ACETIC ACID BY THE CHIYODA/UOP *ACETICA*™ PROCESS

Aspen Model Documentation

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Process Summary

This Aspen Plus model simulates the production of acetic acid by low pressure methanol carbonylation in the presence of a heterogeneous rhodium (Rh) catalyst and the promoter methyl iodide. It is intended to resemble the Chiyoda/UOP *Acetica™* process, a novel heterogeneous methanol process for the production of acetic acid. This technology is based on a heterogeneous Rh catalyst in which the active Rh complex is chemically immobilized on a polyvinylpyridine resin. In the Aspen Plus model, the plant (base case) is designed to produce 800 million lb/yr (363,000 t/yr) of acetic acid from methanol carbonylation. The process consists of both the carbonylation and purification sections. Results from the Aspen Plus simulation shows that the purity of acetic acid obtained is 98.4%. Vent gas (4,304 lb/hr) from two absorbers and heavy by-products (1,150 lb/hr) from the bottom of the heavy-ends stripper are sent to incinerator. The process also generates approximately 65,000 lb/hr of low-pressure (150 psig) steam that supplies a significant portion of the plant energy requirements.

About This Process

Current global capacity for acetic acid exceeds 6.4 million t/yr. Downstream applications for the acid are primarily as a precursor for vinyl acetate monomer synthesis, for acetic anhydride production, and as a solvent in purified terephthalic acid production. Methanol carbonylation to produce acetic acid using a homogeneous Rh catalyst accounts for more than 55% of global capacity, most of which uses the low-pressure process developed by Monsanto and licensed by BP Amoco. Together, BP Amoco and Celanese are responsible for more than 40% of the global acetic acid production. Other major players in the field include Millennium Chemicals and Acetex; several other producers have smaller capacities.

BASF introduced homogeneous methanol carbonylation in 1960. The process used an iodide-promoted cobalt catalyst and operated at an elevated temperature of 230°C (446°F) and pressure of 882 psia (60 atm). In 1970, Monsanto commercialized an improved homogeneous methanol carbonylation process using a methyl iodide-promoted Rh catalyst. Compared with the BASF process, the Monsanto process operates at much milder conditions of 150–200°C (302–392°F) and 440–880 psia (30–60 atm), and exhibits superior results with ~100% conversion of methanol and 98–99% selectivity to acetic acid. The Monsanto process was later improved by the addition of a lithium or sodium iodide promoter to enable operation in a reduced water environment. The reduced water condition mitigates the water gas shift reaction and results in fewer by-products and reduced hydrogen iodide (HI) formation. As a result, raw materials use is improved, and downstream purification costs are lower. We evaluated the Monsanto process in PEP Report 37A, Acetic Acid and Acetic Anhydride (March 1973), and PEP Review 78-3-4, Acetic Acid by Low Pressure Carbonylation of Methane (January 1980).

The use of other less expensive catalyst such as nickel, palladium, and ruthenium in homogeneous systems has also been investigated. In 1996, BP Amoco commercialized the iridium-based Cativa technology, which operates with reactor water levels that are comparable to the improved Monsanto process. The new catalyst is most effective when used in combination with lithium and ruthenium. The Cativa technology is installed in Sterling's Texas City acetic acid plant, which has a capacity of 990 million lb/yr (450,000 t/yr). This technology is also applied in a 330 million lb/yr (150,000 t/yr) plant that Yangtze River Acetyls, a joint venture of BP Amoco and SINOPEC, brought on stream early in 1999. The Cativa process is reported to give an acetic acid yield of 98% and operating savings of 10–30% compared with Rh-based systems.

Drawbacks related to reactor design and catalyst-solubility limitations have been major concerns associated with the widely applied homogeneous methanol carbonylation technology. Consequently, immobilizing the Rh complex on a support was investigated. PEP Review 88-3-4, Acetic Acid by Low Pressure Carbonylation of Methane with a Supported Rhodium Catalyst (February 1990), evaluated the process economics of a low-pressure methanol carbonylation process with a heterogeneous-supported Rh catalyst; the evaluation was based on preliminary findings

by Reilly Industries (501931) that reportedly resulted in a four-fold increase in acetic acid production rates. In 1993, Chiyoda also developed a commercial heterogeneous Rh catalyst system to producef acetic acid (560989). Recently, Chiyoda and UOP jointly developed an improved methanol carbonylation process—the Acetica™ process—that uses a heterogeneous Rh catalyst tio produce acetic acid; the process, which is available for licensing, overcomes the limitations of the homogenous technology and offers several distinct advantages (560988).

