Alternate Fuels and Chemicals from Synthesis Gas:

Vinyl Acetate Monomer

Final Report

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Subcontractor

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A. Abstract

There has been a long-standing desire on the part of industry and the U.S. Department of Energy to replace the existing ethylene-based vinyl acetate monomer (VAM) process with an entirely synthesis gas-based process. Although there are a large number of process options for the conversion of synthesis gas to VAM, Eastman Chemical Company undertook an analytical approach, based on known chemical and economic principles, to reduce the potential candidate processes to a select group of eight processes. The critical technologies that would be required for these routes were:

- 1) the esterification of acetaldehyde (AcH) with ketene to generate VAM,
- 2) the hydrogenation of ketene to acetaldehyde,
- 3) the hydrogenation of acetic acid to acetaldehyde, and
- 4) the reductive carbonylation of methanol to acetaldehyde.

This report describes the selection process for the candidate processes, the successful development of the key technologies, and the economic assessments for the preferred routes. In addition, improvements in the conversion of acetic anhydride and acetaldehyde to VAM are discussed. The conclusion from this study is that, with the technology developed in this study, VAM may be produced from synthesis gas, but the cost of production is about 15% higher than the conventional oxidative acetoxylation of ethylene, primarily due to higher capital associated with the synthesis gas-based processes.

B. Executive Summary

In sponsoring this project, the U.S. Department of Energy set an overall objective to reduce dependence on foreign petroleum by replacing chemical feedstocks based on petroleum with chemical feedstocks based on readily available domestic resources, such as coal or natural gas. Both coal and natural gas are readily converted to synthesis gas (a mixture of hydrogen and carbon monoxide, also referred to simply as syngas) with the release of useable energy. In this specific project, the goal was to explore the potential for generating vinyl acetate monomer (VAM) entirely from synthesis gas in a process that would economically compete with the existing oxidative acetoxylation of ethylene, which is generally derived from petroleum resources.

The target material, vinyl acetate, is a valuable polymer intermediate used in the manufacture of a variety of emulsion polymer products. These emulsion polymers are subsequently used in a variety of applications, the most important being coatings and adhesives. Considering that current production exceeds 6 billion lbs/yr and has a value exceeding \$2 billion/yr and that the U.S. is, by far, the largest current exporter of this material, vinyl acetate has a significant impact on the U.S. economy.

Simple calculations indicate that a totally syngas-based process should have a raw material advantage, and a number of articles already appear in the literature that discuss attempts to capture this advantage. Typical of such investigations is the sequence shown below. Unfortunately, none of these has resulted in an economically competitive process.

AcH = acetaldehyde; AcOMe = methyl acetate; EDA = ethylidene diacetate (1,1-diacetoxyethane)

*recycled to form methyl acetate for carbonylation

Eastman Chemical Company recognized that one of the key reasons these earlier process schemes failed was that they all recycle large volumes of acetic acid to generate methyl acetate. These large acetic acid recycles require that the carbonylation units used within the process (i.e., for reactions [3] and [4]) be exceedingly large, generally requiring total volumes 2.5X the actual production volume of vinyl acetate. Exacerbating the situation is the fact that, to date, all these carbonylation reactors require very expensive corrosion-resistant materials of construction. As a consequence, the capital required to build these large carbonylation units far outweighs any inherent raw material advantage that could be garnered from a process for vinyl acetate based entirely on syngas.

Eastman Chemical Company proposed reducing these massive recycle loops by changing the way acetic acid was used within the process. Eastman Chemical Company saw two potential pathways. In the first process, rather than recycling acetic acid, Eastman Chemical Company proposed the possibility of using the acetic acid generated in reaction [6] as a feedstock for the direct generation of acetaldehyde.

This would not be a trivial undertaking, since the hydrogenation of acetic acid to acetaldehyde is slightly thermodynamically disfavored, and the subsequent hydrogenation of the aldehyde product to an alcohol, which generally uses the same class of catalysts, is thermodynamically quite favorable. Further complicating the picture is the fact that the cracking of 2 moles acetic acid to acetone and carbon dioxide, which is a very favorable process, is also often catalyzed by these same catalysts. As a consequence, few examples of the direct conversion of a carboxylic acid to aldehyde existed prior to this study, and those that did exist used very large excesses of hydrogen and low conversions which would preclude easy isolation of the very volatile acetaldehyde component.

Eastman Chemical Company originally sought to overcome these hurdles by first generating ketene, a very reactive intermediate obtained by high-temperature (and very endothermic) dehydration of acetic acid, and subsequently hydrogenation of ketene to acetaldehyde. A number of catalysts were examined for this hydrogenation, but only catalysts utilizing Pd proved to give both an acceptable selectivity to acetaldehyde and acceptable rates. Key findings in this hydrogenation were that:

- 1) carbon monoxide, a common by-product of ketene formation, was a reversible poison for the ketene hydrogenation, but the poisoning could be overcome with higher temperatures, and
- 2) deactivation was fairly rapid. However, the catalysts could be reactivated with hydrogen. (In a commercial facility, reactivation would have to be performed on a daily basis.)

After conditions for the ketene hydrogenation were defined and its experimental feasibility was demonstrated, a cost estimate for the process was initiated. Although cracking furnaces have been used for over 70 years to generate ketene, no recent information on costing with modern equipment and technology existed. Although the cost of hydrogenation was acceptable, the cost of ketene generation was surprisingly high, and this process was concluded to be an economically unacceptable means of generating the acetaldehyde component.

However, building upon this technology and the recent knowledge base on the hydrogenation of acetic acid, Eastman Chemical Company was able to develop a useful Pd-on-iron oxide catalyst for the direct, *selective* vapor phase hydrogenation of acetic acid to acetaldehyde. This catalyst radically reduced the formation of acetone that plagued earlier hydrogenations and gave acetaldehyde in selectivities of ca. 85% (with most of the remainder being ethyl acetate) at conversions approaching 50%. A commercial catalyst would have to simultaneously meet the following criteria:

- selective and kinetically rapid at higher pressures (ca. 250 psi),

- operable at high conversions, and
- operable at low hydrogen:acetic acid ratios

if it was to be useful for the generation and recovery of acetaldehyde. Through detailed examination of potential catalyst formulations and kinetic measurements, Eastman was able to develop a patentable catalyst formulation that met all these necessary criteria.

The second proposed alternative for eliminating the acetic acid recycle was to replace the two-step esterification of acetaldehyde with acetic anhydride, depicted by reactions [5] and [6], with a direct, one-step, esterification using ketene (again generated by high-temperature dehydration of acetic acid).

Eastman Chemical Company developed a useful, small-scale, vapor-stripped reactor that allowed the generation of vinyl acetate from ketene and acetaldehyde in the presence of an acid catalyst with several solvent options. The reaction generated significant levels of tar, but the esterification was accomplished in commercially useful yields within the small-scale reactors. However, upon scaleup, tar generation rates accelerated and the rates declined within the reactor. While resolution of the differences between the small- and large-scale reactors was attempted, the economic assessments for ketene generation were completed, and it became apparent that this process, while unique and interesting, was not going to compete economically. Eastman Chemical Company then turned its attention to improving the older, well-established technology, developed by Celanese, for the conversion of acetic anhydride and acetaldehyde to VAM.

Prior to the onset of this project, Eastman Chemical Company had examined a reactive distillation of acetaldehyde and acetic anhydride to generate VAM, but the process needed to be optimized. Before discussing this process, it is important to understand that reactions [5] and [6] are actually equilibria, and both reactions strongly favor the formation of EDA. The reactive distillation process developed at Eastman Chemical Company generates a mixture of acetic acid and vinyl acetate by adding a catalyst and acetic anhydride to the midpoint of a column and acetaldehyde at the base. As the acetaldehyde, the lowest boiling component, rises up the column, it encounters an increasingly rich acetic anhydride environment, causing the equilibrium in reaction [5] to continuously shift toward EDA. The EDA, being a high boiler, descends the column where it is undergoing continuous cracking to vinyl acetate and acetic acid via reaction [6]. However, since vinyl acetate and acetic acid are unaffected by the presence of excess acetic anhydride, they are ultimately distilled overhead. When optimized, this process was found to be best operated with excess acetaldehyde (which is easily separated from the product mixture) and at about 4 atm. This process substantially reduced the amount of recycled material and used fewer units of operation than the earlier Celanese process.

At this point, Eastman was able to ascertain that the process most likely to compete with the existing commercial process would consist of the following sequence:

and there were sufficient details to undertake an economic estimate of the integrated process. The result of this economic estimate was that, despite enjoying about a 2 cent/lb advantage in raw materials, the cost of producing and marketing VAM from the new process was 14-17% higher than the conventional technology. The difference is attributable to both higher capital requirements for the production units and higher utility usage. (Both reactions [10] and [11] are endothermic and require an energy input.)

When it became evident that this process, while very close, was not going to be competitive with the conventional ethylene oxidative acetoxylation process, the project was terminated. However, it should be noted that this estimate was for a Gulf Coast type facility. The economics are close enough that this process might still warrant consideration in locations where vinyl acetate is required, but where syngas sources are cheap and ethylene is not readily available.

The final cost of the project was \$1.39 million, with the original budget being set at \$3.45 million (including Eastman Chemical Company cost share). Deliverables for the project included unique processes for:

- 1) the hydrogenation of ketene to acetaldehyde,
- 2) the hydrogenation of acetic acid to acetaldehyde,
- 3) the esterification of acetaldehyde with ketene, and
- 4) an improved process for the conversion of acetic anhydride and acetaldehyde to vinyl acetate.

In addition, a cost estimate of these production components was completed and allowed a rational conclusion to the process.

C. Introduction

1. Project Objectives

In sponsoring this project, the overall objective of the U.S. Department of Energy was to reduce dependence on foreign petroleum by replacing chemical feedstocks based on petroleum with chemical feedstocks based on readily available domestic resources, such as coal or natural gas. Both coal and natural gas are readily converted to synthesis gas (a mixture of hydrogen and carbon monoxide, also referred to simply as syngas) with the release of useable energy. In this specific project, the goal was to explore the potential for generating vinyl acetate monomer (VAM) entirely from synthesis gas in a process that would economically compete with the existing oxidative acetoxylation of ethylene, which is generally derived from petroleum resources.

The target material, vinyl acetate, is a valuable polymer intermediate used in the manufacture of a variety of emulsion polymer products. These emulsion polymers are subsequently used in a variety of applications, the most important being coatings and adhesives. Considering that current worldwide demand exceeds 6 billion lbs/yr and has a value exceeding \$2 billion/yr and that the U.S. is, by far, the largest current exporter of this material, vinyl acetate has a significant impact on the U.S. economy.

The simplest calculations would indicate that a totally syngas-based process should have a raw material advantage, and a number of articles already appear in the literature that discuss attempts to capture this advantage. Typical of such investigations is the sequence shown below:

AcH = acetaldehyde; AcOMe = methyl acetate; EDA = ethylidene diacetate (1,1-diacetoxyethane)

*recycled to form methyl acetate for carbonylation

A number of variations, including processes that combine steps into single processes, have been proposed and investigated.^{1,2} Unfortunately, none of these has resulted in an economically competitive process.

The primary reason none of these earlier processes have proven to be economically viable is the large acetic acid recycle involved in the process. (See reactions [3] and [4].) (In the scheme shown above, one needs to recycle 1.4 lbs of acetic acid for every lb of vinyl acetate, assuming a stoichiometric reaction.) The consequence of this large recycle is that

the upstream plants all need to handle significantly larger masses of material than the ultimate nameplate of the VAM facility. This would not necessarily prohibit the implementation of the process, but unfortunately, several of the upstream reactors require iodine components as promoters, which dictates the use of corrosion-resistant (and very expensive) materials of construction. As a consequence, the capital required for the syngas-based processes has always far outstripped any raw material advantage that synthesis gas might have possessed. None of the proposed solutions to date eliminates this problem.

Given the above, Eastman Chemical Company understood that the likely key to generating an economically competitive synthesis gas-based vinyl acetate process would be to reduce this acetic acid recycle. This would require that Eastman Chemical Company change the way acetic acid was handled in these processes in a very fundamental way. Eastman Chemical Company utilized a rational approach to how this might be accomplished. The development of this approach is described in detail in the next section.

2. Development of the Project Plan.

If one closely examines the fundamental transformations required for a synthesis gas-based process for vinyl acetate, the process can be reduced to just a few key conceptual transformations. These are:

Transformation 1:

Generate an acetyl equivalent from a methanol equivalent.

Transformation 2:

Generate acetaldehyde from a methanol equivalent. (This may be direct or through the reduction of an acetyl equivalent.)

Transformation 3:

Esterify acetaldehyde with the acetyl equivalent to form vinyl acetate. (This may involve the generation of ethylidene diacetate as an intermediate or be a direct conversion to vinyl acetate.)

Although the fundamental steps seem simple, there are a number of possible methanol and acetyl equivalents, and an even larger number of ways of combining and conducting these transformations. To initiate the process, Eastman Chemical Company considered the following materials as potential methanol equivalents in the process:

- methanol
- dimethyl ether
- methyl acetate

The menu of potential acetyl equivalents considered for the esterification were:

- acetic acid
- methyl acetate
- acetic anhydride
- ketene.

This still left a large number of potential processes to investigate. To sort these processes out, Eastman Chemical Company set the following principles to guide the selection process:

1. Only consider processes with reasonably attainable thermodynamics.
2. Only consider processes that do not coproduce net molar quantities of acetic acid. (This is driven by market forces. The major outlet for acetic acid is vinyl acetate. There would no longer be an adequate outlet if the process under investigation was to displace the existing VAM process.)
3. Eliminate major (molar) acetic acid recycles which pass through carbonylation units (based on earlier economic assessments).
4. Do not isolate ethylidene diacetate. (Eastman already had developed a process for the direct conversion of acetaldehyde and acetic anhydride to VAM without isolating EDA.)
5. In systems involving ketene, only consider ketene derived from acetic acid.

After these principles were applied, only eight process options remained, involving a total of six technologies that might need be developed. Of these six technologies:

- two involve new, previously unknown technologies,
- two involve technologies that are currently evolving in the literature, but have no commercial analog, and
- two represent extensions of previously existing commercial technology.

Prior to discussing the eight process options, it would be useful to review the results of the thermodynamic estimates for each possible candidate transformation. These estimates were part of this project, and the results are summarized in Tables C.1 through C.3. Although slightly disfavored processes cannot be ruled out, since the estimation methods may have some inaccuracies and slightly disfavored equilibria can be overcome, several reactions are clearly untenable.

After taking into account the inaccuracies of the estimate, we can consider any reaction with a $\Delta G > +4$ kcal/mol as unlikely to be overcome under ordinary reaction conditions. The thermodynamic assessment of the potential reactions for the esterification of acetaldehyde with an acetyl equivalent are clearly the most informative. (Table C.2.) The only tenable acetyl equivalents for the esterification are ketene and acetic anhydride. Methyl acetate and acetic acid are too unfavorable to be reasonably considered and were removed from consideration.

Once Eastman Chemical Company had assessed the thermodynamics, they could set up a matrix of potential acetaldehyde processes (those shown in Table C.1) and the two candidate esterification processes and look at the overall transformation from methanol to vinyl acetate. The matrix and eight remaining viable processes arising from the analysis are shown in Table C.4.

Table C.1. Thermodynamics for the Generation of Acetaldehyde. (Transformation 2.)

		$\Delta G_{149^{\circ}\text{C}(\text{vapor})}$	$\approx \Delta G_{149^{\circ}\text{C}(\text{liquid})}$
a) Acetate Hydrogenation			
$\text{MeOAc} + \text{H}_2 \longrightarrow$	$\text{AcH} + \text{MeOH}$	+ 5.4 kcal/mol	-3.1 kcal/mol
$\text{AcOH} + \text{H}_2 \longrightarrow$	$\text{AcH} + \text{H}_2\text{O}$	+1.9 kcal/mol	-5.0 kcal/mol
$\text{Ac}_2\text{O} + \text{H}_2 \longrightarrow$	$\text{AcH} + \text{AcOH}$ (EDA Preferred!)	- 8.9 kcal/mol	-15.8 kcal/mol
$\text{H}_2\text{C}=\text{C}=\text{O} + \text{H}_2 \longrightarrow$	AcH	-16.8 kcal/mol	-23.8 kcal/mol
b) Reductive Carbonylation			
$\text{MeOH} + \text{CO} + \text{H}_2 \rightarrow$	$\text{AcH} + \text{H}_2\text{O}$	-11.4 kcal/mol	-18.9 kcal/mol
$\text{MeOAc} + \text{CO} + \text{H}_2 \rightarrow$	$\text{AcH} + \text{AcOH}$	- 8.0 kcal/mol	-17.1 kcal/mol
$\text{DME} + \text{CO} + \text{H}_2 \longrightarrow$	$\text{AcH} + \text{MeOH}$	- 8.1 kcal/mol	-10.8 kcal/mol

Note: Reductive Carbonylation likely needs to be kinetically controlled; not a consecutive process (See Table C.3)

Table C.2. Thermodynamics for Esterification Options (Transformation 3.)

<u>Reaction</u>	$\Delta G_{149^{\circ}\text{C}(\text{vapor})}$	$\approx \Delta G_{149^{\circ}\text{C}(\text{liquid})}$
$\text{AcH} + \text{AcOH} \longrightarrow \text{VAM}$	+13.1 kcal/mol	+11.7 kcal/mol
$\text{AcH} + \text{AcOMe} \longrightarrow \text{VAM} + \text{MeOH}$	+16.5 kcal/mol	+13.5 kcal/mol
$\text{AcH} + \text{Ac}_2\text{O} \longrightarrow \text{VAM} + \text{AcOH}$	+ 2.2 kcal/mol	+1.8 kcal/mol
$\text{AcH} + \text{H}_2\text{C}=\text{C}=\text{O} \longrightarrow \text{VAM}$	- 5.6 kcal/mol	- 7.1 kcal/mol

Table C.3. Thermodynamics for Carbonylation of Various Methanol Equivalents. (Transformation 1)

<u>Reaction</u>	$\Delta G_{149^{\circ}\text{C}(\text{vapor})}$	$\approx \Delta G_{149^{\circ}\text{C}(\text{liquid})}$
$\text{MeOH} + \text{CO} \longrightarrow \text{AcOH}$	-13.3 kcal/mol	-13.9 kcal/mol
$\text{MeOAc} + \text{CO} \longrightarrow \text{Ac}_2\text{O}$	+ 0.9 kcal/mol	-2.3 kcal/mol
$\text{DME} + \text{CO} \longrightarrow \text{MeOAc}$	-13.4 kcal/mol	-15.7 kcal/mol

A. Reductive Carbonylation

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Table C.4. Summary of viable processes for the generation of vinyl acetate from methanol and syngas. (continued)

B. Hydrogenation Processes

AcH Source	Esterification Reagent	
	A. Acetic Anhydride	B. Ketene
1. AcOH Hydrogenation	<p>3 steps - most preferred route</p>	<p>4 steps</p>
2. Ac2O Hydrogenation	Rejected (Recycles Acetic Acid)	<p>4 steps</p>
3. Ketene Hydrogenation	<p>4 steps</p>	<p>4 steps</p>

Most of the transformations in the matrix are already known. The knowledge gaps in each block of the matrix can be extracted and summarized in a single knowledge gap matrix. This matrix appears in Table C.5, which uses the same system and terminology as in Table C.4. Based upon this analysis, Eastman Chemical Company developed a revised work plan that was accepted by the U.S. Department of Energy. (The flow chart, plan, and resultant task outline/timeline are included in an appendix at the end of this section for the reader's convenience.)

The plan called for Eastman Chemical Company to divide its labor into two simultaneous efforts. The first was directed toward demonstrating the esterification of acetaldehyde, with the highest priority being directed toward the demonstration of the previously unknown esterification of acetaldehyde with ketene, which is critical to six of the eight process schemes.

The second portion of Eastman's effort was to be directed toward the hydrogenation of ketene or acetic acid to form acetaldehyde. Of all the processes in Table C.4, the most preferred process, which is reproduced below, would require the hydrogenation of acetic acid, not ketene. Unfortunately, based on the thermodynamics, the likelihood of success for the preferred hydrogenation of acetic acid was less promising than for a ketene hydrogenation. Therefore, given its higher likelihood of success, the ketene hydrogenation was investigated first.

Scheme C.1.

These two efforts would undergo continuous economic assessment until a conclusion could be reached regarding the potential viability of the proposed processes for the generation of vinyl acetate from synthesis gas. The remainder of this report details the background, execution, and conclusions derived from these simultaneous efforts. The first section will deal with the generation of acetaldehyde via the hydrogenation of ketene and acetic acid. Esterification studies and finally the economic assessment will follow this section.

Table C.5. Summary of Knowledge Gaps Associated with Syngas Based Processes to VAM.

<u>Acetaldehyde Process</u>	<u>Esterification Reagent</u>	
	<u>Acetic Anhydride</u>	<u>Ketene</u>
MeOH Reductive Carbonylation	----	MeOH Reductive Carbonylation^b Acetaldehyde Esterification with Ketene^a
MeOAc Reductive Carbonylation	----	<i>MeOAc Reductive Carbonylation</i> Acetaldehyde Esterification with Ketene^a
DME Reductive Carbonylation	----	<i>DME Reductive Carbonylation</i> Acetaldehyde Esterification with Ketene^a
AcOH Hydrogenation	Direct Acetic Acid Hydrogenation^b (reactive distillation, DME carbonylation)	Direct Acetic Acid Hydrogenation^b Acetaldehyde Esterification with Ketene^A
Ac2O Hydrogenation	----	(DME Carbonylation) Acetaldehyde Esterification with Ketene^a
ketene hydrogenation	Ketene Hydrogenation^a (reactive distillation, DME carbonylation)	Acetaldehyde Esterification with Ketene^a Ketene Hydrogenation

^a new, previously unknown technology^b leading edge technologies known in the literature but unproven and incompletely developed.

Processes in parentheses are simple extensions of existing technology.

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2. Gauthier-Lafaye, J. and Perron, R. *Methanol et Carbonylation*, Rhone-Poluenc Recherches, Coubervoie, France, 1986 (English Translation, *Methanol and Carbonylation*, Editions Technip, Paris, and Rhone-Poluenc Recherches, Coubervoie, France, 1987, p. 201)

Appendix
(Section C.)

Scheme C.2. Flow Chart For Investigation of Vinyl Acetate Process
(Eastman Chemical Company)

Statement of Work

Task 1. Acetaldehyde Generation.

The modes of acetaldehyde formation are critical to reducing the quantities of acetic acid recycled within in the overall VAM process and the resultant size of intermediate production facilities. The original proposal called for examinations of a number of potential routes to acetaldehyde. After Eastman examined flowsheets, they could no longer support examinations of the hydrogenation of acetic anhydride since the volumes of acetic anhydride which would need to be regenerated are too large and would be economically unacceptable. However, the examination revealed that the most desirable source of acetaldehyde would be the acetic acid obtained from the EDA cracking to VAM. Other potentially viable sources of acetaldehyde were also identified.

Task 1.1. Generation of Acetaldehyde from Acetic Acid.

Although this would be the most desirable source of acetaldehyde, Eastman is aware of only a few instances of direct **selective** hydrogenation of acetic acid to acetaldehyde, which is thermodynamically disfavored and tends toward the complete hydrogenation to ethanol. None are commercially practiced. Eastman has devised a method for the hydrogenation entailing the generation of ketene as an intermediate. It would however be desirable to perform this transformation without the energy intensive ketene generation step if possible. Therefore, this subtask has been further subdivided into:

Task 1.1.a. Hydrogenation of Acetic Acid via Ketene Intermediates. The generation of ketene from acetic acid has been practiced by Eastman for >60 years. Eastman proposes that they study additional catalysts and optimize the hydrogenation of ketene. Based on the simplicity of the flowsheets using this process and its demonstrated success, Eastman will place top priority on this transformation.

Task 1.1.b. Direct Hydrogenation of Acetic Acid to Acetaldehyde. Eastman hopes to expand upon its progress in Task 1.1.a. to design a process capable of achieving a direct hydrogenation of acetic acid.

Task 1.2. Reductive Carbonylation of Methanol and Methyl Esters.

The original proposal calls for studies of the reductive carbonylation of methanol and methyl esters (either methyl acetate or methyl formate.) Prior investigations of these processes utilized corrosive systems at high pressure. However, initial assessment of the flowsheets indicate that these may remain viable processes and do not necessarily lead to untenable plant sizes. Therefore, these processes should be investigated as proposed in the original Statement of Work. The key will be developing a selective process, which does not proceed to ethanol or its derivatives and which operates under economically advantageous conditions and/or does not require expensive materials of construction. In scheme 4, these transformations are indicated as ***1.2.a.*** for the reductive carbonylation of methanol and ***1.2.b.*** for the reductive carbonylation of methyl acetate.

Task 1.3. Direct Generation of Acetaldehyde from Syngas.

The generation of the acetaldehyde component directly from syngas could prove to be a very fruitful approach as originally proposed. Eastman intends to pursue the direct generation of acetaldehyde from syngas under the contract, likely via studies of several heterogeneous catalysts.

Task 2.1. Process, Economic Evaluations.

The continual economic evaluation of technology under development is important because our objective is to provide a commercially useful process. Eastman intends to conduct formal economic evaluations throughout the program to:

- 1) insure the program continues to provide an economically attractive route to VAM,
- 2) eliminate economically untenable process options before the program expends significant resources on poor choices,
- 3) assist in setting project priorities by identifying the most economically attractive pathways and economically significant knowledge gaps. (The need for this should be obvious given the myriad potential pathways in schemes 4-7.)
- 4) identify key opportunities for process integration between the various units and key knowledge gaps associated with further integration. (Key examples would be the simplification and/or removal of distillation units where the highest purity materials are not required and heat integration.)

Eastman proposes to do these evaluations since it already has access to most of the requisite information and engineering models internally.

Task 2.2. Process, Plan Scale-Up.

Parallel to performing on-going economic evaluations of the proposed technologies, the need to consider plans for process scale-up should be pursued. Some of the chemistry proposed for investigation may be appropriate for examination at DOE's LaPorte, Texas Slurry Phase Alternative Fuels Development Unit. Investigations should be well enough advanced at the milestone to enable a focusing and delineation of future scale-up planes.

Task 3. Acetic Anhydride from Dimethyl Ether.

Given Eastman's success in Task 1.1., dimethyl ether (DME) may be a particularly useful source of acetyls, particularly since it delivers the highest level of carbonylation per pass through the reactor. As shown in scheme 5, this process is dependent upon the successful achievement of Task 1.1. Otherwise, there would be excessive amounts of acetyl generated for which a market outlet might be questionable. The transformation of Eastman's existing methyl acetate carbonylation unit to a DME carbonylation should be straightforward, although it will be necessary to develop a good kinetic model to insure the proper operation of such a facility. (This has a dual use for DOE in that they would like to see if DME from the liquid phase methanol process to be demonstrated at Kingsport can be used within Eastman's carbonylation facility.)

Task 4. Ethylidene Diacetate (EDA) Forming Processes.

Task 4.1. EDA from AcH/Ketene/AcOH. Although Eastman is still early in its investigations of Task 1.1, the capture of the acetaldehyde in the presence of ketene may be necessary, particularly if, as is usually the case, conversion is less than 100%. Although Eastman intends to look at several options for capturing the acetaldehyde in this stream, the direct combination of the stream with acetic acid (obtained from the EDA cracking), with or without a catalyst, may be the most convenient approach and will likely be the first "trapping" process tested. Inherent in this investigation will be some investigations into the kinetics of the formation of EDA from acetaldehyde and acetic anhydride.

Task 4.2. EDA Cracking. If the use of task 4.1. becomes the process of choice, the cracking of EDA to VAM and AcOH will need to be studied. Air Products has existing plans to study this process with the intent of identifying catalysts other than benzene sulfonic acid which leads to benzene contamination in the product via degradation.

Eastman is in possession of several solid acid catalysts and may provide samples to Air Products to test in this phase of the program.

Task 5. Conversion of Acetaldehyde to VAM without Isolation of EDA.

The explicit goal of Task 4 in the original statement of work was to provide EDA for subsequent VAM generation. Although the generation of EDA and its subsequent cracking to VAM was originally envisioned as a two step process, the recent technology advances made at Eastman may obviate any specific EDA isolation. Further, Eastman believes that the processes described in Task 5 may well represent an economically significant improvement in the sequence of transformations required for the potential commercial generation of VAM from syngas. If a good faith effort is to be maintained in this project, Eastman believes Task 5 should be included in the overall plan of work to stay within the spirit of the overall project intent.

Task 5.1. Direct Conversion of Acetaldehyde and Acetic Anhydride to VAM and Acetic Acid - Reactive Distillation.

Outside of the contract, Eastman has demonstrated a reactive distillation process for the conversion of acetaldehyde and acetic anhydride to vinyl acetate and acetic acid without the isolation of EDA. The process, which currently operates as a two column system to generate pure acetic acid and vinyl acetate as the sole effluents, results in significant cost savings over earlier processes for this conversion. Under this revised Proposed Statement of Work, Eastman proposes to incorporate advances in this new technology and undertake further work to:

- 1) identify heavies and more thoroughly study hydrodynamics of the column.
- 2) investigate alternative catalysts and operations which will reduce this to a single column operation.

Task 5.2. Conversion of Acetaldehyde to VAM Using Ketene.

The conversion depicted in scheme 6 would appear initially to be the most desirable process alternative if the acetaldehyde could be induced to react directly with excess ketene to generate the desired VAM product. Unfortunately, the normal mode of addition for ketene to acetaldehyde is to form beta-butyrolactone, a highly undesirable material with carcinogenic properties. However, the presence of catalysts often dramatically effect the modes of ketene addition to aldehydes and ketones. Given the potentially large

economic impact of attaining this conversion and high likelihood of success, Eastman proposes to examine the direct addition acetaldehyde to ketene to see if this transformation can be attained. (This should represent a high priority within Eastman's program.)

Task 6. Evaluation of Commercial Application.

Successful pilot plant demonstration of the developed technology will be accompanied by final stage process concept development, evaluation of the merchant market for the process products, and refinement of the economic evaluations.

D. Generation of Acetaldehyde (Task 1)

1. Overview.

Three acetaldehyde syntheses were investigated in this project: ketene hydrogenation, acetic acid hydrogenation and the reductive carbonylation of methanol. The most successful of these approaches were the ketene hydrogenation and the direct hydrogenation of acetic acid. The ketene hydrogenation study was initiated first because it was thermodynamically advantaged compared to the acetic acid hydrogenation, and it was envisioned that the hydrogenation of ketene could be accomplished under very mild conditions compared with those likely required for acetic acid hydrogenation. Although this vision proved to be true from the viewpoint of molecular efficiency, ketene hydrogenation did not appear to be efficient from an economical viewpoint. Therefore a study of acetic acid hydrogenation was also performed. Although the hydrogenation of acetic acid appeared to be more challenging from a molecular viewpoint than ketene hydrogenation, it appeared to be more efficient from an economical viewpoint than the ketene hydrogenation route. Although the ketene hydrogenation and the acetic acid hydrogenation were examined in a sequential fashion, the reductive carbonylation of methanol was examined in a parallel fashion with the other two approaches.

2. Ketene Hydrogenation Studies (Task 1.1).

Introduction

The philosophy behind the synthesis of acetaldehyde via ketene hydrogenation is to actually accomplish acetic acid hydrogenation in two separate steps. The first of these is the dehydration of acetic acid to form ketene. The formation of ketene by acetic acid dehydration is endothermic by about 32 kcal/mole. However, this reaction has been refined to the point where excellent ketene yields can be achieved by acetic acid pyrolysis at about 720°C and reduced pressure, and the reaction is practiced commercially to ultimately prepare acetic anhydride and higher value products such as sorbates and acetoacetate derivatives. At 100°C the hydrogenation of ketene to acetaldehyde is exothermic by about 17 kcal/mole.¹ It was envisioned that the highly reactive ketene molecule could be hydrogenated to acetaldehyde under very mild conditions, provided the right catalyst could be found.

There are no references in the literature describing the hydrogenation of ketene to acetaldehyde in a continuous fashion. Carr et al. teach that the reaction of ketene with hydrogen atoms produces mainly methane and carbon monoxide.² White et al. describe the interaction of ketene with metal surfaces (Ru and Pt) as studied by spectroscopic techniques.³ Although adsorbed acetaldehyde can be observed in some cases, it either decomposes or polymerizes on the catalyst. No free acetaldehyde is produced. The desorbed products from these reactions are generally methane or higher hydrocarbons and carbon monoxide.

Ponec et al. describe a high-temperature (350°C) hydrogenation of acetic acid over reduced iron oxide catalysts.⁴ Addition of platinum enhances the selectivity somewhat. Ketene was identified as a by-product and possible intermediate. Under conditions where the selectivity to acetaldehyde is good (87-97%), the yield of acetaldehyde is poor (6% or less), even though the reactions are run in a large excess of hydrogen (hydrogen/acetic acid ratio = 60/1). Operation in this mode is impractical from an industrial viewpoint, owing to the dilute product stream, extensive recycle and large temperature extremes required for isolation of the product. Poorer acetaldehyde selectivity (16-40%) is observed at higher yields (13-40%) over a related tin oxide catalyst. By-products of the reaction include acetone along with smaller amounts of methane and carbon dioxide. Platinum metal by itself produced no acetaldehyde in the acetic acid hydrogenation reaction, and the only products observed were methane, water, carbon monoxide and carbon dioxide.

A number of ketene-metal complexes have been described in the literature. Shapley et al. describe a ruthenium-based ketene complex that does not react with hydrogen.⁵ Miyashita et al. describe a platinum-based ketene complex that produces a mixture of acetaldehyde, ethanol and hydrocarbons when treated with hydrogen.⁶ Geoffroy et al. describe an osmium cluster-based ketene complex which decomposes in the presence of hydrogen to form several other osmium clusters, acetic acid and acetaldehyde.⁷ None of these metal complex materials are catalytic in their reaction with hydrogen, and none of the complexes other than the case described by Miyashita et al. was prepared from ketene.

Experimental Methods

General Apparatus, Operation of the Apparatus and Data Analysis. The vast majority of experiments were performed using the following apparatus.⁸ A schematic diagram of the apparatus is provided in Figure D.1. Metered gas flows were provided by four Tylan Model FC-260 mass flow controllers. Electric temperature control and monitoring were provided by a Dow Camile® control system interfaced with a Gateway Model 2000 486DX/33 computer. Tygon® tubing was used for ketene-free gases, and PharMed® tubing was used for ketene-containing gases. Condensers, the cyclone assembly, all traps, reactors and scrubbers were constructed of glass or quartz. Metered gases were fed through on/off valves V1 through V4, and each gas line was teed to a pressure relief column containing water to prevent accidental over-pressurization. Ketene was generated for laboratory use by the method described by Fisher et al. by the pyrolysis of acetic anhydride with minor modifications.⁹ (Although acetic acid pyrolysis is the preferred industrial route to ketene, it is generally not practical on a laboratory scale: any source of ketene can be used, provided it is free of catalyst poisons.) Acetic anhydride (Ac₂O) was fed at 600 ml/hr using a Harvard Apparatus Model 22 syringe infusion pump. The acetic anhydride was fed to a 107-cm-long by 25-mm-O.D. quartz vaporizer/pyrolysis tube, along with 25 standard cubic centimeters per minute (SCCM) helium. The vaporizer/pyrolysis tube was indented at a distance of 27 cm from the top and contained a 9-mm-O.D. quartz thermocouple well extending about two thirds the length of the reactor from top towards the bottom. The portion of the vaporizer/pyrolysis tube extending 22

Figure D.1
Ketene Generator / Hydrogenator

cm up from the indentations also contained quartz chips and was heated with heating tape controlled at 200°C. The lower section of the vaporizer/pyrolysis tube was heated by a Lindberg three-element electric furnace controlled at 520°C. The quenching condenser below the vaporizer/pyrolysis tube was held at about -55°C by circulating methanol cooled in a solid carbon dioxide/acetone bath. The mixture from the quenching condenser passed through two identical cyclones measuring 16 mm O.D. at the top and 80 mm from the top of the cyclone body to the bottom of the tapered section. The inlet and outlet lines of the cyclone were 2 mm I.D., and the liquid from the bottom of the cyclone was drained into a 500-ml flask. The gas displacement tube (10 mm O.D.) connecting the drain flask to the cyclone assembly was bent to provide a liquid seal, as shown in Figure D.1. The misted vapor from the ketene generator cyclone assembly was passed through two demisting traps held at 0°C to a three-way stopcock (SC1). In one position SC1 vented excess ketene-containing vapors from the generator to a water scrubber. In another position SC1 sent the ketene-containing vapors to the ketene inlet line of a trap/vaporizer assembly. The trap/vaporizer assembly was a modified two-piece 32 X 200-mm vacuum trap having the bottom portion of the trap narrowed to 19 mm O.D. and extending an additional 100 mm. A 7-mm-O.D. / 2-mm-I.D. gas inlet tube extended along the outer body of the trap/vaporizer assembly and was connected to the base of the extended tube section. The gas inlet tube was connected to a metered nitrogen line containing a stopcock (SC2). The ketene inlet line was the normal inside 10-mm-O.D. tube found in the standard vacuum trap design. The ketene outlet line was the normal 10-mm-O.D. side tube found in the standard vacuum trap design. The trap/vaporizer assembly was loaded with about 30 ml of liquid ketene by immersing the assembly in a -78°C bath with SC2 closed and SC1 opened to the trap/vaporizer while the ketene generator was operating. During the procedure of loading the trap/vaporizer with ketene, the outlet line was isolated from the reactor and accessed to the water scrubber via stopcocks SC3, SC4 and SC5. Helium (normally set for 50 SCCM) was always flowing through a line leading from valve V2 and mixing with any material exiting the outlet line of the trap/vaporizer, both during the ketene generation procedure and during the hydrogenation procedure. About 15 minutes of ketene generator operation were required to fill the tapered portion of the trap/vaporizer.

After the ketene trap/vaporizer was loaded, it was isolated from the ketene generator by turning SC1 to the position shown in Figure D.1, and SC2 was opened and nitrogen (normal rate 88 SCCM) was metered through the liquid ketene at -78°C. These conditions transpired the ketene from the trap/vaporizer at a rate of 1 mmol/minute (about 22.4 SCCM). Hydrogen (normal rate 44.8 SCCM) was metered through V1 to the temperature-controlled reactor (details of the type of reactor used and reaction conditions are provided in the specific examples). The hydrogenation reaction was begun by turning SC3 to the position shown in Figure D.1 while venting the product vapor to the water scrubber through SC4 and SC5. For vapor phase reactions, a two-necked, 100-ml, round-bottomed flask was connected to the base of the reactor to trap any material that was not volatile at ambient temperature. To collect a sample for analysis, SC5 was turned to the position shown in Figure D.1 to send the product vapors to an analytical scrubber containing methanol (100 ml). The methanol scrubber mixture was circulated by a

Masterflex peristaltic pump. Any unreacted ketene was converted to methyl acetate in the methanol scrubber. Acetaldehyde existed in the methanol as free acetaldehyde and acetaldehyde dimethyl acetal. A condenser containing solid carbon dioxide and acetone was fitted to the top of the scrubber to prevent material loss. After a set period, the product vapor stream was again diverted to the water scrubber via SC5, and the methanol solution was drained from the scrubber base via SC6 and weighed. The scrubber was then replenished with fresh methanol for the subsequent sample.

Products contained in the methanol scrubber solution were analyzed by gas chromatography using a Hewlett Packard Model 5890 gas chromatograph fitted with a 30-m x 0.25-mm FFAP capillary column (0.25 micron film thickness) programmed at 35°C for 7 minutes, 15°C/minute to 220°C and holding at 220°C for 2 minutes using a flame ionization detector held at 280°C (injector temperature = 240°C). Mixtures were prepared for gas chromatographic analysis by adding 5 ml of a tetrahydrofuran solution containing 2 % decane internal standard to an accurately weighed 1-g sample of the methanol scrubber solution.

The following definitions apply to the specific experiments:

Space velocity (SV) = volumes of gas per volume of catalyst per hour under reaction conditions,

Space time yield (STY) = grams of acetaldehyde produced per liter of catalyst per hour,

% ketene conversion = $100(\text{mmoles ketene reacted})/(\text{mmoles ketene fed})$,

% ketene accountability = $100(\text{mmoles ketene recovered} + \text{mmoles acetaldehyde produced})/(\text{mmoles ketene fed})$,

% acetaldehyde selectivity = $100(\text{mmoles acetaldehyde produced})/(\text{mmoles ketene reacted})$.

The volume of any noncatalytic solid (vapor phase operation) or liquid (vapor/liquid/solid operation) material added to the reactor as a diluent is not included in the SV or STY calculations.

Experiment 1. Ketene hydrogenation using a 5% Pd on barium sulfate catalyst in a steam heated reactor.¹⁰ The glass reactor consisted of a 53-cm by 25-mm O.D. tube fitted with a permanent thermowell extending from the base of the reactor. The central portion of the reactor tube was constructed with a condenser jacket which was in turn enclosed in a vacuum jacket to prevent heat loss. The length of the jacketed portion was 37 cm. The 25-mm-O.D. tube had indentations 6 cm above the base of the jacket to support the catalyst bed. The reactor was loaded to a distance extending 25 mm above the indentations with quartz wool covered with 8- X 16-mesh quartz chips. A physical

mixture was made from 5% Pd on barium sulfate powder (1.0015 g = 0.9 ml) and 8- X 16-mesh quartz chips (50 ml), and this mixture was loaded above the quartz chips covering the quartz wool. The catalyst bed length was 15 cm. An additional charge of 4- X 8-mesh quartz chips was loaded on top of the catalyst bed to increase the height of the packed bed an additional 8 cm up to the top of the condenser jacket. Hydrogen was fed to the reactor at 44.8 SCCM and one atmosphere pressure, and the reactor was heated with steam to 97°C. The temperature along the entire length of the catalyst bed was constant to within 0.5°C. The catalyst was treated with hydrogen in this manner for 22 hours, and then a mixture of ketene (1 mmol/minute), nitrogen (88 SCCM) and helium (50 SCCM) was added to the hydrogen stream entering the reactor. The temperature of the catalyst bed remained constant at 97-98°C during the hydrogenation reaction. Samples were taken throughout the day, and at the end of the day, the ketene, nitrogen and helium was diverted from the reactor to the water scrubber, and the reactor was allowed to remain at 97-98°C with hydrogen flowing at 10 SCCM overnight to restore activity to the catalyst. The ketene was allowed to evaporate from the trap/vaporizer, which was then cleaned to prepare it for the next day's operation. The reactor was operated in this manner for 4 days. The following samples were taken at the total time on stream (TTOS, indicated in minutes) that both hydrogen and ketene were contacting the catalyst, and samples were collected over 60- or 90-minute periods:

<u>Sample</u>	<u>TTOS, min.</u>
1-A	286-376
1-B	641-731
1-C	739-799
1-D	994-1084
1-E	1097-1157
1-F	1362-1452

Overnight hydrogenations were performed after TTOS = 376, 731 and 1084 minutes. The results of these experiments are summarized below:

<u>Sample</u>	<u>SV, hr⁻¹</u>	<u>STY, g-l⁻¹-hr⁻¹</u>	<u>% ketene conversion</u>	<u>% ketene accountability</u>	<u>% acetaldehyde selectivity</u>
1-A	18600	1420	78	70	61
1-B	18600	1440	70	79	70
1-C	18600	1680	100	57	57
1-D	18600	1500	66	85	78
1-E	18600	1600	65	90	84
1-F	18600	1370	72	75	65

The differences in performance with time reflect the effects of natural catalyst aging and the elapsed time following overnight hydrogen treatments.

Experiment 2. Ketene hydrogenation using a Pd on barium carbonate catalyst.¹¹ A physical mixture was prepared from 5% Pd on barium carbonate powder (1.0075 g = 0.91

ml) and quartz chips as per example 1. The same reactor, reactor loading sequence, hydrogen pretreatment, flow and temperature settings were used as in the preceding experiment. The following samples were taken at the total time on stream (TTOS, indicated in minutes) that both hydrogen and ketene were contacting the catalyst, and samples were collected over 60- or 90-minute periods:

<u>Sample</u>	<u>TTOS, min.</u>
2-A	286-376
2-B	380-440
2-C	635-725
2-D	729-789
2-E	984-1074
2-F	1350-1440

Overnight hydrogenations were performed after TTOS = 376, 725 and 1074 minutes. The results of these experiments are summarized below:

<u>Sample</u>	<u>SV, hr⁻¹</u>	<u>STY, g-l⁻¹-hr⁻¹</u>	<u>% ketene conversion</u>	<u>% ketene accountability</u>	<u>% acetaldehyde selectivity</u>
2-A	18400	1390	67	81	72
2-B	18400	1550	62	92	87
2-C	18400	1230	57	85	74
2-D	18400	1480	56	95	92
2-E	18400	1310	53	92	86
2-F	18400	1240	56	86	76

The differences in performance with time reflect the effects of natural catalyst aging and the elapsed time following overnight hydrogen treatments.

