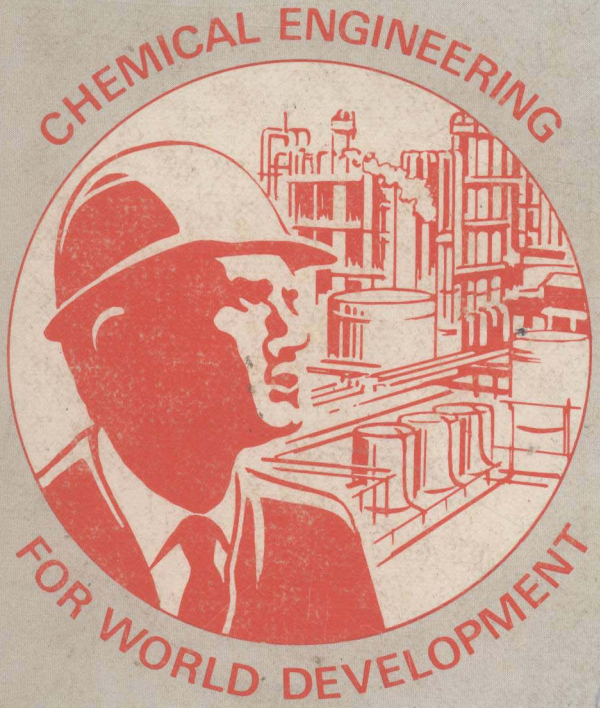

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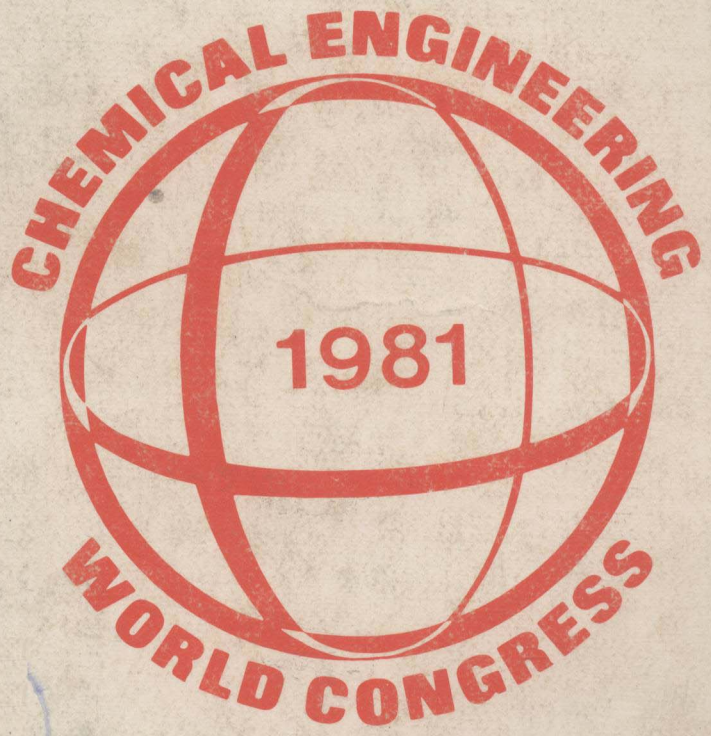

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- Fossil Resource Development — Energy & Petrochemicals
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IX Interamerican Congress of Chemical Engineering

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VOLUME II

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CARBONYLATION CHEMISTRY — THE EMERGING ALTERNATIVE

by John L. Ehrler and Barry Juran, THE HALCON SD GROUP

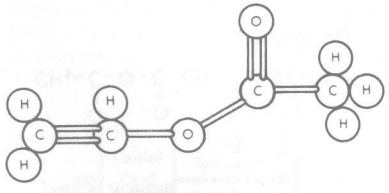
HISTORY AND BACKGROUND

Anyone interested in the commercialization of chemical processes would find a fascinating story by following the history of the major acetyl chemicals in the last three decades. There have been major changes in feedstocks and processes. Before discussing the newest developments which we have made — the production of acetyls by carbonylation without using ethylene or acetic acid — we would like to review briefly the earlier history, emphasizing vinyl acetate and acetic acid.

This historical review was first presented in somewhat shorter form in Ralph Landau's Perkin Medal Address to the SCI on February 13, 1981.

Vinyl acetate monomer is used for the manufacture of polyvinyl acetate polymers and copolymers for water soluble paints, adhesives, textiles and paper coatings. It is also used to make polyvinyl alcohol for textile sizing, fibers and adhesives, to make polyvinyl butyral for windshield safety glass, and for various other end uses. U.S. production of vinyl acetate is now over 900,000 metric tons/yr., and it is the 18th largest organic chemical in the U.S. Vinyl acetate is also produced throughout the world and is a major product of the European and Far East industries.

