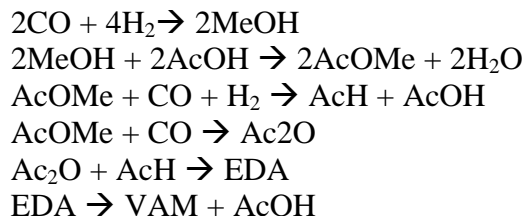# SYNTHESIS OF VINYL ACETATE MONOMER FROM SYNTHESIS GAS

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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 either methyl acetate or dimethyl ether) with acetaldehyde (generated by either hydrogenation of acetic anhydride or hydrocarbonylation of either methanol or a methyl ester) to generate ethylidene diacetate (EDA) which is subsequently cracked to form VAM in a separate step. An exemplary process is shown below.

$$2CO + 4H_2 \rightarrow 2MeOH$$
$$2MeOH + 2AcOH \rightarrow 2AcOMe + 2H_2O$$
$$AcOMe + CO + H_2 \rightarrow AcH + AcOH$$
$$AcOMe + CO \rightarrow Ac2O$$
$$Ac_2O + AcH \rightarrow EDA$$
$$EDA \rightarrow VAM + AcOH$$

MeOH = methanol
AcOH = acetic acid
Ac_2O = acetic anhydride
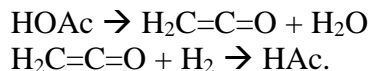AcH = acetaldehyde
AcOMe = methyl acetate

These efforts have failed to generate a commercially viable process to date. One of the key reasons for this failure is the very large quantities of recycled acetic acid (and consequently large commercial facilities) inherent in the earlier proposed processes.

A specific objective of our work is to develop a syngas based process for the production of VAM that avoids the costly recycle of acetic acid to a carbonylation reactor. Although a number of approaches are possible, many of these have been eliminated on thermodynamic grounds or upon the basis of the number of steps involved. We believed that a very important reaction required for the production of VAM was the hydrogenation of acetic acid to acetaldehyde, and, if this could be accomplished, the problem of recycle of acetic acid to the carbonlyation reactor could be solved:

$$HOAc + H_2 \rightarrow HAc + H_2O.$$

Since acetic acid hydrogenation to acetaldehyde is mildly endothermic and further complicated by the formation of acetone and ethanol under the typical conditions of high

temperature and pressure, one approach was to first convert the acetic acid to ketene and then hydrogenate the ketene to acetaldehyde under mild conditions:

$$HOAc \rightarrow H_2C=C=O + H_2O$$
$$H_2C=C=O + H_2 \rightarrow HAc.$$

The potential reactivity of ketene also prompted us to investigate the reaction of acetaldehyde with ketene to produce VAM directly:

$$HAc + H_2C=C=O \rightarrow VAM.$$
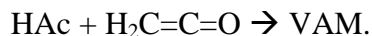
Thus a potential VAM process becomes feasible that totally avoids the large scale manufacture of acetic anhydride or EDA and instead is based on acetic acid (Scheme I):

$$2HOAc \rightarrow 2H_2=C=O + 2H_2O$$
$$H_2C=C=O + H_2 \rightarrow HAc$$
$$HAc + H_2C=C=O \rightarrow VAM.$$
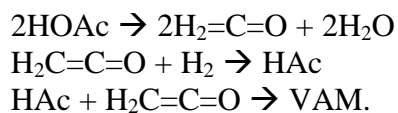
Another route to VAM begins with the carbonylation of dimethyl ether to acetic anhydride, the reaction of acetic anhydride with acetaldehyde in a reactive distillation column to produce VAM and acetic acid which is hydrogenated to provide the acetaldehyde (Scheme II):

$$Me_2O + 2CO \rightarrow Ac_2O$$
$$Ac_2O + HAc \rightarrow VAM + HOAc$$
$$HOAc + H_2 \rightarrow HAc + H_2O.$$
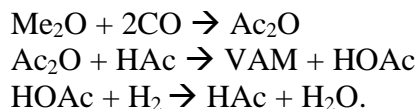
The last reaction, the hydrogenation of acetic acid to acetaldehyde, can take place by the ketene route shown previously. However, since this reaction is so important for all syngas based schemes to VAM, the direct hydrogenation of acetic acid to HAc was also investigated.

The key tasks to be performed were:
1. The hydrogenation of ketene to acetaldehyde.
2. The reaction of ketene with acetaldehyde to produce VAM.
3. The direct hydrogenation of acetic acid to acetaldehyde.
4. The reactive distillation of acetic anhydride with acetaldehyde.
5. Preliminary economic analysis.

Task 4 was performed outside the scope of this project, but an overview is provided to provide more meaning to some of the conclusions in task 5.

