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Green Acetyls

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Report Abstract
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Nexant

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INTRODUCTION

Generally speaking, acetyls are compounds containing the $CH_3C(O)R$ moiety where R represents an atom or group bonded to the carbonyl carbon atom. The acetyls considered in this report are acetic acid and its main derivatives (acetic anhydride, vinyl acetate monomer, ethyl acetate and butyl acetate).

Acetic acid is a multimillion ton market with strong growth potential driven by downstream industry developments in vinyl acetate, polyesters, solvents, and specialties. Acetic acid provides a chemical platform serving several value chains focused on adhesives and coatings, apparel, engineering polymers, generic pharmaceuticals, oilfield chemicals and foodstuffs.

Today, acetic acid is made in large scale mainly by methanol carbonylation, exploiting competitive sources of synthesis gas derived from natural gas and coal, with the latter focused mainly on China. Technology for downstream acetyls production is generally closely held by a few companies, in effect restricting market access, with some exceptions, as for applications like vinyl acetate and pure terephthalic acid, which are more accessible.

Acetic acid can be derived from biomass for the food industry, but this is generally restricted to low scale operations. Hence, the concept behind this study is an analysis of the conversion of biomass into acetyls exploiting combinations of commercial processes at capacities commensurate with commercial scales of biomass processing.

Nexant has examined acetyls production based on both fermentation ethanol and gasification platforms. As a platform chemical, ethanol can support ethylene production via dehydration. Combinations of ethylene and ethanol processing technologies can lead to cost effective acetyls and derivatives production, reflecting some actual commercial examples. The gasification generates syngas that can be exploited in similar manner to the coal-based acetyls operations in the United States and China.

FERMENTATION TECHNOLOGY ROUTES

The main fermentation process options considered here are first and second generation bio-technologies for the production of ethanol. First generation processes use starch and sugar based feedstocks such as corn, wheat and sugarcane, while second generation fermentation technologies can use more complex cellulose-containing bio-feedstock sources, such as wood and various agricultural wastes, for ethanol production. Fermentation routes for bio-butanol, which could be utilized for the production of green butyl acetate, are also discussed.

Ethanol can then be used as the stepping stone or platform for acetyls production. Manufacture of the primary product (acetic acid) is therefore analyzed, with particular reference to the process options that would be feasible within a green acetyls complex. Here, Nexant has considered:

- The direct conversion of ethanol into acetic acid
- Ethanol dehydration to ethylene, with conversion to acetic acid (ethanol dehydration is also necessary for integrated VAM production)

- Production of an acetaldehyde intermediate and latter conversion to acetic acid

The main direct integration opportunities within the fermentation-based green acetyls complex include:

- Ethyl acetate: this would be a logical technical option, as the necessary feedstocks (ethanol and acetic acid) are produced in this complex. In addition, the direct ethanol to ethyl acetate process, allows ethyl acetate production without the acetic acid intermediate process
- Butyl acetate, from the esterification reaction of butanol and acetic acid
- VAM is an ideal downstream product for both fermentation and gasification routes, and its various manufacturing technologies are treated in this report

THERMOCHEMICAL (GASIFICATION) TECHNOLOGY ROUTES

An alternative green route for the production of acetic acid from renewable feedstocks is through the gasification of biomass. As this approach provides a synthesis gas intermediate, it complements approaches based on coal gasification as found in China and to a certain extent natural gas reforming. Gasification provides the synthesis gas, which after suitable treatment can then be converted to methanol. The synthesis gas can also provide carbon monoxide, the other component in the carbonylation process for acetic acid production.

Gasification routes are technically feasible and provide interesting integration opportunities within a green acetyls complex. Related biomass gasification developments aimed at only heat and/or power generation are generally less demanding than chemical-producing end-uses.

The biomass raw materials that have been used for gasification include rice straw, husks of rice, sorghum, wood chips, sawdust, MSW. The gasification technology envelope can also be extended to cover waste products such as “Black Liquor”, a byproduct from the pulp and paper industry. In this report, wood chips gasification is used for the archetype techno-economics.

In addition to the biomass mentioned above for gasification, bio-methane could also be used as feed to a reformer in order to obtain syngas. Bio-methane typically contains a high concentration of carbon dioxide, resulting in relatively low energy content of the bio-methane. However, with specially-designed methane reforming catalyst systems, the high carbon dioxide content can actually benefit the syngas production process by eliminating the need for air separation, carbon dioxide removal, and syngas conditioning units. The ability to utilize carbon dioxide in feed gas, such as bio-methane, can provide higher carbon efficiency and reduce greenhouse gas emissions.

HYBRID ROUTES

Hybrid configurations (acetic acid from gasification and ethanol/ethylene from fermentation) are also possible. A possible configuration for integration opportunities of thermochemical and fermentation based routes is discussed in the report. VAM, acetic anhydride, and acetate esters are all possible candidates for downstream acetyls production, in order to add value to the biomass/ethanol available within the complex.

ACETYL INTEGRATION OPPORTUNITIES

In this Section, some process integration options within a possible Green Acetyls complex are discussed. The main acetic acid derivatives discussed here are acetic anhydride, vinyl acetate and the main esters (ethyl/butyl acetates). Reflecting current industry practice from various licensors (e.g., Kuraray, Nippon Ghosei and Sichuan Vinylon), there is scope for extensive downstream integration into polyvinyl acetate, polyvinyl alcohol, ethylene vinyl acetate copolymers (high ethylene = EVA and high VAM = VAE) and ethylene vinyl alcohol copolymers for specialty barrier films. Downstream integration does, however, lead to implications with regard recycles of acetic acid, methyl acetate, etc, but this is outside the focus of Nexant analysis in this case.