The Heterogeneous Catalyst

Acetica™ technology is based on a heterogeneous Rh catalyst in which the active Rh complex, $[Rh(CO)_2I_2]^{-1}$, is chemically immobilized on a polyvinylpyridine resin. The catalyst is tolerant of elevated temperature and pressure. Under reaction conditions, the Rh is converted to its catalytically active anionic form. The nitrogen atoms of the resin pyridine groups become positively charged after quarternization with methyl iodide. Subsequently, strong ionic bonds between the pyridine nitrogen groups and the Rh complex result in catalyst immobilization (see below). Because the ion exchange equilibrium favors the solid phase, almost all Rh in the reaction mixture is immobilized.[1]

RHODIUM IMMOBILIZATION

Vinylpyridine Resin Active form of Rh at high CO partial pressure Rh Immobilized Catalyst
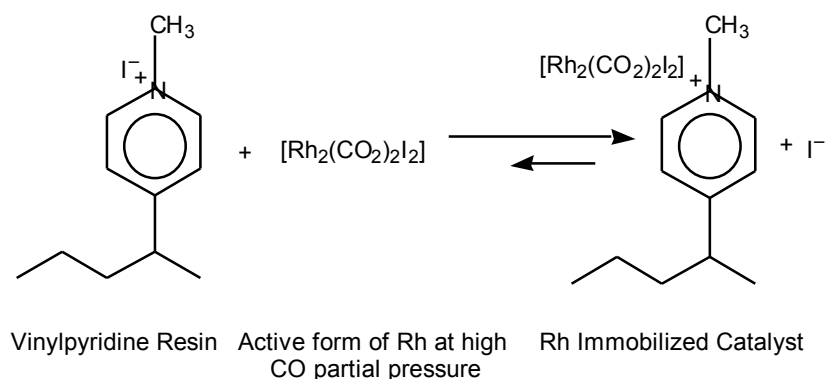
The amount of Rh in the catalyst is preferably 0.1–1 wt%, based on the weight of the insoluble, pyridine-containing polymer (560989). The catalyst is presumably used in an amount of at least 400 ppmw in terms of elemental Rh based on the weight of the solution in the reaction zone (560988). The pyridine ring of the polymer may be in the free base or N-oxide form or quartenized form. The polymer is also preferably in a spherical form, 0.25–0.7 mm in diameter (560988). Commercially available pyridine-containing polymers such as Reillex-425 (a product of Reilly Tar and Chemical) and KEX-316, KEX-501, and KEX-212 (products of Koei Chemical Co.) are suitable for the purpose of this technology.

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[1]   A commercial catalyst stability had been tested at normal operating conditions (with low water content and no Rh or resin makeup), with no decline in performance observed after 7,000 hours of operation.

Reactor Design

The *Acetica*™ process uses a bubble-column reactor (chosen for its excellent three-phase contacting) to minimize catalyst attrition and improve reactor flexibility. Methanol and CO are both introduced at the bottom of the reactor. The compressed CO is fed through a sparger ring to maximize distribution. The two feeds together with the recycle liquid (containing essentially acetic acid, water, methyl iodide, and methyl acetate) and catalyst flow up the reactor, where almost all of the CO is consumed in the carbonylation reaction. A moving impeller is not needed for mixing. The difference in density between the CO-rich riser and CO-depleted downcomer drives the circulation. The agitation provided by the high velocities of the liquid and gaseous reactants rapidly dissolves CO into the liquid phase and the system is thus not mass-transfer limited.

Unreacted CO and other gaseous by-products are vented from the top of the reactor. A portion of the reactor liquid effluent containing the acetic acid product is disengaged by gravity from the solids in the recycle slurry and sent to downstream purification. The remaining catalyst-liquid mixture is routed through the reactor downcomer, cooled, and returned to the bottom of the reactor riser to absorb the large heat of reaction and maintain circulation. The downcomer liquid is cooled with boiler feedwater, and the steam obtained by recovery of reaction heat supplies a large portion of the plant energy requirements. Catalyst retention in the reactor is almost 100%.

The reactor simplifies high-pressure operation and enables the use of low-purity CO. For low-purity CO, the reactor design pressure is increased to maintain the same level of CO partial pressure and CO conversion as achieved when operating with high-purity CO. Leakage is not a concern because no high-pressure mechanical seal is present.

Process Definition

The Aspen Plus model is developed to simulate the steady-state production of acetic acid by low pressure methanol carbonylation in the presence of a heterogeneous rhodium (Rh) catalyst and the promoter methyl iodide. The process is intended to resemble the Chiyoda/UOP *Acetica*™ process, a novel heterogeneous methanol process for the production of acetic acid. Figure 1 in the Aspen Plus model file shows the process flow diagram, which consists of both the carbonylation and purification sections.

In the Aspen model, Radfrac is used to represent the distillation columns. Due to insufficient kinetics information, Aspen Plus RYIELD reactor model is used to represent R-201. The reactor is considered to have two valid phases; vapor and liquid phases.

