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PERP PROGRAM

Report Abstract

Acetic Acid
PERP06/07-1

April 2009

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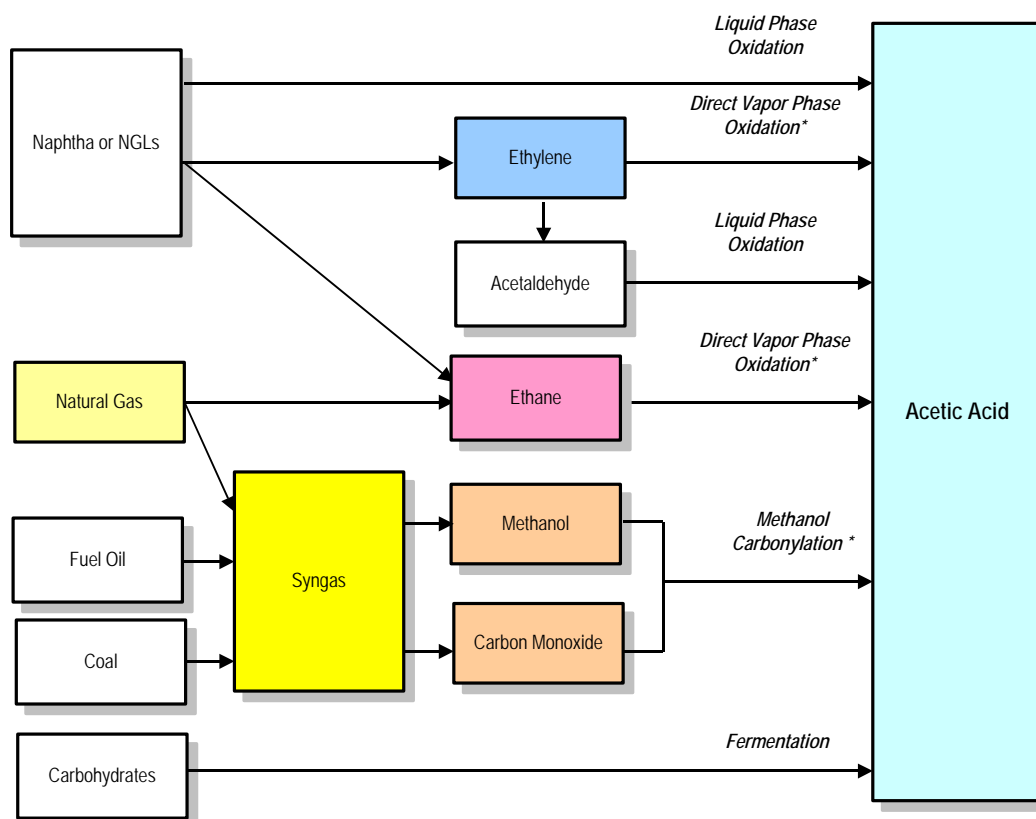
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INTRODUCTION

Acetic acid is a raw material for several key petrochemical intermediates and products including vinyl acetate monomer (VAM), purified terephthalic acid (PTA), acetate esters, cellulose acetate, acetic anhydride, monochloroacetic acid (MCA), etc. The process technology for acetic acid is perhaps the most interesting and diverse of all of the major industrial organic chemicals. No other large volume chemical can claim the varied feedstocks and production approaches that acetic acid can for its commercial synthesis. As shown in the Figure below, commercially employed feedstocks include just about every known source of carbon: (1) natural gas based derivatives methanol and carbon monoxide, (2) ethylene and ethylene derivatives, (3) alkanes such as ethane, butane, and naphtha (4) syngas derived from coal, and (5) renewable natural sources. All of these carbon sources are still in commercial use for acetic acid production; however the proportion that each of these feedstocks contributes to total acetic acid production has changed over time and will continue to change.

Feedstock Choices and Process Routes for Acetic Acid Production



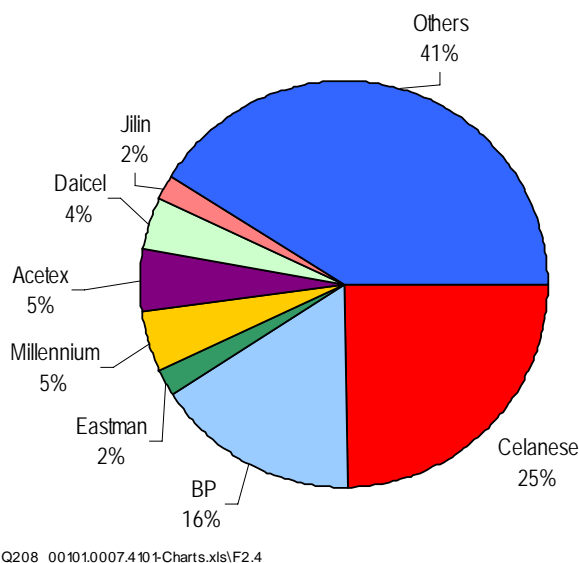
* Comparative process economics analyzed in this study

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Currently, methanol continues to be the main feedstock in acetic acid production as methanol carbonylation technology continues to be the dominant acetic acid production technology.