Experiment 3. Ketene hydrogenation using a Pd on calcium carbonate catalyst.¹² A physical mixture was prepared from 5% Pd on calcium carbonate powder (1.0028 g = 1.4 ml) and quartz chips as per example 1. The same reactor, reactor loading sequence, hydrogen pretreatment, flow and temperature settings were used as per the preceding experiments. The following samples were taken at the total time on stream (TTOS, indicated in minutes) that both hydrogen and ketene were contacting the catalyst, and samples were collected over 60- or 90-minute periods:

<u>Sample</u>	<u>TTOS, min.</u>
3-A	195-285
3-B	573-663
3-C	955-1045
3-D	1146-1206
3-E	1411-1501

Overnight hydrogenations were performed after TTOS = 380, 758 and 1140 minutes. The results of these experiments are summarized below:

<u>Sample</u>	<u>SV, hr⁻¹</u>	<u>STY, g-l⁻¹-hr⁻¹</u>	<u>% ketene conversion</u>	<u>% ketene accountability</u>	<u>% acetaldehyde selectivity</u>
3-A	12000	1210	82	81	78
3-B	12000	1070	85	72	67
3-C	12000	1020	82	71	65
3-D	12000	1220	100	65	65
3-E	12000	1080	100	57	57

The differences in performance with time reflect the effects of natural catalyst aging and the elapsed time following overnight hydrogen treatments.

Experiment 4. Ketene hydrogenation using a lead-poisoned Pd on calcium carbonate catalyst (Lindlar catalyst).¹³ This reaction can be compared to experiment 3 to illustrate the effect of lead poisoning on the performance of the catalyst. A physical mixture was prepared from lead-poisoned 5% Pd on calcium carbonate powder (1.0048 g = 1.2 ml) and quartz chips as per example 1. The same reactor, reactor loading sequence, hydrogen pretreatment, flow and temperature settings were used as per example 1. The following samples were taken at the total time on stream (TTOS, indicated in minutes) that both hydrogen and ketene were contacting the catalyst, and samples were collected over 60- or 90-minute periods:

<u>Sample</u>	<u>TTOS, min.</u>
4-A	188-278
4-B	561-651
4-C	929-1019
4-D	1122-1182
4-E	1382-1472

Overnight hydrogenations were performed after TTOS = 373, 746 and 1114 minutes. The results of these experiments are summarized below:

<u>Sample</u>	<u>SV, hr⁻¹</u>	<u>STY, g-l⁻¹-hr⁻¹</u>	<u>% ketene conversion</u>	<u>% ketene accountability</u>	<u>% acetaldehyde selectivity</u>
4-A	13900	760	77	57	45
4-B	13900	740	71	62	47
4-C	13900	630	66	63	44
4-D	13900	680	100	31	31
4-E	13900	605	62	65	44

The differences in performance with time reflect the effects of natural catalyst aging and the elapsed time following overnight hydrogen treatments.

Experiment 5. Ketene hydrogenation using a Pd on alumina catalyst.¹⁴ This was a long-term experiment in which the total time on stream exceeded 100 hours. A physical mixture was prepared from 1% Pd on alumina, 2-mm sized pellets (5.0186 g = 6 ml) and quartz chips as per experiment 1. The same reactor, reactor loading sequence, hydrogen pretreatment, and reaction conditions were used as per experiment 1. Although reaction conditions were varied during this extended experiment (see experiments 6, 7 and 8 below), the data presented in this experiment were obtained under the flow and temperature settings reported in experiment 1. The following samples were taken at the total time on stream (TTOS, indicated in minutes) that both hydrogen and ketene were contacting the catalyst, and samples were collected over 60 or 90 minute periods:

<u>Sample</u>	<u>TTOS, min.</u>
5-A	260-350
5-B	641-731
5-C	1051-1141
5-D	2363-2423
5-E	2618-2708
5-F	6762-6822

Overnight hydrogenations were performed after TTOS = 350, 731, 1141, 1563, 1971, 2350, 2708, 3116, 3514, 3918, 4311, 4702, 5086, 5464, 5915, 6294 and 6754 minutes. The results of these experiments are summarized below:

<u>Sample</u>	<u>SV, hr⁻¹</u>	<u>STY, g-l⁻¹-hr⁻¹</u>	<u>% ketene conversion</u>	<u>% ketene accountability</u>	<u>% acetaldehyde selectivity</u>
5-A	2800	190	59	84	72
5-B	2800	150	50	84	69
5-C	2790	120	43	84	62
5-D	2790	140	34	96	89
5-E	2790	110	27	99	96
5-F	2790	90	25	94	78

The differences in performance with time reflect the effects of natural catalyst aging and the elapsed time following overnight hydrogen treatments.

Experiment 6. Ketene hydrogenation at different temperatures using a Pd-on-alumina catalyst.¹⁵ The same Pd-on-alumina catalyst described in experiment 5 was used, and the data were obtained during the course of experiment 5. The steam heating system was replaced with a temperature-controlled circulating water bath for data obtained below 90°C. The data were obtained at a point in the catalyst history where changes in activity due to catalyst deactivation were minimal. Flow settings were as per the previous experiments. The following samples were taken at the total time on stream (TTOS, indicated in minutes) that both hydrogen and ketene were contacting the catalyst, and samples were collected over 90-minute periods:

<u>Sample</u>	<u>TTOS, min.</u>	<u>Bed temperature, °C</u>
6-A	5374-5464	98.0
6-B	5730-5820	88.4
6-C	6204-6294	77.8
6-D	5550-5640	69.8
6-E	5986-6076	59.3
6-F	6394-6484	49.4

The results of these experiments are summarized below:

<u>Sample</u>	<u>SV, hr⁻¹</u>	<u>STY, g-l⁻¹-hr⁻¹</u>	<u>% ketene conversion</u>	<u>% ketene accountability</u>	<u>% acetaldehyde selectivity</u>
6-A	2790	91	32	89	65
6-B	2720	62	34	80	41
6-C	2640	41	30	80	31
6-D	2580	41	28	82	33
6-E	2500	24	13	92	41
6-F	2420	15	12	91	29

Experiment 7. Ketene hydrogenation with varying amounts of hydrogen and ketene using a Pd on alumina catalyst.¹⁶ The same Pd-on-alumina catalyst used in experiment 5 was used in this experiment, and the data were obtained during the course of experiment 5. The data were obtained at a point in the catalyst history where changes in activity due to catalyst deactivation were minimal. The temperature of the catalyst was maintained at 98°C, and the space velocity was held essentially constant by changing the amount of diluent helium when other gas flows were changed. A different space velocity was used for the study of varying hydrogen levels than was used for the study for varying ketene levels, and a more dilute gas stream was used when the ketene levels were varied. The following samples were taken at the total time on stream (TTOS, indicated in minutes) that both hydrogen and ketene were contacting the catalyst, and samples were collected over 60- or 90-minute periods:

<u>Sample</u>	<u>TTOS, min.</u>	<u>Mmol ketene/minute</u>	<u>Mmol H₂/minute</u>
7-A	3703-3793	1.0	0.5
7-B	3583-3673	1.0	1.0
7-C	1563-1473	1.0	2.0
7-D	1215-1305	1.0	3.0
7-E	1348-1438	1.0	4.0
7-F	3986-4076	0.5	4.0
7-G	4382-4472	1.0	4.0
7-H	4771-4861	1.5	4.0
7-I	5249-5339	2.0	4.0

The results of these experiments are summarized below:

<u>Sample</u>	<u>SV, hr⁻¹</u>	<u>STY, g-l⁻¹-hr⁻¹</u>	<u>% ketene conversion</u>	<u>% ketene accountability</u>	<u>% acetaldehyde selectivity</u>
7-A	2800	59	23	91	59
7-B	2800	77	37	80	47
7-C	2800	128	47	83	62
7-D	2800	165	51	87	74
7-E	2800	172	49	90	80
7-F	4300	77	46	90	77
7-G	4300	110	36	89	70
7-H	4300	109	33	84	50
7-I	4300	131	34	81	43

Experiment 8. Ketene hydrogenation at varying gas hourly space velocity (SV) using a Pd-on-alumina catalyst.¹⁷ The same Pd-on-alumina catalyst described in experiment 5 was used in this experiment, and the data were obtained during the course of experiment 5. The data were obtained at a point in the catalyst history where changes in activity due to catalyst deactivation were minimal. The temperature of the catalyst was maintained at 98°C, and the gas ratios were the same as described in experiments 1 and 5. The following samples were taken at the total time on stream (TTOS, indicated in minutes) that both hydrogen and ketene were contacting the catalyst, and samples were collected over 60- or 90-minute periods:

<u>Sample</u>	<u>TTOS, min.</u>
8-A	1631-1721
8-B	1473-1563
8-C	1756-1846
8-D	1975-2035

The results of these experiments are summarized below:

<u>Sample</u>	<u>SV, hr⁻¹</u>	<u>STY, g-l⁻¹-hr⁻¹</u>	<u>% ketene conversion</u>	<u>% ketene accountability</u>	<u>% acetaldehyde selectivity</u>
8-A	1400	106	49	99	99
8-B	2800	128	47	82	62
8-C	3700	153	37	87	63
8-D	4910	185	34	87	62

Experiment 9. Ketene hydrogenation using a Pd-on-carbon catalyst.¹⁸ A physical mixture was prepared from 5% Pd-on-carbon powder (1.0026 g = 2.6 ml) and quartz chips as per experiment 1. The same reactor, reactor loading sequence, hydrogen pretreatment, flow and temperature settings were used as per experiment 1. The following samples were taken at the total time on stream (TTOS, indicated in minutes)

that both hydrogen and ketene were contacting the catalyst, and samples were collected over 60- or 90-minute periods:

<u>Sample</u>	<u>TTOS, min.</u>
9-A	336-426
9-B	435-495
9-C	710-800
9-D	1294-1384
9-E	1484-1574

Overnight hydrogenations were performed after TTOS = 426, 800 and 1214 minutes. The results of these experiments are summarized below:

<u>Sample</u>	<u>SV, hr⁻¹</u>	<u>STY, g-l⁻¹-hr⁻¹</u>	<u>% ketene conversion</u>	<u>% ketene accountability</u>	<u>% acetaldehyde selectivity</u>
9-A	6420	585	100	58	58
9-B	6420	663	100	65	65
9-C	6420	607	100	60	60
9-D	6420	589	100	58	58
9-E	6420	552	81	74	67

The differences in performance with time reflect the effects of natural catalyst aging and the elapsed time following overnight hydrogen treatments.

*Experiment 10. Ketene hydrogenation using a Pd-on-titanium dioxide catalyst.*¹⁹ A physical mixture was prepared from 1% Pd on titanium dioxide powder (5.001 g = 6 ml) and quartz chips as per experiment 1. The same reactor, reactor loading sequence, hydrogen pretreatment, flow and temperature settings were used as per experiment 1. The following samples were taken at the total time on stream (TTOS, indicated in minutes) that both hydrogen and ketene were contacting the catalyst, and samples were collected over 90-minute periods:

<u>Sample</u>	<u>TTOS, min.</u>
10-A	262-352
10-B	615-705
10-C	775-865
10-D	1318-1408

Overnight hydrogenations were performed after TTOS = 352, 705 and 1055 minutes. The results of these experiments are summarized below:

<u>Sample</u>	<u>SV, hr⁻¹</u>	<u>STY, g-l⁻¹-hr⁻¹</u>	<u>% ketene conversion</u>	<u>% ketene accountability</u>	<u>% acetaldehyde selectivity</u>
10-A	2800	108	36	89	68
10-B	2800	112	42	83	61

10-C	2800	100	61	61	37
10-D	2800	108	49	76	51

Experiment 11. Ketene hydrogenation using a bulk support-free Pd catalyst.²⁰ A physical mixture was prepared from palladium sponge powder (1.005 g = 0.4 ml) and quartz chips as per experiment 1. The same reactor, reactor loading sequence, hydrogen pretreatment, flow and temperature settings were used as per experiment 1. The following samples were taken at the total time on stream (TTOS, indicated in minutes) that both hydrogen and ketene were contacting the catalyst, and samples were collected over 90-minute periods:

Sample	TTOS, min.
11-A	429-519
11-B	784-874
11-C	1138-1228

Overnight hydrogenations were performed after TTOS = 354, 709 and 1064 minutes. The results of these experiments are summarized below:

Sample	SV, hr ⁻¹	STY, g-l ⁻¹ -hr ⁻¹	% ketene conversion	% ketene accountability	% acetaldehyde selectivity
11-A	41800	1310	24	96	84
11-B	41800	1290	24	95	80
11-C	41800	1310	20	100	100

Experiment 12. Ketene hydrogenation using a Rh-on-alumina catalyst.²¹ The reactor tube used in this experiment was a 25-mm O.D. quartz tube containing an internal quartz thermocouple. The reactor had indentations near the base. The reactor was loaded with quartz chips measuring 12 cm high from the indentations. The catalyst, 0.5% Rh on 3-mm alumina pellets (5.016 g = 5.1 ml), was added. An additional layer of quartz chips measuring 6 cm high was placed on top of the catalyst bed. The reactor was placed in a single-element electric furnace having a 23-cm-long heated zone such that the catalyst was positioned in the center of the heated zone of the furnace. The catalyst was treated overnight with hydrogen (44.8 SCCM) at 200°C and then allowed to cool to ambient temperature. Ketene (1 mmol/minute), helium (25 SCCM), nitrogen (88 SCCM), and hydrogen (44.8 SCCM) were fed to the reactor, and the furnace was not on. The catalyst bed temperature rose from ambient to 30°C, with the space velocity = 2350 hr⁻¹, and the vapor product was sampled over a 90-minute period. The space time yield of acetaldehyde was 56 g-l⁻¹-hr⁻¹ at 11% ketene conversion. The ketene accountability and the acetaldehyde selectivity were 100 and 97%, respectively. The activity of this catalyst for acetaldehyde production decreased to zero during the following hour as the catalyst bed temperature dropped to 24°C. The catalyst once again became active for the production of acetaldehyde when the furnace was set for 100°C, with the space velocity = 3250 and the catalyst bed temperature at 146°C. The sample was collected over 90 minutes, and the space time yield of acetaldehyde was 31 g-l⁻¹-hr⁻¹ at 73% ketene

conversion. The ketene accountability and the acetaldehyde selectivity were 33 and 8%, respectively.

Experiment 13. Ketene hydrogenation using a Pt-on-alumina catalyst.²² The same reactor used in experiment 12 was used in this experiment, and the reactor was packed the same way as per experiment 12, except that the Rh-on-alumina catalyst was replaced with 0.5% Pt on 3-mm alumina pellets (5.0g = 6.1 ml). The same hydrogen pretreatment and reaction conditions as per experiment 12 were used. No acetaldehyde was detected with the furnace at ambient temperature. The furnace was then set for 100°C. The catalyst bed temperature rose to 148°C with the space velocity = 2700 hr⁻¹. The sample was collected over 90 minutes, and the space time yield of acetaldehyde was 45 g-l⁻¹-hr⁻¹ at 68% ketene conversion. The ketene accountability and the acetaldehyde selectivity were 42 and 15%, respectively.

Experiment 14. Ketene hydrogenation performed in the vapor/liquid/solid mode using a gas-stripped reactor.²³ The reaction vessel consisted of a glass cylindrical reaction flask having a ground flanged top joint, gas dispersing stirrer and ground flange reactor head fitted with a precision stirrer bearing, thermocouple and gas outlet port. Dimensions of the cylindrical reaction flask were 5 cm inner diameter by 28 cm high. Two bands of 5 equally spaced 5-cm-high indentations were located with the bottom of the bands at 6 and 15 cm up from the base of the reactor. The bands of indentations acted as baffles, and the indentations of the two bands were staggered. The gas-dispersing stirrer was a hollow 1-cm-O. D. glass tube sealed at the top and opened at the bottom and had two bands of stirrer blades located at the bottom of the stirrer and 11 cm up from the bottom. Each band of stirrer blades contained four 1.5- X 1.5-cm blades, and the blades of the two bands were staggered. The stirrer had a hole in the side that acted as an inlet port for the reactant gases, which were introduced through a side arm on the precision stirrer bearing. The reactor was loaded with 5% Pd on barium carbonate powder (1.0480 g = 0.94 ml) and dodecane (300 ml). The assembled reactor was heated at 95°C in a steam bath overnight with stirring and with hydrogen (44.8 SCCM) sparging through the slurry. Ketene (1 mmol/minute), helium (50 SCCM), and nitrogen (88 SCCM) were then added to the existing hydrogen stream. Products were analyzed from methanol scrubber solutions as per previous experiments, with the product vapor exiting the gas-stripped reactor outlet port contacting the scrubber solution. The slurry temperature remained at 95°C with the space velocity = 17600 hr⁻¹ (based on the catalyst volume). The sample was collected over 60 minutes, and the space time yield of acetaldehyde was 365 g-l⁻¹-hr⁻¹ (based on the catalyst volume) at 21% ketene conversion. The ketene accountability and the acetaldehyde selectivity were 92 and 62%, respectively.

Results and Discussion

The reactor system described in the experimental section was used for most of the reactions studied and provided a purified source of ketene that was essentially free of carbon monoxide. This was very fortunate because later in the project, carbon monoxide was found to be a reversible catalyst poison. The steam-heated reactor was used for most

of the experiments, and this also provided numerous experimental advantages. The use of steam, coupled with diluting the catalyst with quartz chips, allowed for control of the exotherm to about 0.5°C. The temperature of the steam was close to that considered optimal for the reaction (95-100°C). In some of the initial experiments, an electric furnace was used to heat the reactor with an undiluted catalyst bed, and exotherms of about 30°C were often observed. Good temperature control is important with a molecule as reactive as ketene.

Many heterogeneous catalysts were screened for the ketene hydrogenation reaction at 2/1 hydrogen/ketene ratio. Palladium (supported and unsupported) is by far the most active and selective metal for this reaction. Palladium was effective both in the vapor phase reactor and in the slurry phase reactor described in the experimental section. Alumina-supported platinum and rhodium also have some selectivity (see experimental section). Other heterogeneous catalysts examined include reduced iron oxide²⁴ (used by Ponec et al. for acetic acid hydrogenation), 1.2% Ir/C,²⁵ 0.5% Ru/Al₂O₃,²⁶ 1% Co/Al₂O₃,²⁷ supported nickel,²⁸ osmium sponge²⁹ and Cu/Zn/Al mixed oxide³⁰ (commercial methanol catalyst): none of these catalysts produced any detectable acetaldehyde under conditions that were effective with the Pd, Pt and Rh catalysts. Two homogeneous catalysts were examined using the slurry phase reactor: tetrakis(triphenylphosphine)palladium(0)³¹ and tris(triphenylphosphine)rhodium(I) chloride³² (Wilkinson's catalyst) using dodecane as a solvent. Neither of these catalysts produced any acetaldehyde under conditions that were effective with a heterogeneous palladium catalyst.

All heterogeneous palladium catalysts were active for the ketene hydrogenation reaction, regardless of the existence or identity of the support or the presence of various activity modifiers. Tables D.1 and D.2 summarize the performance data for a series of different heterogeneous palladium catalysts under the conditions described in the experimental section (1 mmol ketene/minute, 2 mmol hydrogen/minute, 4 mmol nitrogen/minute and 2.2 mmol helium/minute, 97-101°C, typically 1 g catalyst). During these experiments normally four samples were taken each day, and then the catalyst was left overnight at 97-98°C in a hydrogen stream. The performance data provided in Table D.1 is for the fourth sample taken on the first day of operation. The performance data provided in Table D.2 compares the performance of the fourth sample on the first day with the corresponding sample taken on the fourth day of operation and, therefore, gives information relating to catalyst deactivation. The overnight hydrogenation treatment restores some or all of the catalyst activity, depending on the catalyst. In general, high-surface-area supported catalysts such as 5% Pd/C do not respond well to the regenerative hydrogenation treatment. The low-surface-area bulk Pd catalyst (Pd sponge), on the other hand, responded very well to the overnight hydrogenation treatments. This regenerative behavior, shown in Figure D.2 for Pd sponge, is thought to result from the ability of the entire catalyst surface to hydrogenate off oligomeric by-products. When a large portion of the catalyst surface is support material, some of the oligomeric impurities may not be accessible to the chemisorbed hydrogen. The oligomeric impurities are thought to arise from the dimerization of ketene to produce diketene (vide infra).

TABLE D.1
EXPERIMENTAL RESULTS for the
HYDROGENATION of KETENE to ACETALDEHYDE

Ref. No., X24668-	Catalyst	Surface Area, m ² /g	Metal Dispersion %	STY, gHAc (l-hr) ⁻¹	STY, gHAc (gPd-hr) ⁻¹	STY, gHAc (gPd-hr) ⁻¹ /Metal Dispersion, %	Ketene Accountability, %	HAc Selectivity, %	Ketene Conver- sion, %
014	0.5%Pd/Al ₂ O ₃ pellets	238.0	19.5	188	44.7	2.29	84	72	59
033	5% Pd/BaSO ₄	4.2	2.6	1416	25.4	9.77	70	70	78
038	5% Pd/CaCO ₃ w/Pb	6.42	2.9	736	17.6	6.07	56	43	77
043	5% Pd/CaCO ₃	13.99	10.7	1151	32.1	3.00	79	74	82
048	5% Pd/BaCO ₃	5.21	2.9	1392	25.1	8.66	81	72	67
085	5% Pd/C	1259.0	25.1	713	37.1	1.48	78	76	92
060	5% Pd/Al ₂ O ₃ powder	103.0	17.1	1639	31.3	1.83	82	77	77
066	1% Pd/TiO ₂	9.0	1.7	108	15.8	9.29	88	68	36
072	3% Pd/SiO ₂	55.0	14.4	400	33.3	2.31	83	79	80
058	5%Pd/BaCO ₃	5.21	2.9	559	9.3	3.21	83	54	37
077	Pd Sponge	0.13	0.004	1180	0.47	117.50	91	66	27

Data presented is from the performance of the fourth sample.

All reactions were run in a fixed catalyst bed, steam-heated reactor except for X24668-058 which was run in a slurry phase reactor.

TABLE D.2
% CHANGE in PERFORMANCE
BETWEEN 4th and 16th SAMPLE

Ref. No., X24668-	Catalyst	Rate	Ketene Accountability	HAc Selectivity	Ketene Conversion
014	0.5%Pd/Al ₂ O ₃ pellets	-32	-2	-14	-22
033	5% Pd/BaSO ₄	-3	+7	-7	-8
038	5% Pd/CaCO ₃ w/Pb	-18	+16	+2	-19
043	5% Pd/CaCO ₃	-6	-28	-23	+23
048	5% Pd/BaCO ₃	-11	+6	+6	-16
085	5% Pd/C	-16	+14	+11	-24
060	5% Pd/Al ₂ O ₃ powder	-41	-33	-43	+4
066	1% Pd/TiO ₂	+1	-14	-25	+33
072	3% Pd/SiO ₂	-14	+10	+8	-20
058	5%Pd/BaCO ₃	slurry phase			
077	Pd Sponge	+0.4	+1	+6	-4

Figure D.2

HAc STY Vs Time on Stream

Pd Sponge Catalyst

During the long-term study using Pd on alumina pellets, crude preliminary kinetic studies were performed. These experiments (detailed in the experimental section) were performed at a point in the catalyst life where changes due to natural catalyst deactivation were minimal. Although the ketene conversions were higher than desirable in some of these experiments for good kinetic data, these crude experiments provided an activation energy of 7 kcal/mol and reaction orders for hydrogen and ketene of 0.6 and 0.3, respectively. The possibility of diffusional limitations was not ruled out. Space velocity effects are typical: the higher the space velocity, the higher the rate and the lower the conversion. The low reaction order in ketene is consistent with it being strongly adsorbed on the catalyst surface. This is consistent with the bonding mode presented in the literature for ketene on other metals.³ It is possible that this strong ketene adsorption mode is partly responsible for the excellent selectivity seen in this reaction: most of the adsorbed acetaldehyde could be displaced by ketene rather than hydrogenated. In the presence of unreacted ketene, any ethanol produced from acetaldehyde hydrogenation is converted to ethyl acetate. Normally ethyl acetate was not detected by the analytical method commonly used (gas chromatographic analysis of a methanol scrubber solution). When the reactor effluent from a 3% Pd/SiO₂ catalyst was condensed at -78°C, analysis of the condensate suggested that the ratio of acetaldehyde to ethyl acetate was between about 240 and 120, depending on the conversion. Thus it appears that the selectivity to ethyl acetate is normally less than 1%. The vent gas exiting the methanol scrubber typically contained 0-0.6% CO, 0.5-1% methane and about 0.2-0.5% each of carbon dioxide, ethylene and ethane. In all reactions the quartz catalyst diluent and region below the reactor slowly accumulated thick, oily material. This was the case even when the ketene accountability was close to 100%, and, although the amount of this material could not be quantified, it probably represented very small ketene loss and is likely due to diketene formation. Attempts to identify this oily material by GC-MS were unsuccessful, and, out of many peaks in the chromatogram, only acetaldehyde, acetic acid and acetic anhydride could be positively identified.³⁴ Similar materials form in the absence of a catalyst.

Additional information about deactivation was obtained by comparing the rate of catalyst deactivation when no nitrogen diluent was used (ketene/hydrogen = 1/2) with the rate of catalyst deactivation when the diluent was added (ketene/hydrogen/nitrogen = 1/2/4).³⁵ The reactor was modified to perform the experiments without nitrogen: ketene was produced by acetone pyrolysis and the vapor fed through a continuously operating vapor condensing-liquid feeding trap (to remove CO).³⁶ Comparison of Figures D.3 and D.4 shows that longer catalyst lifetimes were achieved when the ketene was diluted with nitrogen and that, up to the point where irreversible deactivation began, the acetaldehyde production rates are comparable. Thus deactivation rate is more sensitive to ketene concentration than is the acetaldehyde synthesis. This result is also consistent with the deactivation being related to the dimerization of ketene to diketene. In a commercial process the ketene hydrogenation catalyst would probably need to be regenerated on a daily basis.

Figure D.3

HAc STY Vs Time on Stream

3% Pd/SiO₂ w/N₂

Figure D.4

HAc STY Vs Time on Stream

3% Pd/SiO₂ no diluent

A study was initiated to determine the effect of carbon monoxide on the efficiency of the ketene hydrogenation reaction using the acetone pyrolysis method described above for continuous ketene generation. The ketene stream produced by this method contained almost 20% CO when no continuously operating vapor condensing-liquid feeding trap was used.³⁷ This amount of CO was sufficient to totally poison the catalyst. It was learned that, when the continuously operating vapor condensing-liquid feeding trap was used, the gas exiting the analytical scrubber after hydrogenation over 3% Pd on silica contained 1.27% methane and 0.74% CO.³⁸ When the experiment was repeated with the ketene bypassing the reactor (hydrogen still present but mixing with the ketene downstream from the reactor), the gas exiting the analytical scrubber contained 1.04% methane and 0.34% CO.³⁹ This result implies that some CO was coming through the continuously operating vapor condensing-liquid feeding trap (perhaps CO is somewhat soluble in liquid ketene at -78°C). The data are probably not accurate enough to determine if any CO is being generated on the catalyst. In view of these results, it was not too surprising that when the hydrogenation was conducted with hydrogen containing 50 ppm CO, no effect on the efficiency of acetaldehyde production was observed compared to conducting the reaction in pure hydrogen.⁴⁰

Experiments were performed using a custom gas mix containing 95% hydrogen and 5% carbon monoxide.⁴¹ The 5% Pd/C catalyst was used for this series of experiments since it was with this catalyst that the effect of excess CO was discovered. The following results are in chronological order, and the effect of natural catalyst deactivation must be considered along with the effect of CO.

<u>Expt #</u>	<u>% CO in H₂</u>	<u>% ketene conv.</u>	<u>HAc STY, g/(l-hr)</u>
15-1	0	93	448
15-2	5	58	207
15-3	0	76	360
15-4	5	20	123
15-5	5	28	89
15-6	0	48	217
15-7	0	47	304
15-8	2.5	32	149
15-9	2.5	29	123
15-10	0	50	198

These results are shown graphically in Figure D.5. The catalyst was subjected to its normal overnight hydrogenation treatment after experiment numbers 15-3 and 15-6. Even when the natural deactivation is considered, the detrimental effect of CO is apparent from the above data. Actually it is somewhat surprising that the reaction proceeds at all with these high levels of CO. A vent gas analysis of the gas exiting the analytical scrubber of experiment 2 above revealed that it contained 0.791% methane and 5.886% CO. It should be kept in mind that the conditions of the experiments using feed containing 5% CO in hydrogen (about 2/1 H₂/ketene ratio) are roughly equivalent to mixing a ketene stream containing about 10% CO with pure hydrogen. These data

Figure D.5

HAc STY Vs Sample Number

Effect of % Added CO on Rate

provide a rough idea of how much recycle could be tolerated in a process where the ketene feed contained 1-3% CO.

A study was performed to determine the effect of temperature on the ability of CO to inhibit the ketene hydrogenation reaction over 5% Pd/C.⁴² The furnace used in these experiments did not allow for the control that we normally have with the steam-heated reactor (98°C). An inhibitory effect due to the presence of 5% CO was observed at 130-140°C, with the rate falling about 25%. Unfortunately the acetaldehyde selectivity dropped from 90 to 59% when the feed change was made. Neither the rate nor the selectivity returned when the CO-free feed was resumed for the next sample. No inhibitory effect was observed when the 5% CO-containing feed was used at 158-160°C, but the acetaldehyde selectivity remained at only about 50%. At 183°C, a slight increase in the rate (but within the error normally observed) was observed when the CO-containing feed was used, but the acetaldehyde selectivity remained at about 54%. The lack of CO inhibition at higher temperatures coupled with the lowered selectivity are consistent with a large amount of the ketene decomposing to CO and methane at the higher temperatures to the extent that the effect of the 5% CO is masked. Thus, when the temperature is increased sufficiently, the effects of 5% added CO on the rate are not noticeable, but the acetaldehyde selectivity is lower due to decomposition reactions.

Although complicated by the need for frequent catalyst regeneration and some sensitivity to the levels of CO typically present in a ketene stream, with further work, ketene hydrogenation could become a very molecularly efficient way to produce acetaldehyde. However, as shown in the section F, it became apparent that ketene hydrogenation was not an economically efficient way to prepare acetaldehyde. Attention then focused on examination of the direct hydrogenation of acetic acid to acetaldehyde.

Engineering and Process Description

A scoping design for the generation of acetaldehyde via ketene hydrogenation was developed based on these results and is shown schematically in Figure D.6. Ketene and makeup hydrogen are combined with gaseous recycle from a compressor (RC) and fed to the hydrogenation reactor (RX). The reactor effluent is cooled in a series of exchangers (E and ER) before being fed to an absorber (A) for the recovery of acetaldehyde. The liquid product from the absorber (A) is used to cool the reactor (RX) before being sent to a distillation column (D) where acetaldehyde product is separated from the solvent (EtOAc). The solvent is cooled in a series of exchangers (S and SR) before returning to the absorber (A).

Assumptions used to develop the design include: 1) an 8/1 molar ratio of hydrogen to ketene in the reactor (RX) feed and 2) the reactor operates at 98C and 1 atm with 65% ketene conversion to acetaldehyde, 0.5% ketene conversion to CO and methane, and 0.75% conversion of acetaldehyde (and ketene) to ethyl acetate. While most of the experiments discussed above were conducted at 2/1 H₂/ketene, the rapid deactivation observed without dilution suggests catalyst stability may be improved at conditions such as 8/1 H₂/ketene minimizing ketene condensation. While higher pressures are desirable for subsequent acetaldehyde recovery, they cannot be employed to avoid oligomerizing ketene.

Heat and material balances were developed using a process simulator. These balances were used to estimate utility requirements and equipment costs. At the low pressures used, solvent (EtOAc) requirements in the absorber (A) were very high and were a strong function of the desired acetaldehyde recovery. The effect of setting this recovery at values ranging from 85 to 97.8% was studied with results shown below for 39,000 lbs/hr acetaldehyde production:

HAc Recovery, %	85	90	92.5	95	97.8
Solvent Flow, Mlb/hr	0.579	0.691	0.771	0.889	1.298
15# Steam, Klb/hr	47.8	58.0	65.4	76.2	115.9
25F Refrig., MBtu/hr	31.9	34.2	35.8	38.1	47.8
CTW, MBtu/hr	85.9	92.6	97.6	104.8	130.6
Columns, M\$	0.859	0.986	0.986	1.017	1.281
Exchangers, M\$	0.941	1.044	1.094	1.160	1.524

Clearly, low acetaldehyde recoveries are desirable to minimize solvent flow and resulting utility and capital requirements. However, the acetaldehyde concentration in the gas recycle increased from 0.16 to 1.16 mol% upon decreasing HAc recovery from 97.8 to 85%. Higher acetaldehyde levels in the reactor feed may lead to overreduction and subsequently higher ethyl acetate selectivities. Given the HAc concentration in the reactor effluent was still significantly higher than that of the feed at 85% recovery, this potential overreduction was disregarded and 85% recovery was chosen as the design case.

Figure D.6 – Ketene Hydrogenation Process Schematic

The heat and material balances are summarized in Table D.3 for 40,500 lbs/hr acetaldehyde production. The liquid product from the absorber contained very low levels (<0.3 wt%) of ketene and other light gases which were assumed to be separated and purged in stream WASTE. Without this light gas removal, these materials would contaminate the acetaldehyde product. A final design would likely include a further purification step before or after distillation to remove at least reactive ketene. Utility requirements corresponding to these balances are summarized below while an equipment list and estimated costs (30,654 lbs/hr HAc basis) are provided in Table D.4:

<u>Utility</u>	<u>Units</u>	<u>Total</u>
Cooling Water	MBtu/hr	85.9
Electricity	KW	4362
Steam (15#)	Klb/hr	47.8
Refrigeration (25F)	MBtu/hr	31.9

Alternative designs were considered but none were found to be significantly better than the one chosen. Specifically, a scoping design based on the use of a heavier solvent (2-ethylhexyl acetate) was developed but was found to be inferior. Imposing the restriction that ketene cannot be significantly compressed limits potential schemes. If it is assumed that there is simply a ketene partial pressure beyond which oligomerization becomes a problem, there may be other designs incorporating compression before acetaldehyde recovery that prove to be superior.

Table D.3
Ketene Hydrogenation Balance

Stream	ABS1	ABS2	ABS3	BTMS	F1	F2	F3	LIQ	LIQ1
Temperature C	76.3	35.0	0.0	110.1	25.0	69.6	25.0	4.8	4.8
Pressure PSI	15	15	15	40	20	15	20	15	15
Vapor Frac	0.209	0.000	0.000	0.000	1.000	1.000	1.000	0.000	0.000
Total Flow LBMOL/HR	6588.0	6588.0	6588.0	6578.1	1054.0	16414.6	1212.4	7544.1	7496.8
Total Flow LB/HR	578998	578998	578998	578124	43379	220914	2601	620493	618595
Total Flow CUFT/HR	642550	10514	10020	11884	303511	7393680	349116	10924	10878
Enthalpy MBTU/HR	-1309.3	-1349.8	-1367.2	-1307.6	-25.3	-342.8	-0.3	-1441.3	-1439.4
Mole Flow LBMOL/HR									
CO	0.00	0.00	0.00	0.00	10.54	744.61	6.03	0.36	0.00
METHANE	0.00	0.00	0.00	0.00	31.62	1313.13	0.00	1.21	0.00
CO2	0.00	0.00	0.00	0.00	21.08	595.01	0.00	6.35	0.00
H2	0.00	0.00	0.00	0.00	0.00	11458.92	1206.34	1.74	0.00
KETENE	0.00	0.00	0.00	0.00	990.76	1432.37	0.00	37.72	0.00
HAC	32.89	32.89	32.89	32.89	0.00	163.72	0.00	951.52	951.52
ETOAC	6555.13	6555.13	6555.13	6545.21	0.00	706.87	0.00	6545.25	6545.25
Mass Fraction									
CO	0.0000	0.0000	0.0000	0.0000	0.0068	0.0944	0.0650	0.0000	0.0000
METHANE	0.0000	0.0000	0.0000	0.0000	0.0117	0.0954	0.0000	0.0000	0.0000
CO2	0.0000	0.0000	0.0000	0.0000	0.0214	0.1185	0.0000	0.0005	0.0000
H2	0.0000	0.0000	0.0000	0.0000	0.0000	0.1046	0.9350	0.0000	0.0000
KETENE	0.0000	0.0000	0.0000	0.0000	0.9601	0.2726	0.0000	0.0026	0.0000
HAC	0.0025	0.0025	0.0025	0.0025	0.0000	0.0326	0.0000	0.0676	0.0678
ETOAC	0.9975	0.9975	0.9975	0.9975	0.0000	0.2819	0.0000	0.9294	0.9322

Basis.

40,500 lb/hr (330 Mlbs/yr) HAC

Table D.3
Ketene Hydrogenation Balance

Stream	LIQ2	OVHD	P1	P2	P3	PURGE	R1	R2	VAP	WASTE
Temperature C	65.1	49.7	98.0	35.0	0.0	8.0	8.0	77.2	8.0	4.8
Pressure PSI	15	40	15	15	15	10	10	20	15	15
Vapor Frac	0.090	0.000	1.000	1.000	0.973	1.000	1.000	1.000	1.000	1.000
Total Flow LBMOL/HR	7496.8	918.7	15467.2	15467.2	15467.2	362.8	14148.3	14148.3	14511.1	47.4
Total Flow LB/HR	618595	40472	220914	220914	220914	4486	174937	174937	179422	1898
Total Flow CUFT/HR	312330	876	7543490	6263030	5404570	197040	7684580	4788100	5361640	17306
Enthalpy MBTU/HR	-1397.6	-74.6	-384.6	-400.2	-414.7	-8.5	-332.1	-317.3	-340.7	-1.9
Mole Flow LBMOL/HR										
CO	0.00	0.00	747.07	747.07	747.07	18.67	728.04	728.04	746.71	0.36
METHANE	0.00	0.00	1315.60	1315.60	1315.60	32.86	1281.52	1281.52	1314.38	1.21
CO2	0.00	0.00	595.01	595.01	595.01	14.72	573.94	573.94	588.66	6.35
H2	0.00	0.00	10517.21	10517.21	10517.21	262.89	10252.59	10252.59	10515.48	1.74
KETENE	0.00	0.00	490.65	490.65	490.65	11.32	441.60	441.60	452.93	37.72
HAC	951.52	918.63	1086.55	1086.55	1086.55	4.20	163.72	163.72	167.92	0.00
ETOAC	6545.25	0.04	715.08	715.08	715.08	18.13	706.89	706.89	725.02	0.00
Mass Fraction										
CO	0.0000	0.0000	0.0947	0.0947	0.0947	0.1166	0.1166	0.1166	0.1166	0.0053
METHANE	0.0000	0.0000	0.0955	0.0955	0.0955	0.1175	0.1175	0.1175	0.1175	0.0103
CO2	0.0000	0.0000	0.1185	0.1185	0.1185	0.1444	0.1444	0.1444	0.1444	0.1472
H2	0.0000	0.0000	0.0960	0.0960	0.0960	0.1181	0.1181	0.1181	0.1181	0.0018
KETENE	0.0000	0.0000	0.0934	0.0934	0.0934	0.1061	0.1061	0.1061	0.1061	0.8354
HAC	0.0678	0.9999	0.2167	0.2167	0.2167	0.0412	0.0412	0.0412	0.0412	0.0000
ETOAC	0.9322	0.0001	0.2852	0.2852	0.2852	0.3560	0.3560	0.3560	0.3560	0.0000

Basis:

40,500 lb/hr (330 Mlbs/yr) HAC

Table D.4
Ketene Hydrogenation Equipment List

<u>Columns</u>	<u># of Stages</u>	<u># of Trays</u>	<u>Diameter, ft</u>	<u>Height, ft</u>	<u>\$</u>
A	6	30	12.5	107.5	593,900
D	17	34	8.5/10.5	100.5	<u>407,800</u>
					1,001,700
<u>Heat Exchangers</u>	<u>Duty, MBtu/hr</u>	<u>Area, sqft</u>	<u>Shell Side</u>	<u>Tube Side</u>	<u>\$</u>
RX	33.52	4058	LIQ1	F2	100,200
C	23.88	4753	D Ovhd	CW	110,200
RB	36.32	7808	15# Stm	D Btms	158,800
E	11.86	2967	CW	P1	58,500
ER	11.01	3772	23F Refrig	P2	70,100
S	30.72	10517	CW	ABS1	153,600
SR	13.17	4514	23F Refrig	ABS2	<u>80,800</u>
					732,200
<u>Vessels & Tanks</u>		<u>Volume, cuft</u>	<u>Diameter, ft</u>	<u>Height, ft</u>	<u>\$</u>
COL1CON		391	D Accumulator (20 min) & spare		41,300
TANK1		5855	Solvent Holding Tank (14 days)		110,700
TANK2		5067	Product Holding Tank (6 hrs)		96,800
TANK3		251640	D Feed Tank (1 day)		1,390,600
TANK7		3221	A Solvent Feed Tank (20 min)		114,600
TANK4			HAc Product Sphere (2 days)		<u>1,998,900</u>
					3,752,900
<u>Other</u>					
RC		4433 HP centrifugal compressor w/elec motor			1,800,000
FEEDCOMP		Ketene 556 HP centr compressor w/motor			<u>375,000</u>
					2,175,000
Total					7,661,800

Basis:

30,654 lbs/hr (250 Mlbs/yr) HAc

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3. Acetic Acid Hydrogenation Studies (Task 1.2)

Introduction

The carboxylic acid group is generally considered to be among the most difficult functional groups to reduce by catalytic hydrogenation.¹ The aldehyde group, conversely, is considered to be one of the easiest functional groups to reduce by catalytic hydrogenation. Thus, under the forcing conditions required to reduce a carboxylic acid, the aldehyde is often not isolated in good yield because further reduction to the alcohol is facile. Furthermore, when the carboxylic acid contains an α -hydrogen, ketonization can occur with concurrent formation of water and carbon dioxide.² This reaction becomes more prevalent as the number of α -hydrogens increases. Thus acetone can be readily formed from acetic acid at the temperatures typically used for the hydrogenation reaction (300-400°C). The major reactions relevant for hydrogen and acetic acid in the vapor phase are summarized below:

The hydrogenation of acetic acid to acetaldehyde and water is a mildly endothermic reaction. The thermodynamics of the reaction improve as the temperature is increased. The subsequent reaction, the hydrogenation of acetaldehyde to ethanol, is mildly exothermic at 300°C, and the reaction becomes less favorable as the temperature increases. Since the equilibrium of the acetic acid hydrogenation is poor, the reaction must be run in an excess of hydrogen if appreciable acetic acid conversions are desired. Thus, on a thermodynamic basis, ethanol formation will be favored in the region of 300-400°C. The third major reaction, the formation of acetone, is essentially irreversible at all temperatures above 0°C. The formation of acetone becomes more favorable thermodynamically as the temperature is increased. Extending the temperature significantly above 400°C will not likely improve the selectivity to the desired acetaldehyde product because of increasing acetone production. Other reactions, such as the formation of methane, carbon oxides and C_2 hydrocarbons also are relevant in acetic acid hydrogenation chemistry, but are of less importance than the three major reactions described above, unless excessively high temperatures are used. In some circumstances, the formation of ethyl acetate also can lower the selectivity to the desired acetaldehyde. Thus it appears that the challenge in producing acetaldehyde via acetic acid hydrogenation is a definite catalyst design problem: the ideal catalyst should facilitate the initial hydrogenation of acetic acid to acetaldehyde, but should have essentially no activity for the subsequent hydrogenation to ethanol nor for the dimerization reaction producing acetone. If a catalyst has even a small activity for conversion of acetaldehyde

to ethanol or for the conversion of acetic acid into acetone, then extreme losses in acetaldehyde selectivity may occur if the reaction is operated beyond the equilibrium conversion level allowed for converting acetic acid and hydrogen into acetaldehyde and water.

