a by-product.

The acetic anhydride process does not require a plant for acetic acid production. Varying quantities of acetic acid may be generated by reacting some of the anhydride made in carbonylation with some of the feed methanol to yield methyl acetate plus acetic acid.

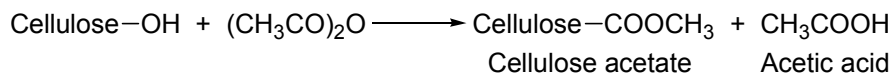
### *Nickel Catalyzed Process*

Halcon, in an effort to eliminate the use of expensive noble metal catalysts, developed a carbonylation process based on nickel catalysts at temperatures in the range of 200-300°C and pressures of up to 84 atmospheres. Eastman has published some results that demonstrate that the severity of these conditions can be significantly reduced by the use of certain promoters.

Eastman has demonstrated a system offering less severe conditions, composed of a nickel catalyst coupled with molybdenum compounds, an iodide promoter, and a phosphine. Under reaction conditions the phosphine exists largely as a phosphonium iodide, some of the phosphine remains unassociated and available to ligate to the catalytically active form of nickel preventing the formation of inactive nickel carbonyl.

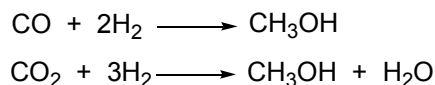
## Methyl Acetate Route to Acetic Anhydride via Coal Gasification

The chemistry for acetic anhydride production via coal is identical to that previously described, except that in the case of the actual Eastman plant in Kingsport, Tennessee, recycle acetic acid is produced in an adjacent facility where acetic anhydride is used to convert cellulose to cellulose acetate, as shown in the following equation.



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Methanol is produced within the complex from synthesis gas produced in a coal gasification plant:



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The plant consists of the following process areas:

- Coal gasification for synthesis gas manufacture
- Raw gas cleanup and separation
- Rectisol process for hydrogen sulfide removal
- Claus/Scot units for sulfur recovery
- Chemical plants to produce methanol, methyl acetate, and acetic anhydride

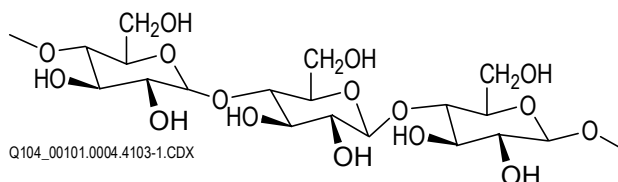
This process starts with coal, which is partially oxidized in Texaco gasifiers to produce synthesis gas, with a H<sub>2</sub> to CO ratio of about 1:1, which is purified. A portion of the syngas is separated into pure CO and pure hydrogen. The pure CO is fed to the methyl acetate carbonylation step while the pure hydrogen is combined with the other portion of the synthesis gas and converted to methanol. Part of the methanol is used to scrub H<sub>2</sub>S from the coal gasification step. The remainder of the methanol is combined with acetic acid to make methyl acetate. The methyl acetate is carbonylated to give acetic anhydride. The acetic anhydride is used to produce cellulose acetate in another process, and the resulting acetic acid is recycled to the esterification section. The acetic anhydride step of the process is catalyzed by rhodium.

The carbonylation process incorporates a rhodium salt, lithium iodide, and methyl iodide as primary catalyst components. The active catalyst form is maintained by the lithium iodide promoter and hydrogen in the carbon monoxide feed to the reaction system. Preferred reaction conditions are a temperature of nearly 190°C and a pressure of 50 bar H<sub>2</sub>/CO. The conversion of methyl acetate to acetic anhydride per pass is between 50 and 75 percent. The overall yield of acetic anhydride based on methanol is approximately 96 percent.

Small amounts of water are present in the system and some acetic acid is produced by hydrolysis of acetic anhydride. Most of the acetic acid is derived from addition of methanol to the reaction mixture. The reaction is conducted under essentially anhydrous conditions.

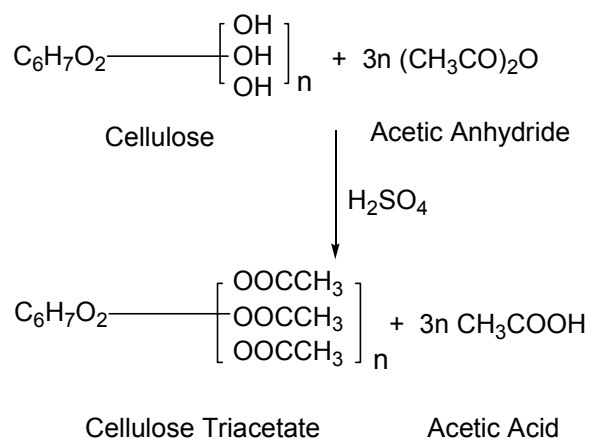
## Cellulose Acetate

Cellulose is one of nature's most abundant materials and is the key building block for most plants. The chemical structure of cellulose is shown below and is composed of repeating segments of anhydroglucose units. Common industrial sources include wood, bagasse, and sugar cane stalks.