2. Results

Task 1. The hydrogenation of Ketene to Acetaldehyde. The reaction of hydrogen with ketene is exothermic by about 17 kcal/mol at 100°C. In order to control the heat produced by this reaction, the reaction was typically performed with 1 ml catalyst diluted

with 50 ml quartz chips in a steam heated reactor at 98°C. Typical reaction conditions are 1 mmol (22.4 ml) ketene/min., 44.8 standard cubic centimeters per minute (SCCM) hydrogen, 50 SCCM helium and 88 SCCM nitrogen at one atmosphere pressure and GSHV = 18600 hr^{-1}. Of all the transition metals surveyed, palladium is by far the most efficient catalyst for this reaction. A low surface area (0.13 m^2/g) Pd sponge catalyst provided acetaldehyde at 1200 g/l-hr at 20 % ketene conversion at 90-100 % selectivity. A high surface area (1259 m^2/g) 5% Pd on carbon provided acetaldehyde at 700 g/l-hr at 92 % ketene conversion at 75 % selectivity. These catalysts deactivate 20-30 % during the first day of operation. The Pd sponge catalyst can be regenerated by maintaining the hydrogen overnight flow in the absence of ketene at normal reaction temperature. The supported catalyst is not totally regenerated by this treatment. The fouling rate increases as the partial pressure of ketene increases. The fouling is likely related to the facile dimerization and subsequent reactions that are well known for ketene. Other products are methane, CO, ethyl acetate and oils. A preliminary kinetic study performed at low ketene conversion revealed the reaction to be approximately 0.6 order in hydrogen, 0.3 order in ketene and had an activation energy = 8 kcal/mole. Carbon monoxide is normally present in industrial ketene streams at a level of about 1 % and is a moderate poison for the reaction. However the reaction will operate at about 50 % efficiency when the feed contains 2.5 % CO.

Task 2. Reaction of Ketene with Acetaldehyde to Produce VAM. This reaction is performed by contacting ketene and acetaldehyde in the presence of a Bronsted acid. Arenesulfonic acids are excellent catalysts. Reaction temperature is preferably in the range between 120-160°C. The reaction is preferably performed in the presence of a solvent, although it has been shown to work in the vapor phase using polymeric sulfonic acid catalysts. Acetic anhydride or 1-methyl-2-pyrrolidinone are excellent solvents for the reaction. Excellent results were obtained using a gas stripped reactor containing acetic anhydride (645 mmol) and p-toluenesulfonic acid (30.6 mmol) through which the ketene (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. Thus the reaction conditions described above provided VAM yields from ketene of 42 %, 78 %, 78 % and 81 % for the first, second, third and fourth days of operation respectively. Attempts to scale this reaction up while running without added diluents have only been moderately successful and have resulted in lower yields from ketene.

Task 3. Direct Hydrogenation of Ketene to Acetaldehyde. The majority of our recent technical efforts have been devoted to the study this reaction. The key barriers to the hydrogenation of acetic acid to acetaldehyde are that the reaction:
   a) is mildly endothermic (ΔG_{300C} = 2.51 kcal/mol),
   b) must compete with a parallel (and thermodynamically favorable) dimerization reaction of acetic acid to acetone (with coproduction of water and carbon dioxide),

c) is subject to a subsequent (also thermodynamically favorable) hydrogenation of acetaldehyde to ethanol, and

d) needs to be performed in a manner allowing a practical means to actually recover the volatile acetaldehyde from the product.

Initial studies concentrated on addressing items a-c to optimize the chemistry and perform kinetic evaluations. Once these were done, efforts turned to item d. We have been examining a series of proprietary catalysts for acetic acid hydrogenation reaction consisting of an essential component (A) and a promoting component (B).). A series of catalysts was prepared and evaluated where the amounts of components A and B were varied. Catalysts studied contained in wt %: 100A-0B, 97.5A-2.5B, 95A-5B, 90A-10B, 80A-20B, 60A-40B, 20A-80B and 0A-100B. Most of the initial studies were performed with the 97.5A-2.5B catalyst under conditions using a vast excess of hydrogen. This catalyst was observed to produce acetaldehyde at a rate of 312 g/l-hr at 25 % acetic acid conversion with 88 % selectivity to acetaldehyde with the other products being ethanol (6 %), acetone (2 %), methane (3 %), and C_2 hydrocarbons (less than 1 %). Catalytic performance remained reasonably steady over 200 hours. Since the selectivity of this catalyst was excellent and its activity fairly stable, it was decided to perform a kinetic study at low and medium conversions so we could later optimize reaction conditions. These studies were complicated somewhat by the observation that, under some conditions, the catalyst becomes oxidized. This condition favors acetone formation. The results of the kinetic studies are summarized below:

Activation Energy Data (kcal/mol)
Acetaldehyde = 16
Acetone = 32 (reduced catalyst), 9 (oxidized catalyst)
Ethanol = 29
Hydrogen Reaction Order
Acetaldehyde = 0.98 (reduced catalyst), 0.79 (oxidized catalyst)
Acetone = -0.08 (reduced catalyst), -0.32 (oxidized catalyst)
Ethanol = 1.76 (reduced catalyst), 1.40 (oxidized catalyst)
Acetic Acid Reaction Order
All products: non-linear behavior (volcano plot).

