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# Eastman Chemical Company's "Chemicals from Coal" program: The first quarter century

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ABSTRACT

Eastman Chemical Company first initiated its Chemicals from Coal program in the mid-1970s. The program led to the successful commercialization of a process to produce acetic anhydride entirely from coal-based synthesis gas in 1983. However, Eastman Chemical Company did not stop to work with on chemicals from coal with the attainment of the acetic anhydride process and they continued to look at the additional processes for chemicals from coal. In this manuscript, Eastman Chemical Company will discuss the case for coal which led Eastman Chemical Company to take a leadership role in the production of chemicals from coal and then present three case studies, including the commercially practiced Eastman acetic anhydride process and potentially competitive processes for vinyl acetate and methacrylic acid, which demonstrate the viability of replacing petroleum and natural gas based processes with processes based entirely on coal derived synthesis gas.

## 1. Introduction

Eastman Chemical Company was established in 1920 in Kingsport, TN as a division of Eastman Kodak. The facility was initially built as a wood products facility to produce methanol and acetic acid by wood distillation. By the end of the decade, the facility was producing cellulose acetate from cellulose and acetic anhydride to produce safety film (replacing nitrocellulose in photographic film) and acetate yarn. In large part, the Northeastern Tennessee location was chosen for its proximity to a large reservoir of wood and mid-Appalachian coal which provided raw materials and energy, respectively, for the new facility. Throughout Eastman Chemical Company's history, coal has continued to constitute the major energy source for the very large, diversified chemical production facility in Kingsport, TN. Natural gas has always been in limited supply at its Kingsport site, and as a consequence, natural gas use for chemicals production at its Kingsport site has normally been limited to use as fuel for ketene furnaces. (Ketene furnaces are used to conduct the highly endothermic dehydration of acetic acid to ketene and water. Reaction of ketene with acetic acid produces acetic anhydride.)

During the mid-1970s, Eastman Chemical Company recognized the value of using coal not only as an energy source, but as a feedstock in place of natural gas. Work began in 1975 on a process to generate acetic anhydride, which represented Eastman Chemical Company's largest volume and most energy intensive chemical, with an entirely coal-based process. This resulted in the start-up of the first modern chemicals from coal facility in 1983, which generated four chemical entities: methanol, methyl acetate, acetic acid, and acetic anhydride entirely from coal.

Eastman Chemical Company's efforts did not terminate with the realization of an acetic anhydride from coal process and several investigations were undertaken to extend the variety of chemicals available from coal. Eastman's overall philosophy from the outset was that, in principle, methods could be developed to use coal-based synthesis gas to generate the full menu of chemical products but would be especially useful for the range of C-1 through C-4 oxygenated products. Eastman Chemical Company's continued efforts have resulted in several processes which have, or may have, commercial viability. (For an earlier brief discussion of Eastman Chemical Company's efforts, see reference [1].)

This report will discuss the case for coal at Eastman Chemical Company and then discuss three case studies for the conversion of coal to chemicals, including the commercially practiced methyl acetate carbonylation to acetic anhydride, and two potential commercial processes for vinyl acetate and methacrylic acid. Each process involved an interactive combination of novel synthetic

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pathways, new chemistries, innovative engineering and often represented first of its kind introduction of new technology.

## 2. The case for coal at Eastman Chemical Company

To fully understand the case for coal at Eastman Chemical Company, we must first examine some additional history. As indicated earlier, the Northeastern Tennessee location for Eastman Chemical Company was chosen, in part, for its proximity to the Central Appalachian coal fields to provide a readily, and regionally, available energy resource to fuel wood distillation units. Throughout its history, Eastman Chemical Company has used coal as its primary fuel source at its main site in Kingsport, TN. As a consequence, Eastman Chemical Company had locally available coal, existing transportation (railroad) infrastructure, and experience in handling coal. However, the choice of location also placed some constraints on the Kingsport site since natural gas was not widely available and often at a premium.

In the 1950s, Eastman Chemical Company established a site in Longview, TX to generate acetaldehyde from ethylene and a hydroformylation facility to generate propionaldehyde and butryraldehyde from ethylene and propylene, respectively. (The aldehydes were shipped to Kingsport, TN where they were oxidized to form the corresponding acids.) While the Longview, TX site provided access to natural gas and oil-based processes, it also provided additional experience with synthesis gas (a mixture of carbon monoxide and hydrogen) which was required as a feedstock for hydroformylation.

Unfortunately, the location in Longview, TX also made Eastman Chemical Company susceptible to the vagaries of oil and natural gas pricing and availability. When the oil crises of the 1970s occurred, Eastman Chemical Company was forced to re-examine its resource base and, given its proximity and familiarity with coal and experiences with synthesis gas, Eastman Chemical Company turned its attention to coal gasification as a carbon source. Further, for Eastman Chemical Company's primary need (acetic anhydride), coal generated a synthesis gas mixture with a more favorable $CO:H_2$ ratio than natural gas and represented a lower transport cost/carbon atom.