In spite of the thermodynamic limitations surrounding the hydrogenation of carboxylic acids to aldehydes, several examples of this reaction appear in the literature. Generally these reactions are performed at about 1 bar pressure in the vapor phase in a large excess of hydrogen at temperatures ranging between 200 and 500°C, and the reaction is most successful with aromatic carboxylic acids or for aliphatic acids containing few α -hydrogens. Van Geem et al. describe a Mn/Zn/Al oxide catalyst that converts benzoic acid to benzaldehyde in the vapor phase at 330°C in a large excess of hydrogen in 88.3% selectivity at 98.9% conversion.⁴ Joentgen et al. describe catalyst systems based on titanium or vanadium oxides in conjunction with one or more metals selected from Cr, Mo, Co, Ni, Zn, Cd and Cu for the hydrogenation of aromatic and aliphatic carboxylic acids containing not more than one α -hydrogen at 325-425°C at 1 bar in the presence of a large excess of hydrogen.⁵ Yokoyama et al. describe the use of zirconium oxide and modified zirconium oxide catalysts for the hydrogenation of aromatic carboxylic acids to aldehydes under similar reaction conditions.⁶ Yokoyama et al. also describe the use of a purified chromium oxide catalyst for the hydrogenation of both aromatic and aliphatic carboxylic acids under similar reaction conditions.⁷ This patent gives several examples of the hydrogenation of high molecular weight acids, such as stearic acid. Acetic acid is also claimed as a suitable acid, but no examples are given. Yokoyama et al. stress that the reason for the high purity requirement in the chromium oxide is to prevent the ketone formation reaction. Welguny et al. describe the use of oxide-supported tin catalysts for hydrogenation of a wide variety of carboxylic acids to aldehydes under the typical high-temperature, high-hydrogen, low-pressure conditions described previously.⁸ Although acetic acid is included in the claims of this patent application, the only examples are for aromatic carboxylic acids and for pivalic acid. Ferrero et al. describe Ru-Sn-B on alumina catalysts for hydrogenation of a wide variety of carboxylic acids to aldehydes under the typical high-temperature, high-hydrogen, low-pressure conditions described previously.⁹ Although the Ferrero patent application gives no examples for acetic acid hydrogenation, it is mentioned in the claims. Most of the Ferrero reference concerns the reduction of senecioic acid to prenal or the reduction of aromatic carboxylic acids to the corresponding aldehydes.

The most definitive work on the acetic acid hydrogenation to acetaldehyde is that of Ponc and coworkers.^{2b, 10} These researchers have proposed a working mechanism for the reaction and have reported several examples of the conversion of acetic acid to acetaldehyde in good selectivity. The base catalysts for these reductions are partially reduced metal oxides having an intermediate metal-oxygen bond strength. Partially reduced iron oxide is the most selective metal oxide, and acetaldehyde selectivities almost as high as 80% could be obtained at 1.2 bar pressure using a hydrogen/acetic acid ratio = 50/1 at 321°C. Addition of 5 wt % Pt to this catalyst further increases the selectivity to acetaldehyde to over 80%. With tin oxide, the addition of the Pt about

doubles the selectivity, increasing it from about 40% to about 80%. Ponec invokes a Mars-Van Krevelen type mechanism for the reaction.¹¹ Acetic acid reacts with an oxygen vacancy present on the surface of the partially reduced metal oxide. This causes the catalyst to become oxidized, forming a surface acetate type species and surface-bonded hydrogen (from the hydroxyl group of the acid or from adsorbed molecular hydrogen). These intermediates react to form acetaldehyde and a surface oxide. The surface oxide is then reduced by adsorbed hydrogen to produce water and the oxygen vacancy. Ketene has been suggested as a possible surface intermediate in these reductions.^{2b, 10b} It is critical that the catalyst be in a correct oxidation state, and the correct oxidation state must be readily regenerated under the reaction conditions. If the catalyst is in an over oxidized state, then acetone becomes the predominant product. The selective catalysts contain a mixture of zero valent metal and metal oxide phases. If the catalyst is in an over reduced state, methane becomes the predominant product. Addition of Pt to the catalyst facilitates the formation and maintenance of the desired oxidation state. Ponec mentions that there is an optimum Pt level, and that increasing the Pt level above 1.25 atomic % actually decreases the selectivity.^{10d}

Although the acetic acid hydrogenation process studied by Ponec and coworkers is very selective to acetaldehyde, it is totally impractical as a commercial way to produce acetaldehyde. The impracticality stems from the need to isolate and collect acetaldehyde (normal boiling point = 19°C) from a vapor stream, where it is present in maximum concentrations of 2-3% (or less, depending on the conversion) at about 1 bar pressure. Water and by-products must be removed from the mixture, and hydrogen and unreacted acetic acid must be recycled to the reactor. These operations require that the temperature be lowered considerably from the 300-400°C reaction temperature. A practical process requires much lower hydrogen/acetic acid ratios and much higher reaction pressures than used by Ponec. As evident from the preceding literature review, the hydrogenation of any carboxylic acid to an aldehyde at low hydrogen/carboxylic acid ratio and elevated pressure is without precedent in the literature. The primary focus of this work was to develop catalysts and conditions that would allow for the practical synthesis and recovery of acetaldehyde via high-pressure acetic acid hydrogenation at low hydrogen/acetic acid ratio.

The philosophy behind our catalyst and process development work was to first optimize the catalyst design and performance of the mixed metallic-metal oxide catalyst system at 1 bar pressure at hydrogen/acetic acid ratio ranging from about 50/1 to 5/1. This would entail kinetic and catalyst characterization studies as well. Once this initial development phase was near completion, the reaction would be operated under the elevated pressure conditions required for good acetaldehyde recovery. Two reactor systems were required for these studies: a very versatile reactor system for one atmosphere operation and a less versatile system for operation at elevated pressure.

Experimental Methods

Low-Pressure Hydrogenation Apparatus and Operation. The vast majority of low-pressure hydrogenation reactions were performed using the apparatus represented schematically in Figure D.7.¹² Metered gas flows were provided by six Tylan Model FC-260 mass flow controllers. Electric temperature control and monitoring were provided by a Dow Camile® control system interfaced with a Gateway Model 2000 486DX/33 computer. All gas delivery lines were teed into pressure relief columns containing water to prevent accidental overpressurization. Acetic acid was fed by metering hydrogen or nitrogen through a temperature-controlled vaporizer containing the acetic acid. The temperature of the vaporizer was maintained by a circulating water/ethylene glycol bath. Product analysis was performed by on-line gas chromatography utilizing a Hewlett-Packard Model 3790A gas chromatograph fitted with a 6-ft. X 1/8-inch stainless steel column containing 80/120 Carbopack B/6.6% Carbowax® 20M. Products were analyzed by this on-line gas chromatograph, with the column programmed for 80°C for 0 minutes, 4°C/minute to 150°C, and 150°C for 0 minute using a flame ionization detector. A 4-port Valco Industries sampling valve was used to send the feed mixture to the reactor or to the gas chromatograph for analysis. Two six-port Valco Industries gas chromatographic sampling valves containing 1-mL volume sample loops were used to sample the reactant stream or the product stream. All tubing lines connecting the exit of the acetic acid vaporizer, bypass valve, reactor, six-port sampling valves and the gas chromatograph were constructed of 1/8-inch stainless steel and were heated with temperature-controlled heating tapes to 150°C. The three sampling valves were heated to 150° using valve ovens. The reactor was constructed of main section of 8-inch long X 8-mm O.D. borosilicate glass fused to a lower section consisting of 6-inch long X 7.5-mm O.D. -3-mm I.D. capillary tubing. The reactor had a 1-inch long X 8-mm O.D. borosilicate side arm situated at 90° and 1 inch down from the top of the 8-mm O.D. glass portion of the main reactor section. The three openings to the reactor were fitted with 2-inch long, 1/4-inch O.D. kovar metal tubing sealed to the end of the glass. Accurately weighed catalyst charges (typically 0.2 g) were loaded into the reactor by first inserting a glass or quartz wool plug from the top of the reactor into the top part of the capillary section and then placing the catalyst charge on top of the glass or quartz wool plug. A thermocouple was inserted through the top of the reactor into the catalyst bed and sealed to the kovar tube with Swagelok® fittings. The reactant mixture was fed through the side arm, and the product exited at the base of the reactor. The kovar portions of the reactor inlet and outlet were connected to the stainless steel transfer lines using Swagelok® fittings. The reactor was heated with a vertically mounted, single-element electric furnace containing a 12-inch long heat zone.

The apparatus allowed for additional hydrogen or inert gas to be metered into the vapor stream exiting the temperature-controlled vaporizer. The acetic acid partial pressure could be controlled by altering the temperature of the vaporizer or by adding hydrogen or inert gas to the vapor stream exiting the temperature-controlled vaporizer. The apparatus could also easily be configured to allow inert gas to be metered to the temperature-controlled vaporizer. This flexibility in setting the feed composition facilitated the study

Figure D.7
Low Pressure Hydrogenation Apparatus

of the reaction kinetics. Normally catalysts were reduced in hydrogen (22.4 standard cubic centimeters per minute, SCCM) overnight at 300°C before feeding the acetic acid and hydrogen mixture. In some cases a higher temperature was used for the reduction. When the reactor was idle between acetic acid hydrogenation experiments with the same catalyst charge, hydrogen flow (22.4 SCCM) was maintained at 300°C.

Some of the initial evaluations were performed before the apparatus was equipped with on-line gas chromatography. In these experiments the output from the reactor was collected in a trap held at -78°C. The liquid from the trap was then weighed and analyzed by gas chromatography using Hewlett Packard Model 5890 gas chromatographs equipped with flame ionization detectors. Acetaldehyde, acetone and acetic acid were analyzed using a 25-m x 0.53-mm FFAP capillary column (1.0 micron film thickness) programmed at 40°C for 5 minutes, 15°C/minute to 235°C and holding at 235°C for 1.67 minutes. For this analysis, mixtures were prepared for gas chromatographic analysis by adding 5 ml of a tetrahydrofuran solution containing 2% decane internal standard to an accurately weighed 1-g sample of the condensate. Qualitative determinations of the relative area percentages of acetaldehyde, acetone and ethanol also were performed by gas chromatography using a Hewlett Packard Model 5890 gas chromatograph fitted with a 30-m x 0.25-mm FFAP capillary column (0.25-micron film thickness) programmed at 35°C for 7 minutes, 15°C/minute to 220°C and holding at 220°C for 2 minutes using a flame ionization detector held at 280°C (injector temperature = 240°C). Gases venting the trap were collected periodically in a gas sampling bottle and analyzed for hydrogen, methane and carbon monoxide by gas chromatography using a 10-m x 0.32-mm, 30-micron film molecular sieve 5A column with a 2-m PoraPLOT Q precolumn held isothermal at 110°C for 120 seconds using a thermal conductivity detector and argon carrier gas. Carbon dioxide, ethylene and ethane were determined using an 8-m x 0.32-mm, 10-micron film PoraPLOT U column with a 1-m PoraPLOT Q precolumn held isothermal at 90°C for 160 seconds using a thermal conductivity detector and helium carrier gas.

High-Pressure Hydrogenation Apparatus and Operation. The vast majority of high-pressure hydrogenation reactions were performed using the apparatus represented schematically in Figure D.8.¹³ The reactor was constructed from a 12-inch length of Hastelloy C tubing having an outer diameter of 1/4 inch. All gas flow, pressure and temperature control devices were controlled by a Camile® Model 3300 process monitoring and control system interfaced with an IBM Model 750-P90 computer. Hydrogen flow was provided by a Brooks mass flow controller, and acetic acid was fed using dual ISCO high-pressure syringe pumps. The device was fitted with a relief valve set for 500 psig. Pressure was controlled by a modified Research Control Valve with a pressure transducer located between the flow controller and the reactor. A 2-micron filter was placed between the reactor and the Research Control Valve. The product exiting the Research Control Valve was fed to a Valco Industries 6-port gas chromatographic sampling valve containing a 1-mL sample loop. The gas chromatographic sampling valve was interfaced to a Hewlett-Packard Model 3790A gas chromatograph fitted with a 6-ft. X 1/8-inch stainless steel column containing 80/120 Carbopack B/6.6% Carbowax®

Figure D.8
MEDIUM PRESSURE HYDROGENATION REACTOR

20M. Products were analyzed by this on-line gas chromatograph, with the column programmed for 80°C for 0 minutes, 4°C/minute to 150°C and 150°C for 0 minute using a flame ionization detector. The transfer lines, filter and Research Control Valve connecting the reactor to the gas chromatographic sampling valve were heated to 200°C by a temperature-controlled heating tape. The gas chromatographic sampling valve and the transfer line connecting it to the gas chromatograph were maintained at 150°C. The reactor tube was loaded to position the accurately weighed catalyst charge (typically 0.2 g) in the middle of the reactor. Quartz fines (1-inch layer), 12 X 20-mesh quartz chips (3.5 inches layer) and quartz or glass wool plugs were placed on both sides of the catalyst charge. The entire length of the reactor was heated with a temperature-controlled heating tape. The acetic acid was delivered to the reactor via a line passing concentrically through the reactor head and about an inch into the upper portion of the heated portion of the reactor. The hydrogen delivery line and the relief valve were also fitted to the reactor head. Thus the upper portion of the heated reactor acted as an acetic acid vaporization and vapor mixing zone.

Catalysts were reduced in hydrogen (25 SCCM) at 10 psig at 300°C in the reactor over night or longer before the feeding of hydrogen and acetic acid. Reactions were started by setting the hydrogen and acetic acid feeds to the desired rates at the 10-psig setting and then setting the pressure to the desired amount. When the reactor was idle between acetic acid hydrogenation experiments with the same catalyst charge, hydrogen flow (22.4 SCCM) at 10 psig was maintained at 300°C.

Definitions. The following definitions apply to the specific experiments:

Space velocity (SV or GHSV) = volumes of gas per volume of catalyst per hour under reaction conditions,

Space time yield (STY) = grams of product produced per liter of catalyst per hour,

% acetic acid conversion = $100(\text{mmoles acetic acid reacted})/(\text{mmoles acetic acid fed})$,

% acetic acid accountability = $100(\text{mmoles acetic acid recovered} + \text{mmoles acetate equivalents in products})/(\text{mmoles acetic acid fed})$,¹⁴

% normalized selectivity = $100(\text{mmoles product})/(\text{total mmoles all products})$.

Preparation of catalysts.

Catalyst No. 1: Fe₂O₃. Fe₂O₃ (Aldrich, lot # DQ15808DQ, 99.98 % purity) was used as received.

Catalyst No. 2: 2.5% Pd on Fe₂O₃.¹⁵ A solution was prepared from Pd(NO₃)₂ x H₂O (442 mg, Alfa lot # 120982, 39.9 % Pd) and water (10 mL). This solution was added to 20 X 40 mesh Catalyst No. 1 (7.1607 g) contained in an evaporating dish. The mixture was dried on the steam bath and calcined in a muffle furnace for 4 hours at 400°C.

Catalyst No. 3: 5% Pd on Fe₂O₃.¹⁶ A solution was prepared from Pd(NO₃)₂ x H₂O (127 mg, Alfa lot # 120982, 39.9% Pd) and water (2 mL). This solution was added to Catalyst No. 1 (1.0294 g) contained in an evaporating dish. The mixture was dried on the steam bath and calcined in a muffle furnace for 5 hours at 400°C.

Catalyst No. 4a: low surface area 10 % Pd on Fe₂O₃.¹⁷ A solution was prepared from Pd(NO₃)₂ x H₂O (264.2 mg, Alfa lot # 120982, 39.9% Pd) and water (4 mL). This solution was added to 20 X 40 mesh Catalyst No. 1 (1.0741g) contained in an evaporating dish. The mixture was dried on the steam bath and calcined in a muffle furnace for 5 hours at 400°C.

Catalyst No. 4b: high surface area 10 % Pd on Fe₂O₃.¹⁷ A solution was prepared from Pd(NO₃)₂ x H₂O (251 mg, Alfa lot # 120982, 39.9% Pd), Fe(NO₃)₃.9H₂O (5.06 g, Mallinckrodt lot # 5032 KHTJ) and water (10 mL). To this solution was added a separate solution prepared from citric acid (2.59 g, Eastman Chemical Company plant material) and water (5 mL). The mixture was evaporated on the steam bath to a scaly mass and then calcined in a muffle furnace for 5 hours at 400°C.

Catalyst No. 5: 20% Pd on Fe₂O₃.¹⁸ A solution was prepared from Pd(NO₃)₂ x H₂O (501 mg, Alfa lot # 120982, 39.9 % Pd), Fe(NO₃)₃.9H₂O (5.06 g, Mallinckrodt lot # 5032 KHTJ) and water (10 mL). To this solution was added a separate solution prepared from citric acid (2.23 g, Eastman Chemical Company plant material) and water (5 mL). The mixture was evaporated on the steam bath to a scaly mass and then calcined in a muffle furnace for 5 hours at 400°C.

Catalyst No. 6: 40% Pd on Fe₂O₃.¹⁸ A solution was prepared from Pd(NO₃)₂ x H₂O (1.0025 g, Alfa lot # 120982, 39.9% Pd), Fe(NO₃)₃.9H₂O (5.06 g, Mallinckrodt lot # 5032 KHTJ) and water (10 mL). To this solution was added a separate solution prepared from citric acid (2.17 g, Eastman Chemical Company plant material) and water (5 mL). The mixture was evaporated on the steam bath to a scaly mass and then calcined in a muffle furnace for 5 hours at 400°C.

Catalyst No. 7: 80% Pd on Fe₂O₃.¹⁸ A solution was prepared from Pd(NO₃)₂ x H₂O (2.005 g, Alfa lot # 120982, 39.9% Pd), Fe(NO₃)₃.9H₂O (1.01 g, Mallinckrodt lot # 5032 KHTJ) and water (10 mL). To this solution was added a separate solution prepared from citric acid (1.93 g, Eastman Chemical Company plant material) and water (5 mL). The mixture was evaporated on the steam bath to a scaly mass and then calcined in a muffle furnace for 5 hours at 400°C.

Catalyst No. 8: Pd sponge. Pd sponge (20 mesh, Alfa lot # 00777) was used as received.

Catalyst No. 9: 5% Pt on Fe_2O_3 .¹⁹ A suspension was prepared from $\text{H}_2\text{Pt}(\text{OH})_6$ (83.5 mg) in water (5 mL) and was acidified with concentrated nitric acid until all of the $\text{H}_2\text{Pt}(\text{OH})_6$ dissolved. This solution was used to impregnate Catalyst No. 1 (1.0095 g) in an evaporating dish. The mixture was evaporated to dryness on the steam bath over a 3-hour period, then calcined for 5 hours at 400°C in a muffle furnace.

Catalyst No. 10: 5% Re on Fe_2O_3 .²⁰ A solution was prepared from ammonium perrhenate (78.1 mg, Aldrich) and water (2 mL). This solution was added to Catalyst No. 1 (1.0126 g) contained in an evaporating dish. The mixture was dried on the steam bath. A portion of this material (0.2097 g) was loaded into the low-pressure microreactor and treated with nitrogen (22.4 standard cubic centimeters per minute, SCCM) overnight at 300°C.

Catalyst No. 11: 5% Rh on Fe_2O_3 .²¹ A solution was prepared from $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ (120.8 mg, Engelhard lot # 143, 42.5% Rh) and water (2 mL). This solution was added to Catalyst No. 1 (1.0288 g) contained in an evaporating dish. The mixture was dried on the steam bath and calcined in a muffle furnace overnight at 400°C.

Catalyst No. 12: 5% Cu on Fe_2O_3 .²² A solution was prepared from $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (187 mg, Aldrich lot # 01830DZ) and water (2 mL). This solution was added to Catalyst No. 1 (1.0033g) contained in an evaporating dish. The mixture was dried on the steam bath and calcined in a muffle furnace overnight at 400°C.

Catalyst No. 13: WO_3 . WO_3 (1.0283g, Alfa lot # 20517) was used as received.

Catalyst No. 14: 5% Pd on WO_3 .²³ A solution was prepared from $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (133.9 mg, Alfa lot # 120982, 39.9% Pd) and water (2 mL). This solution was added to WO_3 (1.0283g, Alfa lot # 20517) contained in an evaporating dish. The mixture was dried on the steam bath and calcined in a muffle furnace for 4 hours at 400°C.

Catalyst No. 15: basic Zn-Cu oxide.²⁴ A first solution was prepared from $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (51.55 g, Aldrich lot # 00727LM), $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (17.28 g, Aldrich lot # 01830D2) and water (500 mL). A second solution was prepared from Na_2CO_3 (28.87 g, Mallinckrodt lot # 7527 KMPB) and water (200 mL). The second solution was added rapidly to the first solution while it was stirred manually, and the stirring was continued for an additional 2 minutes after the completion of the addition. The resulting mixture was centrifuged, the liquid phase was decanted away, and the remaining solids were washed with water. The centrifugation, decantation and washing operations were repeated two more times. The resulting solid was dried overnight at 80°C in an oven, then calcined overnight at 350°C in a muffle furnace. The resulting solid contained 22.7 wt % Cu, 51.5 wt % Zn and 1.84 wt % Na.

Catalyst No. 16: neutral Zn-Cu oxide.²⁵ The preparation of Catalyst No. 14 was repeated except that, after each centrifugation and decantation, the solid was washed by stirring in

water (4 liters) at 80°C for 30 minutes. The resulting solid was dried for 60 hours at 80°C and contained 17.6 wt % Cu, 39.9 wt % Zn and 0.048 wt % Na. The material was then calcined overnight at 350°C in a muffle furnace.

Catalyst No. 17: 0.5% Pd-10% Fe on carbon.²⁶ A solution was prepared from $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (40.4 g, Mallinckrodt lot # 5032 KHTJ) and water (400 mL). To this solution was added concentrated aqueous ammonia (ca. 29 g) until pH 10 was attained. A brown gel formed which was centrifuged, decanted and washed with water. The washing, decantation and centrifugation processes were repeated until the liquid portion was pH 8. The resulting solid was dissolved in a 60°C solution prepared from 88% formic acid (17.3g), oxalic acid dihydrate (18.9 g) and water (1 liter). This solution was used to impregnate in portions activated carbon granules (55 g) contained in an evaporating dish. Each portion was evaporated to dryness on the steam bath. The resulting solid was loaded into a quartz tube and placed in a three-element electric furnace. The solid was treated with a nitrogen stream (100 SCCM) while the temperature was raised to 300°C over a 2-hour period. The temperature was maintained at 300°C for 2 hours and then returned to ambient temperature over a 2-hour period, with the nitrogen feed maintained. After ambient temperature was reached, the solid was treated with a mixture of nitrogen (300 SCCM) and air (10 SCCM). This treatment caused a hot spot (80-100°C) to move down through the bed of solid, and the treatment was continued overnight. The amount of air was slowly increased to be 100% of the feed gas while the nitrogen flow was decreased. The solid (61 g) was recovered from the quartz tube, and a portion of the material (8.0 g) was impregnated with a solution of palladium acetate (76.2 mg) in tetrahydrofuran (15 mL) at room temperature. This mixture was evaporated to dryness on the steam bath to yield Catalyst No.17.

Catalyst No.18: 10% Fe_2O_3 - 2% Pd on SiO_2 .²⁷ Silicon dioxide (Davison grade 57) was ground to 20 X 40 mesh particles (17.43 g). In order to neutralize basic sites, this material was slurried into water (200 mL) containing concentrated nitric acid (1 mL) at pH 1. After an hour, the liquid was decanted away, and the solid was washed with water (4 X 400 mL) to pH 5. The solid was dried in an oven at 115°C for 3 hours and then in a muffle furnace at 300°C for 2.5 hours to yield an acid-washed silica (17.12 g). A portion of this solid (10.0 g) was placed in an evaporating dish and impregnated with a solution prepared from $\text{Pd}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (504 mg, Alfa lot # 120982, 39.9% Pd), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (5.08 g, Mallinckrodt lot # 5032 KHTJ), concentrated nitric acid (ca. 0.5 mL) and water (27.46 g). The mixture was evaporated to dryness on the steam bath, then calcined in the muffle furnace at 400°C for 5 hours.

Catalyst No.19: 10% Fe_2O_3 on SiO_2 .²⁸ A portion of the acid-washed silica used as starting material for the preparation of Catalyst No.18 (5.0 g) was placed in an evaporating dish and impregnated with a solution prepared from $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (2.04 g, Mallinckrodt lot # 5032 KHTJ) and water (13 g). The mixture was evaporated to dryness on the steam bath, then calcined in the muffle furnace at 400°C for 5 hours.

Catalyst No. 20: 10% Fe₂O₃ - 0.5% Pd on SiO₂.²⁹ A portion of Catalyst No. 19 (1.0 g) was placed in an evaporating dish and impregnated with a solution prepared from Pd(NO₃)₂ x H₂O (12.6 mg, Alfa lot # 120982, 39.9% Pd) and water (2 mL) to incipient wetness. The mixture was evaporated to dryness on the steam bath, then calcined in the muffle furnace at 400°C for 5 hours.

Catalyst No. 21: 2.5% Pd on SnO₂.³⁰ A solution was prepared from Pd(NO₃)₂ x H₂O (62.3 mg, Alfa lot # G25G17, 40.12% Pd) and water (1 mL). This solution was added to 325 mesh SnO₂ (1.00 g, Aldrich Lot # 07302BF) in an evaporating dish. The mixture was evaporated to dryness on the steam bath, then calcined in the muffle furnace at 400°C for 5 hours.

Catalyst No. 22: Mixed 30 mole % Cu – 70 mole % Fe oxide catalyst.³¹ A solution was prepared from Cu(NO₃)₂.2.5H₂O (0.70 g, Aldrich lot # 01830DZ), Fe(NO₃)₃.9H₂O (2.04 g, Mallinckrodt lot # 5032 KHTJ) and water (10 mL). This solution was combined with another solution prepared from citric acid (1.92 g, Eastman Chemical Company plant material) and water (5 mL). The mixture was evaporated to dryness on the steam bath and calcined in the muffle furnace at 400°C overnight.

Results and Discussion

Initial screening studies at low pressure without on-line gas chromatography. The results of initial acetic acid screening runs at 1 bar pressure are provided in Table D.5. The first column of Table D.5 lists the catalyst studied along with the corresponding Catalyst No. from the experimental section. The entries in the table are in chronological order. Even though these data were acquired before the apparatus was fitted with on-line gas chromatography, several preliminary trends emerged that helped guide the more definitive work that followed later.

The Fe₂O₃ catalyst studied first was evaluated under the conditions reported by Ponec and coworkers.¹⁰ This material had been pre-reduced in hydrogen at 450°C, and, although it was quite selective for acetaldehyde production, the yield appeared very low. Addition of Pt to the catalyst vastly increased the acetaldehyde yield. The addition of Pt also allowed lowering of the pre-reduction temperature to 300°C and allowed the acetic acid reduction to occur at 300°C rather than the 350°C required in the absence of Pt. It appeared that Rh was about as effective as Pt in promoting the reduction, and Re and Cu were less effective. The screening experiments also suggested that Pd was just as good as or even better than Pt in promoting the reaction. The 2.5 wt % Pd/ Fe₂O₃ catalyst was especially promising because it appeared to maintain its activity and selectivity over an extended period. Because of its excellent activity, selectivity and performance maintenance, palladium appeared to be the best reducing metal. Pd is a poor aldehyde hydrogenation catalyst compared to Pt.⁴⁸ Also it is normally less expensive than Pt. Pd is known to form a bulk metal hydride,⁴⁹ and it was envisioned that this could act as a hydride reservoir, thus aiding in maintaining the iron in the desired oxidation state, especially in

TABLE D.5

Preliminary Acetic Acid Hydrogenation Studies

Catalyst (No.) ^{ref.}	Weight percent			Area ratios HAc/acetone/EtOH	norm. % (max = 2%)		
	HAc	acetone	HOAc		CH ₄	C ₂ H ₄	C ₂ H ₆
Fe ₂ O ₃ (1) ^{*32}	1.01	NA	86.10	1/0.10/0.21	0.03	0	0
Na/Cu/Zn (15) ³³	9.81	10.46	52.37	1/1.38/0.59	0	0	0
Na/Cu/Zn (15) ^{**34}	0.27	6.62	81.18	1/31.6/0	0	0	0
Pt/Fe ₂ O ₃ (9) ³⁵	24.07	1.76	21.88	1/0.09/0.61	0.05	0.10	0
Pt/Fe ₂ O ₃ (9) ³⁶	18.34	1.30	42.04	1/0.09/0.44	0.04	0.05	0
Pt/Fe ₂ O ₃ (9) ^{***36}	20.93	2.00	36.98	1/0.12/0.48	0.08	0.05	0
Cu/Zn (16) ³⁷	12.36	6.42	28.51	1/0.67/1.56	0.01	0	0
Re/Fe ₂ O ₃ (10) ³⁸	11.32	0.46	48.75	1/0.05/0.62	0.13	0.13	0.05
Re/Fe ₂ O ₃ (10) ³⁸	7.29	0.40	64.86	1/0.07/0.76	0.09	0.07	0
Re/Fe ₂ O ₃ (10) ^{***39}	5.39	0.18	68.42	1/0.04/1.03	0.09	0.06	0
Pt/Fe ₂ O ₃ (9) ⁴⁰	19.09	1.28	41.80	1/0.09/0.43	0.05	0.05	0
Pt/Fe ₂ O ₃ (9) ⁴⁰	17.66	1.33	46.17	1/0.10/0.37	0.03	0.04	0
Pt/Fe ₂ O ₃ (9) ^{*40}	10.69	2.52	58.17	1/0.31/0.23	0.11	0.03	0
Pd/Fe ₂ O ₃ (3) ⁴¹	21.97	1.50	10.87	1/0.09/1.24	0.12	0.13	0
Pd/Fe ₂ O ₃ (3) ⁴¹	28.90	1.19	19.46	1/0.05/0.56	0.09	0.05	0
Pd/Fe ₂ O ₃ (3) ^{****41}	8.87	0.31	67.86	1/0.05/0.35	0.01	0	0
Pd/Fe ₂ O ₃ (3) ^{*41}	9.07	0.83	60.30	1/0.12/0.46	0.17	0.06	0
Rh/Fe ₂ O ₃ (11) ⁴²	18.57	0.66	35.36	1/0.05/0.63	0.14	0.08	0
Rh/Fe ₂ O ₃ (11) ⁴²	18.04	0.60	38.00	1/0.04/0.60	0.13	0.06	0
Rh/Fe ₂ O ₃ (11) ⁴²	14.78	0.57	43.84	1/0.05/0.66	0.14	0.06	0
Rh/Fe ₂ O ₃ (11) ⁴²	17.08	0.49	45.63	1/0.04/0.53	0.10	0.05	0
Cu/Fe ₂ O ₃ (12) ⁴³	13.41	0.38	50.72	1/0.04/0.67	0.08	0.06	0
Cu/Fe ₂ O ₃ (12) ⁴³	8.72	0.26	63.30	1/0.04/0.64	0.04	0.04	0
Pd/WO ₃ (14) ⁴⁴	2.26	0.04	78.43	1/0.03/1.05	0.30	0	0.10
.5Pd/10Fe/C(17) ⁴⁵	5.13	2.13	66.46	1/0.53/2.68	0.14	0	0
WO ₃ (13) ⁴⁶	0	0.10	95.24	NA	0.03	0	0
WO ₃ (13) ^{*46}	8.62	0.77	55.86	1/0.12/0.03	0.17	0.51	0
2.5Pd/Fe ₂ O ₃ (2) ⁴⁷	23.02	1.30	24.76	1/0.07/0.89	0.08	0.08	0
2.5Pd/Fe ₂ O ₃ (2) ⁴⁷	25.59	0.88	28.10	1/0.04/0.56	0.05	0.04	0
2.5Pd/Fe ₂ O ₃ (2) ⁴⁷	27.51	0.75	30.92	1/0.04/0.46	0.05	0.03	0
2.5Pd/Fe ₂ O ₃ (2) ⁴⁷	22.25	0.67	41.51	1/0.04/0.45	0.06	0	0

Conditions: 90 SCCM hydrogen containing 2 mol % HOAc, 0.2 g catalyst, 300°C unless otherwise stated, product trapped at -78°C. Metal loading on Fe₂O₃ and WO₃ catalysts = 5 wt. % unless otherwise stated.

*350°C.

**After feeding CO and acetic acid.

***Space velocity lowered by decreasing the hydrogen flow through the acetic acid vaporizer from 90 to 45 SCCM.

****275°C.

situations where the partial pressure of hydrogen is low. For these reasons, Pd was chosen as the reducing metal for more extensive studies.

The low-pressure methanol type catalysts, basic Na/Cu/Zn mixed oxide (Catalyst No. 15) and neutral Cu/Zn oxide (Catalyst No. 16), had activity for the formation of acetaldehyde. It is apparent by comparing the initial data for each catalyst that both catalysts produce excessive amounts of acetone, and that the presence of sodium seems to increase the amount of acetone produced. Treatment of catalyst No. 15 with acetic acid and carbon monoxide destroyed much of its ability to produce acetaldehyde, but it still produced acetone after the hydrogen/acetic acid feed was resumed. Tungsten oxide was examined as a potential catalyst because its average metal oxygen bond strength is similar to that of iron oxide. This catalyst (with or without added Pd) was selective for the formation of acetaldehyde. The best activity for the tungsten oxide catalyst was seen after it was reduced at 450°C and run at 350°C. Although the 0.5 wt % Pd/10 wt % Fe on C catalyst produced acetaldehyde, acetone production was excessive. This may have been due to the presence of oxide impurities commonly found in many carbon supports.

Although the preliminary screening experiments were rather crude, they helped to determine the direction of the next stage of research. It was decided that the 2.5 wt % Pd/Fe₂O₃ catalyst would be the first to be examined in the reactor system when it attained the on-line gas chromatography capability.

Kinetic studies at low pressure with on-line gas chromatography with the 2.5 wt % Pd/Fe₂O₃ catalyst. The 2.5 wt % Pd/Fe₂O₃ catalyst was subjected to a long-term evaluation where the conditions were varied to determine the preliminary kinetic parameters for the hydrogenation reaction. The activity of this catalyst leveled out, and it appears that this type of catalyst may have a very long lifetime (weeks, months or maybe even years). During most of the 254 hours that the catalyst was on stream in the presence of hydrogen and acetic acid, the following conditions were used: one atmosphere pressure, hydrogen/HOAc molar feed ratio = 37/1, GHSV = 71,000 hr⁻¹, and 300°C. However conditions were altered during the run to perform the kinetic experiments summarized in the sections below. Kinetic experiments were often complicated by a "hysteresis" that caused a temporary change in activity during the experiments. Since the activity later returned to normal, it appears that some of the changes in reaction conditions slowly alter the oxidation state or other catalyst structural aspect in a slowly reversible manner. Hydrogenation of the catalyst overnight generally returned the activity to its previous level. Eventually the catalyst was passivated by treating with helium/air mixtures at room temperature, gradually building up to 100% air and then removing it from the reactor.⁵⁰ The passivated catalyst had been removed from the reactor after running several days without the restorative hydrogen treatment. Quite surprisingly, an X-ray diffraction analysis of this catalyst showed that the bulk crystalline phase present was the iron carbide Fe₃C.⁵⁰ The formation of this species could be related to some of the slow reversible deactivation observed during long runs. Hydrogenation of the catalyst would remove a portion of this carbide and restore catalyst activity. In the kinetic studies summarized in the sections below, efforts were made to insure that the studies were being

performed at below equilibrium conversion levels, both by calculation and by deliberately reducing the space velocity to see if a corresponding increase in conversion occurred.

First Activation Energy Study⁵¹

Conditions: 90 SCCM N₂, 20 SCCM H₂, 80 SCCM He, ca. 8 SCCM HOAc, 1 atmosphere, GHSV = 150,000 hr⁻¹. Begin at 281°C, go to 337°C, go back to 283°C, HOAc accountability during run = 96-100%, HOAc conversion ~ 0-4% and HAc selectivity = 82-89%.

Results: Hysteresis observed with catalyst deactivation during temperature rise, giving nearly zero activation energy. However, upon returning to the lower temperature, deactivation was sufficiently low to provide the following activation energies:

For acetaldehyde = 15.5 kcal/mole

For acetone = 9.3 kcal/mole.

The conditions used in this run were sufficient to place the catalyst in an oxidized state, which favors acetone production.

Second Activation Energy Study⁵²

Conditions: 0 SCCM N₂, 90 SCCM H₂, 0 SCCM He, ca. 2 SCCM HOAc, 1 atmosphere, GHSV = 70,000 hr⁻¹. Begin at 301°C, go to 250°C, go back to 308°C, HOAc accountability during run = 90-102%, HOAc conversion ~ 5-41% and HAc selectivity = 82-95%.

Results: No hysteresis observed (data track reproducibly going down or up in temperature). The following activation energies were found:

For acetaldehyde = 17.8 kcal/mole

For acetone = 32 kcal/mole

For ethanol = 28.5 kcal/mole.

The conditions used in this run were sufficient to keep the catalyst in a reduced state, as reflected in the higher activation energy for acetone than seen in the first study. In spite of the fact that this experiment was run at higher than desirable conversions, the activation energy value for acetaldehyde compares well with the value obtained in the first study.

Hydrogen Reaction Order Study⁵³

Conditions: 90 SCCM N₂, ca. 8 SCCM HOAc. Begin at 90 SCCM H₂, then reduce the H₂ flow in steps to 80, 60, 40 and 20 SCCM while concurrently increasing the He flow from 10 SCCM in steps to 20, 40, 60 and 80 SCCM, then reversing the sequence, 1 atmosphere, GHSV = 150,000 hr⁻¹, 301°C, HOAc accountability during run = 96-106%, HOAc conversion = 3-11% and HAc selectivity = 82-95%.

Results: Hysteresis observed, consistent with reducing the amount of hydrogen present in the presence of a relatively large amount of acetic acid, thereby changing the nature of the catalyst. The reaction orders found for the first pass (decreasing the level of hydrogen) and then upon increasing the hydrogen back to the original level (second pass) were:

For acetaldehyde = 0.98 (1st pass) and 0.79 (2nd pass)
For acetone = -0.08 (1st pass) and -0.32 (2nd pass)
For ethanol = 1.76 (1st pass) and 1.40 (2nd pass).

Acetic Acid Reaction Order Study⁵⁴

Conditions: 90 SCCM N₂, 60 SCCM H₂, 40 SCCM He, ca. 2, 4, 6 and 7 SCCM HOAc (space velocity not adjusted since change in space velocity was negligible), then reversing the sequence, 1 atmosphere, GHSV = 150,000 hr⁻¹, 301°C, HOAc accountability during run = 81-99 %, HOAc conversion = 13-33 % (higher than desirable) and HAC selectivity = 93-95 %.

Results: Some hysteresis observed, but it was possible to reverse the sequence without significantly affecting the kinetic results. The results were consistent with those expected for a reaction where one component (acetic acid in this case) is very strongly adsorbed on the catalyst surface, thus causing the apparent reaction order to change as the partial pressure is changed. Thus, for all products, the rate increased and then decreased as the partial pressure of acetic acid was increased. Thus for acetaldehyde, the average reaction order in acetic acid at low partial pressure was 0.66, whereas at higher partial pressure it was -0.77. The overall trend for acetaldehyde was approximately 0.04 order (consistent with the behavior observed earlier where increasing the acetic acid had no effect on the rate). For acetone the approximate overall trend was 0.2 order (not linear), and for ethanol the approximate overall trend was -0.3 order (not linear). This interesting kinetic behavior is possibly responsible for the encouraging effect of total pressure described in the next section.

Effect of Total Pressure⁵⁵

Conditions: Begin with 90 SCCM H₂ passing through acetic acid vaporizer to provide a constant hydrogen/acetic acid ratio = 37/1, decrease the flow rate of hydrogen to 70, 50, 30 and 15 SCCM, while increasing the He flow rate from 0 to 20, 40, 60 and 75 SCCM to maintain constant space velocity, then reversing the sequence, 1 atmosphere, GHSV = 71,000 hr⁻¹, 301°C, HOAc accountability during run = 73-105%, HOAc conversion = 66-71% (1st pass) = 22-61% (2nd pass) and HAC selectivity = 77-93%.

Results: Hysteresis observed with the rate and conversions being less on the second pass, consistent with a change in nature of the catalyst being induced by operating in a hydrogen deficient atmosphere. However, in spite of the hysteresis, the same behavior trend was observed with both passes: **The rate increased with an increase in pressure without significantly affecting the selectivity.** These results suggested that operation at higher pressures might be possible, thereby allowing for efficient recovery of acetaldehyde. The results from the first pass are shown graphically in Figure D.9.

Effect of Conversion⁵¹⁻⁵⁶

Figure D.9 illustrates the effect of conversion on selectivity. These results were obtained under a wide variety of conditions and illustrate that, regardless of the means used to cause an increase in acetic acid conversion, this increase in conversion causes an increase

FIGURE D.9: Effect of H₂ + HOAc Pressure, 2.5 % Pd/Fe₂O₃ Catalyst

in the selectivity to ethanol. This is to be expected with consecutive reactions. Acetone selectivity does not really follow this trend, and the higher levels sometimes seen at low conversions are often possibly the result of reaction conditions that oxidize the catalyst. Up to about 45% acetic acid conversion, the selectivity to acetaldehyde is between 80 and 90%, except in those cases where the conditions favor acetone formation at low conversion. The other principle product, methane (not shown in the figure), increases from about 1% at low conversion to about 7% at higher conversions.

Studies at low pressure using the 5 wt % Pd/ Fe₂O₃ catalyst. The results from the 2.5 wt % Pd/ Fe₂O₃ catalyst were sufficiently encouraging to suggest that increasing the level of Pd may be beneficial. This catalyst was quite active, and the preliminary activation energy study performed early on in the catalyst was thus compromised by the fact that the conversions were typically higher than desired for a kinetic study (observed acetic acid conversions were 12-57%).⁵⁷ The calculated activation energies for acetaldehyde, acetone and ethanol were 15.5, 31.4 and 21.8 kcal/mole, respectively. Thus the activation energy calculated for acetone was the same as that found for the 2.5 wt % Pd/Fe₂O₃ catalyst run at similar conversion range, whereas the values calculated for acetaldehyde were only slightly lower and for ethanol, they were considerably lower. While the lower activation energy for ethanol might suggest a higher selectivity to ethanol under otherwise similar conditions with the 5 wt % Pd/Fe₂O₃ catalyst compared to the 2.5 wt % Pd/ Fe₂O₃ catalyst, this was found not to be the case. In fact, just the opposite appears to be true. The data in Table D.6 summarize the performances of the two catalysts operating under essentially identical conditions and at similar conversions. The data in Table D.6 reveal a slightly higher acetaldehyde selectivity resulting from the catalyst containing more Pd. This observation is in contrast with what Ponec has published.^{10d} Ponec states that increasing the level of the reducing metal beyond 1.25 atomic % decreases the selectivity, whereas the 5 wt % Pd/ Fe₂O₃ catalyst actually contains 3.8 atomic % Pd. Most of the increase in selectivity comes from a decrease in the selectivity to ethanol. This also is surprising since the catalyst should be more reducing as the reducing metal loading increases. While the selectivities to acetone and C₂ hydrocarbons appear slightly lower with the catalyst containing more Pd, the selectivity to methane is slightly higher.

Some experiments were performed with the 5 wt % Pd/ Fe₂O₃ catalyst to determine how the ratio of hydrogen to acetic acid affected rate, selectivity and conversion. Some of these experiments are summarized in Table D.7. The data in the table are entered chronologically, and some of the differences in performance may have resulted from catalyst deactivation. Some caution also must be taken in comparing conversions taken when the acetic acid accountability is low compared to when the accountability is high: if the acetic acid accountability is lower, then the actual conversion is probably lower than listed in the table. Nevertheless the data in the table show some very general trends. When the mole fraction of acetic acid, X_{HOAc}, is low (0.026), the conversion of acetic acid is high, the acetaldehyde rate is high, and the acetaldehyde selectivity is the lowest seen. As the ratio increases, the acetic acid conversion falls, the acetaldehyde rate generally remains reasonably high, and the acetaldehyde selectivity increases, then seems to level out. Decreasing the space velocity (by decreasing the SCCM hydrogen) when the mole

TABLE D.6
Effect of % Pd on the Performance of Fe₂O₃ Catalysts

Wt % Pd	2.5					5			
Reference	58	59	60	61	62	63	64	65	66
% HOAc Conv.	54	50	52	50	45	59	51	48	45
G/(l-hr) HAc	597	621	656	698	527	748	694	674	662
% HAc sel.*	78	79	77	80	73	82	84	84	84
% acetone sel.	0.8	0.8	0.9	0.8	1.6	0.7	0.7	0.6	0.6
% EtOH sel.	15	15	17	14	18	12	10	9	9
% CH ₄ sel.	4.6	4.1	4.4	3.8	6.1	5.2	5.7	5.9	5.9
% C ₂ H. C. sel.**	1.0	0.9	0.9	0.8	1.6	0.7	0.7	0.6	0.6
% HOAc acct.***	91	107	103	103	101	97	101	102	105

Conditions: 90 SCCM H₂ containing 2 mol % HOAc, 0.2 g catalyst, 300°C.

*Selectivities are normalized.

** C₂ Hydrocarbons = ethylene + ethane.

***Acetic acid accountability.

TABLE D.7

Effect of Changing the Mole Fraction of Acetic Acid in Hydrogen
on the Performance of 5 wt. % Pd/Fe₂O₃
at Different Space Velocities.