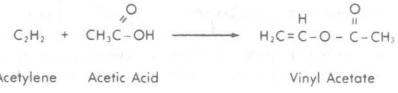
Figure 1
VINYL ACETATE



Vinyl acetate is a complex molecule, as shown in Figure 1. It has four carbon atoms, two oxygen atoms and six hydrogen atoms, and contains a carbon-carbon double bond as well as the carbonyl group, C=0. This complexity has invited many approaches to its production, and a number of processes have been commercialized over the years.

Before World War II, vinyl acetate was made by the German process shown in Figure 2 — the reaction of acetylene with acetic acid. Acetylene came from calcium carbide, and acetic acid was made in several steps from ethanol or acetylene.

Figure 2
EARLY VINYL ACETATE PRODUCTION



However, better processes to make the raw materials for both the vinyl half and the acetate half of the VAM molecule appeared during the 1950's:

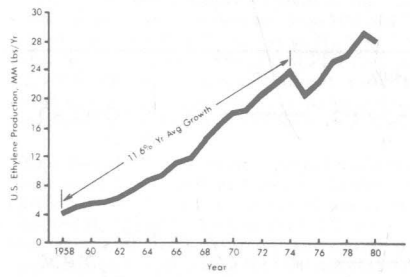
1. BASF's process to make acetylene by methane pyrolysis,
2. Shell's direct hydration of ethylene to ethanol for acetic acid production, and
3. Celanese's oxidation of butanes to acetic acid.

In 1960, virtually all vinyl acetate plants in the world were based on acetylene. However, two radically new processes were being developed that would provide an entirely new pathway to VAM. Wacker simplified the manufacture of acetic acid by the direct oxidation of ethylene to acetaldehyde. Bayer and USI made a second and more important development, the vapor-phase reaction of ethylene and acetic acid to form vinyl acetate.

During the 1960's ethylene usage was booming and larger plants were being built. New plants of 400,000 metric tons/yr. were not uncommon, and still larger ones were being designed and built. Total ethylene capacity rose at a rapid rate, as shown by Figure 3, while the price of ethylene fell steadily. The incentive to switch from acetylene to ethylene for VAM production was compelling. By the end of the 1960's, the all-ethylene route was dominant. The feedstock switch was caused by several new processes coupled with the economies of large-scale ethylene manufacture.

Following these major changes, the 1970's saw two other developments that fundamentally affected the evolution of vinyl acetate manufacture: ICI's low pressure synthesis of methanol

Figure 3
U.S. ETHYLENE PRODUCTION



and Monsanto's low pressure carbonylation of methanol to acetic acid. These emerged just as the "oil shock" of 1973 pushed U.S. ethylene prices from three cents a pound to over twenty cents a pound by 1980 (Figure 4) and caused even greater increases in Europe (Figure 5). Japanese prices also escalated rapidly. As a result, ethylene was too expensive a feedstock for acetic acid, and methanol replaced it. However, even today ethylene is still used for the vinyl half of the VAM molecule.

Figure 4
U.S. ETHYLENE PRICE HISTORY

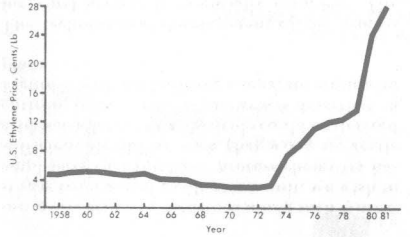
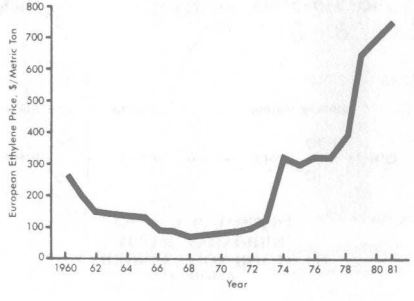


Figure 5
EUROPEAN ETHYLENE PRICE HISTORY



DRIVING FORCES FOR CARBONYLATION

The surge in ethylene prices after October 1973 convinced some companies that carbon monoxide and hydrogen could replace ethylene as an important building block in organic chemical syntheses. The simple carbon monoxide molecule is not as convenient as ethylene for building the more complex organic molecules such as vinyl acetate or acetic anhydride. However, Figure 6 shows that with ethylene at 25¢/lb. or more in the U.S., the value of the carbon contained in ethylene is about 2-3 times that of the carbon contained in CO, even assuming the oxygen part of the CO molecule has no value.