However, the hurdles facing Eastman Chemical Company were significant. Coal gasification had not been widely practiced since the 1940s and modern designs were unproven. Further, coal comes with a number of impurities that needed to be removed and sequestered safely, such as arsenic, sulfur, and mercury. It was particularly critical that Eastman Chemical Company capture mercury since, as a division of Eastman Kodak at the time, it was critical that no mercury be allowed to enter products destined for the photographic market. Moreover, at the time of this decision, there were very few existing synthesis gas based chemical processes. With the sole exception of the Monsanto acetic acid process (the carbonylation of methanol to acetic acid using Rh–MeI catalysts), which had only recently been commercialized at the time of this decision, every synthesis gas based chemical was a C-1 product (methanol, formaldehyde, formic acid, formamide, and HCN) and used natural gas based synthesis gas.

Despite these hurdles, Eastman Chemical Company initiated a study for a Chemicals from Coal program in the mid-1970s and began in earnest in 1977 by commissioning a program whose first phase was to produce acetic anhydride – its most critical and energy intensive intermediate – entirely from coal. The second phase of the program was to demonstrate that other large volume chemicals could be generated entirely from synthesis gas. This program has been ongoing, with varying degrees of effort, since its inauguration in 1977. As stated earlier, it was Eastman's philosophy that, in principle, methods could be developed to use coal-based synthesis gas to generate the full menu of chemical products but would be especially useful for the range of C-1 through C-4 oxygenated products. This report will cover not only the acetic anhydride process, but provide two additional case studies, a vinyl acetate process and a methacrylic acid process, from its further efforts at deriving commodity chemicals from coal.

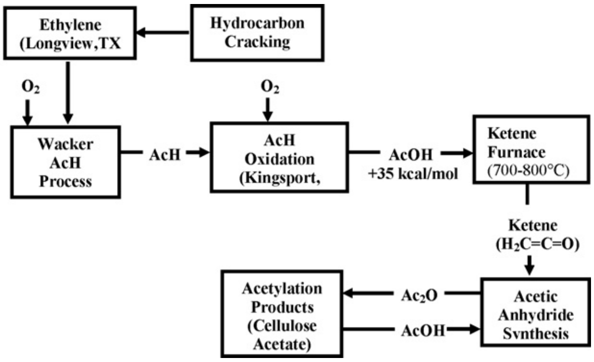

**Fig. 1.** Old acetic anhydride process.

## 3. Case study 1

### 3.1. The acetic anhydride process [2]

In 1977, the existing generation of acetic anhydride was based on ethylene and involved sequential oxidation of ethylene to acetaldehyde, oxidation to acetic acid, ketene generation wherein ketene was converted to acetic anhydride by reaction with recycled acetic acid (see Fig. 1). The key concerns in this process were the high cost of ethylene to feed the Wacker acetaldehyde process and the highly endothermic dehydration of acetic acid to ketene ($\Delta H$ = ca. +35 kcal/mol). The later process (ketene generation) requires rapid water separation from the very reactive ketene and significant amounts of ketene back react to acetic acid, resulting in energy losses. The cost of transporting acetaldehyde, which requires special containers and storage facilities, from Longview, TX to Kingsport, TN further penalized the process.

The coal-based process would involve coal gasification and syngas separation, generation of methanol, esterification of acetic acid, and subsequent carbonylation of methyl acetate to acetic anhydride (see Fig. 2). One critical requirement was that, like the older acetaldehyde–ketene-based process, the coal-based process had to be capable of recycling the acetic acid by-product obtained upon the acetylation of cellulose with acetic anhydride. However, at the outset, only the methanol process was well developed and key developments were going to be required in the areas of gasification, methyl acetate generation, and methyl acetate carbonylation.

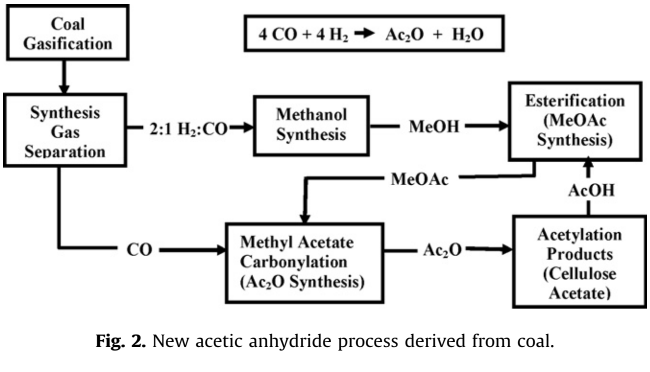

**Fig. 2.** New acetic anhydride process derived from coal.

In the area of gasification, existing coal gasification units had a poor operating history, with typical on-line operating times measured in hours and occasionally stretching to days. Eastman Chemical Company licensed Texaco Gasifiers (technology now owned by GE) and through implementation of several proprietary developments, Eastman Chemical Company rapidly extended on-line operating times first to days and then weeks. Later developments extended this to the order of months. Mercury removal was accomplished using a proprietary Hg removal system which removes >90% of the mercury. Sulfur removal used a licensed Rectisol® process which produces high grade, saleable sulfur useful in the generation of electronics grade sulfuric acid. The gasifiers have provided a reliable, clean source of synthesis gas since their installation in 1983.

When the plant was started, the methanol process was licensed from Lurgi. However, in 1997, Eastman Chemical Company installed, and continues to successfully operate, the first commercial Air Products/Chem Systems Liquid Phase Methanol (LPMeOH™) Process [3–6] to supplement its methanol requirements using coal-based synthesis gas as the feedstock.