Reference	67a	67b	67c	67d	67e	67f	67g	67h
TTOS, min.*	5350	7033	7141	8134	8886	9291	9328	9396
SCCM H ₂	90	30	90	90	90	90	25	25
GHSV, hr ⁻¹	73000	24000	73000	73000	73000	73000	20000	20000
X _{HOAc}	0.057	0.095	0.095	0.026	0.20	0.20	0.20	0.20
% HOAc conv.	38	31	16	66	23	16	17	26
G/(l-hr) HAc	1003	283	497	740	523	899	338	407
% HAc sel.**	87	87	89	79	87	90	89	89
% Acetone sel.	1.1	1.1	0.9	0.9	2.5	1.8	3.9	3.0
% EtOH sel.	8.0	6.8	5.3	15.8	7.5	5.8	4.6	5.4
% CH ₄ sel.	3.2	4.8	3.9	3.7	2.7	1.8	1.9	2.2
% C ₂ H. C. sel.***	0.6	0.8	0.5	0.7	0.2	0.4	0.3	0.6
% HOAc acct.****	86	82	91	92	81	95	96	89

Conditions: 0.2 g catalyst, 300°C.

*TTOS = total time on stream under hydrogen and acetic acid feed.

**Selectivities are normalized.

*** C₂ Hydrocarbons = ethylene + ethane.

****Acetic acid accountability.

fraction of acetic acid is 0.095 about doubled the acetic acid conversion, decreased the acetaldehyde rate, and had little effect on the selectivity. Decreasing the space velocity at the highest acetic acid mole fraction (0.20) had little effect on the conversion and the acetaldehyde selectivity, but a decrease in rate occurs. The failure to increase the conversion in this case may be related to some sort of self-inhibition. Increasing the mole fraction of acetic acid appears to increase the selectivity to acetone. Although it was desired to determine the selectivity at 50% conversion with $X_{\text{HOAc}} = 0.20$, this was not accomplished with this catalyst at low pressure. The data from Table D.7 actually correlate best with the notion that acetaldehyde selectivity is most closely related to acetic acid conversion rather than other reaction parameters, and this is very reminiscent of the situation depicted in Figure D.10 for the 2.5 wt % Pd/ Fe₂O₃ catalyst.

The 5 wt % Pd/ Fe₂O₃ catalyst was used to examine the reaction of some of the products (or potential products). In one experiment, ethanol was fed from the vaporizer held at 20°C by transpiration in 90 SCCM nitrogen across the catalyst at 300°C.⁶⁸ The dehydrogenation reaction yielded about a 10% conversion to acetaldehyde (this is about what the equilibrium value should be). Another experiment examined the possibility of hydrogenating ethyl acetate to ethanol and acetaldehyde.⁶⁹ Ethyl acetate was fed from the vaporizer held at 0°C by transpiration in 25 SCCM hydrogen across the catalyst at 300°C. No reaction was observed. Therefore, it appears that the hydroxyl function is needed for this catalyst to reduce an acetate derivative to acetaldehyde, and this requirement is in accord with the theory of the reaction proposed by Ponec.¹⁰

Studies at low pressure using the 10 wt % Pd/ Fe₂O₃ catalysts. Two versions of this catalyst were prepared and studied: the low-surface-area (18.4 m²/g) material (Catalyst No. 4a) and a high surface-area (113.3 m²/g) material (Catalyst No. 4b). Both catalysts were considerably more active than those containing less or no palladium. In fact, when the standard conditions of $X_{\text{HOAc}} = 0.026$ in 90 SCCM hydrogen at 300°C were used, the conversions of acetic acid were 72-98 % when even the low-surface-area Catalyst No. 4a was used. A comparison of the low-surface-area 10 wt % Pd/Fe₂O₃ catalyst with the 5 wt % Pd/Fe₂O₃ catalyst under conditions of similar feed conditions, conversions, and acetic acid accountability is provided in Table D.8. The addition of more Pd further increased the selectivity to acetaldehyde at similar conversions, and most of the increase in selectivity resulted from a reduction in the amounts of hydrocarbons and ethanol produced. Again, it appears that by increasing the amount of the reducing component palladium, the catalyst acts as a less reducing catalyst. Although several attempts were made to operate at a 5/1 hydrogen/acetic acid ratio, only one sample gave good acetic acid accountability (97 %).⁷¹ This result was obtained by feeding 10 SCCM hydrogen (GHSV = 8080 hr⁻¹) and produced acetaldehyde at a rate of 246 g/(l-hr) and at 29% acetic acid conversion. Normalized selectivities for acetaldehyde, acetone, ethanol methane and C₂ hydrocarbons were 81, 5.2, 9.0, 3.1 and 1.0%, respectively. Note that the selectivity to acetone increases when the mixture becomes leaner in hydrogen.

FIGURE D.10: HOAc Conversion vs. Normalized Selectivities, 2.5 %Pd/Fe₂O₃ Catalyst

TABLE D.8

Effect of % Pd on the Performance of Fe₂O₃ Catalysts:
Comparison at the 5 and 10 Wt. % Levels

Wt % Pd	<u>5</u>		<u>10</u>	
Reference	70a	70b	70c	70d
% HOAc Conv.	98	92	97	91
G/(1-hr) HAc	642	779	773	994
% HAc sel.*	36	47	52	68
% acetone sel.	1.1	0.9	1.0	1.0
% EtOH sel.	44	39	40	27
% CH ₄ sel.	14	11	5.4	3.4
% C ₂ H. C. sel.**	3.7	2.6	1.0	0.6
% HOAc acct.***	98	103	98	103

Conditions: 90 SCCM H₂ containing 2 mol % HOAc, 0.2 g catalyst, 300°C.

*Selectivities are normalized.

** C₂ Hydrocarbons = ethylene + ethane.

***Acetic acid accountability.

The high-surface-area material (Catalyst No. 4b) was also a very active catalyst.⁷² Although the performances of the high- and low-surface catalysts seemed very similar, it unfortunately was not possible to actually compare the two materials definitively under conditions of comparable feed conditions, acetic acid conversions and acetic acid accountabilities.

The high-surface-area material (Catalyst No. 4b) was used to examine the back reaction of acetaldehyde and water to produce acetic acid and hydrogen (since the reaction is theoretically an equilibrium reaction).⁷³ Acetaldehyde was fed by transpiration in nitrogen (31 SCCM) held at 0°C, and this stream was combined with a stream exiting a water vaporizer held at 50°C using nitrogen (227 SCCM) as the transpiration gas. Even when this feed contained added hydrogen (25 SCCM), the catalyst temperature exothermed from 303 to 309°C upon contact with the feed. A sample taken during this exotherm showed no acetic acid production and minor peaks attributed to *cis*- and *trans*-crotonaldehyde (same retention times as an authentic sample). After 15 minutes the catalyst temperature fell to 306°C, and the nitrogen flow to the water vaporizer was reduced to 55 SCCM. The next sample showed slightly elevated levels of acetic acid and crotonaldehyde (both amounting to about 0.8 area %). When the small amount of hydrogen was removed from the feed, the peaks attributed to crotonaldehyde grew in intensity (to 6.7 area %). The catalyst was reduced again overnight, and the feeds were adjusted so that the ratio of hydrogen/water/acetaldehyde was approximately 5/1/1. Under these conditions the catalyst produced some acetic acid (1.4 area %), ethanol (4.1 area %), butyraldehyde (0.9 area %) and small amounts of crotonaldehyde (0.4 area %): the majority of the material was unreacted acetaldehyde (92.7 area %). These experiments suggest that when sufficient water is present and hydrogen is lean, the catalyst becomes oxidized. The result of this oxidation is loss of activity for the conversion of acetaldehyde and water to acetic acid and hydrogen and promotion of the aldol condensation of acetaldehyde due to the formation of acid and/or basic sites on the catalyst. When sufficient hydrogen is present to help keep the catalyst more reduced, some ethanol is formed, some of the crotonaldehyde is reduced to butyraldehyde and a small amount of acetic acid is formed. These results may explain the apparent product inhibition that limits the conversion achievable when the space velocity is reduced at low hydrogen/acetic acid ratio (this was described above for the 5 wt % Pd/ Fe₂O₃ catalyst).

The high-surface-area material was also used to examine the hydrogenation of acetaldehyde.⁷⁴ Acetaldehyde was fed from a vaporizer held at -20° by transpiration in hydrogen (107 SCCM). These conditions provided a hydrogen to acetaldehyde ratio of approximately 5.8. Initially the catalyst (which had been reduced overnight in hydrogen at 300°C) was very active for the formation of ethanol (49 area %) and methane (6.9 area %), with most of the remaining material unreacted acetaldehyde (40.5 area %). After about 6 hours the area percentages were: ethanol = 14.4, methane = 0.8, acetaldehyde = 83.9. Thus the catalyst has a moderate activity for the conversion of acetaldehyde to ethanol when water is absent. We then evaluated the effect of added water on the efficiency of the acetic acid hydrogenation reaction.⁷⁵ We did not observe an inhibitory

effect in this case, but, due to equipment limitations, we were unable to feed at the same molar ratios as in the acetaldehyde experiments. A $H_2/H_2O/HOAc \sim 37/0.62/1$ was used in this case. Therefore, although there is no apparent water inhibitory effect on the acetic acid hydrogenation reaction at high hydrogen level, we cannot make any conclusions at this time about the effect of water at lower hydrogen levels. Note that all of the work done with the high-surface-area catalyst was done with a single catalyst charge, and its performance may have been affected somewhat by its previous history.

Studies at low pressure using 0, 10, 20, 40 and 80 wt % Pd/Fe₂O₃ catalysts and 100 % Pd catalyst. A summary of the performance of this series of catalysts under the standard screening conditions is provided in Table D.9. The 100% Fe₂O₃ catalyst was less active than the catalysts containing 10-80% Pd and only gave 19% acetic acid conversion under the same conditions that the Pd/Fe₂O₃ catalysts provided 81-96% conversion. Because the conversion was low, the 100% Fe₂O₃ catalyst was quite selective to acetaldehyde. However this catalyst produced excessive amounts of methane and C₂ hydrocarbons considering that the conversion was so low. The 100% Pd catalyst (Pd sponge) likewise was not as active as those containing both Pd and iron. The main product resulting when this catalyst was used was methane. The methane make was lowest when the 10 wt % Pd/Fe₂O₃ catalyst was used, even though the conversion was very high. The methane make increased as the amount of Pd increased above 10%, and was especially high when the catalyst containing 80 wt % Pd was used. It is noteworthy that when the hydrogen/acetic acid ratio was reduced to 5/1 using the 40 wt % Pd/Fe₂O₃ catalyst, the methane selectivity fell to only 0.8%, the acetaldehyde selectivity rose to 92% at about 31% acetic acid conversion (acetic acid accountability = 90%).⁷⁷ Selectivities to acetone, ethanol and C₂ hydrocarbons were 3.3, 3.8 and 0.2%, respectively. In view of the cost of Pd compared to that of iron, and, since the rate and acetaldehyde selectivity were the best seen at low pressure, it was decided that the 10 wt % Pd/Fe₂O₃ catalyst would be the best initial candidate for high-pressure studies.

Studies of other catalysts at low pressure using on-line gas chromatography. Two Cu/Fe₂O₃ catalysts were evaluated: one containing 5 wt % Cu (Catalyst No. 12) and a mixed metal oxide containing 30 mole % Cu and 70 mole % iron (Catalyst No. 22). Both catalysts behaved similarly to the unmodified iron oxide. Thus Catalyst No. 12 under standard screening conditions produced acetaldehyde at a rate of 245 g/(l-hr) at 20% acetic acid conversion, with selectivities to acetaldehyde, acetone, ethanol, methane and C₂ hydrocarbons = 75, 0.6, 8.8, 12.3 and 3.6%, respectively (acetic acid accountability = 102 %).⁷⁸ Catalyst No. 22 under standard screening conditions produced acetaldehyde at a rate of 167 g/(l-hr) at 40% acetic acid conversion, with selectivities to acetaldehyde, acetone, ethanol, methane and C₂ hydrocarbons = 73, 2.1, 14.5, 7.5 and 2.6%, respectively (acetic acid accountability = 102 %).⁷⁹

The 2.5 wt % Pd/SnO₂ catalyst was also evaluated under the standard screening conditions. This catalyst had no activity at 300°C.⁸⁰ This result is surprising in view of the results of Ponec.^{10d}

TABLE D.9
Effect of 0 to 100 wt % Pd on the Performance of Fe₂O₃ Catalysts

Wt % Pd	<u>0</u>	<u>10</u>	<u>20</u>	<u>40</u>	<u>80</u>	<u>100</u>
Catalyst No.	1	4b	5	6	7	8
Reference	76a	76b	76c	76d	76e	76f
% HOAc Conv.	19	96	98	99	81	26
G/(l-hr) HAc	280	499	157	79	45	1
% HAc sel.*	80	56	38	35	15	4
% acetone sel.	0.6	3.1	2.7	1.1	0.2	0.3
% EtOH sel.	7	38	50	55	22	0.4
% CH ₄ sel.	10.5	2.7	8.5	8.6	62.9	95.4
% C ₂ H. C. sel.**	3.1	0.1	0.7	0.3	0	0.1
% HOAc acct.***	100	100	108	107	105	100

Conditions: 90 SCCM H₂ containing 2 mol % HOAc, 0.2 g catalyst, 300°C.

*Selectivities are normalized.

** C₂ Hydrocarbons = ethylene + ethane.

***Acetic acid accountability.

Characterization of Fe_2O_3 and $\text{Pd/Fe}_2\text{O}_3$ catalysts. The BET surface areas, XPS and X-ray diffraction (XRD) were determined for a number of catalysts.⁸¹ These results are summarized in Table D.10. Provision was made to reduce the samples in the XPS and XRD instruments without exposure to air between reduction and characterization. The reductions were performed at 300°C in 10% hydrogen in helium (25 SCCM) for 1 hour (in a control run, longer reduction times did not alter the results). Not all samples were completely characterized. XPS data reported in the table indicate atomic percents. Used samples were pacified by the technique described previously. Since this treatment oxidizes the surface of the catalyst, and XPS is a surface technique, the used catalysts evaluated by XPS showed 80 or 100% of the surface iron as Fe (III). The data from Table D.10 indicate that the composition of the reduced catalysts' surfaces by XPS contain more lower valent iron than the composition of the bulk by XRD. Not shown in the table is the fact that the XPS data indicated that a FePd alloy (at least at the surface) was formed in those reduced catalysts containing 2.5-10 wt % Pd. This was indicated by a shift of the Pd 3d to higher binding energy (from 334.2 to 334.6 eV), indicating a reduction in the electron density around the Pd atom consistent with the formation of a Pd-Fe alloy. This alloy was also detected by XRD in the bulk phase in the used catalyst containing 20% Pd and in the reduced catalyst containing 80% Pd. The occurrence of this alloy could have relevance regarding the high selectivity exhibited by the Pd-Fe catalysts. Some of the used catalysts studied contained bulk phase iron carbide (cohenite). The used catalysts also showed enrichment in surface Pd compared to the fresh or reduced-fresh catalysts. Of the used catalysts studied, all had BET surface areas below 20 m²/g, including the catalyst 4b which began with a BET surface area of 113 m²/g.

Studies at elevated pressure. The 10 wt % Pd/Fe₂O₃ catalyst was the first catalyst to be evaluated at elevated pressure. The first 50 hours of operation with this catalyst were complicated by mechanical problems relating to pressure control. Also it was discovered that the on-line gas chromatography data gave much poorer results than observed at low pressure, even when the pressure control valve was working properly. This problem was indirectly caused by the way the Research Control Valve operated (including when it was operating properly). When the valve was operating, and the outlet gases were bubbled through a liquid, it was observed that the valve actually acted as an on/off valve. The gas came out in spurts. The reactor pressure also swung up and down in spurts of 20-30 psig when the valve was operating at a set pressure of 250 psig. When the valve was closed, there was negligible gas flow across the catalyst, and when it was open, the gas flow was huge. Obviously this type of condition caused problems with on-line GC sampling, which takes an instantaneous sample. In one instant the conversion may be exceedingly high and in another instant the conversion may be very low, depending on if the valve is closed or open. Consequently, selectivities and acetic acid accountability varied widely (in most circumstances the bypass area of acetic acid had to be adjusted to provide an accountability of ca. 100%, and the conversion was then estimated). The on-line GC was a much more qualitative device under elevated pressure conditions compared to operation at low pressure, where the flow was uniform. Near the end of the project, some of the sampling was done by trapping the products over a measured time period and analyzing them off line. Another frequent problem at high pressure was plugging of the reactor.

TABLE D.10

Characterization of Fe₂O₃ and Pd/Fe₂O₃ Catalysts

<u>Wt % Pd in Fe₂O₃</u>	<u>XPS before rdn</u>					<u>XPS after rdn</u>					<u>XRD phases before rdn</u>	<u>XRD phases after rdn</u>	<u>BET*</u>
	<u>Pd</u>	<u>Fe</u>	<u>Fe(III)</u>	<u>Fe(II)</u>	<u>Fe(0)</u>	<u>Pd</u>	<u>Fe</u>	<u>Fe(III)</u>	<u>Fe(II)</u>	<u>Fe(0)</u>			
0	---	17.6	100	0	0	---	17.3	50	50	0	Fe ₂ O ₃	Fe ₃ O ₄	20
2.5	---	---	100	0	0	---	---	20	30	50	Fe ₂ O ₃	Fe ₃ O ₄	16
2.5 (used)	---	---	---	---	---	---	---	---	---	---	Fe ₃ C	---	13
5	6.8	15.7	100	0	0	4.5	17.3	0	0	100	Fe ₂ O ₃	Fe ₃ O ₄ , Fe, Pd	15
5 (used)	---	---	---	---	---	---	---	---	---	---	---	---	16
10	38.2	2.5	100	0	0	37.2	11.8	20	60	20	Fe ₂ O ₃	Fe ₃ O ₄ , Fe, Pd	113
10 (used)	---	---	---	---	---	---	---	---	---	---	---	---	18
20	1.7	15.5	100	0	0	2.2	13.5	80	20	0	Fe ₂ O ₃ , PdO	Fe ₃ O ₄ , Pd	80
20 (used)	2.7	7.1	100	0	0	17.7	12.6	25	15	60	Fe, FePd	Fe, FePd	---
40	2.0	14.9	100	0	0	3.5	12.9	80	10	10	Fe ₂ O ₃ , PdO, Pd	Fe ₃ O ₄ , Fe, Pd	35
40(used)	5.2	3.0	80	10	10	12.9	6.3	5	20	75	Fe ₃ C, Pd	Fe ₃ C, Pd	---
80	27.2	6.1	100	0	0	45.4	4.5	0	30	70	PdO	Fe, FePd	24

*BET surface area in m²/g.

This pulsating action from the Research Control Valve may have caused the bed components to move and eventually plug the reactor.

The 10 wt % Pd/Fe₂O₃ catalyst performed best at high hydrogen/acetic acid ratios and better at 100 psig than at 250 psig at 300°C. Thus operation at 10/1 hydrogen/acetic acid ratio at gas hourly space velocity (GHSV) = 25500 hr⁻¹ at 100 psig produced acetaldehyde at a rate of 5750 g/(l-hr) at an estimated acetic acid conversion of about 37%.

Normalized selectivities for acetaldehyde, acetone, ethanol, ethyl acetate, methane and C₂ hydrocarbons were 87.5, 4.1, 7.0, 0.8, 0.6 and less than 0.1%, respectively. When this catalyst was operated at 5/1 hydrogen/acetic acid ratio at 250 psig, the performance of the catalyst deteriorated with time on stream. Losses in rate, estimated conversion and selectivity occurred. These results are summarized in Table D.11. Although ethyl acetate (EtOAc) is normally not a significant product at lower pressure, it becomes a significant product at high pressure, especially as the catalyst's time on stream increases. Acetone selectivity also increases with time on stream. It was speculated that the deterioration in performance was due to the catalyst becoming oxidized at the high acetic acid pressure. This would account for the increased acetone formation, the decline in rate and conversion and would produce the acid sites necessary to catalyze ethyl acetate formation. It was speculated that increasing the amount of Pd in the catalyst would make the catalyst more reducing, and that this would aid in controlling over-oxidation of the catalyst at higher pressures. Therefore the next catalyst evaluated was the 40 wt % Pd/Fe₂O₃ catalyst.

The 40 wt % Pd/Fe₂O₃ catalyst also made less ethanol as the amount of hydrogen was increased. However, unlike the 10 wt % Pd/Fe₂O₃ catalyst, the 40 wt % Pd/Fe₂O₃ catalyst showed no significant decay in acetaldehyde rate or selectivity. These results are summarized in Table D.12. The hydrogen/acetic acid ratio was decreased by decreasing the hydrogen flow rate (from 450 to 315 SCCM) while maintaining the acetic acid flow rate unchanged. Thus the two conditions were run at different space velocities as well as different ratios. However, the apparent conversion at the high hydrogen/acetic acid ratio was very similar to that found for the lower ratio. Nevertheless, the acetaldehyde selectivity was actually better at the high ratio, and this is due to the decrease in selectivity to ethanol and ethyl acetate. It is not immediately obvious why making the reaction conditions more reducing actually makes less of the more reduced products (ethanol and ethyl acetate) at similar apparent conversions, but it should be remembered that the conversion data are the least accurate data because of the pressure control difficulties mentioned above. The accuracy of the data obtained by the on-line GC sampling technique should be verified using bulk sampling techniques. Although some work was done along these lines, these techniques were not providing acceptable acetic acid accountabilities at the time the work under the contract was concluded. Only one bulk sample was taken using this catalyst.⁸⁴ This was taken at 250 psig when the hydrogen/acetic acid ratio was 5/1, and indicated an acetaldehyde selectivity of 54% at 40 % acetic acid conversion and 95% acetic acid accountability. The on-line GC samples taken during the same period suggested acetaldehyde selectivities ranging from 75-82% at 28-36% acetic acid conversion.

TABLE D.11

Effect of Time on Stream on the Performance of 10 wt % Pd/Fe₂O₃
at 250 psig and 5/1 Hydrogen/Acetic Acid Ratio.

TTOS, min*	<u>1739</u>	<u>2089</u>
Reference	82a	82b
% HOAc Conv.	22	10
G/(l-hr) HAc	3350	970
% HAc sel.**	77.9	62.7
% acetone sel.	1.5	4.6
% EtOH sel.	15.0	16.2
% EtOAc sel.	4.6	15.5
% CH ₄ sel.	0.7	0.7
% C ₂ H. C. sel.***	0.2	0.1

Conditions: GHSV = 12200, 300°C.

*TTOS = total time on stream under hydrogen and acetic acid feed.

**Selectivities are normalized.

*** C₂ Hydrocarbons = ethylene + ethane.

TABLE D.12

Effects of Hydrogen/Acetic Acid Ratio and Time on Stream on the
Performance of 40 wt % Pd/Fe₂O₃ at 250 psig.

Reference	83a	83b	83c
TTOS, min*	512	534	2318
H ₂ /HOAc	7	5	5
GHSV, hr-1	3530	2600	2600
% HOAc Conv.	46	42	38
G/(1-hr) HAc	1530	2125	2175
% HAc sel.**	86.4	77.1	77.0
% acetone sel.	1.7	1.3	1.5
% EtOH sel.	9.6	15.9	15.2
% EtOAc sel.	2.1	5.6	6.3
% CH ₄ sel.	0.1	<0.1	<0.1
% C ₂ H. C. sel.***	0	<0.1	<0.1

Conditions: 300°C.

*TTOS = total time on stream under hydrogen and acetic acid feed.

**Selectivities are normalized.

*** C₂ Hydrocarbons = ethylene + ethane.

The 20 wt % Pd/Fe₂O₃ catalyst also was evaluated for the acetic acid hydrogenation reaction at elevated pressure to see if the amount of expensive Pd could be reduced. The evaluation indicated that this catalyst behaved very similarly to the 40 wt % Pd/Fe₂O₃ catalyst, except that it was less active.⁸⁵ Since this catalyst was less active under the same feed conditions, the conversions were lower (about 20-25%), and, therefore the acetaldehyde selectivity was slightly higher. The effect falls within the selectivity vs conversion relationship observed in the low-pressure studies.

In an attempt to save on potential catalyst costs, several supported catalysts were examined. A 10% Fe₂O₃ – 2% Pd on SiO₂ catalyst was evaluated at 240 psig at 7/1 hydrogen/acetic acid ratio.⁸⁶ At 16% acetic acid conversion, this catalyst only had a selectivity to acetaldehyde of 58%, and selectivities to acetone, ethanol and ethyl acetate were 0.3, 32 and 8%, respectively. The low acetaldehyde selectivity at low acetic acid conversion could be related to diffusion limitations, since this material had a BET surface area = 284 m²/g.²⁷ A 10% Fe₂O₃ on SiO₂ catalyst was essentially inactive under similar conditions.⁸⁷ A 10% Fe₂O₃ – 0.5% Pd on SiO₂ catalyst behaved similarly to the catalyst containing 2 wt % Pd, and exhibited similar poor selectivity at low conversion.⁸⁸

The best catalyst found up to this point of the investigation is the 40 wt % Pd/Fe₂O₃ catalyst. The data in Table D.12 suggest that it may be technically feasible to make and recover acetaldehyde at elevated pressure using Pd/Fe catalysts. Work on the acetic acid hydrogenation reaction as a means to produce acetaldehyde for vinyl acetate monomer ceased after economic analysis indicated that, under most conditions, the synthesis gas route to vinyl acetate was not likely to compete with conventional technology.

Engineering and Process Description

Based on these results and some key assumptions, a scoping design was developed for the generation of acetaldehyde via acetic acid hydrogenation. This process consists of two main sections: a reaction section and a recovery section shown schematically in Figures D.11 and D.12, respectively. Acetic acid is converted to acetaldehyde (and water) with excess hydrogen in a fixed-bed reactor (RX) in the reaction section. The acetaldehyde product is recovered via distillation (D) after absorption (A) using the acetic acid-rich distillation bottoms as a solvent after cooling (S). The hydrogen-rich vapor from the absorber is largely recycled to the reactor with a compressor (RC). Unconverted acetic acid is separated from water and other reaction byproducts in the recovery section. This separation takes place primarily in the acetic acid column (AC) using coproduct ethyl acetate as an azeotroping agent. The ethyl acetate-water rich overhead from the acid column separates into organic-rich and water-rich phases in the decanter (DE) after cooling (DC). Ethyl acetate is recovered from the organic phase by first distilling off near ethyl acetate-water azeotrope in the azeotrope column (Z) followed by separation from any acetic acid carryover in the ethyl acetate column (E). Organics in the aqueous phase are largely removed by steam stripping (SS) then separated into waste acetone and near ethyl acetate-water azeotrope streams in the waste acetone column (W). All streams with a composition approximating the ethyl acetate-water azeotrope are combined and fed to the decanter.

Key assumptions used to develop this design are: 1) a 5/1 molar ratio of hydrogen to acetic acid in the reactor (RX) feed, 2) byproduct ethanol is converted to ethyl acetate as dictated by chemical equilibrium at conditions present in the bottom of the acetaldehyde recovery column (D), and 3) the reactor operates at 300C, 250 psig, and 45% acetic acid conversion with a selectivity of 89% to acetaldehyde, 5% to ethanol, 4% to acetone (and CO₂), and 2% to methane and ethene. The assumptions of 5/1 H₂/HOAc and 250 psig are far removed from initial work at 37/1 H₂/HOAc and 1 atm pressure described above but were felt to better represent a commercializable process. Later experimental work largely verified the viability of these conditions. The degree of ethyl acetate formation from ethanol and unconverted acetic acid remains unclear but in practice may be simply catalyzed by adding sulfuric acid to the HOAc-rich solvent before recovery. Certainly the recovery scheme shown in Figure D.12 is highly dependent on this conversion of byproduct ethanol to ethyl acetate and is inappropriate without it.

Heat and material balances were developed for the HOAc hydrogenation process with a capacity of 28,500 lbs/hr (233 Mlbs/yr) acetaldehyde using a process simulator. Utility requirements and equipment costs were estimated from these balances. Limited column optimization was performed in which equipment costs (i.e., diameter and number of stages) were balanced by operating costs (i.e., steam and cooling water requirements) for each column but was not rigorously applied. The separation of HOAc from water and other organics was the most expensive in terms of both equipment (column AC and associated heat exchangers DC and AR) and utility costs so extra effort was made to optimize this separation. Column (AC) specifications on HOAc purity and recovery were varied from 95 to 99% and 99 to 99.9%, respectively, to determine the best strategy for this critical separation.

Figure D.11 – HOAc Hydrogenation Reaction Section

Figure D.12 – HOAC Hydrogenation Recovery Section

HOAc Recovery, %	99.9	99.9	99	99
HOAc Purity, wt%	99	95	99	95
100# Steam, Klb/hr	93.0	90.1	69.9	68.0
Cooling Water, MBtu/hr	85.7	85.2	64.6	65.8
Wastewater COD, lb/hr	331	331	624	631
Equipment Costs (excluding tanks), M\$	1.63	1.40	1.41	1.29

As summarized above, reducing HOAc recovery from 99.9 to 99% lowered steam and cooling water requirements for the recovery section by over 20% while lowering HOAc purity from 99 to 95% reduced equipment costs in the recovery section by about 10%. At a HOAc recovery of 99.9% in the acid column (AC), the ethyl acetate bottoms from the azeotrope column (Z) can meet a 99% purity specification eliminating the need for the ethyl acetate column (E). However, as shown above, it is more cost effective to include equipment to separate ethyl acetate from this carryover acetic acid and relax the recovery specifications on the acid column to 99%. Most of this unrecovered HOAc ends up in the wastewater which will put a lower limit on HOAc recovery in the acid column. This limit was not determined. Lowering the acetic acid purity to 95% may be detrimental to reactor performance and is probably not justified by the small savings in equipment costs. So, 99% HOAc recovery and purity were chosen in the final design.

The heat and material balances for the reaction and recovery sections are summarized in Tables D.13 and D.14, respectively. Because it was assumed that any ethyl acetate in the reactor feed would be hydrolyzed to ethanol and acetic acid over the catalyst, a psuedo-reactor was added to the simulator for convenience to perform this conversion to the reactor feed stream. This adiabatic conversion is not shown in Figure D.11 but is reflected in the material balance between streams 11 and 36. Also, there is a small (<1 MBtu/hr) discrepancy in the energy balance around the waste acetone column (W) in the recovery section due to the pressure difference (15 psi) assumed between the steam stripper (SS) and this column. Reconciling this difference should have no significant impact on the design or estimated costs. Equipment lists and estimated costs corresponding to these balances are provided in Tables D.15 and D.16 for the reaction and recovery sections, respectively. Utility requirements are summarized below:

Utility	Units	Reaction	Recovery	Total
Cooling Water	MBtu/hr	58.84	64.57	123.41
Electricity	KW	650	33	683
Steam (100#)	Klb/hr	0	69.6	69.6
Steam (600#)	Klb/hr	61.8	0	61.8
Natural Gas	MBtu/hr	14.53	0	14.53
Liq. Incineration	lb/hr	0	629	629
WW Treatment	lb COD/hr	0	624	624
WW Flow	Kgal/hr	0	2.044	2.044

Alternative process designs based on the assumption that byproduct ethanol is recovered instead of ethyl acetate should also be considered. This ethyl acetate coproduction effectively lowers potential acetaldehyde yield from acetic acid and may not be easily marketed. Such work was beyond the scope of this project, however. And, without the liquid-liquid phase behavior exhibited in the EtOAc-water system and utilized in the proposed design, the costs for acetic acid recovery may be higher.

Table D.13
HOAc Hydrogenation Reaction Section Balance

Stream	1	2	3	4	5	6	7	8	9	10
Temperature F	572.0	534.4	80.0	214.7	473.4	144.9	102.3	206.1	144.9	144.9
Pressure PSIA	265	250	275	245	270	245	275	245	245	245
Vapor Fraction	1.000	1.000	0.360	0.875	1.000	1.000	0.000	0.000	1.000	1.000
Mole Flow LBMOL/HR	10983.7	10940.0	2506.1	10940.0	10983.7	8563.3	8220.5	10596.6	85.6	8477.6
Mass Flow LB/HR	139080	139080	98059	139080	139080	41435	338024	435640	414	41021
Volume Flow CUFT/HR	458882	466813	20447	283695	407340	226772	5490	7833	2268	224505
Enthalpy MBTU/HR	-307.3	-307.3	-314.2	-357.4	-318.2	-56.3	-1323.9	-1624.9	-0.6	-55.8
Mole Flow LBMOL/HR										
HOAC	1650.00	907.50	1602.55	907.50	1650.00	34.81	4170.42	5042.79	0.35	34.46
H2	8250.00	7432.43	903.55	7432.43	8250.00	7420.66	0.00	11.77	74.21	7346.45
HAC	73.21	734.04	0.00	734.04	73.21	73.95	0.55	660.57	0.74	73.21
METHANE	790.94	823.94	0.00	823.94	790.94	798.93	0.00	25.01	7.99	790.94
ACETONE	5.71	15.61	0.00	15.61	5.71	5.77	49.05	58.89	0.06	5.71
ETHANOL	13.49	50.61	0.00	50.61	13.49	0.51	11.24	61.35	0.01	0.50
ETHENE	62.68	70.93	0.00	70.93	62.68	63.32	0.00	7.62	0.63	62.68
H2O	50.91	808.26	0.00	808.26	50.91	64.55	3813.50	4556.93	0.65	63.90
CO2	86.79	96.69	0.00	96.69	86.79	87.66	0.00	9.02	0.88	86.79
ETOAC	0.00	0.00	0.00	0.00	0.00	13.12	175.78	162.65	0.13	12.99
Mass Fraction										
HOAC	0.7120	0.3920	0.9810	0.3920	0.7120	0.0500	0.7410	0.6950	0.0500	0.0500
H2	0.1200	0.1080	0.0190	0.1080	0.1200	0.3610	0.0000	0.0001	0.3610	0.3610
HAC	0.0230	0.2330	0.0000	0.2330	0.0230	0.0790	0.0001	0.0670	0.0790	0.0790
METHANE	0.0910	0.0950	0.0000	0.0950	0.0910	0.3090	0.0000	0.0009	0.3090	0.3090
ACETONE	0.0020	0.0070	0.0000	0.0070	0.0020	0.0080	0.0080	0.0080	0.0080	0.0080
ETHANOL	0.0040	0.0170	0.0000	0.0170	0.0040	0.0006	0.0020	0.0060	0.0006	0.0006
ETHENE	0.0130	0.0140	0.0000	0.0140	0.0130	0.0430	0.0000	0.0005	0.0430	0.0430
H2O	0.0070	0.1050	0.0000	0.1050	0.0070	0.0280	0.2030	0.1880	0.0280	0.0280
CO2	0.0270	0.0310	0.0000	0.0310	0.0270	0.0930	0.0000	0.0009	0.0930	0.0930
ETOAC	0.0000	0.0000	0.0000	0.0000	0.0000	0.0280	0.0460	0.0330	0.0280	0.0280

Table D.13
HOAc Hydrogenation Reaction Section Balance

Stream	11	13	18	19	23	30	31	33	36
Temperature F	153.2	171.6	100.0	100.0	334.1	334.1	334.1	100.0	152.0
Pressure PSIA	275	275	100	100	95	95	95	40	275
Vapor Fraction	0.848	1.000	1.000	0.000	0.010	0.010	0.010	0.000	0.847
Mole Flow LBMOL/HR	10983.7	8477.6	49.6	701.3	9845.7	1625.2	8220.5	8220.5	10983.7
Mass Flow LB/HR	139080	41021	1125	29663	404851	66827	338024	338024	139080
Volume Flow CUFT/HR	224192	208834	2979	637	16439	2713	13725	5481	223650
Enthalpy MBTU/HR	-368.3	-54.1	-2.0	-58.4	-1540.0	-254.2	-1285.8	-1324.2	-368.3
Mole Flow LBMOL/HR									
HOAC	1637.01	34.46	0.00	0.00	4994.91	824.49	4170.42	4170.42	1650.00
H2	8250.00	7346.45	11.65	0.12	0.00	0.00	0.00	0.00	8250.00
HAC	73.21	73.21	13.11	646.81	0.66	0.11	0.55	0.55	73.21
METHANE	790.94	790.94	18.51	6.49	0.00	0.00	0.00	0.00	790.94
ACETONE	5.71	5.71	0.00	0.14	58.75	9.70	49.05	49.05	5.71
ETHANOL	0.50	0.50	0.00	0.00	13.47	2.22	11.24	11.24	13.49
ETHENE	62.68	62.68	2.82	4.80	0.00	0.00	0.00	0.00	62.68
H2O	63.90	63.90	0.24	37.14	4567.43	753.93	3813.50	3813.50	50.91
CO2	86.79	86.79	3.27	5.75	0.00	0.00	0.00	0.00	86.79
ETOAC	12.99	12.99	0.00	0.00	210.53	34.75	175.78	175.78	0.00
Mass Fraction									
HOAC	0.7070	0.0500	0.0000	0.0000	0.7410	0.7410	0.7410	0.7410	0.7120
H2	0.1200	0.3610	0.0210	0.0000	0.0000	0.0000	0.0000	0.0000	0.1200
HAC	0.0230	0.0790	0.5130	0.9610	0.0001	0.0001	0.0001	0.0001	0.0230
METHANE	0.0910	0.3090	0.2640	0.0040	0.0000	0.0000	0.0000	0.0000	0.0910
ACETONE	0.0020	0.0080	0.0000	0.0003	0.0080	0.0080	0.0080	0.0080	0.0020
ETHANOL	0.0002	0.0006	0.0000	0.0000	0.0020	0.0020	0.0020	0.0020	0.0040
ETHENE	0.0130	0.0430	0.0700	0.0050	0.0000	0.0000	0.0000	0.0000	0.0130
H2O	0.0080	0.0280	0.0040	0.0230	0.2030	0.2030	0.2030	0.2030	0.0070
CO2	0.0270	0.0930	0.1280	0.0090	0.0000	0.0000	0.0000	0.0000	0.0270
ETOAC	0.0080	0.0280	0.0000	0.0000	0.0460	0.0460	0.0460	0.0460	0.0000

Table D.14
HOAc Hydrogenation Recovery Section Balance

Stream	1	2	3	5	7	8	9	12
Temperature F	334.0	206.3	286.7	110.0	110.0	110.0	110.0	216.0
Pressure PSIA	95	30	30	30	30	30	30	30
Vapor Fraction	0.006	1.000	0.000	0.000	0.000	0.000	0.000	0.000
Mole Flow LBMOL/HR	1625.8	3286.4	844.0	2504.6	2642.5	778.8	138.0	37.2
Mass Flow LB/HR	66851	193168	49528	175846	185533	16027	9687	3186
Volume Flow CUFT/HR	2168.4	782949.4	875.2	3160.5	3334.6	269.3	174.1	62.5
Enthalpy MBTU/HR	-254.4	-488.7	-160.6	-448.5	-473.2	-96.9	-24.7	-7.4
Mole Flow LBMOL/HR								
HOAC	824.74	63.35	816.50	55.11	58.15	5.31	3.04	3.00
ACETONE	9.70	192.60	0.00	182.90	192.97	10.94	10.08	0.19
ETHANOL	2.22	24.07	0.00	21.85	23.05	3.52	1.20	0.03
H2O	754.30	1251.58	27.49	524.76	553.67	741.36	28.91	0.02
ETOAC	34.76	1752.79	0.00	1718.02	1812.66	17.60	94.64	33.97
HAC	0.11	2.03	0.00	1.92	2.03	0.11	0.11	0.00
Mass Fraction								
HOAC	0.7410	0.0200	0.9900	0.0190	0.0190	0.0200	0.0190	0.0570
ACETONE	0.0080	0.0580	0.0000	0.0600	0.0600	0.0400	0.0600	0.0040
ETHANOL	0.0020	0.0060	0.0000	0.0060	0.0060	0.0100	0.0060	0.0004
H2O	0.2030	0.1170	0.0100	0.0540	0.0540	0.8330	0.0540	0.0001
ETOAC	0.0460	0.7990	0.0000	0.8610	0.8610	0.0970	0.8610	0.9390
HAC	0.0001	0.0005	0.0000	0.0005	0.0005	0.0003	0.0005	0.0000

Table D.14
HOAc Hydrogenation Recovery Section Balance

Stream	13	15	16	17	20	21	24	25
Temperature F	191.4	166.8	337.6	210.3	194.0	170.8	213.3	262.5
Pressure PSIA	30	15	115	15	30	30	30	30
Vapor Fraction	0.000	1.000	1.000	0.000	0.000	0.000	0.000	0.000
Mole Flow LBMOL/HR	100.8	45.7	116.1	849.3	34.1	11.6	33.8	3.4
Mass Flow LB/HR	6501	2511	2091	15607	1883	629	2963	223
Volume Flow CUFT/HR	126.2	20459.9	8636.5	273.2	36.2	13.6	58.7	4.0
Enthalpy MBTU/HR	-16.8	-6.1	-11.8	-102.6	-5.4	-1.3	-6.7	-0.7
Mole Flow LBMOL/HR								
HOAC	0.04	0.07	0.00	5.24	0.07	0.00	0.28	2.72
ACETONE	9.88	10.27	0.00	0.67	1.44	8.83	0.19	0.00
ETHANOL	1.18	1.41	0.00	2.11	1.32	0.09	0.03	0.00
H2O	28.89	16.22	116.09	841.24	14.55	1.67	0.02	0.00
ETOAC	60.67	17.58	0.00	0.01	16.70	0.88	33.29	0.68
HAC	0.11	0.11	0.00	0.00	0.00	0.11	0.00	0.00
Mass Fraction								
HOAC	0.0003	0.0020	0.0000	0.0200	0.0020	0.0000	0.0060	0.7320
ACETONE	0.0880	0.2370	0.0000	0.0030	0.0450	0.8150	0.0040	0.0002
ETHANOL	0.0080	0.0260	0.0000	0.0060	0.0320	0.0060	0.0004	0.0000
H2O	0.0800	0.1160	1.0000	0.9710	0.1390	0.0480	0.0001	0.0000
ETOAC	0.8220	0.6170	0.0000	0.0001	0.7820	0.1230	0.9900	0.2680
HAC	0.0007	0.0020	0.0000	0.0000	0.0000	0.0080	0.0000	0.0000

Table D.15
Reaction Section Equipment List

<u>Heat Exchangers</u>	<u>Duty, MBtu/hr</u>	<u>Area, sqft</u>	<u>Shell Side</u>	<u>Tube Side</u>	<u>\$</u>
FE	53.20	10858	RX Eff	RX Feed	203,600
C	21.60	8134	D Ovhd	CW	151,500
RB	47.72	4036	600# Stm	D Btms	105,900
S	40.77	5714	CW	A Solvent	88,100
PH	11.55	1230	RX Feed	Hot Oil	46,100
F	11.55	Fired	Gas	Hot Oil	<u>448,700</u>
					1,043,900
<u>Towers</u>	<u># of Stages</u>	<u># of Trays</u>	<u>Diameter, ft</u>	<u>Height, ft</u>	<u>\$</u>
A	4	20	8.5	55	277,600
D	17	40	9.5	94	<u>359,500</u>
					637,100
<u>Vessels</u>		<u>Volume, cuft</u>	<u>Diameter, ft</u>	<u>Height, ft</u>	<u>\$</u>
RX		1695	10.8	24.7	208,900
RC KO Drum		100	4.2	9.6	17,600
TANK1		HOAc Feed Tank (2 days)			780,000
TANK2		HAc Product Sphere (2 days)			<u>1,820,000</u>
					2,826,500
<u>Other</u>		<u>Power, kw</u>	<u>delP, psi</u>	<u>Flow, cuft/hr</u>	<u>\$</u>
RC		486	30	2.40E+05	1,536,900
PU		164	235	5820	<u>40,700</u>
					1,577,600
Total Reaction Section					6,085,100

Table D.16
Recovery Section Equipment List

<u>Heat Exchangers</u>	<u>Duty, MBtu/hr</u>	<u>Area, sqft</u>	<u>Shell Side</u>	<u>Tube Side</u>	<u>\$</u>
AR	56.71	13,986	100# Stm	AC Btms	208,100
DC	62.63	15,062	AC Ovhd	CW	283,500
ZC	4.04	608	Z Ovhd	CW	30,000
ZR	4.53	470	100# Stm	Z Btms	15,800
WC	0.84	173	W Ovhd	CW	15,300
WR	0.84	74	100# Stm	W Btms	6,300
EC	0.94	112	E Ovhd	CW	15,000
ER	0.94	161	100# Stm	E Btms	<u>7,200</u>
					581,200

<u>Towers</u>	<u># of Stages</u>	<u># of Trays</u>	<u>Diameter, ft</u>	<u>Height, ft</u>	<u>\$</u>
AC	14	36	11	125.5	463,700
Z	5	12	5	31	88,900
SS	4	27	2.5	54.25	76,500
W	16	37	2	68.5	92,700
E	8	19	2.5	41.5	<u>60,100</u>
					781,900

<u>Vessels</u>	<u>Volume, cuft</u>	<u>Diameter, ft</u>	<u>Height, ft</u>	<u>\$</u>
DE	1910	9	27	43,600
TANK1	Recovery Feed Tank (2 days)			600,000
TANK2	EtOAc Product Tank (7 days)			<u>200,000</u>
				843,600

<u>Other</u>	<u>Power, kw</u>	<u>delP, psi</u>	<u>Flow, cuft/hr</u>	<u>\$</u>
HOAc Pump	33	245	932	<u>7,300</u>
				7,300

Total Recovery Section 2,214,000

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(88) *ibid.* pp.146-149.