Figure 6
VALUE OF CARBON IN ETHYLENE & CARBON MONOXIDE

MATERIAL	COST, ¢/LB	CARBON VALUE, ¢/LB	COMMENTS
Ethylene	25	21.5	Assumes C And H Valued Equally.
Ethylene	25	19.8	Assumes H_2 @ 56¢/Lb. (Consistent With CO @ 4¢/Lb And H_2 Valued Equally With CO On Volumetric Basis.)
Carbon Monoxide	4	9.3	No Value For Oxygen.

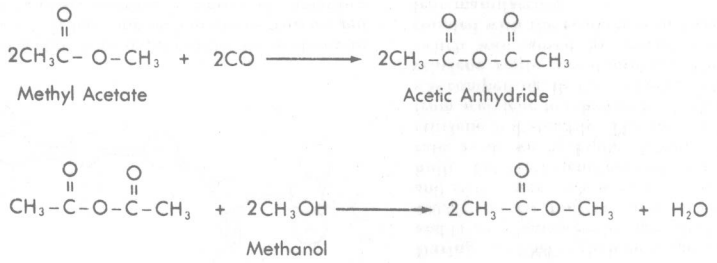
Right now CO is not as available as ethylene in terms of either quantity or number of sources. But there is no doubt that by 1990 many new plants will come on stream producing synthesis gas or intermediate BTU gas (essentially the same material) from coal, lignite, or heavy oil fractions. The large scale of operation applied to the lowest cost feedstocks will result in an ever-widening gap between the value of ethylene and the value of CO. Thus, we at Halcon SD are convinced that two reactive molecules of CO, made from a variety of relatively cheap carbonaceous materials, will produce acetyl chemicals at costs below those when using ethylene.

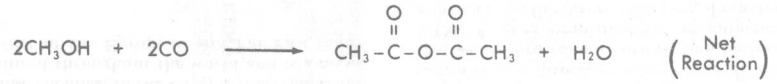
HALCON SD TECHNOLOGY

Driven by this conviction, Halcon SD set out some years ago to develop processes for making acetyls which replaced ethylene with CO and avoided the need for separate manufacture of acetic acid.

In 1980, we announced just such a process for acetic anhydride, and we have now essentially completed the technological development of a similar but more complex process to make vinyl acetate.

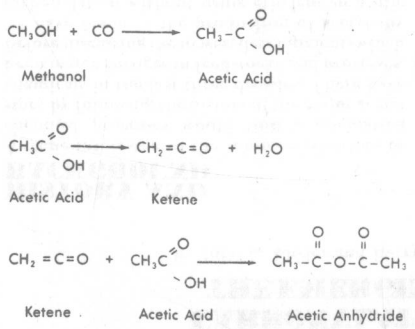
Figure 7
CARBONYLATION ROUTE TO ACETIC ANHYDRIDE
(No Acetic Acid Required)





The chemistry of the acetic anhydride process is shown in Figure 7. Two moles of methyl acetate react with two moles of CO to give two moles of anhydride. One-half the anhydride is recycled and reacted with two moles of methanol to give two moles of methyl acetate and a mole of water. Thus the overall reaction is methanol plus CO to yield acetic anhydride and water. The methanol of course is derived from CO and hydrogen as well, so acetic anhydride made entirely from synthesis gas is the result.

Figure 8
CONVENTIONAL ROUTE TO ACETIC ANHYDRIDE



We believe this new route compares very favorably to the existing three-step process (Figure 8), enumerated as:

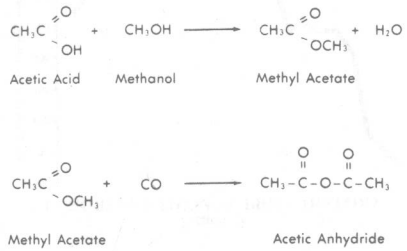
1) Production of acetic acid from methanol and CO;
2) Cracking of acetic acid to ketene; and
3) Addition of acetic acid to ketene to produce the anhydride.

While both routes operate at about the same overall yields, the new route uses significantly less energy.

Last year we reached agreement with Tennessee Eastman Division of Eastman Kodak, who were also working on the conversion of CO to acetic anhydride, to combine our technologies for this chemical. The first commercial plant for producing acetic anhydride by carbonylation technology, and using coal as the ultimate feedstock, is being built by Tennessee Eastman at Kingsport, Tennessee. It will start up in 1983, and the design capacity is 500 MM lbs/yr. Halcon SD is the exclusive worldwide licensor of this technology.