The esterification of the resultant methanol with returned acetic acid represented a significant engineering hurdle since traditional designs required seven units of operation to break a variety of ternary and binary azeotropes. Further, like most esterifications, the conversion of methanol and acetic acid to methyl acetate and water (Eq. (1)) is an equilibrium reaction. To circumvent these issues, Eastman Chemical Company installed the first commercially practiced reactive distillation [7] (see Fig. 3).

$$\mathrm{MeOH} + \mathrm{AcOH} \rightleftarrows \mathrm{MeOAc} + \mathrm{H_2O} \tag{1}$$

As is illustrated in Fig. 3, in the reactive distillation there are three distinct sections in the column, a water/methanol stripping zone at the bottom, a reaction zone in the center, and methyl acetate refinement at the top. Descriptively, methanol (b.p. 65 °C) is added at the bottom of the reaction zone and acetic acid (b.p. 118 °C) and acid catalyst are added at the top of the reaction zone. As methanol ascends up the column it encounters a consistently richer acetic acid concentration, which drives the equilibrium to completion and prevents methanol from leaving the column. Likewise, as acetic acid descends down the column, it also encounters a continuously enriched stream of methanol, which also pushes the equilibrium toward completion and prevents acetic acid from reaching the bottom portion of the column. However, the acetic acid also serves as an extractant for water, breaking the various azeotropes. A short section is left at the base of the distillation column to strip all the methanol and a short section is added at the top of the column to refine methyl acetate and prevent acetic acid from being entrained as the product is distilled overhead in the column. By properly balancing the addition rates, the reaction provides methyl acetate in 100% yield based on both acetic acid and methanol. (Water and acid catalyst are purged from the base.) By operating in this mode, Eastman Chemical Company reduced the methyl acetate process from seven units of operation to one unit of operation consisting of a single distillation column.

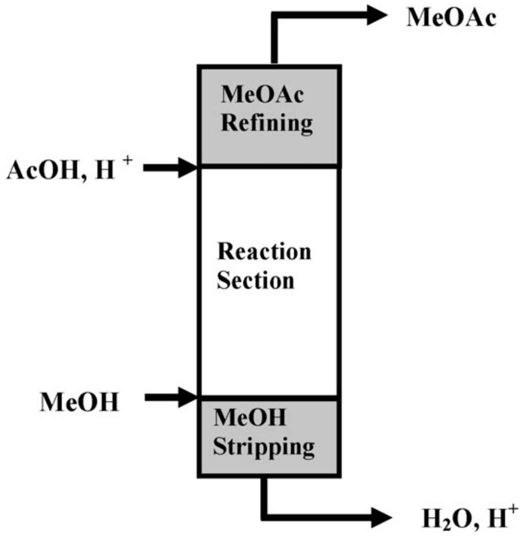

**Fig. 3.** Reactive distillation of methanol and acetic acid to form methyl acetate.

The remaining challenge, and the heart of the process, was the carbonylation of methyl acetate to acetic anhydride [8,9] (see Eq. (2)). While the Rh–MeI carbonylation of methanol [10] in water was known at the time, the catalyst was inoperative for the carbonylation of methyl acetate. There were several reasons. If we examine the reaction mechanism for the carbonylation of methanol, shown in Fig. 4, several important functions are not achievable using the catalyst as it existed. First, the active catalyst failed to form. Rather than the very active $\mathrm{Rh(CO)_2I_2^-}$ anion, the predominant species were the much less reactive neutral species, $\mathrm{Rh(CO)_3I}$ and $\mathrm{[Rh(CO)_2I]_2}$. Whereas water provided hydronium ion as a counterion for the $\mathrm{Rh(CO)_2I_2^-}$ anion in the aqueous methanol carbonylation, there was no analogous source of a cation under anhydrous conditions, so the active catalyst failed to form.

$$\mathrm{MeOAc} + \mathrm{CO} \rightleftarrows \mathrm{Ac_2O} \tag{2}$$

There are further complications. Whereas water reacts readily with acetyl iodide to generate acetic acid and hydrogen iodide, the desired analogous reaction of acetyl iodide with acetic acid to acetic anhydride and HI (reaction (3)) is thermodynamically disfavored and does not proceed. The alternative reaction of acetyl iodide with methyl acetate to form methyl iodide and acetic anhydride is slow at best. As a consequence, even when acetyl iodide is formed, the reaction stops at the production of acetyl iodide and cannot readily proceed.

$$\mathrm{AcI} + \mathrm{AcOH} \rightarrow \mathrm{Ac_2O} + \mathrm{HI} \quad \Delta H = +2.1\ \mathrm{kcal/mol} \tag{3}$$

Further, unlike the methanol carbonylation, which thermodynamically highly favored ($\Delta G_{298\ \mathrm{K}} = -17.8$ kcal/mol), the methyl acetate carbonylation (see Eq. (2)) is only slightly favored ($\Delta G_{298\ \mathrm{K}} = -2.5$ kcal/mol). Under reaction conditions, the value of $\Delta G$ is slightly <1 kcal/mol and the reaction is an equilibrium process. (The impact of the equilibrium limits was partially offset by the application of higher pressures.)