4. Reductive Carbonylation (Tasks 3.2, 7)

Introduction

Within the plan of work, Eastman included an economic assessment of the reductive carbonylation of methanol or methyl acetate (Task 3.2) and optional studies on the process if it was warranted (Optional Task 7). At the outset of the project, it had already become clear that the reductive carbonylation of methyl acetate was unlikely to be useful as it required too many steps compared to other processes (See Table C.4) and was therefore abandoned early. However, the reductive carbonylation of methanol (depicted in reaction [1]) could not be so readily dismissed.

If the reductive carbonylation could be conducted in the same reactor so that we could co-produce acetic acid and acetaldehyde in roughly equal portions; it was believed that this process might be viable. However, the esterification of acetaldehyde with ketene would also have to be both technically and economically acceptable for this process to be viable.

There are a number of examples of the reductive carbonylation of methanol and its derivatives to form acetaldehyde.¹⁻⁶ However, for the reasons cited above, the focus of this investigation had to be on the conversion of methanol to acetaldehyde, without first generating an ester to facilitate the reaction. As described in Sumner and Zoeller,¹ most of these reactions demonstrate inadequate selectivity for commercialization, the key problem being the generation of ethanol. This is particularly true when cobalt-based catalyst systems are used.

However, our attention was drawn to a series of reports by Wegman et al.⁴⁻⁶ In these reports, the authors indicated that the reductive carbonylation of methanol is selective toward acetaldehyde and acetic acid (with selectivities of up to 80% for acetaldehyde) when complexes of 1,3-bis-diphenylphosphino propane with Rh⁶ are used. They further indicated that the only other products were methyl acetate and acetic acid. However, the case was somewhat prejudiced by the use of a 2:1 hydrogen: carbon monoxide ratio.

Rather than developing the catalyst further, Wegman et al. chose to explore the subsequent hydrogenation to ethanol with an added metal (ruthenium) in a single vessel, leaving the ultimate question of selectivity (and its control) toward acetic acid and acetaldehyde inconclusively defined. As part of our report, we examined this reaction and several modifications to see if the process could be used to deliver a product mix approaching the desired 1:1 ratio of acetic acid to acetaldehyde.

As an alternative, we also decided to examine the heterogeneous, vapor phase, reductive carbonylation of methanol to acetaldehyde. There is little in the literature describing this alternative operation³.

Before describing our work in this area, we need to point out that, given that the esterification with ketene was critical to a multiplicity of steps, it was provided a higher priority. When, over the course of the project, we discovered that the esterification with ketene was less cost effective than esterification with acetic anhydride, and acetic acid hydrogenation was found to be feasible, the examinations of the methanol reductive carbonylation were abandoned. Therefore, although we will discuss our efforts, the work in this area was limited.

Results and Discussion

Reductive Carbonylation with Rh/1,3-Bis-(Diphenylphosphino)-Propane

Complexes. The initial work of Wegman et al. used a catalyst generated by the addition of 1 mole equivalent of 1,3-bis-diphenylphosphino propane to dicarbonyl acetylacetonato Rh (I) in the methanol reactant. The catalyst thus formed was then charged with methyl iodide and reacted at 140°C under 1000 psi of 2:1 hydrogen:carbon monoxide. To ascertain the actual selectivity in these processes, we repeated the work exactly, *except* that we used 1:1 hydrogen to carbon monoxide as the feed gas. Under these conditions, the GC analysis indicated that the acetaldehyde (as acetaldehyde and its dimethyl acetal): acetic acid (as acetic acid and methyl acetate) was 1:1.7. (i.e., more selective for acetic acid derivatives than acetaldehyde). Further, the analysis only accounts for 67% of the material present.

We did not pursue the identity of the remaining material, and it is likely that the unaccounted material is present as either ethanol product (from further reduction) or condensation products, such as crotonaldehyde. (We should note that, if the remaining material is ethanol, we would begin to approach the 80% selectivity indicated by Wegman, but it would be for all reduced products, not just acetaldehyde.) Regardless, it was clear that, contrary to the implications in Wegman et al., there were other side-products besides methyl acetate and acetic acid.

Additional attempts were made to improve the catalysis using phase-separated reaction systems. The rationale was based on the observation that the complex is soluble in hydrocarbons, but not in water. Since methyl iodide is the actual active substrate and is also soluble in hydrocarbons, the hope was to react the methyl iodide to form acetic acid and acetaldehyde, which are water soluble and might be extracted into a water layer. If this procedure worked, it would severely reduce the over-hydrogenation of acetaldehyde to alcohol and condensation of acetaldehyde with itself. Unfortunately, conducting the reaction in the presence of water and either toluene or cyclohexane only served to increase the selectivity to acetate products (methyl acetate and acetic acid.)

Reductive Carbonylation of Methanol with Heterogeneous Catalysts. A large number of heterogeneous catalysts were generated containing Rh and Ir; also generated were a large number of bimetallic catalysts containing either Rh or Ir in combination with reducing metals such as Co, Ru, Pt, and Pd. Operation at 240°C with 250 to 350 psi of syngas mixtures never identified a catalyst that yielded more than traces of acetaldehyde.

Conclusion

Although the area of reductive carbonylation is intellectually interesting and could still yield an interesting methodology for the generation of acetaldehyde, our economics dictated we close this avenue of investigation toward the generation of vinyl acetate. If the intent is to generate acetaldehyde, or co-generate acetaldehyde and acetic acid rather than vinyl acetate, this might still be a fruitful and challenging area of research and may be worth revisiting. If investigations in this area are ever resumed, the issue of selectivity, which was inadequately described in the Wegman references, will need to be resolved.

Experimental

Reductive Carbonylation of Methanol to Acetaldehyde with Rh(CO)₂acac/1,3-Bis-(diphenylphosphino)-propane. A 300-mL Hastelloy autoclave was filled with 80 mL of methanol, which was then flushed thoroughly with nitrogen to deaerate the methanol. A physical mixture of 0.76 g (2.9 mmol) of Rh(CO)₂(acac) and 1.23 g (3.0 mmol) of 1,3-bis(diphenylphosphino)-propane was added to the methanol, and the mixture was stirred under nitrogen for ½ hr. The system was then flushed with 1:1 H₂:CO. To initiate the reaction, a solution of 40 mL of methanol and 7.5 mL of methyl iodide was added to the autoclave via a blowcase. The mixture was then heated to 140°C. Upon reaching temperature, it was pressurized to 975 psig using 1:1 CO:H₂. The temperature and pressure were maintained at 140°C and 975 psi, using 1:1 CO:H₂ as feed gas, for 2.5 hrs. The reactor was cooled to less than 18°C and then vented through a dry ice-cooled trap. The contents of the reactor were transferred carefully to insure that the contents were kept at less than 18°C, since the product contained acetaldehyde (bp 19°C), which is a potential carcinogen. After collection from the dry ice trap and autoclave, the product was combined and stored in a refrigerator prior to analysis by GC.

GC analysis of the product mixture gave the following results:

Acetaldehyde:	3.4%
Methyl Iodide:	8.8%
Methyl Acetate:	20.2%
Methanol:	20.3%
Acetic acid:	4.4%
1,1-Dimethoxyethane:	10.7%
(Acetaldehyde dimethyl acetal)	
(Notebook No. X25311-001)	

References

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- (4) Moloy, K. G. and Wegman, R. W. *Organometallics*,**1989**, 8, 2883.
- (5) Wegman, R. W. and Miller, D. S. **1986**, *U. S. Patent* 4,594,463.
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E. Generation of Vinyl Acetate from Acetaldehyde (Task 2)

1. Overview

Two routes to vinyl acetate from acetaldehyde were investigated in this project: the esterification of acetaldehyde with ketene and the esterification with acetic anhydride. The liquid phase esterification of acetaldehyde with ketene is an exothermic reaction (by about 7.1 kcal/mol at 149°C). The reaction had not been satisfactorily demonstrated prior to the beginning of this project, and in general, ketene and aldehydes normally react to form lactones. The liquid phase conversion of acetaldehyde and acetic anhydride to vinyl acetate and acetic acid is mildly endothermic (by about 1.8 kcal/mol at 149°C) and must be driven by the use of an excess of one of the reactants (normally acetic anhydride). Acetaldehyde and acetic anhydride react in the presence of an acid catalyst to form ethylidene diacetate (EDA), which can crack to form starting materials or vinyl acetate monomer (VAM) and acetic acid. The reactive distillation process described herein forces the unfavorable equilibrium by feeding acetaldehyde to the base of a distillation column, while feeding acetic anhydride and acid catalyst counter-currently from near the middle of the distillation column. As acetaldehyde passes up the column, it encounters increasing amounts of acetic anhydride as the EDA intermediate moves down the column, and this forces the equilibrium toward the desired VAM and acetic acid. The reactive distillation process was developed before the contract, but its economic analysis was performed under the contract. During the course of investigation of the esterification of acetaldehyde with ketene, it was discovered by accident that the presence of acetic acid accelerated the EDA formation reaction. The role of EDA will be considered in the description of both VAM processes.

2. Esterification with Ketene (Task 2.1)

Introduction

The production of VAM from acetaldehyde normally proceeds through the formation of the EDA intermediate. The formation of EDA is not required thermodynamically to produce VAM from ketene and acetaldehyde, and an example will be provided that shows in some circumstances EDA may not be an intermediate. However, in most cases, EDA is probably a reaction intermediate.

One of the most efficient ways to make EDA is the reaction of acetaldehyde with acetic anhydride in the presence of a Bronsted acid catalyst, and heating to about 80°C is required for the reaction to proceed at a reasonable rate. Unfortunately the reaction is reversible, and heating the EDA-containing product mixture at elevated temperatures with the catalyst still present can lead to the production of acetaldehyde and acetic anhydride. This is illustrated by equation 1:

However another equilibrium exists when EDA is heated with the catalyst still present, producing vinyl acetate and acetic acid as shown in equation 2:

Both of the equilibria described by equations 1 and 2 favor the formation of EDA. However, since acetaldehyde, acetic anhydride, acetic acid and vinyl acetate are all more volatile than EDA, heating EDA with the acid catalyst present will result in the decomposition of the EDA with the volatilization of acetaldehyde, acetic anhydride, acetic acid and vinyl acetate. If the EDA and catalyst are heated to sufficiently high temperatures (about 140°) that these cracking reactions occur readily and excess acetic anhydride is present, then the equilibria are shifted to produce vinyl acetate and acetic acid by the law of mass action. Although commercial vinyl acetate processes have been based on utilizing the chemistry of combined equations 1 and 2, the process is complicated by the loss of the most volatile component, acetaldehyde, and provisions must be made for its capture and return to the reactor. When EDA and acid catalyst are heated under conditions in which the pressure is sufficiently high to prevent volatilization of the volatile components, the equilibrium levels of acetaldehyde and vinyl acetate present undergo other reactions such as aldol condensation and oligomerization to produce tar-like materials. These secondary reactions that occur under pressurized conditions can account for some of the tar-like materials created in producing EDA from the hydrocarbonylation of methyl acetate or dimethyl ether. Similar difficulties can be encountered when acetic anhydride is hydrogenated under high-pressure acidic conditions.

When ketene is introduced, acetic acid produced from reaction 2 reacts to form acetic anhydride, as shown below:

The reaction of ketene with acetic acid to produce acetic anhydride is essentially irreversible at the temperatures used in the VAM synthesis. The reaction with ketene allows the unfavorable equilibria of equations 1 and 2 to be overcome because one of the products of equation 2 (acetic acid) is continuously being converted into one of the reactants of equation 1 (acetic anhydride). The sum of equations 1-3 becomes the irreversible reaction described by equation 4:

The process depicted by equation 4 has not been described in the literature as a practical reaction. Most of the prior art that uses acetaldehyde as a starting material also uses acetic anhydride as a starting material to make EDA, which is then cracked to acetic acid and vinyl acetate in a second step. The patent literature teaches that the preferred catalysts for the cracking of EDA to acetic acid and vinyl acetate are aromatic hydrocarbon sulfonic acids and that the cracking reaction should be performed in the

presence of at least a three-fold molar excess of acetic anhydride over EDA present to drive the equilibrium to acetic acid and vinyl acetate.¹ The acetic anhydride must continuously be added to the mixture to replace that which is depleted. The commercial process described for the continuous production of vinyl acetate from acetaldehyde and acetic anhydride teaches that acetaldehyde and acetic anhydride are reacted together in one reactor to produce EDA, and that the EDA is then cracked in a separate reactor tower to produce vinyl acetate and acetic acid, which are removed overhead along with acetaldehyde.² A series of distillations is performed to separate and recover vinyl acetate, acetic acid and acetaldehyde. The acetaldehyde is then recycled to the EDA reactor. When ketene is used as a reactant, the continuous introduction of acetic anhydride is not required, and acetic acid is not produced when the reaction is performed under the preferred conditions.

Ketenes and aldehydes react in the presence of Lewis acids to produce beta-lactones.³ Thus ketene and acetaldehyde react at 5-15°C in the presence of the Lewis acid boron trifluoride to produce beta-butyrolactone, and the activity of this catalyst has been compared with that of other Lewis acids such as zinc chloride and iron tetrafluoroborate.⁴ Silica-alumina catalysts (which possess both Lewis and Bronsted acidity) are also active catalysts for the conversion of ketene and acetaldehyde into beta-butyrolactone at 10-15°C.⁵

It is well known that ketenes can react with enolizable ketones in the presence of Bronsted acids to produce enolic esters at 50-100°C.⁶ A Japanese patent application teaches that the efficiency of the reaction of ketene with enolizable carbonyl compounds is related to the ease of enolization of the carbonyl compound.⁷ Thus, in the presence of Bronsted acid catalysts, ethyl acetoacetate reacts with ketene more readily than does acetone to produce the corresponding enol esters. The rate of acid-catalyzed enolization is proportional to the concentration of protonated carbonyl present.⁸ It is also known that it is approximately 1000 times more difficult to protonate an aliphatic aldehyde than it is to protonate an aliphatic ketone.⁹ Thus much of the prior art teaches that it should be very difficult to prepare enol esters from aliphatic aldehydes. The reaction of ketenes with aldehydes to produce unsaturated carboxylic esters in the presence of a strong Bronsted acid catalyst in a preferred temperature range of zero to 80°C has been described by Hull in the patent literature.¹⁰ In this reference it is emphasized that strong acid catalysts, such as sulfuric acid, are preferable to weaker acids such as p-toluenesulfonic acid. Furthermore, even when sulfuric acid is used as the catalyst, the efficiency of the process is low, and, when about 5.4 moles of acetaldehyde are reacted with 2 moles of ketene (bubbled through the acetaldehyde-sulfuric acid mixture at 15°C), only about 21% of the ketene is converted to vinyl acetate after the mixture is distilled. (Note that the numbers provided in Example 1 of this patent are consistent with the ketene conversion vinyl acetate being about 21% rather than the acetaldehyde conversion being 21%. The conversion of acetaldehyde to vinyl acetate calculates to about 8%, based on the Example 1 numbers). The process described in the Hull patent also produces methyl propenyl ketone in addition to acetaldehyde. The process described herein does not produce methyl propenyl ketone and is an improvement over the Hull

patent because higher yields based on both ketene and acetaldehyde are obtained by using higher temperatures and weaker catalysts under continuous conditions.

A process to convert EDA into vinyl acetate in the presence of a ketene stream and an acid catalyst (preferably sulfuric acid) has been described by Denis and co-workers.¹¹ The ketene reacts with acetic acid produced from the EDA cracking, thus creating acetic anhydride, and, as the acetic anhydride level builds up, a modest increase in the amount of vinyl acetate produced is observed compared to that produced in the absence of ketene. However, in the Denis process, much of the ketene is wasted and the vinyl acetate production decreases as the EDA is depleted. The EDA used in the Denis process is produced in a separate step before the cracking reaction is performed. The process described herein is much more efficient than that of Denis because a separate EDA production step is not required since both ketene and acetaldehyde are fed to the reactor, and ketene utilization is much higher.

During the course of investigation of the esterification of acetaldehyde with ketene, it was discovered by accident that the presence of acetic acid accelerated the EDA formation reaction. Only one relevant reference was found relating to this reaction. Waller describes the reaction of acetaldehyde with acetic anhydride in the presence of acetic acid and an iodide source to produce a product mixture containing EDA.¹² The rate of the reaction is enhanced by the use of the acetic acid solvent. Suitable iodide sources are lithium iodide, potassium iodide and methyl iodide. Surprisingly, iodide in the form of the Bronsted acid HI is not a suitable catalyst for the reaction. In view of the work of Waller regarding the unsuitability of the Bronsted acid HI, it is surprising that Bronsted acids of the sulfonic acid type work so well in the presence of acetic acid in the process investigated herein.

Experimental Methods

Part A. General Experimental Methods for the Small-Scale Reaction of Ketene and Acetaldehyde. An overview of the apparatus used in the experiments follows. The apparatus consisted of 7 major sections:

1. a gas delivery system,
2. a ketene generation section,
3. a ketene purification section,
4. a ketene trap/vaporizer section,
5. an acetaldehyde purification and delivery section,
6. a reactor-condenser train section,
7. a scrubber system.

These seven major sections were linked by a series of connecting lines and stopcocks. The gas delivery system provided four separate metered nitrogen flows to various points in the apparatus. The ketene generation section consisted of an acetic anhydride vaporizer/pyrolysis tube, chilled condenser and cyclone assembly. The ketene generation section produced raw ketene by acetic anhydride pyrolysis and accomplished the rapid separation of the ketene from the bulk of the coproduct acetic acid and unreacted acetic

anhydride. The ketene purification section consisted of a demisting trap held at 0°C (trap A) and a trap initially held at -78°C (trap B) for the initial condensation and subsequent distillation of purified ketene to the ketene trap/vaporizer section. The ketene trap/vaporizer section served as a reservoir for purified ketene and also provided for metered delivery of ketene to the reactor. The ketene trap/vaporizer was held at -78°C for the collection of the distilled ketene from trap B and its subsequent delivery to the reactor by transpiration in metered nitrogen. The acetaldehyde purification and delivery section consisted of a graduated cylinder from which acetaldehyde could be distilled and a trap/vaporizer held at -20°C for the collection of the distilled acetaldehyde and subsequent delivery to the reactor by transpiration in metered nitrogen. The reactor-condenser train section consisted of a reactor in which the ketene and acetaldehyde reacted, a water-cooled condenser to return condensable liquid to the reactor and an acetone/solid carbon dioxide condenser and trap (trap C) to collect the bulk of the vinyl acetate, vaporized acetic acid and unreacted acetaldehyde. The scrubber system contained a water scrubber for the destruction of ketene and an analytical scrubber containing acetic acid for the quantification of ketene and for the capture and quantification of any vinyl acetate or acetaldehyde not trapped by trap C of the reactor-condenser train section.

The apparatus was designed to allow the reactants to bypass the reactor as an option. The apparatus also had provision for a continuous flow of nitrogen to prevent back diffusion of scrubber fluids or contamination by air. Details of the construction of each section of the apparatus, how they are connected and the operation of the apparatus are described below.

In the gas delivery section, metered nitrogen gas flows were provided by four Tylan Model FC-260 mass flow controllers. Metered nitrogen gases were fed through four gas lines L1 through L4, and each gas line was teed to a pressure relief column containing water to prevent accidental over pressurization. Two of these gas lines, L1 and L3, provided nitrogen purge to the apparatus. L1 provided nitrogen purge to the acetic anhydride pyrolysis unit, and L3 provided nitrogen purge to the rest of the apparatus at a point teed into the ketene trap/vaporizer outlet line described below. Gas lines L2 and L4 were used to meter ketene and acetaldehyde, respectively, from the ketene trap/vaporizer section and the acetaldehyde trap/vaporizer, respectively, by transpiration.

In the ketene generation section, ketene was generated by the method described by Fisher et al. by the pyrolysis of acetic anhydride with minor modifications. (Although acetic acid pyrolysis is the preferred industrial route to ketene, it is generally not practical on a laboratory scale).¹³ Acetic anhydride feed was provided by a Harvard Apparatus Model 22 syringe infusion pump. The acetic anhydride was fed to the top of a 107-cm-long by 25-mm-O.D. vertical quartz vaporizer/pyrolysis tube, along with nitrogen metered through line L1. Electric temperature control for the vaporizer/pyrolysis tube and monitoring were provided by a Dow Camile® control system interfaced with a Gateway Model 2000 486DX/33 computer. The vaporizer/pyrolysis tube was indented at a distance of 27 cm from the top and contained a 9-mm-O.D. quartz thermocouple well

extending about two thirds the length of the reactor from the top towards the bottom. The portion of the vaporizer/pyrolysis tube extending 22 cm up from the indentations also contained quartz chips and was heated with heating tape controlled at 200°C. The lower section of the vaporizer/pyrolysis tube was heated by two heating tapes controlled at 520°C. The quenching condenser below the vaporizer/pyrolysis tube was held at about -55°C by circulating methanol cooled in an acetone/solid carbon dioxide bath. The mixture from the quenching condenser passed sequentially through two identical cyclones measuring 16 mm O.D. at the top and 80 mm from the top of the cyclone body to the bottom of the tapered section. The inlet and outlet lines of the cyclone were 2 mm I.D., and the liquid from the bottom of the cyclone assembly was drained into a 1-liter bottle. The gas displacement tube (10 mm O.D.) connecting the drain flask to the cyclone assembly was bent to provide a liquid seal. The misted vapor from the ketene generator cyclone assembly was then passed to the ketene purification section.

In the ketene purification section, the ketene-containing vapor passed through a demisting trap held at 0°C (trap A) to remove a portion of the entrained acetic anhydride-acetic acid. The ketene-containing stream exiting trap A then was sent to a trap held at -78°C (trap B), where the ketene was condensed. The outlet line of trap B led to a three-way stopcock (SC1). In one position, SC1 vented excess ketene-containing vapors from trap B to a line teed into the water scrubber. In another position, SC1 sent the ketene-containing vapors to the ketene inlet line of a ketene trap/vaporizer assembly.

The ketene trap/vaporizer assembly was a modified, two-piece, 32-X-200-mm vacuum trap having the bottom portion of the trap narrowed to 19 mm O.D. and extending an additional 100 mm. A 7-mm-O.D. / 2-mm-I.D. gas inlet tube extended along the outer body of the ketene trap/vaporizer assembly and was connected to the base of the extended tube section. The gas inlet tube was connected to the metered nitrogen line L2 containing a stopcock (SC2). The purpose of SC2 was to prevent diffusion of ketene into line L2 when no nitrogen was flowing through it during the ketene generation process and when the ketene trap/vaporizer was being loaded. The ketene inlet line was the normal inside 10-mm-O.D. tube found in the standard vacuum trap design. The ketene trap/vaporizer outlet line was the normal 10-mm-O.D. side tube found in the standard vacuum trap design. The ketene trap/vaporizer outlet line was teed into the nitrogen purge line L3. After the teeing to purge line L3, the ketene trap vaporizer line connected to a three-way stopcock SC3. Further connections to SC3 are described later below.

The acetaldehyde purification and delivery section contained an acetaldehyde trap/vaporizer of identical construction to the ketene trap/vaporizer, except that it was surrounded by a jacket for liquid coolant that was in turn enclosed by a vacuum jacket. Line L4 provided metered nitrogen to the acetaldehyde trap/vaporizer gas inlet tube. The acetaldehyde trap/vaporizer inlet line allowed for the introduction of acetaldehyde distilled from a graduated cylinder. The acetaldehyde trap/vaporizer outlet line was connected to three-way stopcock SC4. Further connections to SC4 are described later below.

The reactor-condenser train contained a reactor, a reflux condenser and an acetone/solid carbon dioxide condenser. Details of the reactor design are provided in the individual experiments. Reactants entered the reactor via line L6. The top of each reactor was fitted to the water-cooled reflux condenser to provide for the return of condensable liquids to the reactor. The top of the reflux condenser was attached to an acetone/solid carbon dioxide condenser. Material condensing in the acetone/solid carbon dioxide condenser was not returned to the reactor, but collected in a trap flask (trap C) fitted to the base of the condenser. Trap C contained *tert*-butylhydroquinone (TBHQ, about 40 mg) polymerization inhibitor, and trap C was also kept chilled with solid carbon dioxide. The majority of the vinyl acetate was found in trap C, along with most of the unreacted acetaldehyde. Any acetic acid vaporizing from the reactor was found in trap C. The outlet of the acetone/solid carbon dioxide condenser was attached to the reactor-condenser train outlet line L7.

The scrubber system contained a water scrubber for the destruction of ketene and an analytical scrubber containing acetic acid for the quantification of ketene (as acetic anhydride) and for the capture and quantification of any vinyl acetate or acetaldehyde not trapped by trap C of the reactor-condenser train section. The acetic acid (about 60 mL) in the analytical scrubber also contained TBHQ (about 40 mg) polymerization inhibitor. The analytical scrubber fluid was circulated by a Masterflex peristaltic pump. A stopcock at the base of the analytical scrubber provided for removal of the scrubber fluid for analysis, and a Claisen adapter at the top of the analytical scrubber allowed for the addition of fresh scrubber fluid. An acetone/solid carbon dioxide condenser was attached to the top of the vertical arm of the Claisen adapter to prevent loss of scrubber fluids. Access to the scrubber system was provided by three-way stopcock SC5. In one position, SC5 sent vapor streams to the water scrubber, and, in another position, SC5 sent vapor streams to the analytical scrubber.

The seven major sections were connected by a series of connecting lines, tees and stopcocks. The three-way stopcock SC3 connected the ketene trap/vaporizer outlet line at the point past the L3 purge tee to the three-way stopcock SC4 via line L5 or to the reactor bypass line. Three-way stopcock SC4 connected line L5 to the acetaldehyde trap/vaporizer outlet line and to the reactor-condenser train inlet line L6. The bypass line attached to SC3 was teed to the reactor-condenser train outlet line L7, and the other arm of the tee was connected to SC5. SC5 directed the gas stream from the reactor-condenser train outlet line L7 or from the bypass line to the water scrubber or to the analytical scrubber as stated above. A description of the operation of the apparatus follows.

Acetic anhydride (600 mL/minute) and nitrogen (25 standard cubic centimeters per minute, SCCM) through L1 were fed to the ketene generation section for 20 minutes, and the product was condensed in trap B held at -78°C by an acetone/solid carbon dioxide bath in the ketene purification section. During the ketene generation/condensation process, vented gases leaving trap B were allowed to pass through SC1 to the ketene trap/vaporizer and then to the water scrubber via stopcock SC3, the bypass line and SC5. Stopcock SC2 was closed during the ketene generation process, and the ketene

trap/vaporizer was kept at -78°C . During the ketene generation process, ketene purification process and at all other times that reactants were not flowing to the reactor, a nitrogen purge (25 SCCM) was flowing through line L3. The -78°C bath was then removed from trap B, and the liquid ketene was then allowed to evaporate and condense in the ketene trap/vaporizer. The evaporation process, which took about an hour, provided about 30 mL pure liquid ketene condensate in the ketene trap/vaporizer. Stopcock SC1 was then turned to disengage the ketene trap/vaporizer from the ketene generation and purification sections and allowed any vapors leaving the ketene generation and purification sections to access the water scrubber.

The acetaldehyde trap/vaporizer was loaded by charging reagent-grade acetaldehyde to a graduated cylinder and then distilling the acetaldehyde with a warm-water bath into the acetaldehyde trap/vaporizer held at -20°C . During the acetaldehyde loading procedure, no gas was flowing through L4, and the acetaldehyde trap/vaporizer outlet line was accessed to the water scrubber through SC4, SC3 and SC5, with nitrogen (25 SCCM) flowing through L3.

The reactant metering was begun by opening SC2 and feeding nitrogen (88 SCCM) to the ketene trap/vaporizer gas inlet tube through line L2, while maintaining the ketene trap/vaporizer at -78°C . These conditions provided 0.7 mmol ketene/minute. Nitrogen (118 SCCM) was fed to the acetaldehyde trap/vaporizer gas inlet tube through line L4, while the acetaldehyde trap/vaporizer was maintained at -20°C . These conditions provided 1.0 mmol acetaldehyde/minute. Stopcocks SC3 and SC4 were positioned with all three ports of each stopcock opened, and SC5 was positioned to provide venting to the water scrubber. With the stopcocks positioned in this manner, the reactants and diluent gases flowed through the bypass line, and no flow to the reactor occurred because the pressure drop across the reactor was greater than the pressure drop across the bypass line. The purge nitrogen to line L3 was then shut off, and access to the bypass line was blocked by turning SC3 to send the nitrogen/ketene stream to SC4 via line L5, where it mixed with the nitrogen/acetaldehyde stream and proceeded to the reactor-condenser train via line L6. At this time stopcock SC5 was positioned to send the vapors exiting the reactor-condenser train to the acetic acid analytical scrubber. The reactor heater was also turned on at this time. Reactions were normally conducted for several hours each day, and the time required to heat the reactor (about 20 minutes) was normally small compared to the total time that the reactor was heated. The reaction was terminated by opening SC3 to access all streams to the bypass line, switching SC5 to the water scrubber, terminating nitrogen flow to L2 and L4, closing SC2, resuming purge nitrogen to L3, and discontinuing the heat to the reactor. The condensed liquid in trap C of the reactor-condenser train was removed, weighed and analyzed. The acetic acid analytical scrubber was allowed to warm up overnight, and the scrubber solution was then drained, weighed and analyzed. Normally reactions were performed for several days in this manner before changing the catalyst charge. When the catalyst solution (the reactor heel) was removed from the liquid phase reactor, it was weighed and analyzed. When the catalyst was removed from the reactor containing an insoluble solid catalyst, the liquid remaining at the base of the reactor (the reactor heel) was weighed and analyzed.

Products obtained from trap C of the reactor-condenser train, acetic acid scrubber solution and reactor heel were analyzed by gas chromatography using Hewlett Packard Model 5890 gas chromatographs with flame ionization detectors. Vinyl acetate, acetaldehyde and acetic acid were analyzed using a 25-m x 0.53-mm FFAP capillary column (1.0 micron film thickness) programmed at 40°C for 5 minutes, 15°C/minute to 235°C and held at 235°C for 1.67 minutes. Acetic anhydride and ethylidene diacetate were analyzed using a 30-m x 0.53-mm DB-5 capillary column (1.5 micron film thickness) programmed at 40°C for 8 minutes, 7°C/minute to 200°C, with a 0 minute holding time at 200°C. Mixtures were prepared for gas chromatographic analysis by adding 5 mL of a tetrahydrofuran solution containing 2 % decane internal standard to an accurately weighed 1-g sample of the reaction product.

The percent yield vinyl acetate is defined as 100 times the moles of vinyl acetate produced divided by the moles of ketene fed.

Experiment 1.¹⁴ This experiment illustrates the reaction of ketene and acetaldehyde performed with the reactor zone containing acetic anhydride solvent and p-toluenesulfonic acid catalyst at 150°C. The experiment also illustrates conditions that provide high yields of vinyl acetate without the production of acetic acid after a steady state has been reached (experiments 1.2 through 1.4). The reactor was a 36-mm-O.D. X 175-mm-long tube sealed on one end. The reactor was mounted vertically with the open end facing upward. The reactor was loaded with acetic anhydride (65.8 g, 0.645 mol), p-toluenesulfonic acid monohydrate (5.8 g, 0.0306 mol) and TBHQ (140 mg, 0.84 mmol) polymerization inhibitor. The reactor tube was placed in a temperature-controlled electric heater. A three-way claisen adapter was attached to the open end of the reactor. A 10-mm O.D. gas delivery tube with the bottom end drawn down to 1 mm I.D. was inserted through the straight vertical arm of the claisen adapter and extended to within about 1 mm of the base of the reactor. A threaded connector bushing at the top of the vertical arm of the claisen adapter held the gas delivery tube in place and provided a seal. The reactor inlet line L6 was connected to the gas delivery tube. The curved side arm of the claisen adapter was attached to the base of the reflux condenser portion of the condenser train assembly. To begin the reaction of experiment number 1.1, stopcock SC3 was positioned to block access to the bypass line, thus sending ketene (0.7 mmol/minute), acetaldehyde (1.0 mmol/minute) and nitrogen (206 SCCM) to the reactor through the gas delivery tube, with the gas exiting the reactor contacting the water-chilled reflux condenser, solid carbon dioxide/acetone cooled condenser and trap flask (trap C) containing TBHQ (40 mg, 0.24 mmol), and SC5 was positioned to send the product exiting the solid carbon dioxide/acetone condenser to the acetic acid (also containing about 40 mg TBHQ) scrubber, and the heater for the reactor was set for 150°C. The 150°C reactor temperature was reached after 20 minutes. The reaction was allowed to continue in this manner for a total of 314 minutes. To terminate the reaction, SC3 was positioned to divert the reactant gases through the reactor bypass line, the heating of the reactor was discontinued, and SC5 was positioned to send all gases to the water scrubber. The gas feeds were shut off, and the reactor system was accessed to nitrogen (25 SCCM) flowing through line L3

during the cooling period, and at all other times it was idle. The liquid contained in trap C was weighed and analyzed by gas chromatography. The acetic acid scrubber was allowed to warm to room temperature and drain overnight. The product recovered from the acetic acid scrubber was weighed and analyzed by gas chromatography. The reactor heel solution was retained in the reactor. Experiment numbers 1.2, 1.3 and 1.4 were performed by conducting the reaction in the manner of experiment number 1.1 for time periods of 301, 300 and 300 minutes, respectively, using the same reactor heel solution. Yields of vinyl acetate isolated from the condenser train trap C and the acetic acid scrubber solutions and the wt % acetic acid contained in trap C (trap C wt % HOAc) follow:

<u>Experiment number</u>	<u>% Yield vinyl acetate</u>	<u>Trap C wt % HOAc</u>
1.1	42	1.13
1.2	78	0
1.3	78	0
1.4	81	0

The reactor heel solution remaining from experiment 1.4 was weighed and analyzed by gas chromatography. The recovered heel solution (86.73 g) contained acetaldehyde (0.31 wt %), vinyl acetate (1.7 wt %), acetic acid (1.14 wt %), acetic anhydride (57.32 wt %) and EDA (28.99 wt %).

Experiment 2.¹⁵ This experiment illustrates the effect of operating the process of experiment 1 at a lower temperature. The experiment also illustrates conditions that provide high yields of vinyl acetate without the production of acetic acid after a steady-state has been reached (experiments 2.2 through 2.5). The same reactor system used in experiment 1 was used in experiment 2. The reactor tube was loaded with acetic anhydride (65.8 g, 0.645 mol), p-toluenesulfonic acid monohydrate (5.8 g, 0.0306 mol) and TBHQ (140 mg, 0.84 mmol) polymerization inhibitor as per experiment 1. The reactor was operated in the same manner as per experiment 1, except that the temperature was set for 140°C. Experiment numbers 2.1, 2.2, 2.3, 2.4 and 2.5 were each conducted for 300 minutes using the same heel solution. Yields of vinyl acetate isolated from trap C and the acetic acid scrubber solutions and the wt % acetic acid contained in trap C (trap C wt % HOAc) follow:

<u>Experiment number</u>	<u>% Yield vinyl acetate</u>	<u>Trap C wt % HOAc</u>
2.1	37	2.81
2.2	75	0
2.3	74	0
2.4	75	0
2.5	80	0

The reactor heel solution recovered from experiment 2.5 was analyzed by gas chromatography. The recovered heel solution (88.18 g) contained acetaldehyde (0.41 wt

%), vinyl acetate (1.59 wt %), acetic acid (1.03 wt %), acetic anhydride (47.65 wt %) and EDA (39.42 wt %).

Experiment 3.¹⁶ This experiment illustrates the effect of operating the process of experiment 1 at a higher temperature. The example also illustrates conditions that provide high yields of vinyl acetate without the production of acetic acid after a steady state has been reached (experiments 3.2 through 3.5). The same reactor system used in experiment 1 was used in experiment 3. The reactor tube was loaded with acetic anhydride (65.8 g, 0.645 mol), p-toluenesulfonic acid monohydrate (5.8 g, 0.0306 mol) and TBHQ (140 mg, 0.84 mmol) polymerization inhibitor, as per experiment 1. The reactor was operated in the same manner as per experiment 1, except that the temperature was set for 160°C. Experiment numbers 3.1, 3.2, 3.3, 3.4 and 3.5 were each conducted for 300 minutes using the same heel solution. Yields of vinyl acetate isolated from trap C and the acetic acid scrubber solutions and the wt % acetic acid contained in trap C (trap C wt % HOAc) follow:

<u>Experiment number</u>	<u>% Yield vinyl acetate</u>	<u>Trap C wt % HOAc</u>
3.1	45	2.94
3.2	76	0
3.3	82	0
3.4	82	0
3.5	82	0

The reactor heel solution recovered from experiment 3.5 was analyzed by gas chromatography. The recovered heel solution (86.31 g) contained acetaldehyde (0.33 wt %), vinyl acetate (1.41 wt %), acetic acid (1.23 wt %), acetic anhydride (56.12 wt %) and EDA (28.82 wt %).

Experiment 4.¹⁷ Experiment 4 illustrates the process of experiment 1 performed with the reactor zone containing N-methyl-2-pyrrolidinone solvent and p-toluenesulfonic acid catalyst at 150°C. The experiment also illustrates conditions that provide high yields of vinyl acetate without the production of acetic acid after a steady state has been reached (experiments 4.2 through 4.5). The same reactor system used in experiment 1 was used in experiment 4. The reactor tube was loaded with N-methyl-2-pyrrolidinone (63.2 g, 0.638 mol), p-toluenesulfonic acid monohydrate (5.8 g, 0.0306 mol) and TBHQ (140 mg, 0.84 mmol) polymerization inhibitor. The reactor was operated in the same manner as per experiment 1 at 150°C. Experiment numbers 4.1, 4.2, 4.3, 4.4 and 4.5 were conducted for 300, 330, 300, 305 and 300 minutes, respectively, using the same heel solution. Yields of vinyl acetate isolated from trap C and the acetic acid scrubber solutions and the wt % acetic acid contained in trap C (trap C wt % HOAc) follow:

<u>Experiment number</u>	<u>% Yield vinyl acetate</u>	<u>Trap C wt % HOAc</u>
4.1	59	0.8
4.2	76	0
4.3	77	0

4.4	71	0
4.5	68	0

The reactor heel solution recovered from experiment 4.5 was analyzed by gas chromatography. The recovered heel solution (80.81 g) contained vinyl acetate (1.04 wt %), acetic acid (1.01 wt %), acetic anhydride (4.73 wt %) and a small amount of EDA (1.13 wt %).

Experiment 5.¹⁸ This experiment illustrates the process of experiment 1, with the reactor zone containing mixed acetic anhydride-acetic acid solvent and p-toluenesulfonic acid catalyst at 150°C. The experiment also illustrates conditions that provide high yields of vinyl acetate without the production of acetic acid after a steady state has been reached (experiments 5.2 through 5.4). The same reactor system used in experiment 1 was used in experiment 5. The reactor tube was loaded with acetic anhydride (59.5 g, 0.583 mol), acetic acid (3.7 g, 0.0616 mol), p-toluenesulfonic acid monohydrate (5.8 g, 0.0306 mol) and TBHQ (140 mg, 0.84 mmol) polymerization inhibitor. The reactor was operated in the same manner as per experiment 1 at 150°C. Experiment numbers 5.1, 5.2, 5.3 and 5.4 were conducted for 340, 300, 300 and 300 minutes, respectively, using the same heel solution. Yields of vinyl acetate isolated from trap C and the acetic acid scrubber solutions and the wt % acetic acid contained in trap C (trap C wt % HOAc) follow:

<u>Experiment number</u>	<u>% Yield vinyl acetate</u>	<u>Trap wt % HOAc</u>
5.1	41	16.2
5.2	86	0
5.3	95	0
5.4	87	0

The reactor heel solution recovered from experiment 5.4 was analyzed by gas chromatography. The recovered heel solution (80.68 g) contained acetaldehyde (0.36 wt %), vinyl acetate (0.71 wt %), acetic anhydride (62.53 wt %) and EDA (35.7 wt %).

Experiment 6.¹⁹ This experiment illustrates the reaction of ketene and acetaldehyde performed with the reactor zone containing mixed acetic anhydride-acetic acid solvent and at 150°C as per experiment 5, but with benzenesulfonic acid catalyst instead. The experiment also shows that the stronger acid catalyst continues to produce acetic acid after the vinyl acetate yield has maximized (experiments 6.2 through 6.4). The same reactor system used in experiment 1 was used in experiment 6. The reactor tube was loaded with acetic anhydride (59.5 g, 0.583 mol), acetic acid (3.7 g, 0.0616 mol), benzenesulfonic acid monohydrate (5.4 g, 0.0306 mol) and TBHQ (140 mg, 0.84 mmol) polymerization inhibitor. The reactor was operated in the same manner as per experiment 1 at 150°C. Experiment numbers 6.1, 6.2, 6.3 and 6.4 were conducted for 305, 300, 300 and 300 minutes, respectively, using the same heel solution. Yields of vinyl acetate isolated from trap C and the acetic acid scrubber solutions and the wt % acetic acid contained in trap C (trap C wt % HOAc) follow:

<u>Experiment number</u>	<u>% Yield vinyl acetate</u>	<u>Trap C wt % HOAc</u>
6.1	50	10.25
6.2	90	2.56
6.3	92	2.52
6.4	78	3.54

The reactor heel solution recovered from experiment 6.4 was analyzed by gas chromatography. The recovered heel solution (83.24 g) contained vinyl acetate (0.55 wt %), acetic acid (3.18 wt %), acetic anhydride (58.7 wt %) and EDA (33.07 wt %).

Experiment 7.²⁰ This experiment illustrates the reaction of ketene and acetaldehyde performed with the reactor zone containing mixed acetic anhydride-acetic acid solvent and at 150°C, as per experiment 6 but with methanesulfonic acid catalyst instead. The experiment also illustrates that acetic acid is not produced when a weaker acid is used, but that the vinyl acetate yield is lowered. The same reactor system used in experiment 1 was used in experiment 7. The reactor tube was loaded with acetic anhydride (59.5 g, 0.583 mol), acetic acid (3.7 g, 0.0616 mol), methanesulfonic acid (2.9 g, 0.0306 mol) and TBHQ (140 mg, 0.84 mmol) polymerization inhibitor. The reactor was operated in the same manner as per experiment 1 at 150°C. Experiment numbers 7.1, 7.2 and 7.3 were conducted for 300, 300 and 305 minutes, respectively, using the same heel solution. Yields of vinyl acetate isolated from trap C and the acetic acid scrubber solutions and the wt % acetic acid contained in trap C (trap C wt % HOAc) follow:

<u>Experiment number</u>	<u>% Yield vinyl acetate</u>	<u>Trap C wt % HOAc</u>
7.1	23	0
7.2	32	0
7.3	26	0

The reactor heel solution recovered from experiment 7.3 was analyzed by gas chromatography. The recovered heel solution (75.31 g) contained vinyl acetate (0.91 wt %), acetic acid (1.22 wt %), acetic anhydride (79.9 wt %) and EDA (9.69 wt %).

Experiment 8.²¹ This experiment illustrates the reaction of ketene and acetaldehyde performed with the reactor zone containing mixed acetic anhydride-acetic acid solvent and at 150°C, as per experiment 7 but with sulfuric acid catalyst instead. The experiment also illustrates that strong acids lower the vinyl acetate yield and produce acetic acid. The same reactor system used in experiment 1 was used in experiment 8. The reactor tube was loaded with acetic anhydride (59.5 g, 0.583 mol), acetic acid (3.7 g, 0.0616 mol), 96.8 % sulfuric acid (3.1 g, 0.0306 mol) and TBHQ (140 mg, 0.84 mmol) polymerization inhibitor. The reactor was operated in the same manner as per experiment 1, with the temperature set for 150°C for 300 minutes. The yield of vinyl acetate isolated from trap C and the acetic acid scrubber was 12%, and trap C contained 19.28 wt % acetic acid. Plugging of the gas delivery tube due to excessive char formation prevented further operation of the reactor containing this heel solution. The liquid portion (58.28 g) of the heel mixture was recovered, and it contained acetic acid (21.14 wt %), acetic anhydride (55.83 wt %) and EDA (24.95 wt %).

