

SYNTHESIS OF VINYL ACETATE MONOMER FROM SYNTHESIS GAS

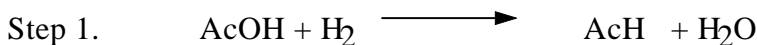
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1. Introduction

The overall objective of this project is to develop a commercially viable process for the generation of vinyl acetate monomer (VAM) based entirely upon coal-generated syngas. Previous attempts at this objective have generally involved the combination of acetic anhydride (generated by carbonylation of dimethyl ether or methyl acetate) with acetaldehyde (generated by hydrocarbonylation of methanol or a methyl ester) to generate ethylidene diacetate (EDA) which is subsequently cracked to form VAM and acetic acid in a separate step. Owing primarily to the need to recycle or otherwise dispose of huge quantities of the acetic acid byproduct, these efforts have failed to generate a commercially viable process to date.

Eastman's proposal centers around the generation of acetaldehyde from acetic acid (AcOH) rather than methanol or a methyl ester. The proposed linchpin technology was to develop and apply a proprietary method for generating transient, higher energy acetic acid species (referred to hereafter as activated acetic acid or AAA) thus permitting the normally endothermic hydrogenation of acetic acid to acetaldehyde (AcH) to proceed in high conversions, at acceptably low pressures, and moderate temperatures without subsequent hydrogenation to ordinarily thermodynamically favored ethanol.

The acetaldehyde thus formed could be converted to EDA and subsequently to VAM by known methods (i.e. combining acetic anhydride with acetaldehyde to form EDA followed by subsequent cracking to VAM and AcOH.) Within the proposal, Eastman presented several methods for improving this known process. However, Eastman also proposed a very speculative application of the same (or modified) proprietary technology for the generation of activated acetic acid to the direct esterification of acetaldehyde to yield VAM. The normally endothermic esterification of acetic acid with acetaldehyde would also become favorable if the endothermic AAA generation process could be coupled with an exothermic reaction of AAA with acetaldehyde to produce VAM. If this overall speculative conversion came to fruition, the overall process would be represented by the following equations:



and would represent a synthesis of VAM entirely from acetic acid. (The commercially preferred route to acetic acid, methanol carbonylation, is already based entirely upon syngas.)

The key initial tasks to be performed were for Eastman to:

1. Explore the possibility of using its activation process to permit selective acetic acid hydrogenation to acetaldehyde.
2. Explore the possibility of applying similar activation technology to the direct esterification of acetaldehyde.
3. Initiate a preliminary economic estimate to determine whether the proposed process could be competitive with the existing, commercial vinyl acetate processes.

2. Results

Task 1. Acetaldehyde Process Since the inception of this project, Eastman has been exploring several alternative reactor configurations for generating activated acetic acid and alternatives for the introduction of the reactive species into a hydrogenation unit. Several of the designs have proved suitable for the examination of the hydrogenation and Eastman completed an initial screening of a number of catalysts for this transformation. A number of catalysts have been found that provide high yields of acetaldehyde while operating at moderate temperatures (50-175°C) and very low pressures (1 atmosphere or less) in the vapor phase. The preferred catalysts are heterogeneous and contain palladium. Typical conditions for the activated acetic acid hydrogenation used 1 mL catalyst powder diluted with 50 mL 8x16 mesh quartz chips contained in a steam-heated 25 mm O.D. glass reactor containing a 9 mm thermowell. The bed temperature was maintained at 98°C throughout the entire catalyst bed using this reactor configuration during the hydrogenation reaction. The feed to the reactor contained diluents, and typical feed conditions were 1 mmol (22.4 mL at STP AAA/minute, 44.8 SCCM (standard cubic centimeters per minute), 188 SCCM N₂, 50 SCCM He. Typical space velocity, based on the volumes of gases passing the volume of the catalyst at reaction conditions per hour was 18600 hr Table 1 summarizes the performances of a number of different palladium catalysts and provides surface area and dispersion data for the catalysts. The data in Table 1 were obtained after about 5 hours of operation and were taken with the fourth sample of the day. The catalysts were regenerated by continuing the hydrogen treatment overnight at 98°C without any AAA present. With the exception of the catalyst of Ref. No. X24668-058, which was run in a slurry mode, all of the catalysts were subjected to three regenerations, and 16 product samples were collected for each catalyst. Table 2 provides comparisons of the performances of the 4th and 16th samples for each catalyst and thus provides information about the deactivation rates of the various catalysts. The Pd sponge catalyst is noteworthy because its performance could be almost completely restored by the mild overnight hydrogenation treatment.

Eastman now has constructed a total of three units for the activation of acetic acid which could be used to study this process. Two of the reactors have the capability of reducing the use of diluent gases within the process and one of the reactors will allow a ca. 10 fold increase in scale. Using these new reactors, Eastman began to study the hydrogenation of activated acetic acid to acetaldehyde in detail. Several key observations were made regarding catalyst behavior, particularly the mode of deactivation.

The most significant observation upon scale-up is that at least one of the minor by-products of the activation process acts as a reversible poison for the hydrogenation when the byproduct is present in sufficient quantity. Improvements in the activation process can reduce, even eliminate, this poison

Identification of a catalyst which is not poisoned by the minor by-products is desirable. Therefore, although Eastman intends to continue its detailed study of the previously identified catalysts in the near future, a greater portion of Eastman's activity within this task will be devoted to identifying (or attempting to identify) a catalyst which is not poisoned by the minor by-products.

Task 2. VAM Generation Process Eastman has discovered that its acetic acid activation process is useful for the direct esterification of acetaldehyde to vinyl acetate, providing proper reactor designs and catalysts are employed. Excellent results were obtained using a gas stripped reactor containing a solvent (645 mmol) and catalyst (30.6 mmol) through which the AAA (0.7 mmol/minute), acetaldehyde (1.0 mmol/minute) and diluent nitrogen (9.2 mmol/minute) were sparged at 150°C. A reflux condenser attached to the top of the reactor returned condensable liquids to the reactor, and the VAM and unreacted acetaldehyde were collected in a subsequent dry ice trap. Reactions were performed for 5-6 hours per day for 4 days. All reactions require a period to come to steady state, and then the performance either reaches a maximum then declines or, depending on the solvent, reaches a somewhat lower maximum but does not decline over the time period examined. The most active system provided VAM yields from AAA of 41 %, 86 %, 95 % and 87 % for the first, second, third and fourth days of operation respectively. A different solvent system provided VAM yields from AAA of 42 %, 78 %, 78 % and 81 % for the first, second, third and fourth days of operation respectively.

Eastman is currently scaling the reaction by a factor of about 10 in both reactant feed rate and in reactor volume. The larger reactors will be used to optimize conditions including the best reactor designs and reaction conditions to take advantage of balancing mass transfer effects with chemical kinetic effects.

Task 3. Economics. Having identified operable processes at the laboratory scale level for both the hydrogenation of acetic acid and the direct esterification of acetaldehyde, Eastman now has sufficient information to undertake preliminary economic estimates for the overall process. These studies are underway, and a number of the components of the model are already in place. Longer term, economic estimates will be refined as the knowledge base grows and Eastman's engineers start integrating the processes.

3. Summary.

Eastman has improved upon their methods for the:

- 1) generation of activated acetic acid,

- 2) selective, low temperature and low pressure hydrogenation of acetic acid, including the identification a key inhibitor for the process, and
 - 3) direct esterification of acetaldehyde with activated acetic acid.
- Economic studies currently are in progress.