These problems were resolved by the addition of LiI. First, the addition of a soluble salt allowed the active anionic catalyst,

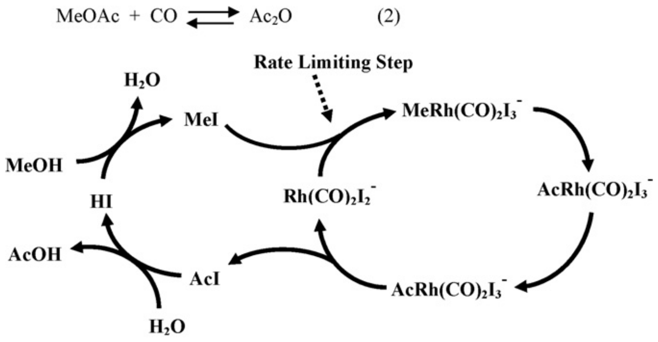

**Fig. 4.** Rh–MeI catalyzed carbonylation of methanol.

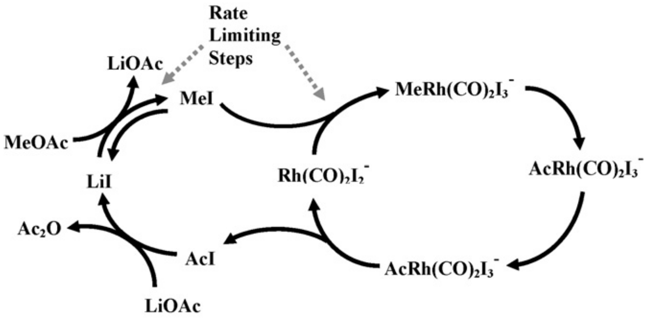

**Fig. 5.** Rh–Li–MeI catalyzed carbonylation of methyl acetate.

$Rh(CO)_2I_2^-$, to form. However, Li also allowed the organic cycle to proceed readily. LiI reacts with methyl acetate in an equilibrium process to form LiOAc and MeI (see Eq. (4)). LiOAc in turn reacts readily with acetyl iodide allowing the reaction to proceed. While many cations could serve as a counterion for the $Rh(CO)_2I_2^-$ catalyst, Li was unique in its efficacy in accelerating the organic portion of the catalytic cycle.

$$\mathrm{LiI} + \mathrm{MeOAc} \rightleftarrows \mathrm{LiOAc} + \mathrm{MeI} \quad K_{\mathrm{eq}(190\,^\circ\mathrm{C})} = 0.39 \tag{4}$$

The catalytic cycle using Li as a cocatalyst is shown in Fig. 5. The reaction has two potentially rate-limiting steps, namely the generation of MeI from MeOAc via the equilibrium reaction shown in Eq. (3) and the oxidative addition of methyl iodide to Rh. As expected, the kinetics were very complicated since the reaction consists of two consecutive reactions with a pre-equilibrium. Further, LiOAc, MeI, MeOAc, and LiI are not independent variables and at higher conversions one must also consider the reverse reaction since this is an equilibrium-limited process. To get the most efficient use of Rh, the process is operated with large excesses of Li to minimize the contribution of equilibrium (4) and, under these conditions, the initial reaction rates approach first order behavior in MeI and Rh.

However, there was an additional complication. In the methyl acetate carbonylation, the catalyst rapidly deactivated forming the inactive Rh(III) species, $Rh(CO)_2I_4^-$. A small amount of hydrogen was required to reduce the oxidized rhodium species back to the active Rh(I) species, $Rh(CO)_2I_2^-$. (In the earlier aqueous methanol carbonylation water gas shift provided the small quantities of hydrogen required to reverse oxidation of the catalyst.)

With the attainment of a successful process for the carbonylation of methyl acetate Eastman Chemical Company had achieved its first objective, the generation of acetic anhydride entirely from coal. The process saves the equivalent of >1 million barrels of oil per year. The initial goal of replacing ethylene only accounts for a portion of this savings since there were also substantial energy savings achieved by the elimination of natural gas as a fuel for ketene furnaces. Essentially, Eastman Chemical Company had shifted the dehydration step from a highly endothermic, entropically driven ketene generation to a nearly thermodynamically neutral esterification. By shifting to a reactive distillation column Eastman also realized substantial savings in distillation costs. In ketene furnaces, a wet acetic acid stream is obtained and water needs to be removed overhead by distillation with a high-energy penalty. However, in the reactive distillation, water is not distilled overhead, but instead is purged as a high boiling stream from the base of the column. As a consequence, there is no energy lost distilling the water by-product from the product or starting material streams.

The Eastman Chemical Company coal to acetic anhydride process entailed several commercial "firsts". It was the first commercial demonstration of modern coal gasification, the first commercial application of reactive distillation, and the first commercial demonstration of methyl acetate carbonylation. Later, it would include the first commercial demonstration of the Air Products/Chem Systems Liquid Phase Methanol process.

At the end of this successful endeavor, Eastman Chemical Company had successfully demonstrated that coal was a reliable and clean source of synthesis gas and energy. Eastman Chemical Company had successfully converted the coal-based synthesis gas to methanol, methyl acetate, acetic acid, and acetic anhydride. Eastman Chemical Company was now prepared to proceed to the next phase of its Chemicals from Coal program and examine additional large-scale products that might be generated entirely from coal-based synthesis gas. Two additional case studies appear below.