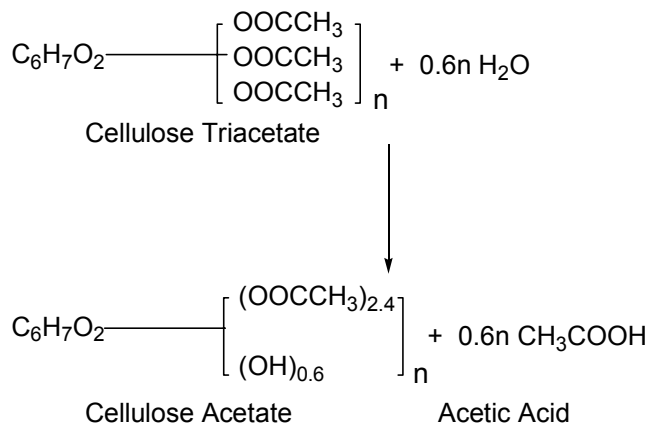
Cellulose acetate is the partially acetylated reaction product of high-purity cellulose (from wood pulp) and acetic anhydride. It is obtained by acid catalyzed hydrolysis of the triacetate to an average degree of substitution of 2.4 acetyl groups per glucose unit. Cellulose triacetate contains approximately 2.9-3.0 acetyl groups per glucose unit.

Cellulose will react under anhydrous conditions, in the presence of an acid catalyst, with acetic anhydride to form cellulose triacetate according to the following simplified equation:



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The fully acetylated cellulose triacetate is then hydrolyzed to give cellulose acetate according to the following simplified equation:



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## Economic Considerations

The report presents cost of production estimates for the ketene-route and the methyl acetate carbonylation route, each at capacities of 227 and 110 thousand metric tons per year. The methyl acetate carbonylation route shows over a 14 cent per pound advantage in variable costs on a US Gulf Coast, fourth quarter 2002 basis, more than sufficient to offset this route's somewhat higher capital-related costs.

Cost of production estimates are provided on the same basis for cellulose acetate flake and tow production at a capacity of 60 thousand metric tons per year. Net acetyl raw materials cost (acetic anhydride cost less acetic acid credit) approaches 60 percent of total raw materials cost, with cellulose making up the rest.

## Applications

Acetic anhydride is used in the manufacture of pharmaceuticals and detergents, but the vast majority, 77 percent, is used for the production of cellulose acetate flake, which is then used as the raw material for cigarette filter tow and yarn, as well as a minor amount of engineering plastics.

Acetic anhydride is a reactive chemical intermediate in the synthesis of a number of pharmaceuticals such as aspirin and paracetamol. Acetic anhydride is also used in the manufacture of the bleach activator Tetra-Acetyl Ethylene Diamine (TAED), which is used extensively in European washing powder formulations. Other acetic anhydride outlets include specialty esters such as triacetin, herbicide and pesticide manufacture, dyes, and food ingredients.

Cellulose acetate plastics in general have excellent properties. They are molded and extruded into various consumer products such as brush handles, tool handles, toys, steering wheels, and a range of other miscellaneous items. Cellulose acetates are used in lacquers and protective coatings for

various substrates such as paper, glass, metal, leather, and wood. Photographic and cinematographic film, as well as x-ray film, microfilm, and graphic film, are made from cellulose acetate. Special castings of cellulose acetate films are also used for water purification, for blood purification dialysis, for air separation, and for a wide variety of biotechnology applications.

### **Supply/Demand/Trade**

The report breaks out acetic anhydride demand by three regions. Acetic anhydride capacity is categorized by seven regions and also by three technology alternatives.

Cellulose acetate flake consumption is presented for four regions in 1997 and 2002. Breakdown of cellulose acetate regional demand into filter tow, textiles, and plastics/other is also provided.

Cellulose acetate demand is flat or declining in developed regions and growing slightly in developing regions, resulting in little overall growth. Historically, North America has exported over 200 million pounds per year of cellulose acetate flake, more than any region, but this has been declining gradually over the past few years due to increased production of filter tow overseas. China has historically imported at least half of its cellulose acetate requirements, but is planning to expand captive cellulose acetate capacity over the next few years.

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