Acetic anhydride will be made by Tennessee Eastman in two steps, as shown in Figure 9. Since acetic acid is available from another unit at the Kingsport site, the first step will be to use it to esterify methanol to methyl acetate. This will then be reacted with CO to give acetic anhydride. While Tennessee Eastman has chosen to

Figure 9
CARBONYLATION ROUTE TO ACETIC ANHYDRIDE
(Acetic Acid Available)



use acetic acid as a feedstock along with synthesis gas from a coal gasification unit, we wish to emphasize that the basic process chemistry has sufficient flexibility such that when no acetic acid is available the anhydride could be derived entirely from synthesis gas, as was described in Figure 7, without building a separate acetic acid plant.

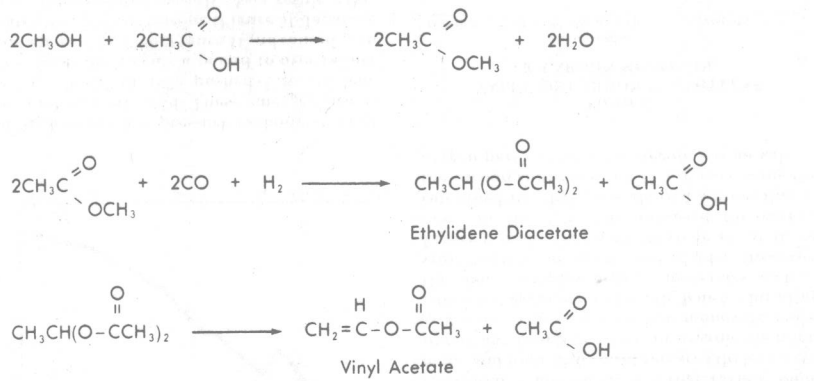
The technological development of the process for vinyl acetate is essentially complete. The chemistry again offers considerable flexibility, with the possibility of producing VAM alone as well as VAM with by-product acetic acid or acetic anhydride, if desired.

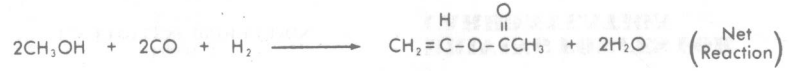
Production of VAM entirely from syn gas, without by-products and without the need for external acetic acid or acetaldehyde feedstock, is shown in Figure 10. Methanol is esterified with acetic acid, and the methyl acetate product is reacted with CO and hydrogen to form ethylidene diacetate (EDA) and acetic acid. The last step is the cracking of the EDA to VAM and more acetic acid. All the acid is recycled to the esterification step, so that the net reaction is methanol plus CO plus hydrogen to yield VAM and water.

The carbonylation of methyl acetate to EDA is the critical step. We have investigated several different process routes in fully integrated pilot operations, using a large number of different catalyst systems, to determine which routes and which catalysts give the best overall results.

By-product acetic acid can be made in various ratios to VAM by the proper combinations of the reactions already described. A typical case of interest might be equal quantities of VAM and acetic acid. Of course, the quantities of methanol, CO and hydrogen will vary with product ratio. The synthesis gas used for methanol manufacture and the carbonylation reactions is likely to require some upgrading or separation to achieve the desired ratio of CO to hydrogen. This will only add a small amount to the cost of CO and hydrogen.

Figure 10
CARBONYLATION ROUTE TO VINYL ACETATE





The points to remember for these new routes to VAM and acetic anhydride, which we call the emerging alternative, are:

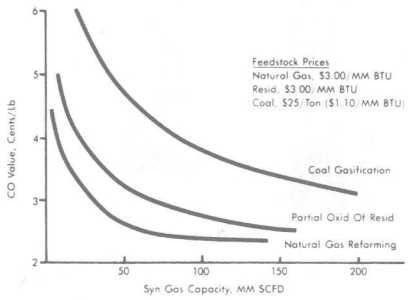
1) You do not need ethylene.
2) You do not need a separate acetic acid plant.
3) You do not *have* to make a co-product. You can readily design a plant for 100% acetic anhydride, 100% vinyl acetate, or any ratio in between.
4) You can also make acetic acid or acetaldehyde.
5) Methyl acetate, where available, can be very advantageously used as a feedstock.
6) In making acetic anhydride, you do not need ketene furnaces.

COMMERCIALIZING HALCON SD TECHNOLOGY

As stated earlier, Tennessee Eastman is combining their technology with Halcon SD's to build a carbonylation plant to produce acetic anhydride from synthesis gas and methanol. Separately from this, Halcon SD has developed a carbonylation route to vinyl acetate that is technologically ready for commercialization now.