BP and Celanese are by far the largest producers of acetic acid in the world. Although the figure below shows Celanese as having a larger capacity share, it should be noted that BP currently has a number of new planned projects and expansions. The next tier of producers is Eastman, Millennium, Acetex, and Daicel, with each having about 2 to 5 percent of global acetic acid capacity.

World Acetic Acid Capacity by Producers, 2007



A new player to the acetic acid market will be Saudi International Petrochemical Company (Sipchem). The company has licensed Eastman's proprietary acetyl co-production technology for the production of acetic acid and acetic anhydride. This technology will be used to establish Sipchem's world-scale acetyls complex in Al-Jubail. Commercial operations of this plant are scheduled to start in 2009.

The organization for this ChemSystems report is as follows:

- Section 3 (Commercial Technologies) presents the detailed chemistry and process description for the current commercial and emerging technologies employing methanol carbonylation (Monsanto/BP, Celanese AO Plus, BP Cativa, and Chiyoda Acetica processes), direct ethylene oxidation (Showa Denko process), and direct ethane oxidation (SABIC acetic acid process via direct ethane oxidation with air or oxygen).
- Section 4 (Patent Survey and Recent Developments) presents the recent developments in acetic acid technologies and processes. This section begins with the discussion of new developments in direct ethane oxidation by BP, Celanese, and others. It is followed by a discussion of direct methane conversion to acetic acid, mainly by Natural Resource Canada. Finally, the developments of acetic acid production via biocatalysis route are also discussed.

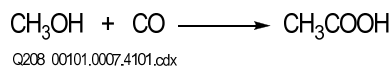
- Section 5 (Economic Assessment) presents the process economics of acetic acid technologies discussed in Section 3. Economics of methanol carbonylation, direct ethylene oxidation, and direct ethane oxidation are analyzed and compared. The effects of feedstocks, capital investment, and capacity, are examined. Additionally, acetic acid economics at a remote Middle East location using the above technologies are analyzed and compared.
- Section 6 (Commercial) presents the commercial assessment of the acetic acid market. The global acetic acid production capacity in operation at the end of 2007 is presented. The projected supply/demand balances for the global and the major regional acetic acid markets including North America, Western Europe, Japan, and East Asia are also examined.

COMMERCIAL TECHNOLOGIES

In this section, the detailed chemistry and process descriptions for the current commercial technologies employing methanol carbonylation (Monsanto/BP, Celanese AO Plus, BP Cativa, and Chiyoda Acetica processes), direct ethylene oxidation (Showa Denko process), and the direct ethane oxidation route (SABIC acetic acid process via direct ethane oxidation with air or oxygen) are presented.

Methanol Carbonylation

In 1913, BASF discovered that methanol could be carbonylated to acetic acid. The reaction takes place according to the following simple equation:



It was not until the late 1950s that corrosion resistant molybdenum/nickel alloys (Hastelloy) permitted the construction of the first pilot plant. BASF started its first methanol carbonylation plant in 1960 using cobalt iodide (CoI₂) as a catalyst.

In the 1970s, Monsanto developed the rhodium/iodide catalyst system for methanol carbonylation. In 1986 ownership of the Monsanto technology was acquired by BP, which has further developed the process. This technology features acetic acid selectivity greater than 99 percent based on methanol.

This process is discussed further in the report:

- The process developed by Monsanto/BP as discussed in this report is representative of the basic methanol carbonylation technology.
- In the 1980s, Celanese developed the proprietary AO Plus (Acid Optimization Plus), which improved the Monsanto process significantly, and is briefly outlined.
- The BP Cativa Process is discussed.

Direct Ethylene Oxidation

The production of acetic acid from ethylene via acetaldehyde intermediate is one of the earliest acetic acid technologies developed. Since acetaldehyde is usually prepared by the oxidation of ethylene, and acetic acid is made by subsequent oxidation of acetaldehyde, combining both processes into one has always been conceptually attractive to chemists. Much developmental work has been undertaken over the years to produce a simpler single stage process for producing acetic acid directly from ethylene.

This is discussed further in the report:

- Showa Denko's one step, vapor phase process for the production of acetic acid by direct oxidation of ethylene is discussed

Direct Ethane Oxidation

- SABIC Direct Ethane Oxidation to Acetic Acid process is described.