Experiment 9.²² This experiment illustrates the reaction of ketene and acetaldehyde performed with the reactor zone containing mixed acetic anhydride-acetic acid solvent and at 150°C, as per experiment 8 but with phosphoric acid catalyst instead. The experiment also illustrates that strong acids lower the vinyl acetate yield and produce acetic acid. The same reactor system used in experiment 1 was used in experiment 9. The reactor tube was loaded with acetic anhydride (59.5 g, 0.583 mol), acetic acid (3.7 g, 0.0616 mol), 85 % phosphoric acid (3.53 g, 0.0306 mol) and TBHQ (140 mg, 0.84 mmol) polymerization inhibitor. The reactor was operated in the same manner as per experiment 1, with the temperature set for 150°C for 300 minutes. The yield of vinyl acetate isolated from trap C and the acetic acid scrubber was 19%, and trap C contained 13.84 wt % acetic acid. Plugging of the gas delivery tube due to excessive char formation allowed for further operation of the reactor containing this heel solution for only 65 minutes. The liquid portion (72.25 g) of the heel mixture was recovered, and it contained vinyl acetate (0.84 wt %), acetic acid (1.98 wt %), acetic anhydride (77.55 wt %) and EDA (32.78 wt %).

Experiment 10.²³ This experiment illustrates the reaction of ketene and acetaldehyde with the reactor zone containing the insoluble solid acid catalyst Amberlyst 15 and no added solvent. The glass reactor used in this experiment consisted of a 74-cm by 25-mm-O.D. tube fitted with a permanent thermowell extending from the base of the reactor. The central portion of the reactor tube was constructed with a condenser jacket which was in turn enclosed with a vacuum jacket to prevent heat loss. The length of the jacketed portion was 61 cm. The 25-mm-O.D. tube had indentations 5 cm above the base of the jacket to support the catalyst bed. A physical mixture of Amberlyst 15 resin (17 mL, 10.26 g, ca. 31 meq -SO₃H) and 16 X 24 mesh quartz chips (50 mL) was prepared. The base of the reactor was loaded with 6 X 6-mm Raschig rings to a height of 6 cm above the indentations, and a 1-cm-high layer of 4 X 8 mesh quartz chips was placed on top of the Raschig rings. The entire mixture of Amberlyst 15 and 16 X 24 mesh quartz chips was then placed in the reactor. The length of the catalyst + quartz mixture charge was 20 cm. An additional 5-cm-high layer of 4 X 8 mesh quartz chips was placed on top of the catalyst bed. A 100-mL, 2-necked flask was attached to the bottom of the reactor. The reactor inlet line L6 was attached to the other neck of the 100 mL 2-necked flask. The bottom of the reflux condenser portion condenser train was attached to the top of the reactor to allow for the return of condensable liquids to the reactor. The 100-mL 2-necked flask served as a heel reservoir for any liquid draining from the reactor. Under the conditions of the experiment, liquid did not flow into the heel reservoir until after the reaction feed flows to the reactor were terminated. Ketene, acetaldehyde and nitrogen were delivered to the reactor at the same rate as per experiment 1 to begin experiment 10.1. The temperature of the catalyst bed slowly rose from 19.6 to 83.3°C, after which steam was delivered to the reactor condenser jacket. The catalyst bed temperature continued to slowly rise to 110.6°C and then slowly decreased and leveled out at 98.7°C. During the process of experiment 10.1, the catalyst bed slowly wetted. The reaction was terminated as per experiment 1 after 360 minutes, after which a portion of the liquid wetting the catalyst bed drained into the reservoir. In experiments 10.2 through 10.5, the

reactor was operated in the same fashion as per experiment 10.1, except that steam heating of the reactor was commenced when the feeds were initially delivered to the reactor. Experiments 10.2, 10.3, 10.4 and 10.5 were performed over periods of 300, 330, 300 and 352 minutes, respectively, using the same catalyst bed. Yields of vinyl acetate isolated from trap C and the acetic acid scrubber solutions and the wt % acetic acid contained in trap C (trap C wt % HOAc) follow:

<u>Experiment number</u>	<u>% Yield vinyl acetate</u>	<u>Trap C wt % HOAc</u>
10.1	10	14.44
10.2	44	0
10.3	37	1.97
10.4	34	0
10.5	31	0

The reactor heel solution recovered from the reservoir after completion of the reaction of experiment 10.5 was analyzed by gas chromatography. The recovered heel solution (8.1 g) contained acetaldehyde (3.46 wt %), acetic acid (1.17 wt %), acetic anhydride (2.01 wt %) and EDA (39.9 wt %).

Experiment 11.²⁴ This experiment illustrates the use of a single contact zone for the production of vinyl acetate from ketene and hydrogen. The same reactor system used in experiment 1 was used in experiment 11, but the feed system was modified by blocking off the acetaldehyde feed system and by replacing the nitrogen feed to the ketene trap/vaporizer with hydrogen feed controlled by a hydrogen mass flow controller, thus allowing the ketene to be transpired in a hydrogen stream. The analytical scrubber was loaded with methanol in place of acetic acid. The reactor was loaded with 5% Pd on carbon powder (2.0151 g), acetic anhydride (65.8 g, 0.645 mol), p-toluenesulfonic acid monohydrate (5.8 g, 0.0306 mol) and TBHQ (160 mg, 0.963 mmol). The reactor was operated as per experiment 1 at 140°C for 317 minutes, but with the feed consisting only of ketene (0.7 mmol/minute) and hydrogen (88 SCCM). The material isolated from trap C (4.32 g) contained acetaldehyde (11.2 wt %), vinyl acetate (26.7 wt %), acetic acid (37.7 wt %) and EDA (2.1 wt %). The material isolated from the methanol scrubber (76.6 g) contained methyl acetate (0.95 wt %).

Experiment 12.²⁵ This experiment illustrates the accelerated reaction of acetaldehyde and acetic anhydride conducted in acetic acid present in a 78 molar % excess over equal molar amounts of acetaldehyde and acetic acid (compare to experiment 13 below). Acetic acid (38.4 g), acetic anhydride (36.75 g) and benzenesulfonic acid monohydrate (1.29 g) were charged into a bottle and stirred magnetically at ambient temperature (about 20-23°C). Acetaldehyde (15.9 g), cooled to about 0°C, was added to the stirred mixture. After stirring for 20 minutes, the temperature of the mixture was 50°C. About two hours after initially mixing the reagents, the mixture was analyzed by gas chromatography using Hewlett Packard Model 5890 gas chromatographs with flame ionization detectors. Vinyl acetate, acetaldehyde, paraldehyde and acetic acid were analyzed using a 25-m x 0.53-mm

FFAP capillary column (1.0 micron film thickness) programmed at 40°C for 5 minutes, 15°C/minute to 235°C and holding at 235°C for 1.67 minutes. Acetic anhydride and ethylidene diacetate were analyzed using a 30-m x 0.53-mm DB-5 capillary column (1.5 micron film thickness) programmed at 40°C for 8 minutes, 7°C/minute to 200°C with a 0 minute holding time at 200°C. Analyses were accurate to within about 5%. Mixtures were prepared for gas chromatographic analysis by adding 5 mL of a tetrahydrofuran solution containing 2% decane internal standard to an accurately weighed 1-g sample of the reaction product. The mixture analyzed as containing 1.9 wt % acetaldehyde, 0 wt % paraldehyde, 43.8 wt % acetic acid, 11.8 wt % acetic anhydride, 0 wt % vinyl acetate and 46.0 wt % EDA.

Experiment 13 (comparative).²⁶ This experiment illustrates the effect of omitting the acetic acid promoter using additional acetic anhydride to allow for the concentrations of acetaldehyde and benzenesulfonic acid comparable to those used in experiment 12. Acetic anhydride (65.2 g) and benzenesulfonic acid monohydrate (1.29 g) were charged into a bottle and stirred magnetically at ambient temperature (about 20-23°C). Acetaldehyde (15.9 g), cooled to about 0°C, was added to the stirred mixture. After stirring for 20 minutes, the temperature of the mixture was 26°C. About three hours after initially mixing the reagents, the mixture was analyzed by gas chromatography as per experiment 12. The mixture contained 14.3 wt % acetaldehyde, 1.6 wt % paraldehyde, 85.2 wt % acetic anhydride and 2.1 wt % EDA.

Experiments using the ReactIR 1000. Experiments 14-16 used the following instrument to analyze the reaction. The ReactIR 1000 by Applied Systems is a compact bench-top instrument designed for real-time, in-situ analysis of chemical reactions. The ReactIR 1000 is based on mid-infrared Fourier transform spectroscopy, and is typically used to identify and track the concentration of starting materials, intermediates, and products, thereby providing both reaction pathway and kinetics information. The DiComp probe is a very rugged probe that will withstand many corrosive chemical environments. It has a six-reflection bi-layer ATR element with a temperature range of -80 to 230°C. The pressure range for the DiComp probe is 10 torr to 200 psig. The probe has a wavelength range from 4000 to 2200 cm⁻¹ and from 1900 to 700 cm⁻¹. The probe is equipped with a sliding 24/40 ground glass joint so it can be used on various sizes of reaction flasks and at various depths. Spectra were collected at 4 cm⁻¹ resolution, and 32 scans were co-added.

Experiment 14.²⁷ This experiment illustrates the promotion of the reaction of acetic anhydride and acetaldehyde performed at a level of acetic acid promoter sufficient to induce an initial rate enhancement, yet at too low a level to promote the reaction to completion. Acetic anhydride (200 g), acetic acid (1.0 g) and benzenesulfonic acid monohydrate (0.5 g) were charged into a 500-mL, 2-necked bottle and stirred magnetically. The DiComp probe was inserted into the reaction mixture through one of the necks of the 500-mL, 2-necked bottle while the mixture was stirred magnetically at ambient temperature. Acetaldehyde (10.3 g) was added to the stirred mixture as rapidly as possible, and the absorbance of the infrared absorption uniquely characteristic of EDA

occurring at 951.3 cm^{-1} was monitored by recording the spectrum every 60 seconds. Relevant absorbance data as a function of time follow:

<u>Time after acetaldehyde addition, sec.</u>	<u>Absorbance</u>
0	0.0007
60	0.0267
120	0.0426
180	0.0472
240	0.0534
600	0.0553
1200	0.0566
2400	0.0587
4200	0.0635

At the concentrations used in the experiment, the absorbance at total conversion of the acetaldehyde to EDA is about 0.32-0.34.

Experiment 15.²⁸ This experiment illustrates the promotion of the reaction of acetic anhydride and acetaldehyde performed at a level of acetic acid promoter higher than that used in experiment 14, the level being sufficient to induce an initial rate enhancement followed by a lesser extent of promotion of the reaction to completion. Acetic anhydride (200 g), acetic acid (10.3 g) and benzenesulfonic acid monohydrate (0.5 g) were charged into a 500-mL, 2-necked bottle and stirred magnetically. The reaction was initiated by adding acetaldehyde (10.3 g) as rapidly as possible, and the reaction was monitored as per experiment 14, except that the spectra were recorded every 45 seconds. In the data that follow, the acetaldehyde was added between 45 and 90 seconds after the spectrophotometer began recording spectra.

<u>Time after recording the first spectrum, sec.</u>	<u>Absorbance</u>
0	0.0019
45	-0.003
90	0.0980
135	0.1558
180	0.1656
360	0.1777
720	0.1898
1500	0.2426
3900	0.3214

At the concentrations used in the experiment, the absorbance at total conversion of the acetaldehyde to EDA is about 0.32-0.34.

Experiment 16.²⁹ This experiment illustrates the promotion of the reaction of acetic anhydride and acetaldehyde performed at a level of acetic acid promoter higher than that used in experiment 15, the level being sufficient to induce a rate enhancement that

persists unabated throughout the entire course of the reaction. Acetic anhydride (200 g), acetic acid (20.6 g) and benzenesulfonic acid monohydrate (0.5 g) were charged into a 500-mL, 2-necked bottle and stirred magnetically. The reaction was initiated by adding acetaldehyde (10.3 g) as rapidly as possible, and the reaction was monitored as per experiments 14 and 15, and the spectra were recorded every 45 seconds. In the data that follow, the acetaldehyde was added between 45 and 90 seconds after the spectrophotometer began recording spectra.

<u>Time after recording the first spectrum, sec.</u>	<u>Absorbance</u>
0	0.0004
45	0.0016
90	0.1445
135	0.2234
180	0.2375
360	0.2786
720	0.3018
1500	0.3089
3900	0.3190

At the concentrations used in the experiment, the absorbance at total conversion of the acetaldehyde to EDA is about 0.32-0.34.

Experiment 17.³⁰ This experiment illustrates the use of the process of the accelerated reaction of acetic anhydride and acetaldehyde as a means to scrub diluted ketene and acetaldehyde from a gas stream forming EDA by contacting the gas with acetic acid containing benzenesulfonic acid catalyst. The scrubber system was the same type as described previously. The scrubber reservoir was loaded with a solution of acetic acid (60 mL) containing benzenesulfonic acid monohydrate (1.29 g), and this mixture was circulated through the scrubber system. Nitrogen gas metering was provided by Tylan Model FC-260 mass flow controllers. Ketene was generated and delivered by the method described previously. Ketene feed rate was 0.7 mmol/minute under these conditions. Acetaldehyde in nitrogen also was fed by the method described previously. Acetaldehyde feed rate was 1.0 mmol/minute. The nitrogen/ketene and nitrogen/acetaldehyde streams were combined and mixed with an additional nitrogen stream metered at 25 SCCM. The combined nitrogen/ketene/acetaldehyde stream was fed to the inlet line of the scrubber reservoir for six hours while the scrubber fluid circulated. The fluid was then drained from the scrubber reservoir and analyzed by gas chromatography as per experiment 12. The scrubber fluid analyzed as containing 2.9 wt % acetaldehyde, 0.1 wt % paraldehyde, 54.1 wt % acetic acid, 0 wt % acetic anhydride and 44.5 wt % EDA.

Part B. Construction and Operation of Large-Scale, Continuous Reactor for the Reaction of Ketene with Acetaldehyde.³¹ The apparatus used for these experiments is outlined in Figure E.1. It consisted of a ketene generation (diketene pyrolysis) section, reactor/distillation section and effluent scrubber section. Each section and its operation will be described separately. All connections between equipment used Pharmmed®

Figure E.1. Overall Schematic for the Large Scale Production of VAM from Ketene and Acetaldehyde.

flexible tubing. All joints were secured with plastic clips. (*Use extreme caution where ketene may be present as acute ketene toxicity is similar to that of phosgene.*)

Ketene Generation. The source of ketene for these experiments was diketene, which was freshly obtained from Eastman Chemical Company's diketene facility and stored frozen until use. (*Caution! Diketene is a very reactive substance with acute toxicity. Since it generates significant pressure as it decomposes, diketene must be stored in plastic bottles, with a small vent hole in the cap to avoid the possibility of explosion and resultant injury.*) The ketene required for the reaction was generated by pumping diketene from a reservoir to a pyrolysis tube using a Masterflex® C/L pump for small-diameter tubing.

The pyrolysis tube consisted of a 14-in.-long, 1-in.-diameter quartz tube which had male 24/40 joints with spring hooks at each end and dimples at about 2 inches above one of the joints. A small plug of quartz wool was placed in the bottom of the reactor and the reactor attached to a head of the configuration shown below. (Each joint on the head had two spring hooks.) The head was secured to Joint 1 with a spring.

Joint 2 was fitted with a 10-in.-long, 1/4-in.-diameter quartz thermowell and secured with a spring. Via joint 3, the pyrolysis tube was filled to within an inch of the upper joint with coarse quartz chips, using care not to dislodge the quartz wool plug at the bottom. Joint 3 was then capped with a female glass stopper with a spring hook. The cap was secured in place with a spring.

The pyrolysis assembly was then placed and secured in a 10-in. electric furnace. Joint 3 was connected to a nitrogen inlet, which could be used to purge the reactor prior to operating the apparatus and to provide a minute nitrogen purge in the course of the reaction. This inlet had some particular safety features that need to be reviewed.

The overall nitrogen inlet system for the ketene generation section was constructed as follows:

- 1) the nitrogen source was connected to a two-way bubbler filled with oil so that we could verify that it was operating,

- 2) the exit of the nitrogen bubbler was connected to a tee, one side of which was connected to the pyrolysis reactor, using an appropriate 10/30 male inlet in joint 3, and
- 3) the remaining side of the tee was connected to a relief device.

The relief device, which was connected at various points in the process for safety reasons, consisted of four 1/4-in. glass tubes of ca. 42 inches length that had been inserted into a 5-hole rubber stopper that fit a 2-in-diameter tube. This collection of tubes was inserted into a 2-in. diameter glass tube of ca. 3 feet in length that had one end sealed. The relief device was filled with water to within 1-2 inches of the top of the tube, and each of the 1/4 in. tubes was inserted so that they were within an inch of the base of the relief device.

A one-way valve was placed in the line leading to the pressure relief device to prevent water from being drawn back into the reactor. (This one-way valve is present in any line leading to the relief device.) ***(Caution! It is very important that this relief device be used. If the pyrolysis reactor should plug, this is the only outlet for the ketene gas that is generated in the process. Ketene is very reactive with water, and this represents a very efficient method of removal.)***

After securing joint 3 to the nitrogen inlet with a spring, the last joint was fitted with a 10/30 male joint which had a small inlet sized to fit very snugly the tubing from the diketene feed pump. (From this point forward, all equipment used 24/40 joints unless specified otherwise.) A thermocouple was then placed in the thermowell, connected to a temperature controller, and the furnace connected to the same controller.

The base of the pyrolysis tube was fitted with a 1-foot-long, water-chilled condenser, which was connected to a Claisen head. The bottom of the Claisen head was connected to a 250-mL, round-bottomed flask with a stopcock at the bottom to drain the liquid by-products from the reactor. The second outlet was connected to second condenser chilled to 10°C and whose outlet passed via flexible tubing to a demister.

The demister consisted of a 500-mL addition funnel that was jacketed for cooling with an external coolant. The funnel was filled loosely with glass wool, and a gas inlet tube pushed through the glass wool. (Either Lab Glass LG-1990 or LG-2050 were suitable gas inlet tubes.) A 100-mL, round-bottomed flask was attached at the bottom of the addition funnel to allow drainage of the demister if necessary. (Throughout the entire series of runs, no more than a few drops of material at the base of the demister was ever collected.) The demister was cooled with ethylene glycol/water mixture chilled to 10°C.

The output from the ketene generation system was then connected to a three-way stopcock (labeled 1 in Figure E.1). One outlet was connected to the scrubbing system, the other to the reactor. To operate the reactor, the entire system was first flushed thoroughly with nitrogen, and the pyrolysis unit was heated to and maintained at 550°C using the aforementioned temperature controller. Diketene was fed from the diketene reservoir at a rate of about 60 g/h of diketene, using a calibrated pump. However, the ketene output

needed to be calibrated prior to use in each experiment; this calibration is described below. The feed rates of diketene were adjusted until a generation rate of ca. 1 mol of ketene/h was obtained.

Since we already knew that the reaction yield for the pyrolysis was about 70%, (i.e., 1.4 moles of ketene are generated per mole of diketene fed), we could quickly estimate the diketene feed rate that would be required. To accurately calibrate the unit, we needed to take the effluent from the ketene reactor to an analytical (methanol) scrubber that converts the ketene quantitatively to methyl acetate, which can be measured by GC. The operation of the analytical scrubber is described below.

Scrubber Section

Analytical Scrubber. The analytical scrubber, which could be fed from the exit of either the ketene generator or the reactor section, was very similar to those described in earlier sections of this report. However, due to the volume of ketene used and subsequent temperature rise, some modifications had to be made in the base of the scrubber, both in volume and cooling. (The reaction of ketene and methanol to form methyl acetate is very exothermic.) For this system, the base consisted of an apparatus that is depicted below:

The key difference between this base and the one used in the small-scale examinations was that we used a larger volume and, due to the large amount of heat generated, we needed to provide cooling, which we did at the base of the scrubber.

The scrubbing section consisted of 2-foot-long, 1-in.-diameter tube with a 24/40 female joint at the top, a 24/40 male joint at the bottom, and indentations at the base to support a packing. The tube was filled with Raschig® rings and inserted in the scrubber. At the top of the scrubbing column was placed a methanol inlet, which is depicted below:

At the top of the methanol inlet was placed a Claisen head. The first port of the Claisen head was used to introduce fresh methanol when operating and was stoppered during operation. The remaining head was connected to a dry ice condenser whose exit port was connected to a drying tube and the remaining gases vented to the hood fan.

The analytical column was connected so that we could feed either the ketene gas from the generator, to allow calibration of the ketene generator, or feed the gaseous effluent from the reactor section. Provisions were also made to allow ketene from the ketene generator and reactor to bypass the analytical scrubber and pass to a water scrubber, which will be described later. This required a somewhat complex plumbing system which is depicted in Figure E.1. The figure shows that a three-way stopcock (labeled 2) was placed in one of the lines leading from three-way stopcock 1 (the exit of the ketene generation section). One port was connected to the water scrubber, described below, and the other was connected to a tee. One end of the tee was connected to the ketene inlet of the analytical scrubber, and the second was connected to a third three-way stopcock (labeled 3 on the diagram), which connected to the reactor.

To operate the unit, either for ketene calibration or to scrub the gases from the reactor, the dry ice condenser was filled with dry ice/acetone, the methanol reservoir was filled (through the Claisen head) with 240 g of methanol, and the base was chilled to -10°C . Using flexible tubing (Pharmed®) and a Masterflex® pump, the chilled methanol was circulated at a rate to insure that the entire column was continually wetted, but not fast enough to allow flooding of the column.

During calibration, ketene generation was initiated as described above; the stopcocks were first opened to the water scrubber for about five minutes to flush the system. (Stopcock 3 from the reactor was shut off so that the ketene did not bypass the scrubber.) Stopcock 2 was turned to send the feed now to the scrubber, and the ketene was allowed to pass into the reactor for 30 min. The stopcock was then turned to divert the ketene to the water scrubber and the methanol pump was reversed. All the methanol was drained and the material was analyzed by GC using the same methods described in earlier vapor stripped reactor experiments.

When a reaction was undertaken, the operation was the same, except that stopcock 1 was opened to the reactor, stopcock 3 was opened to the analytical scrubber, and stopcock 2 was closed. During reactions, the analytical scrubber was operated for variable lengths of time between samples, generally 1.5-2 hours. (The time interval between samples was accurately determined using a stopwatch.) The reactor sample contained methyl acetate

and acetaldehyde (and its dimethyl acetal), in addition to unreacted methanol, and was analyzed by GC as described in the vapor stripped reactor section. (*Caution: when samples are removed in an ongoing reaction, the ketene-containing effluent stream is always diverted temporarily to the water scrubber to avoid exposure to ketene!*)

Water Scrubber. The water scrubber was constructed from a base with a 500-mL, round-bottomed flask equipped with a side arm and an overflow sidearm. This is shown below.

The round bottom was connected to a scrubbing tube identical to the one used for the methanol scrubber (including the Raschig® rings) and an adapter (Lab Glass LG 1330-100) which allowed us to connect to a water source placed at the top. Tap water was introduced continuously from the top, and ketene was effectively scrubbed and discarded as acetic acid. The additional gases that might have been generated in the reaction were vented in the hood.

Reactor Section. The reactor section will be described starting with the exit from stopcock 1 in Figure E.1. Stopcock 1 was connected to a 3-necked, 500 mL, round bottomed flask. The three necks had the following items inserted:

- 1) the first neck was connected to the relief device (again using a one-way valve in the line to prevent sucking the contents of the water tower into the reactor);
- 2) the second (center) neck was fitted with a gas inlet adapter (Lab Glass LG-2050 or LG-1990) whose tube length had been reduced to fit the round-bottomed flask. The connections were the reverse of those normally used. The side normally used as the inlet (the long tube) was connected to the reactor, and the second port (generally used as the exit) was used for the ketene inlet;
- 3) the third was connected via a gas adapter with a stopcock (Lab Glass LG-1710 or 1711) which was connected to a nitrogen source (a nitrogen line that could be diverted entirely to the reactor if necessary).

This round bottom is not shown in Figure E.1, but served an important purpose:

- 1) It provided a point for the release of ketene if the reactor plugged. (In operation this happens as the reaction proceeds, and one can quickly tell when the reactor is plugged by observing the occurrence of bubbles in the water tower. The reactor is shut down immediately if any ketene begins to travel to

the water tower. More commonly, pressure gradually builds and is evidenced by the reduced water height in the tower).

2) It also acted as a buffer between the ketene generator and the reactor. This is necessary because, unless the reactor is purged thoroughly with nitrogen, the very reactive ketene is very rapidly consumed and the reactor will back up the lines very rapidly.

The ketene that passed through this unit was introduced into the reactor through a gas dispersion tube (Lab Glass LG-1971-102) that had been altered to include a small inlet to accept a piece of Pharmed® precision capillary tubing. When the reactor was operated, acetaldehyde was introduced through this inlet using Pharmed® precision capillary tubing connected to two 50-mL plastic syringes placed on a syringe pump that had been calibrated for these syringes. The setting on the syringe pump was altered as needed to alter the ratio of ketene/acetaldehyde, as this was the easier addition to reset. The low-boiling acetaldehyde was retained in these syringes by placing a cold pack over the two syringes to keep them cold. (It is important that plastic syringes be used, as other syringe types either seize or leak upon cooling.)

The gas dispersion tube was fitted into one of the side ports on a 3-necked head of a kettle reactor. Using a 1-L reaction kettle with indentations (to facilitate mixing), the reactor kettle was filled with acetic anhydride (ca. 560 g), acid catalyst, and a small amount of t-butyl hydroquinone (t-BHQ, a polymerization inhibitor.) The exact quantity of each used is indicated in the results section. Since the reactor was stirred magnetically, an efficient stirbar such as Lab Glass LG-9557T-104, was added prior to sealing the reactor. The head was secured on the reactor using a Kalres® seal, and the kettle was placed in a heating jacket over a magnetic stirrer motor. In the remaining side port was placed a thermowell with a little oil. A thermocouple was placed in this thermowell to monitor temperature in the reactor bottom.

The center port was fitted with a distillation unit consisting of a 15-tray Oldershaw column (silvered), a splitter, and a condenser (cooled with tap water) for the top of the column. A small plug of copper wool was placed at the top of the Oldershaw column to minimize polymerization in the column. When the reactor is operated experimentally, the base is heated until vapor reaches distillation head and then the acetaldehyde and ketene are introduced. The splitter was operated at a 3/1 reflux ratio (9 seconds on, 27 seconds off). The offgas from the reactor was sent to a tee. The tee was connected to the analytical scrubber stopcock 3 where it could be sent to the analytical scrubber or to the water scrubber. The gaseous output was sent to the analytical scrubber during a reaction run to allow us to ascertain the levels of unreacted acetaldehyde and ketene, and was only sent to the water scrubber during the very short period when we were draining and refilling the analytical scrubber.

The second port of the tee was connected to the vent for the product receiver, which was connected to the splitter. Since the splitter used a ball joint, this required fitting the unit with an adapter to convert the ball joint to a 24/40 joint and connecting this to the

receiver using a three-way 24/40 adapter (Lab Glass LG-1440-100). The receiver consisted of a jacketed 250-mL graduated cylindrical separatory funnel similar to Lab Glass LG-8359T-102, except it was graduated (as in Lab Glass LG-8362T-102) and the glass stopper was replaced with a 24/40 joint. In operation, the receiver was cooled to 10°C to retain any acetaldehyde.

The top of the three-way adapter was fitted with a "glass plug balloon adapter" (Lab Glass IG-22-104.) The glass plug balloon adapter was not used to introduce gas, but to allow us a vent for the reactor and access for introducing stabilizer while the reaction was underway. To do this, we placed a rubber septum over the upright outlet (the one at 180° to the 24/40 joint) of the adapter to allow us to insert a syringe into the receiver. The second outlet (the one at a 90° to the 24/40 joint) was used as a vent to the analytical scrubber. (This is the receiver vent referred to earlier in this section.)

In operation, the "glass plug balloon adapter" was open to the vent leading to the analytical scrubber throughout the run, except when we needed to introduce stabilizer. At the outset of every reaction, we introduced a solution of 0.2 g t-BHQ in 1 mL of acetic acid into the receiver. The rates in these reactions were sufficient to fill the receiver over several hours. As the receiver began to get full, it would be drained, weighed and analyzed. After draining, a new charge of stabilizer (polymerization inhibitor) would need to be introduced. To introduce the stabilizer, the "glass plug balloon adapter" was turned to the serum capped inlet and a fresh charge of stabilizer added. The stopcock was then immediately returned to the vent position. Samples removed from the product receiver were analyzed by the same methods as the product effluent from the vapor stripped reactors.

Overall Operation. Having described the equipment and operation of each unit in detail, we can now describe the overall operation of the unit using Experiment 1 as typical. To start the reaction, the kettle was filled with acetic anhydride, 560 g acetic anhydride, 30 g of p-toluenesulfonic acid, and 2 mL of a solution containing 0.2 g t-BHQ/mL. This kettle was connected to the apparatus described above and heated with stirring, with a gentle purge of nitrogen until reflux started. The nitrogen source was that described in the reaction section (independent of that provided to the ketene section), and during this heat-up, the nitrogen effluent was sent to the water scrubber.

As the reactor was heating, the ketene generation section was thoroughly purged with nitrogen, and diketene feed was started into the ketene generation section. Since this was already calibrated to generate about 1 mol of ketene/h, the ketene generated from this reactor was sent to the analytical scrubber as described above to ascertain the exact ketene feed rate. (As we operated equipment parts, these settings changed slightly, so this recheck is necessary.) After an analytical sample was obtained, the ketene was diverted to the water scrubber, and then the diketene feed was turned off until the reactor was ready.

After the reactor attained reflux, the acetaldehyde syringes were filled, the ketene section was again flushed with nitrogen, and the diketene feed resumed. The ketene from this start-up was sent to the water scrubber for about 5-10 minutes, the nitrogen feed to the reactor was then closed off (the small purge to the ketene generation section was retained, however), and then the ketene was diverted to the reactor. Acetaldehyde feed was turned on immediately, and the reactor gases were diverted to the analytical scrubber, which had been refilled with a fresh methanol charge.

Over the course of the day, the analytical scrubber was drained on the average of 4 times. (Daily reaction times were from 6-7.5 hrs, depending upon the duration of the start-up.) It was refilled through the Claisen head on the analytical scrubber, as indicated earlier. The ketene was diverted to the water scrubber during this operation for safety reasons, and the draining and refilling process required only a few minutes. The product receiver typically needed to be drained a total of 2-3 times over the course of the day. Both the analytical scrubber and product receiver contents were analyzed as indicated above.

At the end of a day, the reactor was shut down by first shutting down the acetaldehyde feed, diverting the reactor gases to the water scrubber, and then introducing a strong nitrogen purge to the reactor section. The ketene feed was then diverted to the water scrubber, and the reactor was allowed to cool under a slow nitrogen purge. (The nitrogen purge could be reduced, but not shut off after several minutes.) ***(Caution! Failure to follow this procedure for the reactor shutdown will result in the contents of the reactor being sucked back into the 500-mL buffer.)***

All product and analytical samples were removed from the reactor and analyzed at the end of a day. These generally needed to be stored overnight in a freezer prior to analysis. (It should be noted that sometimes these samples became colored overnight and subsequently darkened considerably over the course of several days.)

Over the course of a day's reaction, the pyrolysis tube in the ketene generator became very dark and tarry. This was remedied by leaving the reactor at 550°C overnight with a purge of air. This gave a completely clean quartz surface in several hours. (The effluent from this "reactivation" was sent to the water scrubber.) Prior to restarting the next day, any of the traps that required it were drained, and the system was purged thoroughly with nitrogen. The reactions were restarted the next day by repeating the procedure above.

All the reactions used this same procedure with only one slight alteration for the examinations with methanesulfonic acid. Since methanesulfonic acid is slightly volatile, a bed of 2-polyvinylpyridine, supported by a fritted glass filter, was inserted just after the three-way adapter connecting the splitter to the receiver in the reactor section (i.e., between the three-way adapter and the receiver).

Results and Discussion

Part A. Small-Scale Reactor Studies. Most of the significant results for the small-scale reaction of ketene and acetaldehyde have been detailed in the experimental section. All of the small-scale experiments were performed using large quantities of nitrogen diluent, and the molar ratio of acetaldehyde to ketene to nitrogen was 1/0.7/9.2. Normal acetaldehyde feed rate was 1 mmole per minute, and the gases were sparged through a heated mixture of solvent and Bronsted acid catalyst. When acetic anhydride is used as a solvent, there is a definite buildup of EDA in the heel solution. Most of this buildup of EDA occurs during the first day of operation. After the first day, the level of EDA is apparently at a steady state, and it is being consumed at the same rate that it is being created. When EDA reaches steady state, the yield of VAM is highest. Often acetic acid is evolved from the reaction mixture during the first day of operation. This could be the result of water present in the initial charges, and most of the acid catalysts used contained waters of hydration. Any water present is converted to acetic acid by reaction with acetic anhydride or ketene.

The evolution of significant amounts of acetic acid from the reaction after the first day of operation is indicative of the acid catalyst being too strong. Thus acetic acid is not evolved after the first day when p-toluenesulfonic acid is the catalyst, but is evolved on subsequent days when an equivalent amount of benzenesulfonic acid is used under the same conditions (experiment 6). When the weaker methanesulfonic acid is used, no acetic acid is evolved, and the vinyl acetate yield is lower. This acid also produced less EDA in the reactor heel, and most of the reactants passed through the reactor without reacting. Thus, there appears to be an optimum acid strength suitable for the reaction at the typical concentrations used, and p-toluenesulfonic acid appears to be one of the most efficient catalysts. Acids such as sulfuric and phosphoric not only cause excessive amounts of acetic acid to evolve, but also cause extensive charring. The evolved acetic acid is believed to be the result of aldol condensations of acetaldehyde, and this type of product has been identified by GC-MS.³² The mole of water produced from the aldol condensation can generate two moles of acetic acid by reaction with acetic anhydride or ketene.

The discovery that acetic acid vastly accelerates the rate of EDA formation (see experiments 12-17) may have relevance in the reaction of ketene and acetaldehyde to produce VAM. The highest yield of VAM (95% based on ketene) was obtained when a small amount of acetic acid was added to the reactor solution (experiment 5). The reactor heel obtained after running the reaction in the presence of added acetic acid contained 35.7 wt % EDA, whereas that obtained under similar conditions without the added acetic acid contained only 28.99 wt % EDA (experiment 1). The mechanism of the promotion of the EDA formation rate by the presence of acetic acid is not understood at this time. Among possible causes might be the formation of a small equilibrium amount of highly reactive hydroxy acetate produced from the reaction of acetaldehyde with acetic acid, or it could be a solvent effect. Although it may seem contrary to common sense to add acetic acid to a reaction that is driven to completion by the consumption of acetic acid, perhaps

this added acid has the more beneficial effect of accelerating the rate of EDA buildup early on in the reaction. Also, since all of the reactor heel solutions contain some acetic acid, there could be some degree of self-promotion occurring in all of the reactions in acetic anhydride solvent. Although this notion is purely speculative, the large kinetic effect resulting from the influence of acetic acid on EDA formation could be greater than the negative effect it has on the VAM-acetic acid-EDA equilibrium.

Although EDA is very likely the source of VAM in reactions conducted in acetic anhydride solvent, it may or may not be the intermediate in reactions conducted in N-methyl-2-pyrrolidinone solvent (NMP). When NMP was used as the solvent, the reactor heel only contained 1.13 wt % EDA (experiment 4). Nevertheless this reaction was quite efficient in converting ketene and acetaldehyde to VAM.

The reaction of ketene and acetaldehyde to produce VAM also can occur in the absence of solvent by delivering the reactant vapors to a bed of solid acid catalyst such as Amberlyst 15 sulfonic acid resin (experiment 10). However, the catalyst eventually becomes covered with a film of liquid, and thus the reaction actually becomes a gas-liquid-solid reaction. Since Amberlyst 15 is not stable at the temperatures normally in the VAM synthesis, yields were modest.

Studies were performed to better understand the role of diluent gases and space velocity effects. The results of the diluent study are summarized in Figures E.2, E.3 and E.4, depicting the VAM yield from ketene, VAM production rate and the volatile acetic anhydride collected, respectively, as a function of time.³² The points on the graph labeled "N2" were performed with a 48% increased flow of diluents, with the effective space velocity through the reactor thus also increasing by about the same amount. The liquid phase in the reactor was the normal charge of 30.6 mmol p-toluenesulfonic acid and 645 mmol acetic anhydride. Under the control conditions, 0.7 mmol ketene/min., 1.2-1.4 mmol acetaldehyde/min. and 213 SCCM carrier gases were fed to the reactor heated to 150°C. An additional 103 SCCM nitrogen was added in the experiments labeled "N2". Although the added diluent decreased the VAM yield from ketene, it did not decrease it by 48%. The analysis is complicated by the fact that the reaction efficiency typically increases during the first three days (i.e., the first three points) and then decreases with time on stream under normal conditions. Also, it was noticed that the increased diluents volatilized some of the acetic anhydride (see Figure E.4). This probably upset the steady-state conditions (EDA/acetic anhydride balance) to some degree, and this probably also influenced the results somewhat. Under the conditions of low space velocity (low S.V.), no additional diluent nitrogen was added, but all of the feeds, including the nitrogen of the standard conditions, were decreased by about 48%. Under conditions of high space velocity (high S.V.), no additional diluent nitrogen was added, but all the feeds including the nitrogen of the standard conditions, were increased by about 48%. The results taken on the third day of operation (where performance is usually at a maximum) are summarized below:

Figure E.2.

Figure E.3.

VAM PRODUCTION RATE

Figure E.4

<u>Conditions</u>	<u>Rate VAM production, mmol/min.</u>	<u>% yield from ketene</u>
standard ³⁴	0.80	114
diluent ³⁵	0.70	99
low S.V. ³⁶	0.38	103
high S.V. ³⁷	0.84	81

The results are complicated by the fact that changing the reaction conditions upsets the steady state, and more acetic anhydride is carried out of the mixture at high space velocities. The results are further complicated by a rather poor material balance around ketene (the mass flow meter was out of calibration during these experiments) and acetaldehyde (vaporizer temperature control difficulties). However, in spite of these complications, increasing the space velocity appears to increase the rate, but decrease the conversion of ketene and vice versa. Addition of the diluent also increases the space velocity, but lowers the concentration of the reactants, thus lowering the rate and the conversion. The standard conditions, where diluents are present as well, appear to be adequate to provide time for the reactants to diffuse from the bubbles and for all of the ketene to react. This does not appear to be the case at high space velocity, and some of the ketene leaves the reactor before reacting.

Another series of experiments attempted to determine whether or not diffusion from the gas to the liquid phase was important.³⁸ Instead of performing the reaction in the tubular gas stripped reactor, the reaction was performed in a heated scrubber. In an effort to maximize liquid/gas contact area and time, the scrubber was constructed from two Hempel columns filled with 6 X 6-mm Rashig rings. The feed was to the zone between the two columns. The top column was 17 inches long, and the bottom column was 15.5 inches long. The two columns and the feed zone were heated by separate heat tapes set for 140°C. The solvent/catalyst mixture was circulated from the scrubber base reservoir to top of the scrubber, and no provision was made to heat the reservoir or the return line. The remainder of the reactor system was as described previously. This reactor was operated under conditions otherwise identical to those used in the normal tubular gas stripped reactor (0.76 mmol ketene/minute, 1.0 mmol acetaldehyde/minute 177 SCCM nitrogen, 645 mmol acetic anhydride, 30.6 mmol p-toluenesulfonic acid, 140°C). The VAM yields from ketene resulting from the scrubber/reactor were actually slightly lower (45% on the third day) than those from the normal tubular gas stripped reactor (53% on the third day). This result suggests that the rate of mass transfer of gas to the liquid normally is not a critical factor in determining the reaction efficiency. The slightly lower yields from the scrubber/reactor could be due to the fact that a fraction of mass of the reaction solvent/catalyst mixture was at the preferred temperature compared to the entire mass with the normal tubular gas stripped reactor. The information obtained from the small-scale reaction studies suggests that, under standard operating conditions, the rate probably is limited by the intrinsic chemical kinetics of the reaction. As the space velocity increases, it becomes increasingly probable that the rate becomes limited by mass transfer effects.

Part B. Scaled-Up (Large-Scale) Reactor Studies. Given the encouraging results from the esterification of acetaldehyde with ketene in the small-scale, vapor-stripped reactors, we initiated an examination of the reaction on a larger scale using conditions and operations which would be more representative of a commercial operation. The key changes we needed to make were to both radically increase the scale and significantly reduce, and ultimately eliminate, the diluent gases.

The scaleup and ketene delivery were somewhat problematic. If we were to reduce and ultimately eliminate the diluent gases, we could no longer condense either ketene or acetaldehyde and subsequently aspirate them into the reactor. Instead, to deliver ketene, we needed a continuous means of generating and delivering relatively clean ketene to the reactor. Further, we needed a means of adding the acetaldehyde to the reactor.

For generating and delivering ketene, we examined two reactor types. The first used a commercially available ketene generator (Ace Glass, Inc., Part. No. 7470) which generates ketene via acetone pyrolysis, as shown in the following equation:

Nominally, this apparatus delivers 0.1-1 moles of ketene feed/hr. Whereas, we could operate the apparatus as described, and the reactor delivers high-quality ketene, it is still accompanied by a mole of methane. To accomplish our goal of removing diluent gases, the ketene needed to be separated from the methane. To do this, we used a unit which utilized a U tube with a longer J-tube at the lowest point, all contained in a dry ice jacket. The gas was passed through the U-tube to condense ketene and, as the J-tube filled, the ketene spilled over into an evaporator that delivered ketene to the reactor. Although a significant amount of ketene bypassed the condenser, this delivered a reproducible level of ketene on a continuous basis in calibration runs. Unfortunately, it proved inadequate in the longer term because the back pressure of a column in the continuous reactor, which can fluctuate, reduced the delivery of ketene and, worse, the pressure fluctuations caused the delivery rate to vary significantly.^{39,40}

We needed to develop an alternative means of delivering the ketene and turned to the cracking of diketene (see reaction [6]).³¹

This process delivers ketene without significant amounts of any by-product gas. Unfortunately, the process does carry some dark, higher boiling liquids which are present as a mist and harder to remove than in the case of acetone cracking. These could be reduced to acceptable levels (but not absolutely eliminated) by using additional condensers and a demisting chamber.

More difficult is obtaining a source of diketene. The commercially available diketene (Aldrich) is quite dark and of variable quality and composition. Most of this inconsistency is due to improper handling. To get consistent results, we obtained freshly generated and purified diketene from the Eastman Chemical Company facility and froze it prior to use. Samples were never stored or allowed to remain as liquids for more than a couple of hours, nor were they stored for extensive periods.

Using this pure, freshly generated and purified diketene, we could deliver a wide range of ketene feed rates at very reproducible rates. The rate of ketene addition to the reactor could now be controlled quite simply by the rate of diketene addition to the cracker. Although we could feed at even faster rates, our examinations were conducted at between 0.9-1.2 moles of ketene feed/hr. Acetaldehyde could be readily controlled using a syringe pump, providing the syringes were chilled with ice packs.

To study the reaction of acetaldehyde and ketene, the ketene and acetaldehyde were introduced through a gas dispersion tube into a boiling mixture of acetic anhydride and acid catalyst in a kettle reactor. (The kettle reactor was chosen so since it has more vertical contact with the gases.) The vapor from this reactor was passed through a 15-tray Oldershaw column to separate out most of the acetic anhydride and any ethylidene diacetate which might be present. The top of the Oldershaw column was fitted with a splitter, and the product was obtained using a 3/1 reflux ratio with the condenser and product storage vessel maintained at 10°C. The gaseous effluent was trapped with chilled (10°C) methanol to measure unreacted ketene and to recover any acetaldehyde that bypassed the reactor.

Using this approach, we were able to obtain reaction rates and material balances at several conditions. A summary of these results appears in Tables E.1 and E.2. A complete data set for all the runs appears in the appendix for this chapter. Runs 1-3 were performed using p-toluenesulfonic acid as the catalyst and designed to both demonstrate that scaleup was achievable and to test the effect of differing relative ketene:acetaldehyde ratios. Although we demonstrated that we could generate large quantities of vinyl acetate in the scaled-up process, the scaled-up processes were less satisfactory than the small-scale, vapor-stripped processes in all respects, except the rate of VAM generation. The fourth run was focused on using methanesulfonic acid, where we could obtain higher acid concentrations, as an alternative to p-toluenesulfonic acid.

Throughout this set of experiments, we were focusing on the following key areas:

1. Attainable run duration and the accumulation of high boilers,
2. Material balances including:
 - a) Conversion,
 - b) Selectivity,
 - c) Accountability, and
3. Reaction rates

Our observations in each key area are discussed in more detail below.