One of the requirements for favorable economics for the carbonylation route to VAM or acetic anhydride is low-priced carbon monoxide. Figure 11 shows that the value of CO in the U.S. is about 3-4¢/lb. when produced by partial oxidation of residual oil on a large scale, say 50-100 MM SCFD or more.

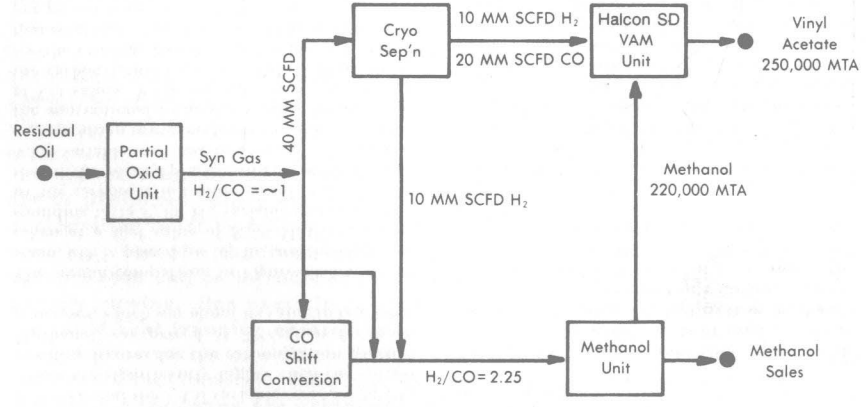
Figure 11
CO COST IN SYN GAS VS CAPACITY (1980 Basis)



This price for CO results from the production of syn gas on a scale larger than is required for the vinyl acetate unit alone, and from the absence of by-product hydrogen. By integrating methanol manufacture into the complex, either with or without sales of methanol, all syn gas is fully consumed, and the CO and hydrogen components of the syn gas can be valued equally on a volumetric basis.

Figure 12 shows one possible schematic block flowsheet for a vinyl acetate-methanol complex, starting from resid. To produce 250,000 metric tons per year of VAM, you need about 20 MM SCFD of CO (535,000 NM^3/day) and 10 MM SCFD of H_2 (270,000 NM^3/day) along with

Figure 12
VINYL ACETATE - METHANOL COMPLEX



220,000 MTA of methanol. If no methanol export is desired, a methanol plant of this size could be built with a feed of about 60 MM SCFD of syn gas (1.6 MM NM^3/day) at an H_2/CO ratio of 2.25/1. Thus a total of 90 MM SCFD of syn gas (2.4 MM NM^3/day) would be required. A partial oxidation unit built for such a complex is large enough to realize most of the benefits of scale.

Note that the syn gas from a partial oxidation unit must be divided and treated further to arrive at the desired quantities of gas at the desired H_2/CO ratios for both the VAM unit and the methanol plant. The syn gas leaves the partial oxidation unit at an H_2/CO ratio of about 1.0, and 40 MM SCFD are sent to a cold box for separation. Some 10 MM SCFD of H_2 are taken off to be used in methanol synthesis while the 20 MM SCFD of CO and the remaining 10 MM SCFD of H_2 are used in the VAM plant.

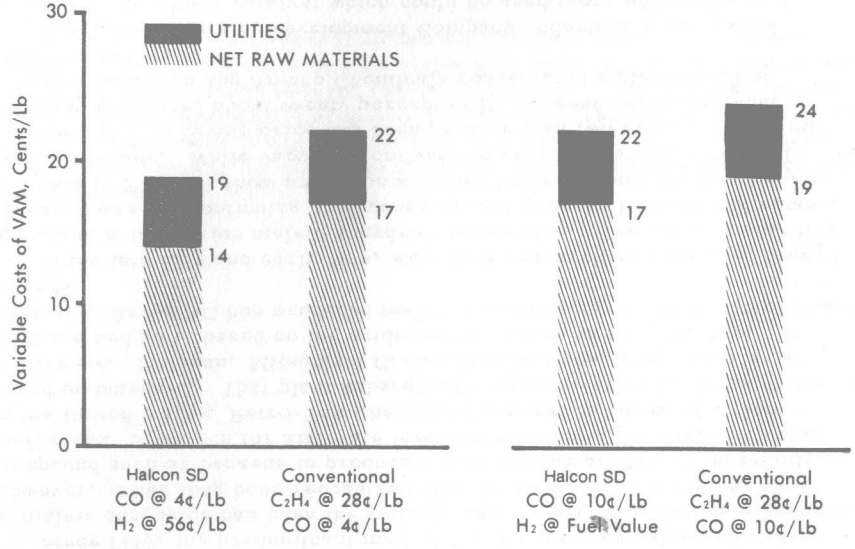
The syn gas not sent to the cold box is divided again, with a portion going through a shift conversion unit in which CO is reacted with steam to produce hydrogen and carbon dioxide. The amount of gas sent to the shift converter is determined by the material balance to satisfy the required amount and H_2/CO ratio of the syn gas feed to the methanol unit.