## 4. Case study 2

### 4.1. *Vinyl acetate [11]*

Vinyl acetate (vinyl acetate monomer, VAM) has been a favored target for a synthesis gas based process [12,13]. The current commercial process involves the oxidative acetoxylation of ethylene with acetic acid [13–16] and is outlined in Fig. 6. Besides the cost of ethylene (as opposed to synthesis gas) the key reaction of acetic acid with ethylene and oxygen (reaction (5)) has some key limitations, since:

(i) The reaction must run below the explosion limits, resulting in a limited conversion.
(ii) Like many oxidations, it is difficult to limit overoxidation to $CO_2$ leading to reduced yields and, unfortunately, the reaction is inhibited by $CO_2$ requiring a complex $CO_2$ removal system to maintain the reaction. (Ethylene yields are only about 87–94% depending on the age of the catalyst, acetic acid yields are somewhat higher, 98–99% but this is misleading since some of the ethylene is converted to acetic acid.)
(iii) The catalyst (Pd/Au) is expensive and lifetimes are moderate (about 1–1.5 years).

$$\mathrm{AcOH} + \mathrm{H_2C{=}CH_2} + (1/2)\mathrm{O_2} \rightarrow (\mathrm{AcO})\mathrm{HC{=}CH_2} + \mathrm{H_2O} \tag{5}$$

By 1980, while a large portion of acetic acid produced commercially was still generated from ethylene, methanol carbonylation had displaced acetaldehyde oxidation as the preferred method of producing acetic acid. Therefore, since the acetic acid portion of the process was already undergoing conversion to a synthesis gas based process, the focus of the completely synthesis gas based processes for vinyl acetate was to replace the ethylene component and cumbersome oxidative acetoxylation.

Initial synthesis gas based vinyl acetate concepts recycled large quantities of acetic acid and carbonylated large amounts of methyl

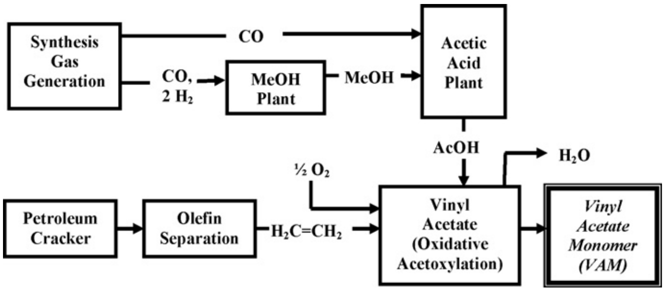

**Fig. 6.** Current commercial vinyl acetate monomer (VAM) process.

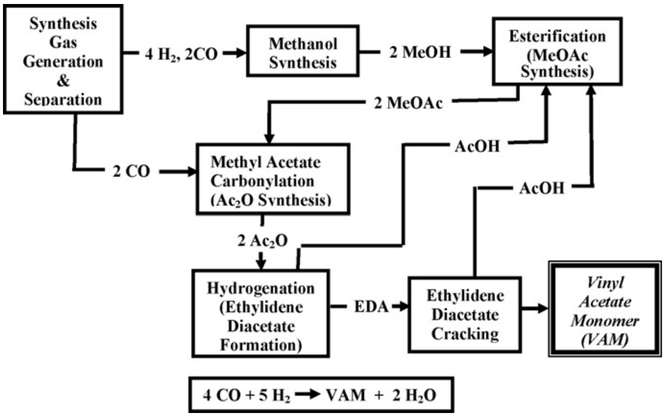

**Fig. 7.** Prior proposals for an all synthesis gas based route to vinyl acetate [14,16] (EDA = 1,1-diacetoxy ethane; ethylidene diacetate).

acetate [12,13]. An example is shown in Fig. 7. The most capital intensive part of the process was the carbonylation of methyl acetate. Unfortunately, these earlier schemes would have required a plant that would have generated 2.37 kg of acetic anhydride, 2.40 kg of ethylidene diacetate (EDA, 1,1-diacetoxyethane) and recycled 1.40 kg of acetic acid for each kilogram of vinyl acetate produced if every reaction operated stoichiometrically. Therefore, while these earlier processes had lower feedstock costs, they were overwhelmed by capital costs and were never viable.