The observation that the rate increases then decreases with increasing acetic acid partial pressure is consistent with it being strongly adsorbed on the catalyst. The activation energy study was very useful in revealing the need to keep the catalyst reduced to minimize acetone formation and in selecting the temperature for optimum selectivity.

The next step in the development was determining which conditions allowed the amount of hydrogen to be lowered while maintaining the catalyst in the reduced state. Optimum performance using a 5/1 hydrogen/acetic acid ratio was found with the 90A-10B catalyst. This material produced acetaldehyde at a rate of 278 g/l-hr at 48 % acetic acid conversion, and the following selectivities were observed: acetaldehyde = 89 %, acetone = 4 %, ethanol = 5 %, methane + C_2 hydrocarbon = 2 %. The fresh 90A-10B catalyst was analyzed by XPS and XRD before reduction and after reduction and contained different

phases than the 95A-5B catalyst after reduction but similar phases before reduction. By using different preparative techniques, two versions of the 90A-10B catalysts were prepared. The surface area of one of these was four times that of the other. The high surface area material had higher activity than the low surface area material, but, when the space velocity was adjusted so both catalysts were operating at the same conversion, the selectivities were very similar.

Task 4. Reactive Distillation of Acetic Anhydride with Acetaldehyde. Although this process was investigated outside of the scope of this project, it is pertinent to review it because of its relevance in producing VAM from acetic anhydride and acetaldehyde. This production of VAM by this chemistry involves 2 equilibria:

$$Ac_2O + HAc = EDA$$
$$EDA = VAM + HOAc.$$

Both of these equilibria favor EDA. When EDA is heated in the presence of an acid catalyst, it will produce acetic anhydride, acetaldehyde, VAM and acetic acid as volatile products even though the desired products are only acetic acid and VAM. Previous routes to VAM utilizing EDA cracking crack the EDA in the presence of excess acetic anhydride to drive the equilibrium towards VAM and acetic acid, but these processes require several distillation columns to capture acetaldehyde and other components for recycle. The process of reactive distillation overcomes many of these limitations by feeding recycled catalyst solution and acetic anhydride to the middle of a distillation column while feeding acetaldehyde to the base of the column. Any acetaldehyde that rises up the column encounters a stream that is increasingly rich in acetic anhydride thus continuously pushing the equilibrium toward VAM and acetic acid which are collected from the top of the column. This process has been demonstrated in our laboratories.

Task 5. Preliminary Economic Analysis. SRI style economics were performed on the processes of Schemes I and II and the conventional ethylene oxidative acetoxylation route to calculate a product value at 15 % ROI. Raw materials were methanol, carbon monoxide, hydrogen, ethylene and oxygen. Acetic acid was assumed to be produced in the appropriately sized plant required for 450 Mlb VAM/year. Data for the dimethyl ether carbonylation were estimated from the SRI study for methyl acetate carbonylation. Data for the new processes were estimated from process simulation using ASPEN models and laboratory data. The process of Scheme I is disadvantaged due to the high capital and utility costs associated with producing the large quantities of ketene required to produce one mole of VAM from two moles of ketene. The process of Scheme II is better, but is still disadvantaged compared to conventional VAM under typical current raw material prices. Product by Scheme II would cost about 20 % more than that produced by conventional technology based on ethylene. The main costs arise from the large capital required for the large-scale dimethyl ether carbonylation plant and the utilities required for the reactive distillation. A sensitivity study varying the battery limits capital estimates and the methanol, CO and ethylene prices produced no reasonable regions where the product value of VAM produced from scheme II overlapped with that produced by the conventional route. If the price of ethylene more than doubled, then the process of Scheme II becomes more competitive.

3. **Summary.**

Three new technologies have been discovered during our work on this project: ketene hydrogenation to acetaldehyde, the synthesis of VAM from ketene and acetaldehyde and the direct hydrogenation of acetic acid to acetaldehyde. Even though these syngas based routes have a raw material cost advantage, this advantage is lost because of capital and utility costs. However, if the cost of ethylene became prohibitive, then these syngas based processes are well worth considering because the chemistry works very well.