Should methanol for sale be desired, a methanol plant with capacity greater than 220,000 MTA could be built. The partial oxidation unit grows considerably in size to 106 MM SCFD for 1,000 T/D (300,000 MTA) of methanol and to 188 MM SCFD for 2,000 T/D (600,000 MTA) of methanol. This further reduces the CO cost and improves the VAM economics. Because of the inclusion of methanol production in the complex, there is no excess hydrogen (as a matter of fact the hydrogen contained in the syn gas is insufficient to meet all needs and some CO must be shifted).

Variable costs for VAM production are shown in Figure 13 for the Halcon SD carbonylation route and the conventional ethylene oxidation route. For the carbonylation, two different CO prices have been assumed. The first corresponds to syn gas with CO and hydrogen priced equally at about $3/MSCF, which might be the cost after a portion of the product from a partial oxidation unit is separated in a cold box as was shown in Figure 12. On this basis, CO is worth 4¢/lb., H_2 is worth 56¢/lb. and the VAM variable cost is 19¢/lb. for this first case.

For the conventional technology including acetic acid manufacture in a large Monsanto plant, with ethylene priced at 28¢/lb. and CO at 4¢/lb.,

Figure 13
VARIABLE COSTS OF VINYL ACETATE PRODUCTION
(1980 Basis; Methanol @ 70¢/Gallon)



it is seen that the VAM variable costs are 22¢/lb. These are significantly higher than the corresponding figures for the carbonylation process. Methanol was priced at 70¢/gallon for both processes, which was about its value in late 1980.

The second comparison in Figure 13 shows that when CO is priced at 10¢/lb. and hydrogen is taken at a fuel value of $2.50/MMBTU, corresponding to 15.3¢/lb. H_2, variable costs for VAM by the carbonylation route go up to 22¢/lb. For the ethylene-based process with CO at 10¢/lb., the VAM variable costs rise to over 24¢/lb. Thus the carbonylation route has lower variable costs than the conventional technology over a broad range of CO values. While capital-related charges for the carbonylation route are slightly above those for the ethylene-based route, we have estimated that total cost of production will be several cents per pound lower for the CO-based process at the lower end of the range of CO prices.

We expect that ethylene prices, related to crude oil, will increase at a rapid rate over the next several years, and that construction of large partial oxidation plants and later large coal gasification plants will keep the price of syn gas from escalating at as rapid a rate as ethylene. Being a new process, there will also be continuing improvements in the carbonylation route to vinyl acetate. Hence it is clear that economics will increasingly favor the CO-based process in the years ahead.

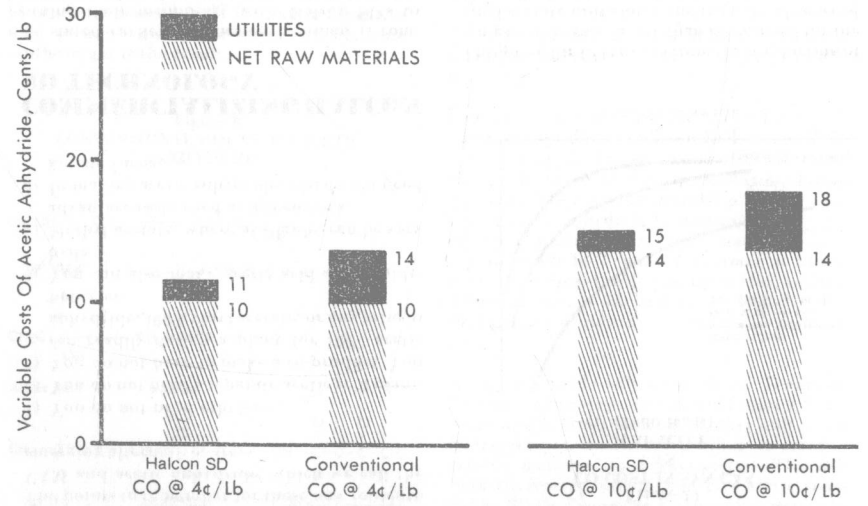
With regard to acetic anhydride, compare in Figure 14 the variable costs of production for the carbonylation route starting from methanol and CO with the ketene route including acetic acid manufacture. With CO at 4¢/lb. and methanol at 70¢/gallon, the net variable cost for the Halcon SD/Tennessee Eastman process is about 11¢/lb.