While early Eastman Chemical Company efforts followed pathways similar to these earlier proposals, Eastman Chemical Company ultimately devised a much simpler production scheme (see Fig. 8) which eliminated the large acetic acid recycle stream and significantly reduced the size of the intermediate plants. The key features were replacing the methyl acetate carbonylation with a carbonylation of dimethyl ether (reaction (6)), hydrogenation of the acetic acid co-product from the production of vinyl acetate to generate acetaldehyde (reaction (7)), and a reactive distillation that represented a marked improvement for the conversion of acetic anhydride and acetaldehyde to form VAM. As a consequence, the plant sizes shrink markedly. For example, the expensive carbonylation step is now halved. A comparison of the stoichiometric volumes required for the older synthesis gas based processes for VAM and the Eastman Chemical Company synthesis gas based process is shown in Fig. 9.

$$\mathrm{Me_2O + 2CO \rightarrow Ac_2O} \qquad (6)$$

$$\mathrm{AcOH + H_2 \rightarrow AcH + H_2O} \qquad (7)$$

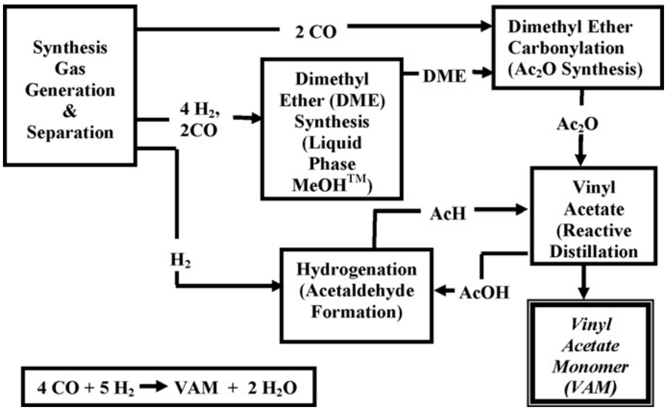

**Fig. 8.** Eastman Chemical Company all synthesis gas based route to vinyl acetate [11].

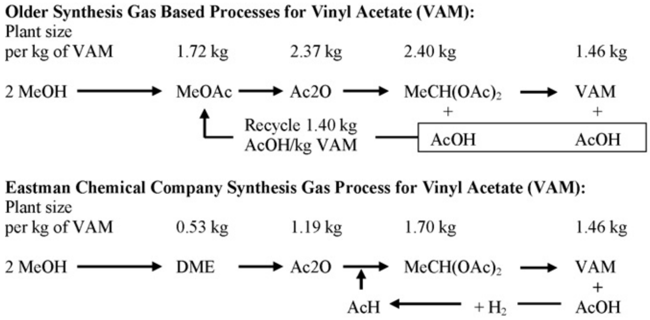

**Fig. 9.** Comparison of syntheisis gas based processes to vinyl acetate. (Based on stoichiomtery.)

The dimethyl ether required as a feedstock could be provided by the Liquid Phase Methanol™ process [6] or by the very well-established dehydration of methanol over γ-alumina. The carbonylation of dimethyl ether is also now well known and past processes have used the same catalysts as the methyl acetate carbonylation [17,18]. (Most patents granted for the generation of acetic anhydride by carbonylation include claims and examples demonstrating that the catalysts are applicable to both dimethyl ether and methyl acetate carbonylation.) The key chemical and engineering breakthroughs were in the area of vinyl acetate generation from acetaldehyde and acetic anhydride and the hydrogenation of acetic acid to acetaldehyde.

While the conversion of acetic anhydride and acetaldehyde was known and had been commercially practiced [19], the process used five to six units of operation and required extensive recycling. Eastman Chemical Company devised a reactive distillation that could be used to reduce this process to two units of operation. However, operating a reactive distillation for the conversion of acetic anhydride and acetaldehyde to vinyl acetate would be much more complex than the earlier reactive distillation of acetic acid and methanol to methyl acetate for several reasons. First, unlike the earlier reactive distillation to form methyl acetate, the formation of vinyl acetate from acetic anhydride and acetaldehyde consisted of two equilibria as shown in reactions (8) and (9), both of which are acid catalyzed.

$$\mathrm{AcH + Ac_2O \rightleftarrows CH_3CH(OAc)_2} \quad K_{\mathrm{eq}(140\,^\circ\mathrm{C})} = 25 \qquad (8)$$

$$\mathrm{CH_3CH(OAc)_2 \rightleftarrows AcOH + H_2C{=}CH(OAc)} \quad K_{\mathrm{eq}(140\,^\circ\mathrm{C})} = 0.01 \qquad (9)$$

Further, unlike the methyl acetate reactive distillation, the vinyl acetate product was an intermediate boiling component not the lowest boiling component in the mixture. Instead, the starting material (AcH) is the lowest boiling component. Furthermore, an intermediate (ethylidene diacetate, $CH_3CH(OAc)_2$) is formed as the most thermodynamically favored product and represents the highest boiling component in the mixture. An additional complication arose during the demonstration of the process which presents a design challenge. When operated, the column had a peculiar temperature profile wherein the mid-point of the column is the hottest point in the column, not the base. (The reason for the odd temperature profile will become clear as the operation is described further.)