Before entering the carbonylation reactor, the fresh methanol (technical grade) feed is split and fed to two countercurrent absorbers. Methanol is contacted with the reactor offgas (primarily unconverted CO) in high-pressure absorber C-202 and also with light gases generated and released downstream in low-pressure absorber C-201. This absorption scheme maximizes the recovery of valuable methyl acetate and methyl iodide that would otherwise exit the system with the vent gas, causing unnecessarily high chemical consumption and yield loss. The methanol feed streams (together with the recovered methyl acetate and methyl iodide) exiting the absorbers are recombined, heated in E-202, and then mixed with the effluent from the recycle surge drum to yield the combined liquid feed stream to carbonylation reactor R-201.

Compressed, 98.6% pure CO is introduced at the bottom of R-201. The carbonylation reaction is carried out continuously at about 180°C (356°F) and 638 psig (42 atm). The heat of reaction is removed by passing the catalyst-liquid mixture through the reactor downcomer to generate low-pressure steam that supplies a significant portion of the plant energy requirements. Catalyst retention in the reactor is essentially 100%.

Most of the unreacted CO and other gaseous by-products are separated from the liquid effluent in V-201. The liquid effluent from V-201 containing product acetic acid, is introduced to crude fractionating column C-301 to recover the net acetic acid product, and to reject dissolved CO and light by-product gases into the combined low-pressure offgas line. The lighter liquids are phase-separated into aqueous and organic fractions in reflux drum V-302, with 99% of the aqueous material (mostly water) returned to the reaction system and all of the organic liquid (mostly methyl iodide promoter and methyl acetate intermediate) recycled to the reactor. The recovered net acetic product is sent to downstream purification. The portion of liquid not vaporized is mixed with other recycle streams, and returned to the reactor for absorption and recovery of the reaction heat.

The crude acetic acid is sent to the dehydration column C-302 to remove most of the remaining water and residual organic materials. Excess water is purged from the system through column C-303. The dried acetic acid is routed to refining column C-304. The product is withdrawn as a side stream below the top plate of column C-304, cooled in E-301, and sent to storage. The bottom effluent from column C-304 is sent to column C-305, where heavy by-products (primarily propionic acid) are removed in the bottom drawoff. The vapor stream from column C-305 is recycled to column C-304.

Process Conditions

Table 1 provides the list of important blocks, design bases and assumptions for the process:

TABLE 1. ACETIC ACID BY THE CHIYODA/UOP *ACETICA*™ PROCESS
DESIGN BASES AND ASSUMPTIONS
Capacity: 800 million lb/yr (363,000 t/yr)
Acetic Acid at 0.90 stream factor

References	560989, 560988, 501931
Carbonylation conditions	
Temperature, °C (°F)	160–200 (320–390)
Pressure, psig (atm)	638 (42)
Catalyst	
Support	Poly-4-vinylpyridines, Reillex™ [a] 425 N-oxide
$RhCl_3 \cdot 3H_2O$ content, % Rh metal loading	0.8
Promoter	Methyl iodide
Solvent	Acetic acid
Space time yield, mole of acetic acid/L/hr	8.0
Methanol conversion, %	~100
CO conversion, %	92
Selectivity of methanol to acetic acid, %	99
Allowance for plant losses, % of product	1
Overall plant yield based on methanol (theoretical), %	98
Column Internals	
C-201, LP Absorber	Ring packing
C-202, HP Absorber	Ring packing
C-301, Crude Fractionation Column	Valve trays
C-302, Dehydration Column Design Spec	Valve trays Mass recovery of acetic acid in the bottom stream = 78.0 %
C-303, Excess Water Column	Ring packing
C-304, Refining Column Design Spec	Valve trays Mass purity of acetic acid in the side product stream = 98.44 %
C-305, Heavy-ends Stripper	Ring packing

Components

Carbon monoxide	Raw material
N_2, H_2, CO_2, CH_4	By-product / Constituent of raw material
Hydrogen iodide	By-product
Methyl acetate	By-product
Methanol	Raw material
Formic acid	By-product
Water	By-product / Constituent of raw material
Acetic Acid	Product
Propionic acid	By-product

Physical Property Methods and Data

The Aspen Plus simulation uses the NRTL physical property method. The NRTL model can describe VLE and LLE of strongly non-ideal solutions. The NRTL model requires binary parameters. Many binary parameters for VLE and LLE, from literature and from regression of experimental data, are included in the ASPEN PLUS databanks.

Separate data sets can be used for the NRTL binary parameters to model properties or equilibrium at different conditions. The NRTL model can also handle any combination of polar and non-polar compounds, up to very strong non-ideality. Parameters should be fitted in the temperature, pressure, and composition range of operation. No component should be close to its critical temperature.