For the ketene route starting with CO and methanol also, the variable costs per pound of acetic anhydride are 14¢/lb. with CO at 4¢/lb. These are considerably greater than the corresponding costs for the carbonylation process. Similarly, comparing on the right side of Figure 14 the variable costs of conventional anhydride technology with carbonylation technology using CO at 10¢/lb., it is likewise seen that the latter holds a significant advantage.

In summary, the carbonylation routes to two major acetyl chemicals are more attractive today than the ethylene-based routes. The process for acetic anhydride will begin operations on a very large scale in 1983 while the process to VAM is only slightly behind in technological development.

Last, the advantage for these routes will improve futher as commercial experience reduces costs and the ethylene-syn gas price gap grows.

Figure 14
VARIABLE COSTS OF ACETIC ANHYDRIDE PRODUCTION
(1980 Basis; Methanol @ 70¢/Gallon)



FLUIDIZED BED CATALYTIC OXIDATION OF BUTANE TO MALEIC ANHYDRIDE - *G.S. Schaffel, S.S. Chen, J.J. Graham, The Badger Company Inc., Cambride, MA 02142

Since 1933, the predominant method for the commercial manufacture of maleic anhydride has been the vapor phase, catalytic oxidation of benzene. However, it has long been recognized that the oxidation of a six-carbon compound such as benzene to produce a four-carbon product is inherently inefficient. A search for alternate feedstocks began in the early 50's and, in the United States, Petro-Tex Chemical Corporation operated a plant based on butene-2. That plant subsequently was converted to the oxidation of benzene. In Japan, Mitsubishi Chemical Industries, Ltd. operates a fluidized bed plant based on the oxidation of butenes in a C_4 fraction. In Germany, Bayer AG has produced maleic anhydride by the oxidation of mixed butenes.

In the late 60's and early 70's, extensive research was directed toward the use of n-butane for maleic anhydride production. The incentive for this research was the continuing divergence in cost between benzene and butane. The data in Figure 1 show prices on a weight basis for both feedstocks over the past decade. While varying from year to year, the average ratio of benzene price to butane price has been greater than two to one. Monsanto Company converted about twenty percent of its benzene oxidation capacity to butane oxidation and Amoco Chemicals constructed a plant based on butane oxidation.

Mobil Research and Development Company undertook a successful program to develop a catalyst which could be used more efficiently in the oxidation of butane. It was subsequently discovered that this catalyst was not only effective for production of maleic anhydride in good yield but also had attrition resistant properties which forecast the potential for successful use in a fluidized bed operation. Therefore, first in conjunction with Mobil and, subsequently alone after acquisition of Mobil's patent rights, The Badger Company undertook the development and commercialization of the process to be described. In early 1981, operation of a demonstration plant (shown in photograph) was completed, during which optimum operating conditions, scale-up factors, and process yields were confirmed. This demonstration plant, located at Denka Chemical Corporation's maleic anhydride plant at Houston, Texas is now operating as a small production unit.

Process Description

A schematic flow diagram for the Badger process is shown in Figure 2. Air is filtered, compressed, and fed to the reactor, fluidizing the catalyst. Butane is vaporized and injected directly into the fluidized catalyst bed. Rapid motion of the fine solid particles prevents formation of localized hot spots, resulting in an isothermal catalytic bed with precise temperature control. Although the reaction is highly exothermic, reaction heat is removed readily by direct steam generation in cooling coils immersed in the catalyst. Cooling surface area is relatively small because of the high heat transfer coefficients on both the water side and the process side of the coils.

The reactor effluent passes through a cooler to generate additional steam and then enters a condenser cooled with tempered water. A substantial fraction of the maleic anhydride is condensed and recovered as a liquid. Any product remaining in the gas stream is absorbed in water as a maleic acid solution. Vent gas from the scrubber, which contains unconverted butane, carbon monoxide, and carbon dioxide has a high heating value and is fed to an incinerator or boiler to generate additional steam, without the requirement

to add supplementary fuel to support combustion.