Regardless of the difficulties, Eastman Chemical Company was able to demonstrate the reactive distillation of acetaldehyde and acetic anhydride to vinyl acetate and acetic acid [11,20]. An illustration of how the bench scale demonstration was operated is shown in Fig. 10. Descriptively, the reactive distillation consisted of two sections, a reaction section at the bottom and

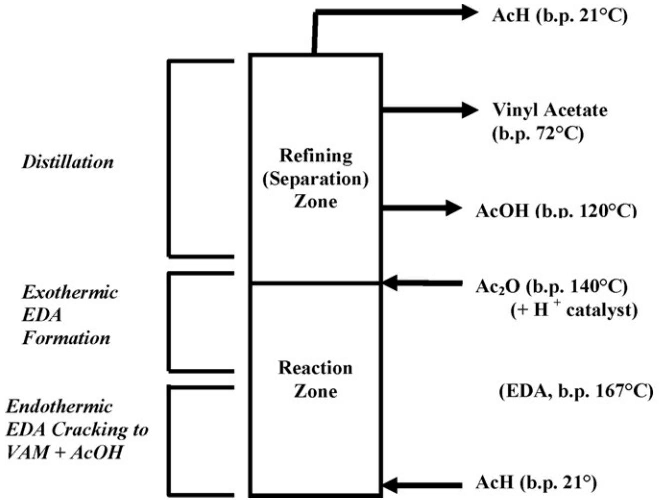

**Fig. 10.** Reactive distillation of acetaldehyde and acetic anhydride to vinyl acetate (EDA = ethylidene diacetate; 1,1-diacetoxyethane).

a refining section at the top. Acetic anhydride (b.p. 140 °C) and a strong acid catalyst were added at the top of the reaction section and acetaldehyde was added at or close to the bottom of the reactor section. Conceptually, as the acetaldehyde (b.p. 21 °C) ascended the column, it encountered an increasingly rich acetic anhydride stream, forcing the formation of ethylidene diacetate (b.p. 167 °C) which, as the highest boiling component, began to descend down the column. As the ethylidene diacetate descended down the column it began to crack to form acetic acid (b.p. 118–120 °C) and vinyl acetate (b.p. 72 °C) in a disfavorable equilibrium. However, the acetic acid and vinyl acetate have lower boiling points than acetic anhydride or ethylidene diacetate. Although they are continuously undergoing equilibration to reform ethylidene diacetate, they were eventually distilled out of the reaction zone and into the refining zone, where, since they were now free of acid catalyst, equilibration ceased and they were now readily separated.

Although the hope was to capture all the acetaldehyde in the reaction zone, in practice an excess of acetaldehyde (1.2–2.3 AcH mol/mol $Ac_2O$) was required to operate the reactive distillation. (The actual amount of excess acetaldehyde required was dependent on the pressure used in the reactor.) The excess acetaldehyde was distilled overhead. In the bench scale unit, the yields were 100% based on acetic anhydride added and 80% based on acetaldehyde. However, the acetaldehyde yields are somewhat deceiving since the primary yield loss was attributable to incomplete acetaldehyde recovery since the bench scale unit lacked the refrigeration unit or compressor that would have been required for efficient recovery of acetaldehyde. The bench scale unit provided purified vinyl acetate and acetic acid containing minor amounts of vinyl acetate. Although the vinyl acetate product obtained in the laboratory initially met specifications, a second unit of operation would likely be required to insure the complete removal of any trace quantities of acetaldehyde from the vinyl acetate product.

The reason for the peculiar temperature profile observed in the column becomes clear when we look at Fig. 10. At the point acetic anhydride and acid catalyst was introduced, an exothermic reaction between acetaldehyde and acetic anhydride to form ethylidene diacetate (reaction (8)) ensued rapidly. As the ethylidene diacetate descends the column it then begins to crack in an endothermic reaction, which cools the lower portion of the column. While causing design difficulties, the high mid-point temperature does accelerate the removal of vinyl acetate and acetic acid from the reaction zone into the refining section.

The acetaldehyde required to feed the reactive distillation was obtained from the acetic acid co-produced from the reactive distillation. However, the hydrogenation of acetic acid to acetaldehyde (reaction (7)) is not a trivial reaction to conduct since the reaction is slightly endothermic ($\Delta G_{300\,^{\circ}\mathrm{C}} = +2.5$ kcal/mol), and, therefore, is slightly disfavored. Unfortunately, the subsequent hydrogenation of acetaldehyde to ethanol is highly exothermic and very favorable. To overcome this problem, the hydrogenation of carboxylic acids to aldehydes is normally conducted in the presence of a very large excess of hydrogen to force the reaction to proceed and is operated at low conversion to avoid further reduction to the alcohol. Unfortunately, this approach fails in practice for the hydrogenation of acetic acid to acetaldehyde since, due to its low boiling point (b.p. 19–21 °C), acetaldehyde becomes difficult to recover if the ratio of $H_2$:AcH is too high.

Further complicating the hydrogenation was the presence of additional side reactions. For example, formation of symmetrical ketones, due to decarboxylative condensation of the acid starting material, is often a problem in carboxylic acid hydrogenation. In addition, over reduction to the alkane or decarboxylation (leading to a hydrocarbon with one less carbon than the parent carboxylic acid) are also often observed. These potential side reactions are shown for the case of acetic acid in reactions (10)–(12) below.

$$2\mathrm{AcOH} \rightarrow \text{acetone} + \mathrm{CO_2} + 2\mathrm{H_2O} \tag{10}$$

$$\mathrm{AcOH} + 3\mathrm{H_2} \rightarrow \text{ethane} + 2\mathrm{H_2O} \tag{11}$$

$$\mathrm{AcOH} \rightarrow \mathrm{CH_4} + \mathrm{CO_2} \tag{12}$$

Therefore, the challenge that faced Eastman Chemical Company was to identify a catalyst that simultaneously:

(1) Operated at hydrogen: acetaldehyde ratios that are amenable to the recovery of the acetaldehyde product.
(2) Minimized the further reduction of acetaldehyde over ethanol.
(3) Minimized the formation of acetone.
(4) Did not lead to the co-production of hydrocarbons.