PATENT SURVEY AND RECENT DEVELOPMENTS

- A survey of patents granted to BP, Celanese, SABIC, Showa Denko, Chiyoda, Mitsubishi, and Natural Resources Canada, for acetic acid related technologies is listed in this section (by date, title, patent number for each individual producer considered).
- Natural Resources Canada's developing oxidation of methane to acetic acid process is described.
- A biocatalytic route to acetic acid being explored by Celanese in collaboration with Diversa is briefly described.
- A selective, one-step catalytic process that converts methane directly to acetic acid has also been developed by a research team at the University of Southern California (USC) and is briefly mentioned.

ECONOMIC ASSESSMENT

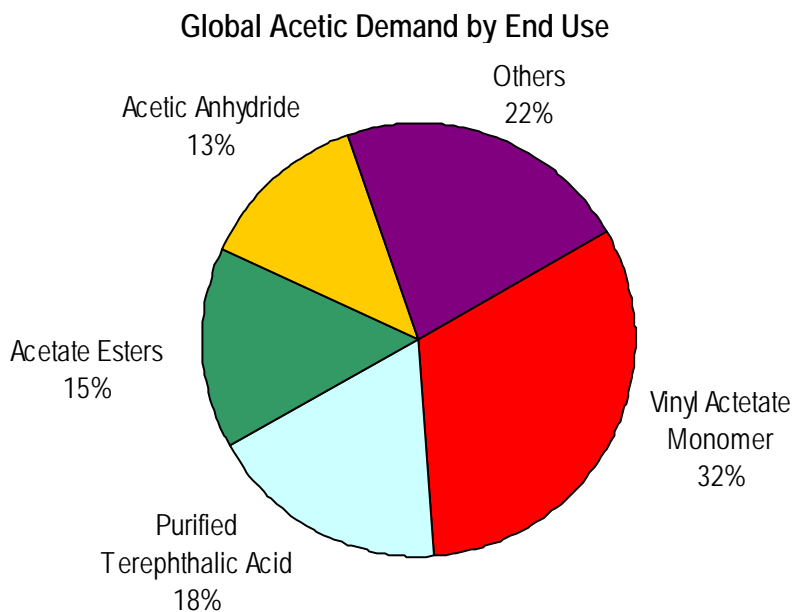
Cost of production estimates for the following acetic acid production economics at the U.S. Gulf Coast and a Middle East remote location are presented:

- SABIC Direct Ethane Oxidation with Oxygen and with Recycle.
- Effects of ethane price, effects of oxygen price, effects of capacity and effects of capital investment on cost of production are evaluated for the USGC case.
- SABIC Direct Ethane Oxidation with Air and without Recycle.
- Effects of ethane price, effects of capacity and effects of capital investment on cost of production are evaluated for the USGC case.
- Showa Denko Direct Ethylene Oxidation
Effects of ethylene and oxygen prices, effects of capacity and effects of capital investment on cost of production are evaluated for the USGC case.

- **Monsanto/BP Methanol Carbonylation Process**
Effects of methanol and carbon monoxide prices, effects of hydrogen by-product credit (in the production of carbon monoxide), effects of capacity and effects of capital investment on cost of production are evaluated for the USGC case.
- **Chiyoda Acetica Process**
Effects of methanol and carbon monoxide prices, effects of capacity and effects of capital investment on cost of production are evaluated for the USGC case.
- **Celanese AO Plus Process**
Effects of methanol and carbon monoxide prices, effects of capacity and effects of capital investment on cost of production are evaluated for the USGC case.
- **BP Cativa Process**
Effects of methanol and carbon monoxide prices, effects of capacity and effects of capital investment on cost of production are evaluated for the USGC case.

COMMERCIAL SECTION

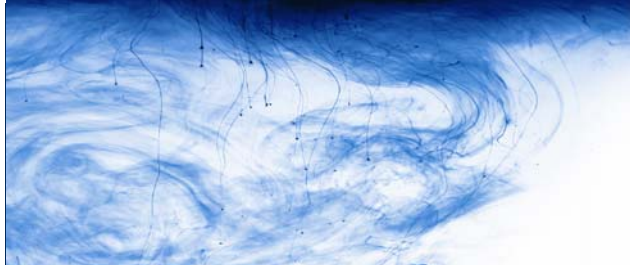
Acetic acid markets, supply and demand are discussed. As shown in the figure below, the largest, and one of the most rapidly growing end use sectors is for vinyl acetate monomer (VAM). VAM is an intermediate in the production of a range of chemical derivatives, of which polyvinyl acetate and polyvinyl alcohol are the most important. Its major end uses are in the emulsion paints, adhesives and coating sectors.



Total Global Demand: 10.7 Million Metric Tons

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- Acetic Acid Production Capacity for each of the following regions: United States, Western Europe, East Asia, Japan, South America and the Rest of the World, is tabulated by company, specific plant location and capacity; new acetic acid projects are also tabulated.
- Supply/Demand balance each of the following regions: North America, Western Europe, East Asia, Global is tabulated.
- Supply/Demand outlook is given.



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