The maleic acid solution from the scrubber, which contains slight traces of non-selective oxidation products, is fed continuously to a dehydration column where water is removed and the maleic acid is dehydrated to maleic anhydride. The dehydration can be performed at decreased pressure in short residence time devices or, preferably, at atmospheric pressure using a water entraining agent such as xylene. The liquid stream from the partial condenser is combined with the product from the dehydration column and then is purified in the refining column. Since the catalyst permits the attainment of very high selectivity, removal of trace impurities is simplified and the product is of exceptional purity.

Process Economics

Figure 3 shows the estimated capital investment for a fluidized bed butane oxidation plant, as a function of plant capacity, compared with estimated investments for plants based on benzene and on butane with fixed bed reactors. The latter are shown as continuous functions even though discontinuities would result when the capacity of unit fixed bed reactors is exceeded. In contrast, a single fluid bed reactor can be constructed and operated at capacities exceeding those shown in Figure 3.

Figure 4 shows the estimated transfer price for maleic anhydride produced from butane in a fluid bed reactor plant, as a function of plant capacity. Also, estimated transfer prices for maleic anhydride produced from benzene and from butane in fixed bed reactor plants are shown.

The reasons underlying the significant economic advantages of a fluid bed oxidation process can be described as follows.

It is well known that catalysts used in fixed bed tubular reactors have a limited useful life. This is attributed to the "hot spot" effect, i.e., to the inability to conduct highly exothermic reactions isothermally in fixed catalytic beds. Operating conditions and reactor design can be modified to minimize the "hot spot", but the occurrence of high temperatures causes undesirable and irreversible changes in both the conversion and selectivity. As a result, the catalyst must be removed from thousands of tubes per reactor and replaced, which is labor intensive and time-consuming. This requires reactor shut-down for several weeks and results in a capacity decrease together with high maintenance costs. In contrast, a fluidized bed reactor can operate continuously and isothermally ($\pm 1^{\circ}F$ throughout the catalyst bed), resulting in no change in catalyst performance with time. Small quantities of catalyst are lost because of attrition, but can be replaced in a simplified manner without disturbance of the reactor operation. The economic advantages of continuous operation at a steady, constant yield are self-evident.

Use of a multitubular fixed bed reactor requires that the hydrocarbon and air be premixed before entering each catalytic bed. Therefore, the feed composition must be maintained outside of the flammability envelope. In contrast, use of a fluidized bed does not involve such a constraint since the hydrocarbon can be introduced into the air stream in the presence of the rapidly moving, fine particle catalyst. The heat capacity of the catalyst and the rapid heat transfer created by the movement of the catalyst particles prevents formation of a flame front. Therefore, butane/air mixtures at the required stoichiometric ratio can be used. As a result, several important economic advantages are achieved.

Since air-to-hydrocarbon ratio can be reduced by more than 50%, the size of the air compressor can be reduced accordingly, resulting not only in a capital cost reduction but also a significant reduction in consumption of utilities required to drive the compressor.

The higher concentration of maleic anhydride in the fluid bed reactor effluent enables the partial condensation of a large fraction of the product. Thus, the size and cost of partial condensation equipment are reduced. Further, since a smaller fraction of the product must be absorbed, the size and cost of dehydration facilities are reduced, accompanied by a reduction in utilities required for dehydration. The absorber is sized on the basis of total gas flow. Use of a smaller air-to-hydrocarbon ratio thus results in reduction of the size and cost of the absorber.

All butane oxidation processes operate at less than 100% conversion in order to maximize yield. Unconverted butane must be eliminated from the scrubber effluent stream by incineration. The effluent from the fluid bed process, because of the lower air requirement, sustains combustion in the incinerator without the requirement for an auxiliary fuel, in contrast to that from a typical fixed bed operation where a significant fuel requirement results in a higher utility cost.

A major economic advantage stems from the low capital investment associated with fluidized bed reactors. No costly molten salt cooling system is used. Moreover, a single reactor train is feasible at capacities well in excess of 100 million pounds per year of maleic anhydride. In contrast, multiple fixed bed reactors, each containing tens of thousands of tubes, must be employed at plant capacities in excess of approximately 30 million pounds per year. Such reaction systems contribute significantly to increased capital investment.

As a result of the ability to use low temperatures isothermally in a fluidized bed, the number and quantity of non-selective impurities are low. Consequently, surface fouling is minimized and on-stream time is extended. This contributes significantly to reduction of operating cost.

In summary, the Badger fluidized bed catalytic oxidation of butane produces maleic anhydride at good yields with reduced utilities requirements and with a substantially lowered capital investment. This results from the discovery and development of an attrition resistant catalyst whose performance does not change with time, together with an optimum fluidized bed reactor design and optimally efficient operating conditions. The process is now being offered for license by The Badger Company, Inc.