Chemistry/Kinetics

Reactors

The Aspen Plus model simulates the steady-state production of acetic acid by low pressure methanol carbonylation in the presence of a heterogeneous rhodium (Rh) catalyst and the promoter methyl iodide. The process is intended to resemble the Chiyoda/UOP *Acetica*™ process, a novel heterogeneous methanol process for the production of acetic acid.

The *Acetica*™ process operates at a moderate temperature of 160–200°C (320–392°F) and pressure of 44–880 psia (30–60 atm) in the presence of a heterogeneous-supported Rh catalyst and methyl iodide promoter in a bubble-column reactor. Even more crucial than the total pressure is the CO partial pressure of 100–425 psig (6–28 atm), which depends on CO feed purity, reaction composition, and temperature. A minimum CO partial pressure is needed to maintain Rh in its catalytically active anionic form so that it will remain immobilized. Reaction kinetics at normal operating conditions are generally governed by the concentrations of Rh and methyl iodide promoter, and by temperature. Selectivity to acetic acid is approximately 99%. Expected product yields are >99% and 92% of theoretical values, based on methanol and CO consumption, respectively.

The chemistry of the carbonylation reaction is presumably similar to the use of homogeneous catalyst in the Monsanto process; namely, the reaction proceeds by way of a five-step mechanism, proceeding through the production of the intermediates dimethyl ether and methyl acetate before the final acetic acid product is produced. The net reaction in the carbonylation of methanol to acetic acid is as follows:

$$CH_3OH + CO \longrightarrow CH_3COOH$$
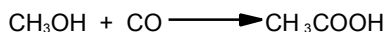
Although excess water is not required with the *Acetica*™ process for active Rh complex stability, water is present in approximately 3 to 8 wt% as a result of the esterification and etherification reactions:

$$CH_3OH + CH_3COOH \rightleftharpoons CH_3COOCH_3 + H_2O$$
$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$$
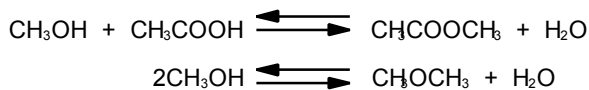
Aqueous HI is also present in the reaction mixture as a result of the reaction between methyl iodide promoter and water:

$$CH_3OH + HI \rightleftharpoons CH_3I + H_2O$$
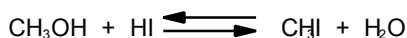
By-product formation reactions, such as a water-gas shift and methane formation, also occur. However, the CO and methanol lost by these mechanisms amount to less than 1% of the total feed:

$$CO + H_2O \longrightarrow CO_2 + H_2$$
$$CH_3OH + H_2 \longrightarrow CH_4 + H_2O$$
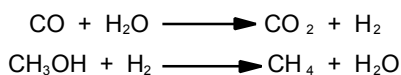
Presumably, the *Acetica*™ process also produces small amounts of other by-products such as methyl acetate, formic acid, and propionic acid under conditions similar to processes based on homogenous Rh catalyst. The presence of water affects the ratio of methyl acetate and acetic acid in the reaction mixture. At a high water:ester molar ratio of 1.5:1 to 3.0:1, acetic acid is favorably produced; at a low ratio of 0.5:1 to 1.0:1, ester production is favored. The ratio of methyl acetate and acetic acid also depends on the amounts of methyl acetate in the reaction mixture, as shown below:

Methanol:Methyl Acetate Mole Ratio	Major Product
0.001:1 to 2:1	Acetic acid
2:1 to 10:1	Mixture of acetic acid and methyl acetate
10:1 to 10,000:1, with methanol conversion <90%	Methyl acetate
10:1 to 10,000:1, with methanol conversion >90%	Acetic acid

The yields used to model the RYIELD reactor R-201 in the Aspen Plus model are as follow:

Components	Yields Per Unit Mass of Non-Inert Feed (Not normalized)
CO	3,545
CO2	350
H2	0
CH4	75
HI	60
CH3I	10,9440
M-Acetate	8,235
Methanol	403
Formic-A	1,843
Water	52,000
Acetic-A	399,000
Propionic-A	4,065
N2	Inert

Cited References

560989   Minami, T., et al., "The (novel) Chiyoda/UOP Acetica™ Process for the Production of Acetic Acid," API Document No. 4600677 (November 29, 1998)

560988   Noriyuki, Y., et al. (to Chiyoda), "Process for the Production of Acetic Acid from Methanol and Carbon Dioxide using Supported Rhodium Catalyst," US 5,334,755, (April 21, 1993)

501931   Marston, C.R. et al. (to Reilly Tar & Chemical), "Process for Acetic Acid Preparation and Heterogeneous Catalyst for Same," European 277,824 (August 10, 1988)

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Takaoka, S., *Acetic Acid and Acetic Anhydride*, PEP Report 37A, Supplement A, Process Economics Program, Stanford Research Institute, Menlo Park, California (March 1973)

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August 19, 1999