Table E.1. Rate Data for Large Scale VAM Production from Ketene and Acetaldehyde

Example	Catalyst (identity & Quantity in g)	Time Online (h)	Ketene Feed Rate (mol/h)	AcH Feed Rate (mol/h)	VAM Production Rate (mol/L-h)
1	pTsOH (30.2 g)	19.6	1.09	1.07	0.56
2	pTsOH (30.2 g)	16.5	1.17	1.37	0.7
3	pTsOH (30.2 g)	17.2	0.92	0.69	0.43
4	MeSO ₃ H(82 g)	11.3	0.95	1.07	0.55

Table E.2. Material Balances for Large Scale VAM Production Examples in Table 1.

Ketene Material Balances					Acetaldehyde Material Balances			
Example	Ketene Feed Rate (mol/h)	Ketene Conversion (%)	Acetate* Accountability (%)	Selectivity to VAM (%)	AcH Feed Rate (mol/h)	AcH Conversion (%)	AcH Accountability (%)	Selectivity to VAM (%)
1	1.09	57%	86%	55%	1.07	59%	76%	53%
2	1.17	85%	72%	42%	1.37	61%	77%	50%
3	0.92	63%	82%	45%	0.69	59%	85%	64%
4	0.95	91%	91%	38%	1.07	72%	77%	42%

*Acetic anhydride was as solvent and was occasionally renewed with additional acetic anhydride.

Accountability was determined for as total acetyl added which sums ketene, acetic acid, and acetic anhydride sources.

Attainable Run Duration/High Boiler Formation. The ultimate determinant of attainable run duration is the rate at which high boilers ("tars") begin to accumulate, which forces us to cease operating the unit. In the scaled-up reactors, attainable run times were shorter than in the smaller scale vapor stripped reactors, as the accumulation of higher boiling components was much faster. The rate at which the high boiling components were formed appeared to be deleteriously effected by increased acid concentration, and the very high acid loading used with methanesulfonic acid resulted in formation rates of tar which shut down the reactor in less than 8 hours. (An attempt at running the reaction in neat methanesulfonic acid failed since the entire contents of the reactor solidified in about an hour.)

Further, based on observing the rate of temperature rise in the base and apparent viscosity of the liquid, it appears that the formation of high boilers is not constant, but accelerates as the reaction proceeds. Although we did not make any attempt to quantify the rate, once the formation of high boiling materials starts, its growth rate appears to be self accelerating. A key to making this reaction run longer would likely involve providing for the continuous removal of high-boiling components. We had designed a system for accomplishing this exact operation, but abandoned it when it became apparent that the economically preferred route would not involve esterification of acetaldehyde with ketene. (It should be noted that this same observation was made in the vapor-stripped reactors. However, the acceleration and overall high boiler formation rate in the scaled up reactors is significantly faster.)

We believe one reason the scaled-up reactors had such high rates of high boiler formation compared to the vapor stripped reactors is the higher concentrations of reactants in the reactor and longer retention times of the VAM product in the absence of a gas purge. The ketene and acetaldehyde starting materials are both very reactive materials, with a high propensity to react with themselves, giving diketene from ketene and crotonaldehyde from acetaldehyde. These materials will be retained in the reactor and are susceptible to myriad further reactions once they have been formed.

As for the product vinyl acetate, we do not believe the formation of high-boiling components is due to the more common free radical polymerization. We took extensive precautions against this event by adding a large amount of inhibitor (t-butyl hydroquinone) at the outset, and Cu was continuously added from the corrosion of a Cu wool plug at the head of the column. (This plug was included for this purpose.)

However, the intervention of an acid-catalyzed polymerization appears quite reasonable and is consistent with observations, particularly the acceleration with higher acid concentrations and the observation that faster stripping of the VAM in the vapor-stripped reactor leads to higher selectivities toward VAM. If any further attempts are made to practice this chemistry, one key would be to optimize the acid strength and concentration to minimize the formation of high boilers without significant sacrifices in the rate of VAM formation.

Lastly, as described in the introduction, the interaction of ketene with acetaldehyde may give not only the desired vinyl acetate, but also may yield β -butyrolactone by a 2+2 addition process. β -Butyrolactone would likely be retained in the reactor if it is formed. Although we did not see gross amounts of β -butyrolactone in the reactor at the end of the reaction, it is a reasonable reactive material that can polymerize, or more likely under the acid catalyzed conditions, open to form crotonic acid. Unfortunately, we did not analyze for crotonic acid, although the high boilers had a strong odor similar to that of crotonic acid. Like vinyl acetate, the crotonic acid is also prone to polymerization.

Conversion, Selectivity, Accountability, Production Rates. In all cases, the scaled-up reactor displayed poorer conversions, selectivities, and material accountabilities than the smaller scale vapor stripped reactors. We tested feed ratios using balanced feeds of ketene and acetaldehyde, as well as cases where each of the reactants was fed in excess. Under any of the conditions tested, the selectivities were unacceptable (ca. 40-65%), which represented the most dramatic (and disappointing) change upon scaleup.

These poor selectivities are also mirrored in the mediocre material accountabilities. It is likely that these poor material accountabilities are a direct consequence of the higher rate of high boiler formation, and we are seeing a diversion of the material to higher molecular weight products ("tars").

The best conversions and rates were obtained with a slight excess of acetaldehyde over ketene, but ketene selectivity suffered considerably under these conditions. It is likely that the condensation of acetaldehyde with itself, which would be expected to increase with excess acetaldehyde, generated more water, which scavenges ketene very effectively.

Finally, whereas we targeted a production rate of ca. 2 mol/L-hr, we never approached these rates; the highest rates obtained were 0.7 mol/L-h. About half of the difference was just unreacted starting materials passing through the reactor system; however, the remainder was primarily in material losses attributable to the poor selectivities.

One last difficulty was encountered with the product from the scaled-up reactors. Unlike product from the gas-stripped reactors, the VAM samples obtained from the scaled-up reactor were not stable to storage. Whereas the product is initially obtained as a clear, visually colorless (or nearly colorless) liquid, it darkens considerably (generally turning red) over the course of several days in a refrigerator.

From the scaleup work we can conclude that, should we ever choose to reexamine the esterification of acetaldehyde, or for that matter any other aldehyde or ketone, with ketene, the key to success will be mastering the issue of selectivity upon scaleup. The directions to be taken are discernible in the comparison of the small-scale vapor phase reactor and the larger scale reactor, where we simply depended upon distillative removal. The most important differences between the small-scale, vapor-stripped reactor are:

- 1) the residence times of the product and reactants in the process, and
- 2) the concentration of the components.

It may well be that one must strip the reactor continuously with a nitrogen purge to attain acceptable selectivities. We had several additional concepts regarding means of increasing mass transfer into the reactor and removing product quickly, including the use of co-solvents and separate feeds for the reactants and a stripping gas, but these were abandoned when the economic analysis indicated that we should move toward non-ketene based processes.

Engineering and Process Description

Background

A process model for the generation of VAM via the reaction of ketene and acetaldehyde was developed earlier by Scott Barnicki and was used as a starting point for the current work. While the modeled system was inexpensive (the gas-stripped reactor tower was only 6 feet in diameter), its performance was poor. Vinyl acetate yields were low (59% based on acetaldehyde). In addition, the model did not have any post-reactor cleanup columns.

Rough liquid phase kinetic data for reactions 3 and 4 were developed by Zoeller, Lane, Cwirko, Fuller, and Barnicki for an invention report before the contract was entered.⁴¹ Mixed-phase thermodynamics for the reaction of liquid acetic acid with gaseous ketene to form liquid acetic anhydride was modified from vapor phase thermodynamics using Gibbs Free Energies of Vaporization.⁴²

A number of design options were considered, including acetic acid sidedraws from the gas-stripped tower leading to separate ketene reactors. Figure E.5. shows the ASPEN flowsheet of the current process model. The material balance for the model is contained in Tables E.3-E.6. Unless otherwise noted, all components are constructed of 316 stainless steel.

Gas-Stripped Reactor

The gas-stripped reactor, GAS-STR, was modeled using a RADFRAC column with a liquid holdup of 12,500 ft³ in the reboiler. In reality, this large reboiler would actually represent a separate reactor. For costing purposes, the reactor was modeled as a V-VESSEL. Important specifications for the gas-stripped column and reactor are included in Table E.7.

Equimolar quantities (715 lbmol hr⁻¹) of acetaldehyde (Stream 1) and ketene (Stream 2) are introduced to the block. An extra 5 lbmol hr⁻¹ of HAc is present for modeling purposes, and is removed in Stream 13. Stream 1 mixes with a broken acetaldehyde recycle loop (Stream 3) in mixing block MIX1. The total ratio of acetaldehyde (Stream 4) to ketene being fed to the reactor is 1.16:1. An AKT reboiler with titanium tubes and a BFM condenser were specified.

Table E.3. Material balance for gas-stripped reactor block, streams 1-5.

Stream:	1	2	3	4	5
From Block:	From			MIX1	GAS-STR
To Block:	MIX1	GAS-STR	MIX1	GAS-STR	MIX2
Phase:	VAPOR	VAPOR	VAPOR	VAPOR	LIQUID
Mole Flow LBMOL/HR					
HOAC	0.0000	0.0000	0.0000	0.0000	0.2510
EDA	0.0000	0.0000	0.0000	0.0000	7.7965
VAM	0.0000	0.0000	27.8360	27.8360	4.8469
HAC	720.0000	0.0000	109.2400	829.2400	0.1733
AC2O	0.0000	0.0000	0.0000	0.0000	16.9322
KET	0.0000	715.0000	0.2973	0.2973	0.0001
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Mole Frac					
HOAC	0.0000	0.0000	0.0000	0.0000	0.0084
EDA	0.0000	0.0000	0.0000	0.0000	0.2599
VAM	0.0000	0.0000	0.2026	0.0325	0.1616
HAC	1.0000	0.0000	0.7952	0.9672	0.0058
AC2O	0.0000	0.0000	0.0000	0.0000	0.5644
KET	0.0000	1.0000	0.0022	0.0003	0.0000
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Mass Flow LB/HR					
HOAC	0.0000	0.0000	0.0000	0.0000	15.0725
EDA	0.0000	0.0000	0.0000	0.0000	1139.4090
VAM	0.0000	0.0000	2396.4140	2396.4140	417.2677
HAC	31718.2800	0.0000	4812.3670	36530.6400	7.6351
AC2O	0.0000	0.0000	0.0000	0.0000	1728.6090
KET	0.0000	30056.6500	12.4977	12.4977	0.0029
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Mass Frac					
HOAC	0.0000	0.0000	0.0000	0.0000	0.0046
EDA	0.0000	0.0000	0.0000	0.0000	0.3444
VAM	0.0000	0.0000	0.3319	0.0615	0.1261
HAC	1.0000	0.0000	0.6664	0.9381	0.0023
AC2O	0.0000	0.0000	0.0000	0.0000	0.5226
KET	0.0000	1.0000	0.0017	0.0003	0.0000
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Total Flow LBMOL/HR	720.0000	715.0000	137.3733	857.3733	30.0000
Total Flow LB/HR	31718.2800	30056.6500	7221.2780	38939.5500	3307.9970
Total Flow CUFT/HR	235247.0000	233614.0000	44884.3200	280132.0000	56.9358
Temperature C	50.0000	50.0000	50.0000	50.0000	123.6073
Pressure ATM	1.3000	1.3000	1.3000	1.3000	1.3000
Vapor Frac	1.0000	1.0000	1.0000	1.0000	0.0000

Table E.4. Material balance for gas-stripped reactor block, streams 6-10.

Stream:	6	7	8	9	10
From Block:		MIX2	MIX2	GAS-STR	SPLIT1
To Block:	MIX2		GAS-STR	SPLIT1	
Phase:	LIQUID	MISSING	LIQUID	VAPOR	LIQUID
Mole Flow LBMOL/HR					
HOAC	3.5000	0.0000	3.7510	3.4538	3.4538
EDA	0.0000	0.0000	7.7963	0.0000	0.0000
VAM	0.0000	0.0000	4.8468	742.7896	0.0000
HAC	0.0000	0.0000	0.1733	114.2861	0.0000
AC2O	0.0000	0.0000	16.9321	0.0457	0.0000
KET	0.0000	0.0000	0.0001	0.2975	0.0000
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Mole Frac					
HOAC	1.0000	0.0000	0.1120	0.0040	1.0000
EDA	0.0000	0.0000	0.2327	0.0000	0.0000
VAM	0.0000	0.0000	0.1447	0.8628	0.0000
HAC	0.0000	0.0000	0.0052	0.1328	0.0000
AC2O	0.0000	0.0000	0.5054	0.0001	0.0000
KET	0.0000	0.0000	0.0000	0.0003	0.0000
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Mass Flow LB/HR					
HOAC	210.1840	0.0000	225.2553	207.4100	207.4100
EDA	0.0000	0.0000	1139.3670	0.0000	0.0000
VAM	0.0000	0.0000	417.2627	63947.0800	0.0000
HAC	0.0000	0.0000	7.6354	5034.6630	0.0000
AC2O	0.0000	0.0000	1728.5940	4.6691	0.0000
KET	0.0000	0.0000	0.0029	12.5050	0.0000
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Mass Frac					
HOAC	1.0000		0.0640	0.0030	1.0000
EDA	0.0000		0.3239	0.0000	0.0000
VAM	0.0000		0.1186	0.9240	0.0000
HAC	0.0000		0.0022	0.0727	0.0000
AC2O	0.0000		0.4913	0.0001	0.0000
KET	0.0000		0.0000	0.0002	0.0000
WATER	0.0000		0.0000	0.0000	0.0000
Total Flow LBMOL/HR	3.5000	0.0000	33.4995	860.8727	3.4538
Total Flow LB/HR	210.1840	0.0000	3518.1180	69206.3300	207.4100
Total Flow CUFT/HR	3.3134	0.0000	61.0681	476001.0000	3.3169
Temperature C	50.0000		129.3909	63.5091	63.5091
Pressure ATM	1.3000	1.5000	1.5000	0.8000	0.8000
Vapor Frac	0.0000		0.0000	1.0000	0.0000

Table E.5. Material balance for gas-stripped reactor block, streams 11-15.

Stream:	11	12	13	14	15
From Block:	SPLIT1	HAC-COL	SPLIT2	SPLIT2	COMPRESS
To Block:	HAC-COL	SPLIT2		COMPRESS	
Phase:	VAPOR	VAPOR	VAPOR	MIXED	VAPOR
Mole Flow LBMOL/HR					
HOAC	0.0000	0.0000	0.0000	0.0000	0.0000
EDA	0.0000	0.0000	0.0000	0.0000	0.0000
VAM	742.7896	27.8546	0.0000	27.8546	27.8546
HAC	114.2861	114.2289	5.0000	109.2289	109.2289
AC2O	0.0457	0.0000	0.0000	0.0000	0.0000
KET	0.2975	0.2975	0.0000	0.2975	0.2975
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Mole Frac					
HOAC	0.0000	0.0000	0.0000	0.0000	0.0000
EDA	0.0000	0.0000	0.0000	0.0000	0.0000
VAM	0.8663	0.1956	0.0000	0.2028	0.2028
HAC	0.1333	0.8023	1.0000	0.7951	0.7951
AC2O	0.0001	0.0000	0.0000	0.0000	0.0000
KET	0.0003	0.0021	0.0000	0.0022	0.0022
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Mass Flow LB/HR					
HOAC	0.0000	0.0000	0.0000	0.0000	0.0000
EDA	0.0000	0.0000	0.0000	0.0000	0.0000
VAM	63947.0800	2398.0160	0.0000	2398.0160	2398.0160
HAC	5034.6630	5032.1450	220.2658	4811.8790	4811.8790
AC2O	4.6691	0.0000	0.0000	0.0000	0.0000
KET	12.5050	12.5050	0.0000	12.5050	12.5050
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Mass Frac					
HOAC	0.0000	0.0000	0.0000	0.0000	0.0000
EDA	0.0000	0.0000	0.0000	0.0000	0.0000
VAM	0.9268	0.3222	0.0000	0.3320	0.3320
HAC	0.0730	0.6761	1.0000	0.6662	0.6662
AC2O	0.0001	0.0000	0.0000	0.0000	0.0000
KET	0.0002	0.0017	0.0000	0.0017	0.0017
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Total Flow LBMOL/HR	857.4189	142.3810	5.0000	137.3810	137.3810
Total Flow LB/HR	68998.9200	7442.6660	220.2658	7222.4000	7222.4000
Total Flow CUFT/HR	474269.0000	71977.1600	2527.6250	68374.2100	44886.8400
Temperature C	63.5091	34.5313	34.5313	34.5313	50.0000
Pressure ATM	0.8000	0.8000	0.8000	0.8000	1.3000
Vapor Frac	1.0000	1.0000	1.0000	0.9845	1.0000

Table E.6. Material balance for gas-stripped reactor block, streams 16-18.

Stream:	16	17	18
From Block:	HAC-COL	VAM-COL	VAM-COL
To Block:	VAM-COL		
Phase:	LIQUID	LIQUID	LIQUID
Mole Flow LBMOL/HR			
HOAC	0.0000	0.0000	0.0000
EDA	0.0000	0.0000	0.0000
VAM	714.9350	707.8243	7.1107
HAC	0.0571	0.0571	0.0000
AC2O	0.0457	0.0065	0.0393
KET	0.0000	0.0000	0.0000
WATER	0.0000	0.0000	0.0000
Mole Frac			
HOAC	0.0000	0.0000	0.0000
EDA	0.0000	0.0000	0.0000
VAM	0.9999	0.9999	0.9945
HAC	0.0001	0.0001	0.0000
AC2O	0.0001	0.0000	0.0055
KET	0.0000	0.0000	0.0000
WATER	0.0000	0.0000	0.0000
Mass Flow LB/HR			
HOAC	0.0000	0.0000	0.0000
EDA	0.0000	0.0000	0.0000
VAM	61549.0700	60936.9100	612.1630
HAC	2.5173	2.5173	0.0000
AC2O	4.6691	0.6586	4.0105
KET	0.0000	0.0000	0.0000
WATER	0.0000	0.0000	0.0000
Mass Frac			
HOAC	0.0000	0.0000	0.0000
EDA	0.0000	0.0000	0.0000
VAM	0.9999	0.9999	0.9934
HAC	0.0000	0.0000	0.0000
AC2O	0.0001	0.0000	0.0065
KET	0.0000	0.0000	0.0000
WATER	0.0000	0.0000	0.0000
Total Flow LBMOL/HR	715.0378	707.8875	7.1504
Total Flow LB/HR	61556.2500	60940.0500	616.2078
Total Flow CUFT/HR	1129.3410	1109.0310	11.2970
Temperature C	66.3690	61.0603	66.5210
Pressure ATM	0.8000	0.6600	0.8000
Vapor Frac	0.0000	0.0000	0.0000

Table E.7. Gas-stripped reactor specifications.

Tray Type	Sieve
Column Diameter, ft	8.15
Column Height, ft	65.0
Molar Reflux Ratio	1.0
Tray Efficiency	50%
Tray Spacing, ft	2.0
Actual Number of Trays	26
Liquid Holdup in Reactor, ft ³	12,500
Bottoms Flow Rate, lbmol hr ⁻¹	30
Distillate Vapor Fraction	1.0
Pressure Profile (top to bottom), atm	0.8-1.3
Temperature Profile (top to bottom), °C	63.5-123.6
Actual Volume of Reactor, ft ³	16,000
Reactor Diameter, ft	22.9
Reactor Height, ft	52.3

Table E.8. Acetaldehyde recovery column specifications.

Tray Type	Sieve
Column Diameter, ft	5.50
Column Height, ft	34.0
Molar Reflux Ratio	1.90
Tray Efficiency	50%
Tray Spacing, ft	1.5
Actual Number of Trays	14
HAc Recovery in Distillate	99.95%
VAM Recovery in Distillate	3.75%
Distillate Vapor Fraction	1.0
Pressure Profile (top to bottom), atm	0.8-0.8
Temperature Profile (top to bottom), °C	34.5-66.4

Streams 5, 7, and 8 simply represent a circulating reboiler loop for the reactor and column. Acetic acid ($3.5 \text{ lbmol hr}^{-1}$) is introduced in Stream 6 for modeling purposes and is mostly removed in Stream 10. Stream 9 exits the column as a vapor distillate.

Acetaldehyde Recovery Column

Stream 11 enters the HAc recovery column, HAC-COL, from the gas-stripped reactor, containing predominantly VAM and HAc. The acetaldehyde recovery column was designed using the DSTWU shortcut model. Important column specifications are included in Table E.8. An AKT reboiler and a BFM condenser were specified.

Stream 12, the vapor distillate from the acetaldehyde recovery column, passes through a conceptual splitting block (SPLIT2) before being compressed to 1.30 atm at 50°C. This broken recycle stream (15) becomes Stream 3, which feeds MIX1 and returns to the reactor.

Vinyl Acetate Color Column

The bottoms stream from the HAc recovery column (Stream 16) contains high-purity VAM (99.99%_{mass}). These bottoms are then passed through a VAM color column, modeled using a DISTL shortcut model. Important column specifications are contained in Table E.9. An AKT reboiler and BFM condenser were specified.

Ninety-nine percent of the feed to the color column is recovered as Stream 17, which contains 99.99%_{mass} VAM. The bottoms from the color column (Stream 18) contain 99.34% vinyl acetate and most of the remaining acetic anhydride.

Equipment Costs and Utility Usages

Table E.10 includes an equipment list for each column section, as well as rough capital cost estimates (generated using ASPEN) and utility usages. Equipment capital for the overall gas-stripped reactor block is relatively low, with most of the cost in the large reactor and compressor. The electric power required to drive the compressor is relatively low (34.8 hp).

Summary

A working model for the gas-stripped reaction of ketene with acetaldehyde to form vinyl acetate was developed and optimized for VAM production and cost. Equipment capital and utility usage for the process are within reason. Work is currently underway to obtain improved kinetic parameters for the reaction of HAc with Ac_2O to form EDA, and the decomposition of EDA to form HOAc and VAM. Improved kinetic and/or thermodynamic parameters for the mixed-phase reaction of ketene with acetic acid to form acetic anhydride should be obtained.

Table E.9. Vinyl acetate color column specifications.

Tray Type	Sieve
Column Diameter, ft	6.5
Column Height, ft	74.0
Molar Reflux Ratio	0.10
Tray Efficiency	10%
Tray Spacing, ft	2.0
Actual Number of Trays	30
Distillate: Feed	0.99
Pressure Profile (top to bottom), atm	0.63-0.80
Temperature Profile (top to bottom), °C	61.1-66.5

Table E.10. Equipment list and utilities usages.

Section	Equipment Item	Equipment Capital	Utility Type	Utility Usage (MBTU hr ⁻¹)
Gas-Stripped Reactor	Accumulator	\$62,000	—	—
	Column	\$241,800	—	—
	Condenser	\$73,800	Cooling Water	-12.1
	Reactor	\$649,800	—	—
	Reboiler	\$222,700	600 psi Steam	18.5
Acetaldehyde Recovery	Accumulator	\$17,200	—	—
	Column	\$102,000	—	—
	Condenser	\$21,600	Cooling Water	-0.58
	Reboiler	\$67,300	100 psi Steam	10.4
	Recycle Compressor	\$1,133,300	—	—
Vinyl Acetate Color Column	Accumulator	\$51,600	—	—
	Column	\$227,100	—	—
	Condenser	\$74,600	Cooling Water	-10.9
	Reboiler	\$67,600	100 psi Steam	10.6
Net	—	\$3,012,400	—	—

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3. Esterification of Acetaldehyde With Acetic Anhydride (Task 2.2)

Introduction

Historically, the esterification of acetaldehyde with acetic anhydride (see reaction [1]) played a very important role in the generation of vinyl acetate. The Celanese Corporation of America operated a facility for this conversion from 1953 until 1968 in Pampa, TX. (It was ultimately displaced by the current commercially practiced oxidative acetoxylation of ethylene.) The production capacity at this facility in 1964 was estimated to be 50 million lb/yr.¹ Figure E.6 shows a simplified process diagram for the plant, which is described in detail elsewhere.²⁻⁵ Various sources list vinyl acetate yields of 80-100%,^{2,3} with 99.9% purity.⁵

A closer examination of the reaction reveals that the conversion depicted in reaction [1] actually is composed of two reactions, both of which are equilibria. These are shown below:

(The equilibrium constants were obtained from Halcon SD⁶.) The fact these equilibria are unfavorable for the formation of vinyl acetate has always been problematic. Further, as one heats the reaction, despite the favorable equilibrium, reaction [2] has a tendency to reverse quickly, since the very low boiling acetaldehyde is preferentially distilled out of the reaction mixture while there is any trace of catalyst still present. Celanese used large excesses of acetic anhydride to push the equilibria further in favor of EDA to reduce this problem, but this practice required the recycle of large volumes of acetic anhydride.

Prior to the joint research contract, Eastman had conceived a novel approach to improving this process and reduced it to practice on a bench scale. The concept sought to simplify the overall process and increase the per-pass yields by applying principles of reactive distillation similar to those Eastman used to develop its methyl acetate process.⁷⁻⁹ This will be more difficult in the generation of VAM, since it involves more than one equilibrium. Although the literature references give a more thorough discussion of the process, it might be useful to briefly discuss the concept of reactive distillation.

A reactive distillation column is best applied to processes involving two reactants (one of which must be higher boiling than the desired final product) that are undergoing dynamic equilibria. The column consists of two parts, a reaction zone and a separation zone. The two reactants are introduced to the column at different points: the highest boiling reactant (and catalyst if necessary) are introduced at a point above the introduction of lower boiling starting material. Introduction of the higher boiling reactant above the lower boiling component creates a unique component profile in the column. Essentially, this is an inversion of a normal column, in which a

high-boiling component is now richest at a midpoint, not at the base, and a low boiler is now richest in the base, not at the top of the column. As a consequence, as the lower boiling starting material begins to distill up the column, it encounters an increasingly rich concentration of the higher boiling starting material. Conversely, the higher boiling starting material sees an increasing concentration of the more volatile reactant as it descends the column, forcing its consumption to rise: thus the consumption of both components is actually enhanced by the process.

This effectively forces the equilibrium toward the product side without the use of large excesses of one starting material. (In Eastman Chemical Company's methyl acetate, the acetic acid and methanol components are added in balance.) The product(s) distills into the refinement zone where the product(s) is distilled from the higher boiling starting material. (Remember that the desired product must boil at a point lower than the highest boiling starting material.)

In their application to the esterification of acetaldehyde with acetic anhydride, Eastman Chemical Company added the acetic anhydride to the mid-point of a distillation column, along with an acid catalyst, and added the other reactant, acetaldehyde, to the base. If one examines the different boiling points of the materials, which are listed below, the consequences of this mode of operation become apparent. The use of large excesses of acetic anhydride is circumvented since, as acetaldehyde rises up the column, it will encounter a continuously enriched acetic anhydride environment, effectively shifting equilibrium [2] toward the formation of EDA without requiring the use of huge excesses of acetic anhydride. The EDA, being the highest boiling component in the reaction mixture, descends the column. In the second reaction, the cracking of EDA to vinyl acetate and acetic acid (equilibrium [3]), the equilibrium is independent of acetic anhydride, so the vinyl acetate and acetic acid are eventually distilled from the reaction zone. We have illustrated this operation in Figure E.7.

<u>Component</u>	<u>Boiling Point(°C)</u>
Acetaldehyde	19
Vinyl Acetate	72-73
Acetic Acid	118-119
Acetic Anhydride	140
Ethylidene Diacetate	167

Work conducted prior to the contract did indicate that, due to the volatility of acetaldehyde, we would be hard pressed to operate the reactive distillation without purging some excess acetaldehyde. Further, to enhance the concentration within the reactive section and reduce the amount of acetaldehyde distilled overhead, it would be best to operate under moderate pressure. The demonstration column used in the work preceding the contract was operated for extended periods over two pressure conditions and was used as a source of "kinetic" data to further develop the process.

Figure E.7.
Idealized Reactive Distillation for the Conversion of Acetaldehyde and Acetic Anhydride to Vinyl Acetate and Acetic Acid

Within the term of the contract, Eastman Chemical Company continued to optimize the reactive distillation using a series of computer simulation techniques that utilized the data obtained from their bench-scale unit before they entered the joint research program. There were multiple iterations of the model, and we have included the last rendition in the section below.

One important difference between the Eastman Chemical Company process and the earlier Celanese process emerged from this optimization. To reduce column sizes, and thus the capital investment, Eastman Chemical Company had to move toward increasingly larger acetaldehyde purges from the reactive distillation column as it drove toward complete conversion of the acetic anhydride. Ultimately, the Eastman Chemical Company process involved the use of excess acetaldehyde, rather than the large excess of acetic anhydride used by Celanese.

Development of the Process Model

Prior Work (Background). As mentioned in the introduction, the source of Eastman Chemical Company's initial data for the optimization was the bench-scale unit operated prior to the contract and the equilibrium data from Halcon SD. Further, several models were developed prior to the joint project, although they were primarily developed for guidance and were not completely optimized. The important operating parameters developed in this earlier work are included in

Table E.11 and represent the starting point for the latest process model. Details for the latest model appear in the following section.

Current Process Model. The current process model uses three units of operation, the reactive distillation column, an acetaldehyde recovery column, and a vinyl acetate recovery (purification) column. Each unit of operation is discussed in detail.

Reactive Distillation Column

Figure E.8 shows the current process model flowsheet for the reactive distillation block. The material balance for the model is contained in Tables E.12-E.14. Stream 1, containing 100% HAc, is fed to mixing block MIX1, in which it merges with recycle HAc (Stream 12) to form Stream 3. Stream 3 feeds the reactive distillation column, RX-DST, at the reboiler. It should be noted that Stream 1 contains an extra 5 lbmol hr⁻¹ of HAc for modeling purposes (this quantity of HAc is purged in Stream 11).

Stream 2, containing an essentially stoichiometric amount of Ac₂O compared to the HAc in Stream 1, merges with Stream 6 in mixing block MIX2. This combined stream (4) enters the reactive distillation column 10 theoretical stages above the reboiler.

The reactive distillation column, RX-DST, was modeled using a RADFRAC column model. The tower is 35 theoretical stages tall, with the bottom 10 theoretical stages specified as the reactive portion of the column. Reactions were assumed to occur in the liquid phase, using rough experimental kinetic data developed by Zoeller, Lane, Cwirko, Fuller, and Barnicki for an invention report.⁹ Important column specifications are included in Table E.15. The pressure within the column ranged from 3.64 to 4.14 atm (top to bottom), and the temperature ranged from 74.1 to 183.1°C. The bottoms stream (5) flows to a splitting block (SPLIT1) and is split into Streams 6 and 7. Stream 7 is a conceptual purge stream with zero flow. Stream 6 joins Stream 2 in mixing block MIX2. For the actual process, this reboil/fresh feed loop would be the mechanism by which the catalyst is circulated in the reactive portion. The molar ratio of acetaldehyde to acetic anhydride feeding the column is roughly 3.9:1. An AKT kettle reboiler was specified for the column, constructed with a SS316 shell and titanium tubes. All other column components were assumed to be SS316. A two-pass shell BFM condenser was specified.

Acetaldehyde Recovery Column

The fully-condensed distillate from the reactive distillation column (Stream 8) feeds the acetaldehyde recovery column, HAC-COL. The distillate contains HAc, HOAc, and VAM. HAC-COL was modeled using the DSTWU shortcut model. Important column specifications are included in Table E.16. The column was assumed to operate at a roughly constant pressure of 3.64 atm. At this pressure, acetaldehyde can be recycled as a liquid without the use of refrigerant. The reflux ratio was defined to be 20% greater than the minimum reflux ratio. Condenser and reboiler input specifications were identical to those in the reactive distillation column, with the exception of SS316 tubes in the reboiler. SS316 was used for all equipment items.

Stream 9, the liquid distillate from HAC-COL, is cooled in a heat exchanger (COOLER), and emerges as Stream 10. This stream is predominantly acetaldehyde, with trace vinyl acetate present. Stream 10 passes through a conceptual splitting block (HACSPLIT) and is recycled as Stream 12 to MIX1.

Vinyl Acetate Recovery Column

Stream 13 emerges from the bottoms of HAC-COL and contains mostly VAM and HOAc. This stream feeds the vinyl acetate recovery column, VAM-COL. VAM-COL was modeled using the DSTWU shortcut model. Important column specifications are included in Table E.17. The column operates at 3.00 atm, with a reflux ratio 20% larger than the minimum. The bottoms product, 99+% HOAc, emerges as Stream 14 (which can be hydrogenated to produce the HAC required for the reactive distillation). High-purity liquid VAM exits the column as the distillate (Stream 15) in roughly stoichiometric yields.

Equipment Costs and Utility Usages

Table E.18 includes an equipment list for each column, as well as rough capital cost estimates (generated using ASPEN) and utility usages. The high utility usages for the reactive distillation column reboiler and condenser are somewhat alarming. These high usages are a result of moving essentially all of the material entering the column out as an overhead stream, and appear to be required with the current design.

Process Optimization. In an effort to improve both the performance and costs of the reactive distillation block, the effects of a number of variables were studied. These variables included the locations of the feed stages, volume of liquid holdup in the reactive portion, the number of trays for both the reactive and non-reactive portions, bottoms flow rate, reflux ratio, tray spacing, and the HAC recycle flow rate (hence the ratio of acetaldehyde to acetic anhydride in the column). The most important variables appear to be the reflux ratio and the size of the acetaldehyde recycle loop.

Reflux ratio (RR) has a considerable effect on the diameter of the reactive distillation column. Figure E.3 shows the impact of reflux ratio and total (fresh + recycle) acetaldehyde fed to the reactive distillation column on the column diameter. The initial model had a reflux ratio of 8.0, requiring column diameters of 20-25 feet under the flow conditions (HAc recycle flow rates) necessary to achieve high vinyl acetate yields. Sensitivity studies revealed that a reflux ratio of 2.0 requires columns only 10-15 feet in diameter under the necessary conditions.

Figure E.4 illustrates the dependence of vinyl acetate production on the acetaldehyde feed rate (fresh + recycle) and reflux ratio. With a reflux ratio of 8.0, only 1000-1200 lbmol hr⁻¹ of HAC is required to achieve quantitative yields of VAM (715 lbmol hr⁻¹). With a reflux ratio of 2.0, quantitative yields of VAM can be achieved with HAC flows of 2800-3000 lbmol hr⁻¹. Lowering the reflux ratio to 1.0 requires much larger HAC flows. It can therefore be seen from Figures E.9 and E.10 that optimum conditions for high vinyl acetate production and low column diameter exist with a reflux ratio of 2.0 and a total acetaldehyde feed of 2800 lbmol hr⁻¹.

Economic Comparison. The positive impacts of this optimization work are readily seen by an equipment capital cost comparison for the initial and optimized versions of the reactive distillation model (Figure E.11). The cost of the acetaldehyde recovery column has increased from roughly \$500,000 to \$1,000,000 due to increases in the size of the acetaldehyde recycle loop. The benefits of the modifications are readily seen in the 40% capital reduction for the reactive distillation column. There was little change in the cost of the vinyl acetate cleanup column. Overall, there was a 26% equipment capital reduction for the reactive distillation block due to modifications in the reflux ratio and size of the HAc recycle loop. In addition, the utility capital has been reduced by roughly 10%.

Summary. A reactive distillation process model for the synthesis of vinyl acetate has been developed, optimized, and costed using ASPEN 9.2 Model Manager. Significant improvements in equipment capital costs have been made through modifications of the reflux ratio for the reactive distillation column and the size of the acetaldehyde recycle loop.

Table E.11

Important Parameters for Reactive Distillation Model (Reactive Distillation Column) developed by Scott Barnicki, Fall 1996

Tray Type	Valve
Column Diameter, ft	20.3
Column Height, ft	200
Reflux Ratio	8.0
Tray Efficiency	50%
Tray Spacing, ft	2.79
Actual Number of Trays	66
Liquid Holdup in Reactive Portion, ft ³	233.3
Percent of Space Between Trays Occupied by Liquid Holdup	25.8%
Bottoms Flow, lbmol hr ⁻¹	30.0
Distillate Vapor Fraction	0.0

Table E.12. Material balance for optimized reactive distillation model, streams 1-5.

Stream:	1	2	3	4	5
From Block:			MIX1	MIX2	RX-DST
To Block:	MIX1	MIX2	RX-DST	RX-DST	SPLIT1
Phase:	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
Mole Flow LBMOL/HR					
HOAC	0.0000	0.0000	0.0000	1.4633	1.4633
EDA	0.0000	0.0000	0.0000	22.6133	22.6133
VAM	0.0000	0.0000	7.2106	0.3381	0.3381
HAC	720.0000	0.0000	2865.4260	1.0305	1.0305
AC2O	0.0000	715.0000	0.0000	719.5549	4.5549
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Mole Frac					
HOAC	0.0000	0.0000	0.0000	0.0020	0.0488
EDA	0.0000	0.0000	0.0000	0.0304	0.7538
VAM	0.0000	0.0000	0.0025	0.0005	0.0113
HAC	1.0000	0.0000	0.9975	0.0014	0.0344
AC2O	0.0000	1.0000	0.0000	0.9658	0.1518
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Mass Flow LB/HR					
HOAC	0.0000	0.0000	0.0000	87.8739	87.8739
EDA	0.0000	0.0000	0.0000	3304.7780	3304.7780
VAM	0.0000	0.0000	620.7659	29.1087	29.1087
HAC	31718.2800	0.0000	126231.0000	45.3973	45.3973
AC2O	0.0000	72994.2300	0.0000	73459.2400	465.0067
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Mass Frac					
HOAC	0.0000	0.0000	0.0000	0.0011	0.0223
EDA	0.0000	0.0000	0.0000	0.0430	0.8404
VAM	0.0000	0.0000	0.0049	0.0004	0.0074
HAC	1.0000	0.0000	0.9951	0.0006	0.0115
AC2O	0.0000	1.0000	0.0000	0.9549	0.1183
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Total Flow LBMOL/HR	720.0000	715.0000	2872.6370	745.0001	30.0001
Total Flow LB/HR	31718.2800	72994.2300	126852.0000	76926.4000	3932.1650
Total Flow CUFT/HR	680.2406	1105.7340	2718.2280	1177.4740	72.4370
Temperature C	45.0000	40.0000	45.0000	48.5329	183.1048
Pressure ATM	4.2000	4.0000	3.6400	4.2000	4.1400
Vapor Frac	0.0000	0.0000	0.0000	0.0000	0.0000

Table E.13. Material balance for optimized reactive distillation model, streams 6-10.

Stream:	6	7	8	9	10
From Block:	SPLIT1	SPLIT1	RX-DST	HAC-COL	COOLER
To Block:	MIX2		HAC-COL	COOLER	HACSPLIT
Phase:	MIXED	MISSING	LIQUID	LIQUID	LIQUID
Mole Flow LBMOL/HR					
HOAC	1.4633	0.0000	713.8514	0.0000	0.0000
EDA	22.6133	0.0000	0.0000	0.0000	0.0000
VAM	0.3381	0.0000	721.0619	7.2106	7.2106
HAC	1.0305	0.0000	2151.5750	2150.4990	2150.4990
AC2O	4.5549	0.0000	1.1487	0.0000	0.0000
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Mole Frac					
HOAC	0.0488	0.0000	0.1990	0.0000	0.0000
EDA	0.7538	0.0000	0.0000	0.0000	0.0000
VAM	0.0113	0.0000	0.2010	0.0033	0.0033
HAC	0.0344	0.0000	0.5997	0.9967	0.9967
AC2O	0.1518	0.0000	0.0003	0.0000	0.0000
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Mass Flow LB/HR					
HOAC	87.8739	0.0000	42868.6100	0.0000	0.0000
EDA	3304.7780	0.0000	0.0000	0.0000	0.0000
VAM	29.1087	0.0000	62076.5400	620.7654	620.7654
HAC	45.3973	0.0000	94783.6700	94736.2800	94736.2800
AC2O	465.0067	0.0000	117.2738	0.0000	0.0000
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Mass Frac					
HOAC	0.0223		0.2145	0.0000	0.0000
EDA	0.8404		0.0000	0.0000	0.0000
VAM	0.0074		0.3106	0.0065	0.0065
HAC	0.0115		0.4743	0.9935	0.9935
AC2O	0.1183		0.0006	0.0000	0.0000
WATER	0.0000		0.0000	0.0000	0.0000
Total Flow LBMOL/HR	30.0001	0.0000	3587.6370	2157.7100	2157.7100
Total Flow LB/HR	3932.1650	0.0000	199846.0000	95357.0500	95357.0500
Total Flow CUFT/HR	72.4536	0.0000	4005.1050	2098.9430	2042.7800
Temperature C	183.1066		74.0784	58.8773	45.0000
Pressure ATM	4.1400		3.6400	3.6400	3.6400
Vapor Frac	0.0000		0.0000	0.0000	0.0000

Table E.14. Material balance for optimized reactive distillation model, streams 11-15.

Stream:	11	12	13	14	15
From Block:	HACSPLIT	HACSPLIT	HAC-COL	VAM-COL	VAM-COL
To Block:		MIX1	VAM-COL		
Phase:	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
Mole Flow LBMOL/HR					
HOAC	0.0000	0.0000	713.8514	713.8157	0.0357
EDA	0.0000	0.0000	0.0000	0.0000	0.0000
VAM	0.0000	7.2106	713.8513	0.7139	713.1375
HAC	5.0000	2145.4990	1.0758	0.0000	1.0758
AC2O	0.0000	0.0000	1.1487	1.1487	0.0000
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Mole Frac					
HOAC	0.0000	0.0000	0.4992	0.9974	0.0000
EDA	0.0000	0.0000	0.0000	0.0000	0.0000
VAM	0.0000	0.0033	0.4992	0.0010	0.9984
HAC	1.0000	0.9967	0.0008	0.0000	0.0015
AC2O	0.0000	0.0000	0.0008	0.0016	0.0000
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Mass Flow LB/HR					
HOAC	0.0000	0.0000	42868.6100	42866.4600	2.1434
EDA	0.0000	0.0000	0.0000	0.0000	0.0000
VAM	0.0000	620.7654	61455.7700	61.4558	61394.3200
HAC	220.2658	94516.0200	47.3918	0.0000	47.3918
AC2O	0.0000	0.0000	117.2738	117.2735	0.0003
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Mass Frac					
HOAC	0.0000	0.0000	0.4103	0.9958	0.0000
EDA	0.0000	0.0000	0.0000	0.0000	0.0000
VAM	0.0000	0.0065	0.5882	0.0014	0.9992
HAC	1.0000	0.9935	0.0005	0.0000	0.0008
AC2O	0.0000	0.0000	0.0011	0.0027	0.0000
WATER	0.0000	0.0000	0.0000	0.0000	0.0000
Total Flow LBMOL/HR	5.0000	2152.7100	1429.9270	715.6783	714.2489
Total Flow LB/HR	220.2658	95136.7800	104489.0000	43045.1900	61443.8500
Total Flow CUFT/HR	4.7239	2038.0560	2005.9690	777.0761	1210.9090
Temperature C	45.0000	45.0000	128.9385	158.2643	108.5060
Pressure ATM	3.6400	3.6400	3.6400	3.0000	3.0000
Vapor Frac	0.0000	0.0000	0.0000	0.0000	0.0000

Table E.15

Optimized Reactive Distillation Column Specifications

Tray Type	Valve
Column Diameter, ft	14.6
Column Height, ft	180
Reflux Ratio	2.0
Tray Efficiency	50%
Tray Spacing, ft	2.50
Actual Number of Trays	66
Liquid Holdup in Reactive Portion, ft ³	150
Percent of Space Between Trays Occupied by Liquid Holdup	35.8%
Bottoms Flow, lbmol hr ⁻¹	30.0
Distillate Vapor Fraction	0.0

Table E.16

Optimized Acetaldehyde Recovery Column Specifications

Tray Type	Sieve
Column Diameter, ft	10.0
Column Height, ft	151.0
Reflux Ratio	0.53
Tray Efficiency	50%
Tray Spacing, ft	3.00
Actual Number of Trays	45
HAc Recovery in Distillate	99.95%
VAM Recovery in Distillate	1.00%
Distillate Vapor Fraction	0.0

Table E.17

Optimized Vinyl Acetate Recovery Column Specifications

Tray Type	Sieve
Column Diameter, ft	7.0
Column Height, ft	116.0
Reflux Ratio	0.75
Tray Efficiency	50%
Tray Spacing, ft	2.00
Actual Number of Trays	51
VAM Recovery in Distillate	99.90%
HOAc Recovery in Distillate	0.0050%
Distillate Vapor Fraction	0.0

Table E.18

Equipment Capital and Utility Usage

Section	Equipment Item	Equipment Capital	Utility Type	Utility Usage (MBTU hr ⁻¹)
Reactive Distillation	Accumulator	\$163,600	—	—
	Column	\$1,372,600	—	—
	Condenser	\$299,200	Cooling Water	-130
	Reboiler	\$1,779,600	600 psi Steam	140
Acetaldehyde Recovery	Accumulator	\$63,400	—	—
	Column	\$539,300	—	—
	Condenser	\$161,300	Cooling Water	-32
	Reboiler	\$212,500	100 psi Steam	36
	Recycle Cooler	\$25,100	Cooling Water	-2.1
Vinyl Acetate Recovery	Accumulator	\$44,900	—	—
	Column	\$316,900	—	—
	Condenser	\$48,600	Cooling Water	-17
	Reboiler	\$306,600	100 psi Steam	17
	Product Tank	\$1,300,000		
Net	—	\$6,633,600	—	—

Figure F.6. Celanese process for vinyl acetate synthesis [8].