ECONOMICS ANALYSIS

This report discusses the techno-economics for the processes mentioned above. The approach used in this report has been to include all the capital costs for the various process steps as if they were stand-alone units. It is noted that considerable cost savings are possible if using an integrated approach. Such underlying factors are discussed in the technoeconomic section of this report.

Fermentation Approach

Ethanol production is the platform for the fermentation routes discussed in this report. Cost of production estimates for the following ethanol production technologies are provided:

- First generation fermentation corn-based (dry milling) route in the United States
- First generation fermentation sugar-based route in Brazil
- First generation fermentation wheat-based route in Europe
- Second generation bio-technologies from biomass

Estimates for the costs of acetyls production are then given via the following routes:

- Direct conversion of ethanol into acetic acid
- Direct ethyl acetate production from ethanol
- Ethanol dehydration to ethylene, with conversion to acetic acid
  - The ethanol dehydration step would be necessary for the following VAM production. Two main processes are discussed for the ethylene conversion to acetic acid, through acetaldehyde and via the direct Showa Denko process.

Thermochemical Approach

For the thermochemical route to acetyls from biomass, the economic potential of the following processes is analyzed:

- Gasification of biomass to syngas
- Separation of carbon monoxide from syngas for acetic acid production and to adjust H_2:CO ratio at the methanol unit with the use of the hydrogen rich stream
- Conversion of part of the synthesis gas to methanol

- Reaction of part of the carbon monoxide produced in the gasification with methanol to make acetic acid via carbonylation

Downstream Green Acetyls Production

Margins for acetic acid production reflect its status of a commodity chemical produced all around the world in large scale plants. To fully exploit the green factor of production from renewable sources, downstream integration could be vital to project implementation of the green acetyls complex. In order to add value to the green acetic acid produced via the fermentation or the gasification routes, downstream production of other acetyls could be implemented. In the following, economics for some of the usual suspects for downstream acetyls integration are reviewed:

– Acetic anhydride via the ketene route

– Acetic anhydride via methyl acetate carbonylation

– Vinyl acetate via Conventional Fixed-Bed, Vapor-Phase Ethylene Acetoxylation

– Ethyl acetate via Davy process

– Ethyl acetate via esterification of acetic acid

– Ethyl acetate using Wacker / Tishchenko process via Acetaldehyde

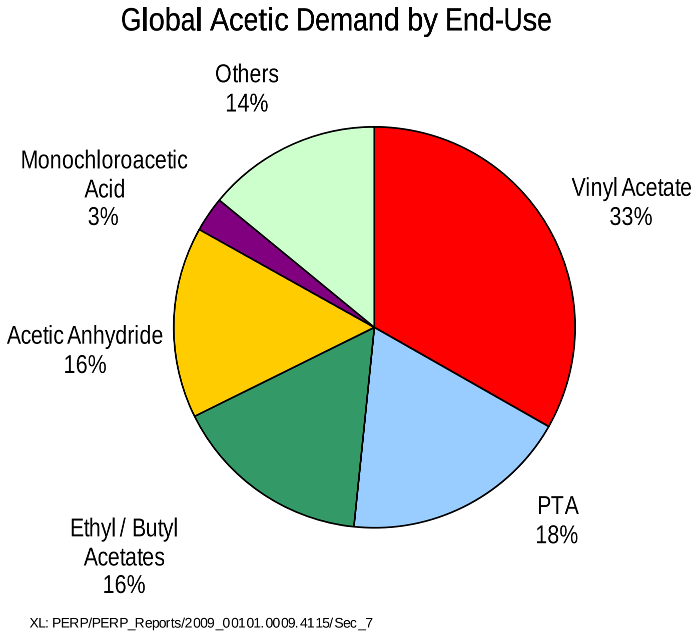
– Butanol production via Blashek et al. Advanced Continuous ABE - C Beijerinckii BA 101

– Butyl acetate via esterification for acetic acid

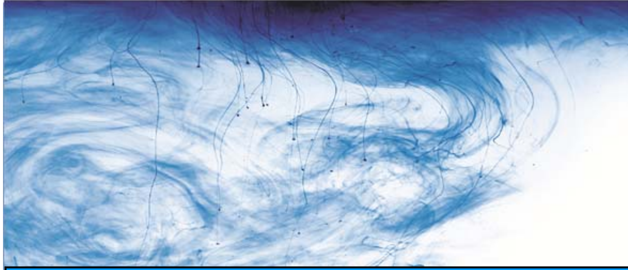
COMMERCIAL MARKET ANALYSIS

The business market value for the main acetyls discussed in this report (acetic acid, VAM, acetic anhydride and acetate esters) are discussed.

The main product among the acetyls considered in this report is acetic acid. As shown in the figure below, acetic acid is a raw material/solvent used for the production of several key petrochemical intermediates and products including vinyl acetate monomer, purified terephthalic acid, acetate esters, cellulose acetate, acetic anhydride, monochloroacetic acid, etc.



- A summary of Nexant's projected supply/demand balance for the global and the major regional acetic acid markets including North America, Western Europe, and East Asia is given
- Acetic Acid Production capacity listings detailing specific plant, location and plant capacity for North America, South America, Western Europe, East Asia, India and the Middle-Eats is given
- Main acetyls and end-use applications are briefly outlined



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