Figure E.9. Dependence of column diameter on total acetaldehyde fed to the reactive distillation column and reflux ratio.

Figure E.10. Dependence of vinyl acetate production on total acetaldehyde fed to the reactive distillation column and reflux ratio.

Figure E.11. Equipment capital cost comparison for original and optimized reactive distillation process models.

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Appendix
for
Section E.

VAM Generation - Large Scale Reactor**Diketene Method:** Tracy Zoll, Sept. 1996 - 1:1 ketene:AcH**Run No.:** 1

<u>Initial Charge:</u>	<u>Wt</u>	<u>Moles</u>
pTsOH.H ₂ O	30.2 g	0.159
Ac ₂ O(total added)	713.7 g	7.00
EDA	0 g	0.00
tBHQ	0.2 g	
total	744.10 g	

Feed Rates:

Ketene:	1.09	mol/hr
AcH:	1.07	mol/hr

Total Time Run 19.6 Hours
Total Product Produced 1052.6 g

BASE:**GC Analysis**

<u>Wt</u>	<u>AcH</u>	<u>VAM</u>	<u>AcOH</u>	<u>Ac₂O</u>	<u>EDA</u>
490.9	0.2%	0.1%	0.0%	50%	22%

Minimum 27% Tar**Material Balances:**

	<u>Moles Added</u>	<u>Moles Recovered</u>	<u>% Recovery</u>	<u>Conversion</u>		<u>Selectivity to VAM (%)</u>
Acetate Equivalents:	35.3	30.3	86%	57%	(ketene)	55%
AcH Equivalents:	21.0	15.9	76%	59%		53%

VAM Generation - Large Scale Reactor

Diketene Method: Tracy Zoll, Sept 1996 - 1:1 ketene:AcH

Run No.: 1

Initial Charge:	Wt	Moles
pTsOH H ₂ O	30.2 g	0.159
Ac ₂ O (total added)	713.7 g	7.00
EDA	0 g	0.00
tBHQ	0.2 g	
total	744.10 g	

Feed Rates:

Ketene:	1.09 mol/hr
AcH:	1.07 mol/hr

Methanol Scrubber:

Day	Hrs. On-Line	Sample Number	Dilution Factors		Total Wt.	GC Analysis			Mole Equiv.	
			Sample	MeOH Diluent		MeOAc	AcH	MeCH(OMe) ₂	AcH	Ketene
1	6.17	1	0.3254	0.7388	323.76	7.9	2.2	0	0.5294	1.1304
		2	0.5287	0.5377	321.89	9.59	3	0	0.4427	0.8414
		3	0.4947	0.5217	331.9	9.745	3.455	0	0.5355	0.8980
		4	0.5217	0.5369	306.43	7.41	2.723	0	0.3848	0.6226
2	6.67	1	0.5287	0.5377	317.85	7.639	4.393	0	0.6401	0.6618
		2	0.5045	0.508	325.36	7.926	4.066	0	0.6034	0.6994
		3	0.513	0.5307	295.96	6.316	2.538	0	0.3473	0.5139
		4	0.336	0.6909	351.77	6.147	2.961	0	0.7235	0.8931
3	6.75	1	0.5125	0.4996	300.37	7.493	3.111	0	0.4194	0.6006
		2	0.5251	0.5322	285.98	6.645	2.448	0	0.3204	0.5171
		3	0.5168	0.5357	299.16	6.203	2.041	0	0.2826	0.5107
		4	0.5218	0.5293	327.07	8.162	3.608	0	0.5402	0.7267
		5	0.5346	0.5202	309.64	6.98	3.45	0	0.4790	0.5763
Totals	19.59								6.2483	9.1920

Liquid Take-Off

Day	Sample Number	Wt	GC Analysis					Mole Equivalents				
			AcH	VAM	AcOH	Ac ₂ O	EDA	AcH	VAM	AcOH	Ac ₂ O	EDA
1	1	143.81	4.34	19.52	8.98	67.39	0.5	0.142	0.326	0.215	0.950	0.005
	2	159.31	8.68	70.65	1.366	23.75	0	0.314	1.309	0.036	0.371	0.000
2	1	118.59	12.66	64.72	0.92	24.86	0	0.341	0.892	0.018	0.289	0.000
	2	125.58	12	64.66	1.12	25.98	0	0.342	0.944	0.023	0.320	0.000
	3	91.12	10.93	60.86	1.92	29.58	0	0.226	0.645	0.029	0.264	0.000
3	1	135.73	8.61	49.99	2.02	42.59	0	0.266	0.789	0.046	0.567	0.000
	2	111.76	7.99	45.7	1.33	48.43	0	0.203	0.594	0.025	0.531	0.000
	3	166.67	10.67	58.18	1.37	34.16	0	0.404	1.128	0.038	0.558	0.000
Totals		1052.57						2.239	6.627	0.431	3.850	0.005

BASE:

GC Analysis					
Wt	AcH	VAM	AcOH	Ac2O	EDA
490.9	0.22	0.12	0	50.312	22.242

Mole Equivalents

AcH	VAM	AcOH	Ac2O	EDA
0.025	0.007	0.000	2.421	0.748
Net :				
8.512	6.634	0.113	-0.567	0.753

(accounts for water in catalyst)

Material Balances:

	Moles Added	Moles Recovered	% Recovery	Conversion	Selectivity to VAM (%)
Acetate Equivalents:	35.35	30.30	85.7%	57%	(ketene) 55%
AcH Equivalents:	20.96	15.90	75.8%	59%	53%

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Methanol Scrubber
Run #1

Liquid Take-Off
Run #1

VAM Generation - Large Scale Reactor**Diketene Method:** Tracy Zoll, Sept. 1996 - High Acetaldehyde**Run No.:** 2

<u>Initial Charge:</u>	<u>Wt</u>	<u>Moles</u>
pTsOH.H ₂ O	30.4 g	0.160
Ac ₂ O(total added)	991.9 g	9.72
EDA	0 g	0.00
tBHQ	0.2 g	
total	1022.50 g	

Feed Rates:

Ketene:	1.17	mol/hr
AcH:	1.37	mol/hr

Total Time Run 16.5 Hours**Total Product Produced** 1482.8 g**BASE:****GC Analysis**

<u>Wt</u>	<u>AcH</u>	<u>VAM</u>	<u>AcOH</u>	<u>Ac₂O</u>	<u>EDA</u>
564.8	0.2%	0.0%	0.0%	25%	41%

Minimum 33% Tar**Material Balances:**

	<u>Moles Added</u>	<u>Moles Recovered</u>	<u>% Recovery</u>	<u>Conversion</u>		<u>Selectivity to VAM (%)</u>
Acetate Equivalents:	38.8	27.9	72%	85%	(ketene)	42%
AcH Equivalents:	22.6	17.4	77%	61%		50%

VAM Generation - Large Scale Reactor

Diketene Method: Tracy Zoll, Sept. 1996 - High Acetaldehyde

Run No.: 2

Initial Charge:	Wt	Moles
pTsOH.H ₂ O	30.4 g	0.160
Ac ₂ O(total added)	991.9 g	9.72
EDA	0 g	0.00
IBHQ	0.2 g	
total	1022.50 g	

Feed Rates:

Ketene:	1.17	mol/hr
AcH:	1.37	mol/hr

Methanol Scrubber:

Day	Hrs. On-Line	Sample Number	(Dilution Factors)		Total Wt.	GC Analysis			Mole Equiv.	
			Sample	MeOH Diluent		MeOAc	AcH	MeCH(OMe) ₂	AcH	Ketene
1	5	1	0.5451	0.4962	262.97	2.94	2.29	0	0.2615	0.1996
		2	0.541	0.5217	322.1	8.91	4.92	0	0.7075	0.7618
		3	0.5155	0.5186	283.32	4.56	2.96	0	0.3823	0.3502
		4	0.5368	0.5306	291.42	5.25	3.63	0	0.4781	0.4111
2	7.25	1	0.5423	0.5207	303.62	5.05	7.08	0	0.9576	0.4061
		2	0.5222	0.4903	297.14	4.68	4.77	0	0.6246	0.3644
		3	0.5205	0.492	288.7	3.83	4.05	0	0.5169	0.2907
		4	0.541	0.5196	279.58	2.12	3.56	0	0.4435	0.1570
3	4.27	1	0.518	0.5167	243.31	0.206	0	0	0.0000	0.0135
		2	0.5104	0.5167	284.73	0.294	0.59	0.229	0.0914	0.0228

Totals 16.52

4.4634 2.9772

Liquid Take-Off

Day	Sample Number	Wt	GC Analysis					Mole Equivalents				
			AcH	VAM	AcOH	Ac ₂ O	EDA	AcH	VAM	AcOH	Ac ₂ O	EDA
1	1	307.34	8.98	27.24	3.99	56.62	0.33	0.627	0.973	0.204	1.706	0.007
	2	257.67	11.42	36.11	2.5	49.47	0	0.669	1.082	0.107	1.250	0.000
2	1	233.68	14.15	46.3	2.51	38.79	0	0.751	1.258	0.098	0.889	0.000
	2	241.1	15.36	45.87	1.42	38.53	0	0.842	1.286	0.057	0.911	0.000
	3	243.64	18.14	43.9	1.88	37.16	0	1.004	1.244	0.076	0.888	0.000
3	1	32.98	21.36	66.91	1.69	0.566	0	0.160	0.257	0.009	0.002	0.000
	2	166.38	9.9	41.44	7.38	0.131	0	0.374	0.802	0.205	0.002	0.000
Totals		1482.79						4.428	6.901	0.757	5.647	0.007

BASE:

GC Analysis					
Wt	AcH	VAM	AcQH	Ac2O	EDA
564.8	0.17	0	0	25.108	41.249

Mole Equivalents

AcH	VAM	AcQH	Ac2O	EDA
0.022	0.000	0.000	1.390	1.596

Net :

8.913	6.901	0.437	-2.528	1.603
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(accounts for water in catalyst)

Material Balances:

	Moles Added	Moles Recovered	% Recovery	Conversion	Selectivity to VAM (%)
Acetate Equivalents:	38.78	27.91	72.0%	84.597%	(ketene) 42.21%
AcH Equivalents:	22.63	17.42	77.0%	60.62%	50.31%

Methanol Scrubber
Run #2

Liquid Take-Off
Run #2

VAM Generation - Large Scale Reactor

Diketene Method: Tracy Zoll, Oct. 1996 - High ketene

Run No.: 3

<u>Initial Charge:</u>	<u>Wt</u>	<u>Moles</u>
pTsOH.H ₂ O	30.91 g	0.163
Ac ₂ O(total added)	980.49 g	9.61
EDA	0 g	0.00
tBHQ	0.2 g	
total	1011.60 g	

Feed Rates:

Ketene:	0.92	mol/hr
AcH:	0.69	mol/hr

Total Time Run 17.2 Hours
Total Product Produced 1007.2 g

BASE:GC Analysis

<u>Wt</u>	<u>AcH</u>	<u>VAM</u>	<u>AcOH</u>	<u>Ac₂O</u>	<u>EDA</u>
585.36	0.4%	1.0%	27%	32%	17%

Minimum 23% Tar

Material Balances:

	<u>Moles Added</u>	<u>Moles Recovered</u>	<u>% Recovery</u>	<u>Conversion</u>		<u>Selectivity to VAM (%)</u>
Acetate Equivalents:	35.0	28.9	82%	63%	(ketene)	45%
AcH Equivalents:	11.9	10.1	85%	59%		64%

VAM Generation - Large Scale Reactor

Diketene Method: Tracy Zoll, Oct. 1996 - High ketene

Run No.: 3

Initial Charge:

	Wt	Moles
pTsOH H2O	30.91 g	0.163
Ac2O(total added)	980.49 g	9.61
EDA	0 g	0.00
IBHQ	0.2 g	
total	1011.60 g	

Feed Rates:

Ketene	0.92 mol/hr
AcH	0.69 mol/hr

Methanol Scrubber:

Day	Hrs. On-Line	Sample Number	(Dilution Factors)		Total Wt.	GC Analysis			Mole Equiv.	
			Sample	MeOH Diluent		MeOAc	AcH	MeCH(OMe)2	AcH	Ketene
1	5.5	1	0.5167	0.5059	283.55	8.28	1.39	0	0.1773	0.6279
		2	0.5093	0.5017	302.63	10.86	2.03	0	0.2772	0.8816
		3	0.502	0.5125	338.7	13.49	3.52	0	0.5476	1.2478
2	6.5	1	0.5078	0.503	296	7.84	3.31	0	0.4432	0.6242
		2	0.5252	0.5427	326.2	9.64	3.52	0	0.5306	0.8640
		3	0.5267	0.5164	309.54	6.82	3.05	0	0.4249	0.5650
3	5.2	1	0.5068	0.5159	286.26	4.83	3.26	0	0.4280	0.3770
		2	0.501	0.5174	291.2	5.72	3.2	0	0.4305	0.4575
		3	0.5076	0.5047	267.89	3.11	1.77	0	0.2149	0.2245

Totals 17.2

3.4742 5.8697

Liquid Take-Off

Day	Sample Number	Wt	GC Analysis					Mole Equivalents				
			AcH	VAM	AcOH	Ac2O	EDA	AcH	VAM	AcOH	Ac2O	EDA
1	1	168.39	2.56	8.02	7.25	76.2	0.71	0.098	0.157	0.203	1.258	0.008
	2	165.71	4.45	21.9	3.01	67.62	0.23	0.168	0.422	0.083	1.099	0.003
	3	186.45	5.67	26.48	2.26	63.76	0.24	0.240	0.574	0.070	1.165	0.003
2	1	168.05	6.57	52.44	1.93	41.8	0	0.251	1.025	0.054	0.689	0.000
	2	110.37	7.64	53.7	2.18	39.65	0	0.192	0.689	0.040	0.429	0.000
3	1	159.57	8.39	61.2	2.29	28.05	0	0.304	1.136	0.061	0.439	0.000
	2	48.7	11.07	66.39	1.53	23.53	0	0.123	0.376	0.012	0.112	0.000
Totals		1007.24						0.000	0.000	0.000	0.000	0.000
								1.375	4.378	0.524	5.191	0.014

BASE:

GC Analysis					
Wt	AcH	VAM	AcOH	Ac2O	EDA
585.36	0.39	0.98	26.66	31.52	17.34

Mole Equivalents

	AcH	VAM	AcOH	Ac2O	EDA
	0.052	0.067	2.601	1.809	0.695
Net :	4.901	4.445	2.800	-2.450	0.709
(accounts for water in catalyst)					

Material Balances:

	Moles Added	Moles Recovered	% Recovery	Conversion	Selectivity to VAM (%)
Acetate Equivalents:	35.05	28.86	82.3%	62.91%	(ketene) 44.66%
AcH Equivalents:	11.87	10.06	84.7%	58.70%	63.81%

Methanol Scrubber
Run #3

Liquid Take-Off Run #3

VAM Generation - Large Scale Reactor**Diketene Method:** Tracy Zoll, Oct. 1996 - 1:1 ketene:AcH**Run No.:** 4

<u>Initial Charge:</u>	<u>Wt</u>	<u>Moles</u>
Methanesulfonic Acid	81.96 g	0.853
Ac2O(total added)	594.7 g	5.83
EDA	0 g	0.00
tBHQ	0.2 g	
total	676.86 g	

Feed Rates:

Ketene:	0.95	mol/hr
AcH:	1.07	mol/hr

Total Time Run 11.3 Hours**Total Product Produced** 826.3 g**BASE:****GC Analysis**

<u>Wt</u>	<u>AcH</u>	<u>VAM</u>	<u>AcOH</u>	<u>Ac2O</u>	<u>EDA</u>
562.4	0.2%	0.1%	10%	25%	59%

Minimum 6% Tar**Material Balances:**

	<u>Moles Added</u>	<u>Moles Recovered</u>	<u>% Recovery</u>	<u>Conversion</u>	<u>Selectivity to VAM (%)</u>
Acetate Equivalents:	22.4	20.4	91%	91%	(ketene) 38%
AcH Equivalents:	12.1	8.8	77%	72%	42%

VAM Generation - Large Scale Reactor

Diketene Method: Tracy Zoll, Oct. 1996 - 1:1 ketene:AcH

Run No.: 1

Initial Charge:	Wt	Moles
Methanesulfonic Acid	81.96 g	0.853
Ac2O(total added)	594.7 g	5.83
EDA	0 g	0.00
tBHQ	0.2 g	
total	676.86 g	

Feed Rates:

Ketene:	0.95	mol/hr
AcH:	1.07	mol/hr

Methanol Scrubber:

Day	Hrs. On-Line	Sample Number	(Dilution Factors)		Total Wt.	GC Analysis			Mole Equiv.	
			Sample	MeOH Diluent		MeOAc	AcH	MeCH(OMe)2	AcH	Ketene
1	5.58	1	0.5	0.53	291.7	5.101	3.039	0	0.4150	0.4142
		2	0.5	0.52	310.58	5.74	3.56	0	0.5126	0.4915
		3	0.5	0.53	242.02	0.383	0.245	0	0.0278	0.0258
2	5.75	1	0.5	0.52	324.62	0.433	0.553	18.878	1.4723	0.0387
Totals	11.33								2.4277	0.9702

Liquid Take-Off

Day	Sample Number	Wt	GC Analysis					Mole Equivalents				
			AcH	VAM	AcOH	Ac2O	EDA	AcH	VAM	AcOH	Ac2O	EDA
1	1	154.61	3.03	34.45	30.7	27.14	0.34	0.106	0.619	0.791	0.411	0.004
	2	185.55	6.76	91.05	1.18	4.017	0	0.285	1.964	0.036	0.073	0.000
2	1	271.56	5.1	21.03	53.2	14.48	0.1	0.315	0.664	2.408	0.386	0.002
	2	214.62	3.88	18.72	64.25	3.677	0.11	0.189	0.467	2.298	0.077	0.002
Totals		826.34						0.896	3.715	5.534	0.947	0.007

BASE:

GC Analysis					
Wt	AcH	VAM	AcOH	Ac2O	EDA
562.4	0.24	0.09	9.96	25.174	59.31

Mole Equivalents

AcH	VAM	AcOH	Ac2O	EDA
0.031	0.006	0.934	1.388	2.285

Net :

3.354	3.721	4.761	-2.642	2.292
(accounts for water in catalyst)				

Material Balances:

	Moles Added	Moles Recovered	% Recovery	Conversion	Selectivity to VAM (%)
Acetate Equivalents:	22.42	20.41	91.0%	90.986%	(ketene) 37.99%
AcH Equivalents:	12.12	9.37	77.3%	72.33%	42.43%

Methanol Scrubber
Run #4

Liquid Take-Off
Run #4

F. Economic Assessment of Processes (Tasks 3 and 5)

1. Introduction

The objective of Tasks 3 and 5 was to evaluate preliminary and detailed economics to compare the syngas-based VAM routes developed in this project with the conventional (ethylene oxyacetylation) VAM route. These tasks overlapped since preliminary (partial) economics were used to guide the project (i.e., the choice of routes) and more detailed (complete) economics were used to report results.

Anticipated Trade-Offs

The predominant process for VAM involves oxyacetylation of ethylene, where acetic acid (HOAc) for the oxyacetylation can be generated by carbonylation of methanol (MeOH). The overall chemistry for this two-step route is:

(See Section F.2 for chemistry of the individual steps.)

We considered several syngas-based routes for VAM. While these routes involved different intermediates, they all exhibited the same overall chemistry:

Based on this overall chemistry and the raw material prices that Eastman assumed at the beginning of this project, we expected the syngas-based routes to show an approximately 2¢/lb VAM raw material cost advantage over the conventional VAM route. (This cost advantage dropped to ~1¢/lb using the raw material prices supplied by Air Products, as shown in Table F.3.) Thus, our challenge was to develop syngas-based routes that did not squander this raw material cost advantage by using excessive capital or utilities, or by having excessive raw material yield losses.

Selection of Syngas-Based Routes

A large number of routes can be generated, depending upon:

- The choice of acetyl used to esterify acetaldehyde (HAc) to produce VAM: ketene, acetic anhydride (Ac₂O), acetic acid (HOAc) or methyl acetate (MeOAc);
- The chemistry used to generate HAc: ketene hydrogenation, HOAc hydrogenation, MeOH carbonylation, MeOAc reductive carbonylation, etc.
- The chemistry used to generate Ac₂O: dimethyl ether (DME) carbonylation, MeOAc carbonylation, reaction of ketene with HOAc, etc.

[We only considered one way to deliberately generate HOAc (MeOH carbonylation) and one way to generate ketene (HOAc cracking).]

Some of these routes are shown in Section C.2, which also discusses the heuristics we used to reduce the number of alternatives. All remaining routes involved the use of zero, one or two

moles of ketene to generate each mole of VAM. At first, we did not know which extreme would be most economical:

- a “no-ketene” route involving esterification of HAc with Ac_2O and generation of HAc from HOAc hydrogenation, or
- an “all-ketene” route involving two moles of ketene for each mole of VAM: one mole of ketene for esterification of HAc and another mole of ketene to produce HAc (by ketene hydrogenation).

Nearly all the other routes involve one mole of ketene per mole of VAM. We believe the economics for these two extremes should bracket the economics for the other favorable routes discussed in Section C.2. Thus, we chose these two extremes for economic evaluation.

As a basis, we chose a 450M (million) lb/yr VAM plant. SRI¹ used 600M lb/yr to represent a world-scale VAM plant. However, they assumed two parallel trains of 300M lb/yr each. SRI² used 450M lb/yr in a previous study that appears to represent a single-train plant.

2. Overall Routes—Descriptions, and Material and Energy Balances

Conventional VAM Route

The “conventional” ethylene-based VAM process was used as an economic benchmark with which to compare the syngas-based VAM routes. This route consists of two blocks (Figure F.1):

1. Carbonylation of methanol (MeOH) to acetic acid (HOAc) [details in Reference 3]:

2. Oxyacetylation of ethylene to VAM [details in Reference 1]:

For this benchmark case, we assumed the use of a (small) dedicated HOAc plant.

Both of these blocks represent known processes. We took the material balances, utility usages and labor requirements for both blocks from the references cited above. This route exhibits overall VAM yields of 93% from MeOH, 86% from CO, 90% from ethylene and 90% from O_2 .

Figure F.1

No-Ketene Route (PATENT HOLD on HOAc Hydrogenation)

The no-ketene route consists of five blocks (Figure F.2):

1. Dehydration of methanol (MeOH) to dimethyl ether (DME) [information taken from Air Products⁴]:

2. Carbonylation of DME (and co-fed MeOH) to acetic anhydride (Ac₂O) [and acetic acid (HOAc)] [by analogy to the methyl acetate carbonylation process in Reference 5]:

3. Hydrogenation of acetic acid (HOAc) to acetaldehyde (HAc) (details in Section D.3):

4. Esterification of HAc with Ac₂O to produce VAM and HOAc (details in Section E.3):

5. Recovery of HOAc and ethyl acetate (EtOAc) (details in Section D.3).

The last three blocks—HOAc hydrogenation to HAc, HOAc/EtOAc recovery (associated with HOAc hydrogenation), and esterification of HAc with Ac₂O—are new processes. The first block—MeOH dehydration to DME—represents a known process. The second block—DME carbonylation to Ac₂O—is a well-known analog to the existing process for carbonylation of MeOAc to Ac₂O.

We took material balances for existing blocks from the references cited above. Material balances for new blocks were generated using a process simulator (ASPEN); these results are discussed in the report sections cited above. We used an Excel spreadsheet to scale and coordinate the material balance results from individual blocks, and thus to create the overall material balance.

The no-ketene route exhibits overall VAM yields of 86% from MeOH, 80% from CO and 64% from H₂. Table F.1 breaks down these yield losses.

We took the utility usages directly from the references and ASPEN models cited above. Note the relatively high steam usage for esterification of HAc with Ac₂O (in a rather large reactive distillation column). Labor requirements for existing blocks were also taken from the references cited above. We estimated labor requirements for new blocks based on the number of major equipment items using the correlation in Reference 6.

Figure F.2.

Table F.1

Yield Losses from Primary Raw Materials (Percent)—No-Ketene Route

	MeOH	CO	H ₂
DME Carbonylation			
HOAc Purge (Marketable)	1.0	0.9	0.0
Ac ₂ O and EDA to Incineration	1.5	1.4	0.4
Gas Purge	0.0	7.0	8.3
<i>Total</i>	2.5	9.3	8.7
HOAc Hydrogenation and HOAc/EtOAc Recovery			
EtOAc (Marketable)	4.8	4.4	7.1
Acetone to Incineration	1.4	1.3	0.0
EtOH in Wastewater	0.2	0.2	0.4
HAc in Gas Purge	0.9	0.9	1.4
C ₂ H ₄ and CH ₄ in Gas Purge	1.7	1.6	8.3
H ₂ in Gas Purge	0.0	0.0	8.3
<i>Total</i>	9.0	8.4	25.5
Esterification of HAc with Ac₂O			
Tars to Incineration ¹	2.7	2.5	2.0
<i>Total</i>	2.7	2.5	2.0
Total Yield Loss	14.2	20.2	36.2

¹Assumed equivalent to 3% VAM loss*All-Ketene Route*

The all-ketene route consists of five blocks (Figure 3):

1. Carbonylation of methanol (MeOH) to acetic acid (HOAc) [details in Reference 3]:

2. Thermal cracking of HOAc to ketene [details in Reference 7]:

3. Hydrogenation of ketene to acetaldehyde (HAc) (details in Section D.2):

4. Esterification of HAc with ketene to produce VAM (details in Section E.2):

5. Acetic acid recovery (Acid Con) [details in Reference 7].

Blocks 3 and 4—ketene hydrogenation to HAc, and esterification of HAc with ketene to produce VAM—are new processes. The other blocks—MeOH carbonylation to HOAc, thermal cracking of HOAc to ketene, and HOAc recovery (associated with ketene production)—represent existing processes.

We took material balance information for individual blocks from the references cited above (for existing processes) and from process simulation models described in the report sections cited above (for new processes). We used an Excel spreadsheet to coordinate the material balance results from individual blocks, and thus to create the overall material balance.

We took utility usages directly from the references and ASPEN models cited above. Note the use of relatively expensive natural gas *and* refrigeration for HOAc cracking, and refrigeration (to condense HAc) in ketene hydrogenation (which is limited to 1 atm operation due to ketene compressibility constraints). We took labor requirements for existing blocks from the references cited above, and estimated labor requirements for new blocks from the correlation in Reference 6.

Figure F.3.
Block Flow Diagram—All-Ketene Route

3. Capital Cost Estimates for Overall Routes

Methodology and Assumptions

Purchased equipment costs for known blocks were taken from the references cited in Section F.2, inflated to 1997 dollars. For new blocks, we estimated purchased equipment costs using ASPEN and cost correlations available in the literature. Details for the new blocks (including equipment lists) are included in the report sections cited in Section F.2.

Battery limits capital was estimated from total purchased equipment cost using a Lang factor of 4.0, and a contingency factor (multiplied on top of Lang factor) that depended upon the state of knowledge of the block. For known processes with limited engineering (e.g., blocks taken from the cited references), we used a contingency factor of 35%. For new blocks, we used a contingency factor of 50%.

Battery limits capital was scaled to the required capacity using the “six-tenths” rule. For known blocks, we took scaling exponents from the cited references. For new processes, we used an exponent of 0.6.

Off-sites capital was estimated as a percentage of battery limits capital. For known blocks, we took off-sites percentages from the cited references. For new blocks, we assumed off-sites capital to be 100% of battery limits capital.

Results and Discussion

Table F.2 and Figure F.4 present a side-by-side comparison of battery limits capital, off-sites capital and total fixed capital for the conventional, no-ketene and all-ketene routes.

Conventional VAM Route

Battery limits capital for the conventional VAM route is ~\$180M (million). The oxyacetylation block is somewhat capital intensive for a commodity chemical (23¢ per annual lb of VAM throughput) because a large ethylene recycle is required to keep ethylene-oxygen mixtures above their upper explosive limit. The MeOH carbonylation step is also somewhat capital intensive (23¢ per annual lb HOAc), since we assumed a small, dedicated HOAc plant rather than a large, world-scale plant.

No-Ketene Route

Battery limits capital for the no-ketene route (~\$250M) is 39% more expensive than that of the conventional VAM route (~\$180M).

Excluding DME carbonylation, the battery limits capital of all the blocks in the no-ketene route (~\$110M) is about the same as that of the oxyacetylation block in the conventional route (~\$100M). However, the DME carbonylation block in the no-ketene route is larger (761 Mlb/yr Ac_2O and HOAc), and hence more expensive, than the MeOH carbonylation block in the conventional VAM route (330 Mlb/yr HOAc). There are two reasons for this:

1. In the conventional VAM route, only “half” the VAM molecule (more precisely, half the carbon in the VAM molecule) passes through carbonylation (via HOAc):

However, in the no-ketene route, *all* the VAM molecule—except for hydrogen added during HOAc hydrogenation—passes through carbonylation (via Ac_2O):

HOAc Hydrogenation

Esterification of HAc with Ac_2O

Net Reaction

2. The DME carbonylation reactor in the no-ketene route requires the presence of HOAc solvent that is not needed elsewhere in the overall route. This solvent is recycled through the reactor and a large part of the separation system in the DME carbonylation block, thus increasing the size and cost of most of the equipment in the block. [This recycle is shown in Figure F.2. The amount of recycle was based on the analogous MeOAc process in Reference 5.]

DME carbonylation constitutes 55% of the battery limits capital for the no-ketene route.

All-Ketene Route

Battery limits capital for the all-ketene route (~\$290M) is 18% higher than that of the no-ketene route (~\$250M). Relatively high capital for cracking furnaces and higher capital for hydrogenation and HOAc recovery more than offset lower capital for carbonylation and esterification.

- Multiple, parallel furnaces are required to crack HOAc to ketene. Thus, the capital cost of HOAc cracking does not scale well with capacity.
- Ketene hydrogenation is limited to ~1 atm pressure to avoid diketene formation. Thus, a relatively large absorber is required to remove relatively dilute HAc from the reactor effluent. In contrast, HOAc hydrogenation, for the no-ketene route, can be operated at higher pressures, which reduces the cost of HAc isolation.
- MeOH carbonylation is slightly cheaper than DME carbonylation in the no-ketene route, mainly because of slightly lower throughput, but also because of a somewhat simpler flowsheet and less tar handling.

- The HAC esterification block (using ketene in a gas-stripped reactor) is cheaper than that of the no-ketene route (using Ac_2O in a reactive distillation column), mainly because the gas-stripped reactor is smaller than the reactive distillation column for the same VAM production rate.

Table F.2

Comparison of Battery Limits, Off-Site and Total Fixed Capital

	Conventional VAM	No-Ketene Route	All-Ketene Route
Battery Limits Capital			
MeOH Dehydration (to DME)		20	
DME or MeOH Carbonylation (to Ac_2O or HOAc)	76	136	128
HOAc Cracking (to Ketene)			68
HOAc or Ketene Hydrogenation (to HAc)		39	46
Acid Con (to recover HOAc and/or EtOAc)		14	30
Oxyacetylation or Esterification (to VAM)	103	38	21
Total Battery Limits Capital	179	248	294
Off-Sites Capital	118	168	180
Total Fixed Capital	297	416	474

Figure F.4

Comparison of Battery Limits, Off-Site and Total Fixed Capital

4. Economic Estimates for Overall Routes

Methodology and Assumptions

SRI-style spreadsheets were used to estimate the VAM “product value” (direct production cost + allocated overhead costs + 10% depreciation + 15% ROI, *not* including distribution and freight) for the conventional, no-ketene and all-ketene routes. We used unit raw material, utility and labor costs furnished by Air Products. We also used a unit HOAc by-product credit furnished by Air Products, and assumed the EtOAc byproduct credit to be $\sim 2/3^{\text{rds}}$ of the CMR spot price.⁸ Other factors (maintenance, overhead, taxes and insurance, depreciation, ROI) were taken from SRI and Air Products. We used the same “General & Administrative, Sales, and R&D” costs as SRI,¹ and assumed these costs to be independent of the route used to make VAM.

“Nominal” Results

Table F.3 and Figure F.4 present a side-by-side comparison of the major components of product value for the conventional, no-ketene and all-ketene routes.

Conventional VAM Route

The conventional VAM route has an estimated product value of $\sim 38\text{¢/lb}$ (assuming a small, dedicated HOAc plant). This is consistent with a short-term contract price of $\sim 35\text{--}40\text{¢/lb}$.⁹

No-Ketene Route

The product value for the no-ketene route ($\sim 44\text{¢/lb}$) is 18% higher than that of the conventional VAM route. Before credit for by-product sales is taken, the no-ketene route has about the same raw material costs as the conventional VAM route. The anticipated 1–2¢/lb VAM raw material cost has disappeared due to higher yield losses, mainly in HOAc hydrogenation (Table F.1) Table F.4 summarizes the raw material usages, yields (to VAM, marketable by-products and unrecoverable losses), and contributions to VAM product value of each of these yield losses.

After credit for by-product sales is taken, the no-ketene route exhibits $\sim 2.5\text{¢/lb}$ *net* raw material cost advantage over the conventional route. However, this cost advantage is negated by higher capital (Figure F.4)—as reflected in higher maintenance costs, taxes and insurance, depreciation and ROI in Figure F.5—and by 80% higher utility costs—mostly due to high steam usage for esterification of HAc with Ac_2O in the reactive distillation column.

All-Ketene Route

The product value for the all-ketene route ($\sim 51\text{¢/lb}$) is 16% higher than that of the no-ketene route. The all-ketene route does not exhibit a raw material cost advantage over the conventional route. The all-ketene route also suffers higher capital than the no-ketene route (Figure F.4), as well as higher utility costs (mostly due to natural gas *and* refrigeration for HOAc cracking, as well as refrigeration of HAc in ketene hydrogenation).

Table F.3

Product Value Comparison (15% ROI)

	Conventional VAM	No-Ketene Route	All-Ketene Route
Raw Material Costs			
Methanol @ 9.1¢/lb	0.036	0.079	0.079
CO @ 5.4¢/lb	0.021	0.044	0.045
H ₂ @ 37.7¢/lb		0.014	0.013
Ethylene @ 20¢/lb	0.072		
Oxygen @ 1.9¢/lb	0.004		
Other	0.004		
Total Raw Material Cost	0.138	0.137	0.138
HOAc Credit @ 12¢/lb		(0.002)	
EtOAc Credit @ 38¢/lb		(0.021)	
Net Raw Material Cost	0.138	0.113	0.138
Utility Costs	0.015	0.027	0.033
Labor Costs	0.011	0.015	0.016
Maint & Oper Matls	0.006	0.009	0.010
Plant Overhead	0.009	0.012	0.013
Taxes and Insurance	0.013	0.018	0.021
10% Depreciation	0.066	0.092	0.105
Gen & Adm, Sales, Res	0.017	0.017	0.017
15% ROI (before taxes)	0.099	0.139	0.158
Product Value (fob)	0.375	0.441	0.511

Figure F.5

Product Value Comparison (15% ROI)

Table F.4
Raw Material Usage, Yield and Cost Comparisons—Conventional and No-Ketene Routes

	Conventional Route			No-Ketene Route					
	Raw Material Usage (lb/lb VAM)	Raw Material Usage Distribution (% Yield)	Contribution to VAM Product Value (¢/lb VAM)	Raw Material Usage (lb/lb VAM)	Raw Material Usage Distribution (% Yield)	Contribution to VAM Product Value (¢/lb VAM)			
		Stoichiometric (VAM) Unrecoverable Losses Marketable Byproducts (HOAc, EtOAc)	Stoichiometric (VAM) Unrecoverable Losses Marketable Byproducts (HOAc, EtOAc)		Stoichiometric (VAM) Unrecoverable Losses Marketable Byproducts (HOAc, EtOAc)	Stoichiometric (VAM) Unrecoverable Losses Marketable Byproducts (HOAc, EtOAc)			
Raw Material Costs			Total			Total			
	Methanol @ 9.1¢/lb	0.400	93.1%	6.9%	0.0%	3.4	0.3	0.0	3.6
	CO @ 5.4¢/lb	0.382	85.2%	14.8%	0.0%	1.8	0.3	0.0	2.1
	H2 @ 37.7¢/lb								
	Ethylene @ 20¢/lb	0.362	90.0%	10.0%	0.0%	6.5	0.7	0.0	7.2
Oxygen @ 1.9¢/lb	0.207	89.9%	10.1%	0.0%	0.4	0.0	0.0	0.4	
Other Chemicals					0.4			0.4	
Total Raw Material Costs					12.5	1.3	0.0	13.8	
HOAc Credit @ 12¢/lb									
EtOAc Credit @ 38¢/lb									
Net Raw Material Cost					12.5	1.3	0.0	13.8	

Sensitivity Studies

Conventional VAM Route

Sensitivity of product value for the conventional VAM route to one-variable-at-a-time changes in capital and raw material costs is shown in the “tornado diagram” in Figure F.6. Product value ranges from 33 to 43¢/lb, and is most sensitive to the assumed uncertainties in total fixed capital and MeOH and ethylene prices. The uncertainty ranges for MeOH and ethylene prices were taken as the historical U.S. price ranges since 1988.¹⁰

No-Ketene Route

Figure F.6 shows the sensitivity of product value for the no-ketene route to uncertainties in capital, raw material costs, by-product EtOAc credit and steam usage. The product value ranges from 37 to 56¢/lb, and is most sensitive to total fixed capital and MeOH price. Note that for the assumed uncertainties in total fixed capital (and fixed, nominal values of raw material costs, by-product credits and steam usages), the product value ranges for the conventional and no-ketene routes overlap by about 6¢/lb (from 37.3 to 43.3¢/lb).

All-Ketene Route

Sensitivity of product value for the all-ketene route to uncertainties in raw material costs and battery limits capital is shown in Figure F.7. The product value ranges from 43 to 63¢/lb, and is most sensitive to total fixed capital and MeOH price.

Simultaneous Changes in Methanol and Ethylene Prices

Sensitivity of product value to simultaneous changes in MeOH and ethylene prices is shown in Figure F.8 for both the conventional (ethylene oxyacetylation) and no-ketene routes. (Note that the no-ketene route does not depend upon ethylene.) Uncertainty in total fixed capital superimposes error bars of about -4/+6 and -7/+10 ¢/lb VAM on the conventional and no-ketene routes, respectively (based on the capital cost bars in Figure F.6 and Figure F.7). Ignoring uncertainty in capital, product values for the conventional and no-ketene routes begin to overlap at combinations of historically high U.S. ethylene and historically low U.S. MeOH prices. Considering uncertainty in capital, VAM product values do overlap at the values of MeOH and ethylene prices assumed for the nominal economics (as indicated in Figure F.6 and Figure F.7).

Conclusions

One-variable-at-a-time changes may make the no-ketene route competitive with the conventional VAM route. In particular, for the assumed, nominal values of MeOH and ethylene prices, it may be possible to reduce the total fixed capital of the no-ketene route enough to make it competitive with the conventional VAM route. Reducing the capital cost of the no-ketene route most likely depends upon reducing the size and/or cost of DME carbonylation, since carbonylation capital constitutes ~55% of overall battery limits capital (Figure F.2 and Table F.4).

Two-variable-at-a-time changes are more likely to make the no-ketene route competitive with the conventional VAM route. In particular, the no-ketene route may compete with the conventional VAM route in parts of the world where ethylene is scarce (i.e., expensive), but MeOH (from

syngas) is not so scarce. This is particularly true if the capital cost of the no-ketene route can be reduced, or chemical yields increased to improve the raw material cost advantage.

Figure F.7. Sensitivity Study—No-Ketene Route

Figure F.8
Sensitivity Study—All-Ketene Route

Figure F.9

Sensitivity to Ethylene and Methanol Prices—Conventional and No-Ketene Routes

5. References

- (1) SRI, PEP Rept. 15B, *Vinyl Acetate/Polyvinyl Acetate*, Chap. 4, "Vinyl Acetate by Vapor Phase Oxyacetylation of Ethylene" (1996).
- (2) SRI, *1994 PEP Yearbook International*, Vol. 1 (1995).
- (3) SRI, PEP Rept. 37B, *Acetic Acid and Acetic Anhydride*, Chap. 4, "Acetic Acid by Low Pressure Carbonylation of Methanol" (1994).
- (4) Moore, Bob and Fran Waller; Air Products and Chemicals, Inc.; personal communication (June 25, 1997 FAX).
- (5) SRI, PEP Rept. 37B, *Acetic Acid and Acetic Anhydride*, Chap. 5, "Acetic Acid and Acetic Anhydride (Eastman Process)" (1994).
- (6) SRI, PEP Rept. 140, *Operating Costs in the Chemical Industry and Their Estimation* (1981).
- (7) SRI, PEP Rept. 146, *Bulk Chemicals from Synthesis Gas*, "Acetic Anhydride via Acetic Acid and Ketene," pp. 33–56 (1982).
- (8) *Chemical Marketing Reporter* **251**, 20 (May 19, 1997).
- (9) TECNON, *Acetic Acid–Vinyl Acetate Monthly Newsletter* (Sept. 1997).
- (10) TECNON, *Acetic Acid–Vinyl Acetate Monthly Newsletter* (April 1997).

G. Conclusion

Eastman Chemical Company undertook a careful examination of the numerous potential processes for the generation of vinyl acetate from synthesis gas. Using fundamental chemical and engineering principles, Eastman Chemical Company was able to narrow the number of potential candidates to only eight potentially viable processes. These revolved around six technologies, two of which were simple extensions of known processes. The remaining four technologies were:

- 1) the esterification of acetaldehyde (AcH) with ketene to generate VAM,
- 2) the hydrogenation of ketene to acetaldehyde,
- 3) the hydrogenation of acetic acid to acetaldehyde, and
- 4) the reductive carbonylation of methanol to acetaldehyde.

Eastman Chemical Company examined each of these technologies and the economics associated with the individual steps. Eastman Chemical Company was able to demonstrate unique, likely patentable, technology for each of the first three processes. (The last was abandoned based on the economic projections.)

In addition, when Eastman Chemical Company recognized that the preferred route would not involve ketene (for economic reasons), they applied (and improved) technology for the conversion of acetic anhydride and acetaldehyde to vinyl acetate, which Eastman Chemical Company had discovered and reported prior to the contract. The economic estimates indicated that, despite the successful attainment of the key technologies, the cost to produce and sell vinyl acetate using the best synthesis gas-based routes is about 15% higher than when using the conventional oxidative acetoxylation of ethylene.

H. Inventory of Intellectual Property

1. File Locations and Contract Numbers:

- a) Internal Auditing File No.: 1995-11-15 000082
- b) U.S. Dept. of Energy/Air Products and Chemicals, Inc., Prime Contract No.: DE-FC22-95PC93052
- c) Air Products and Chemicals, Inc. Subcontract No.: P.O. # PT-M0014

2. Notebooks

X25188 (Justin Abnee)
X25229 (Renee Atkinson)
X24668 (Leslie DePew)
X25497 (Leslie DePew)
X24988 (Regina Moncier)
X25312, p.16 (Andy Singleton)
X24518 (Gerald Tustin)
X25940 (Gerald Tustin)
X24343 (Joseph Zoeller)
X25311 (Tracey Zoll)

3. Invention Reports

- a) G. C. Tustin, L. S. DePew, "Process for the Preparation of Acetaldehyde.", Docket No. 70283 (Issued as US Pat. No. 5,679,870.)
- b) G. C. Tustin, J. R. Zoeller, L. S. DePew, "Process for the Preparation of Vinyl Acetate.", Docket No. 70448 (Notice of Allowance received, publication pending)
- c) G. C. Tustin, J. R. Zoeller, and L. S. Depew, "Preparation of Vinyl Acetate", Docket No. 70520 (Notice of Allowance Received, publication pending.)
- d) G. C. Tustin, T. J. Dickson, "Carboxylic Acid Accelerated Formation of Diesters." Docket No. 70519.
- e) G. C. Tustin, L. S. DePew, N. A. Collins, "Process for the Preparation and Recovery of Acetaldehyde.", in preparation.