While a significant challenge, this was accomplished with a Pd catalyst supported on iron oxide. While a complete description is provided in the literature [11], this catalyst, when operated at 300 °C, 18 atm of pressure, a $H_2$:AcOH ratio of 7:1, and ca. 40% acetic acid conversion, provided acetaldehyde with a selectivity of >86%. AcH could be readily recovered from a stream with this composition and there was very little acetone formation (<1.5%) and very little hydrocarbon (methane, ethane, or ethylene) formation (<0.1% of product). The remaining products were ethanol and ethyl acetate resulting from over reduction to ethanol. These results were well within the desired target parameters.

There were two critical parameters in successfully operating the hydrogenation of acetic acid to acetaldehyde. First, the iron oxide support needed to be reduced to Fe(II) to minimize acetone formation and for maximal activity. Second, it was critical to correctly optimize the acetic acid partial pressure. The rate and selectivity for the hydrogenation of acetic acid to acetaldehyde initially increased as a function of increasing acetic acid partial pressure, reached a maximum, beyond which point any additional acetic acid increasingly inhibited the reaction and reduced selectivity. (This behavior is common in heterogeneous catalysis and the graphs are often referred to as “volcano” plots.) Locating this maximum was critical to the good performance of this catalyst.

With the identification of an adequate hydrogenation catalyst for acetic acid to acetaldehyde and the demonstration of a reactive distillation for the conversion of acetaldehyde and acetic anhydride to vinyl acetate, Eastman Chemical Company had successfully demonstrated a synthesis of vinyl acetate entirely from synthesis gas. By using reactive distillation, employing fewer steps, and eliminating large acetic acid recycles, the Eastman Chemical Company process used a minimum number of units of operation and reduced the scale of each operation resulting in substantially lower capital investment and, consequently, the conversion of synthesis gas to vinyl acetate could now be seriously considered as a potential replacement process. Additional approaches to shortening the reaction paths involving esterification of acetaldehyde with ketene and ketene hydrogenation to generate acetaldehyde in high yield and high selectivity have also been described by Eastman Chemical Company and can be found in the literature [11].

## 5. Case study 3

### 5.1. Methacrylic acid [21]

The existing process for methacrylic acid consists of the addition of hydrogen cyanide to acetone to form acetone cyanohydrin, subsequent dehydration to methacrylonitrile and subsequent hydrolysis of methacrylonitrile to methacrylic acid. (The dehydration and hydrolysis may be operated sequentially or in a single unit depending on the producer.) The acetone feedstock is ultimately derived from propylene and may be formed intentionally, or more commonly, as a by-product from other manufacturing processes. The real downfall of this process is that the hydrolysis of methacrylonitrile with sulfuric acid results in 1.1 kg of ammonium bisulfate by-product for each kilogram of methacrylic acid produced. The ammonium bisulfate must be discarded, with a substantial environmental penalty, or laboriously recycled to reform hydrogen cyanide (although recycle still produces a sulfate waste stream).

Eastman Chemical Company in cooperation with Research Triangle Institute, sought to displace this environmentally challenged process with a more environmentally friendly synthesis gas based process. The synthetic scheme chosen for this investigation is shown in Fig. 11 and the key technologies were a unique Mo catalyzed carbonylation of ethylene to form propionic acid (or a derivative) [21–23] and a $Nb_2O_5$–$SiO_2$ catalyzed condensation of formaldehyde with a propionate derivative [21,24]. The ethylene feedstock could be generated using a methanol to olefins process (a process commercially licensed by UOP/HYDRO), dehydration of ethanol, or if desired, could tap into the existing ethylene infrastructure.

The unique Mo catalyzed carbonylation of ethylene (reaction (13)) to form propionic acid, propionic anhydride, or methyl propionate, was a homogeneous catalyst composed of inexpensive zerovalent $Mo(CO)_6$, ethyl iodide, and an iodide salt. A small amount of hydrogen was required to maintain catalyst activity [22,23]. When operated at 160 °C and less than 45 atm of pressure, turnover frequencies exceeded 360 mol propionate/mol of Mo/h. Unlike many other ethylene carbonylation catalysts the Mo catalyst can be used to generate propionic acid, propionic anhydride, or methyl propionate with equal alacrity.

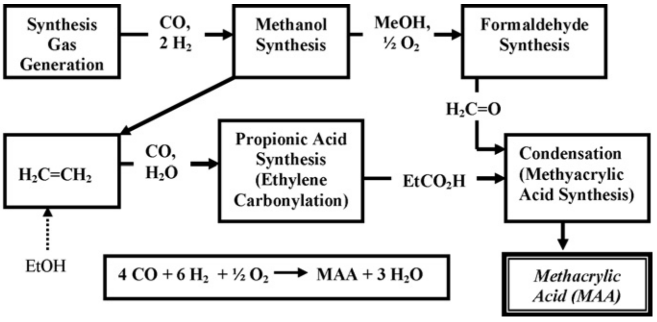

**Fig. 11.** Synthesis gas based route to methacrylic acid.

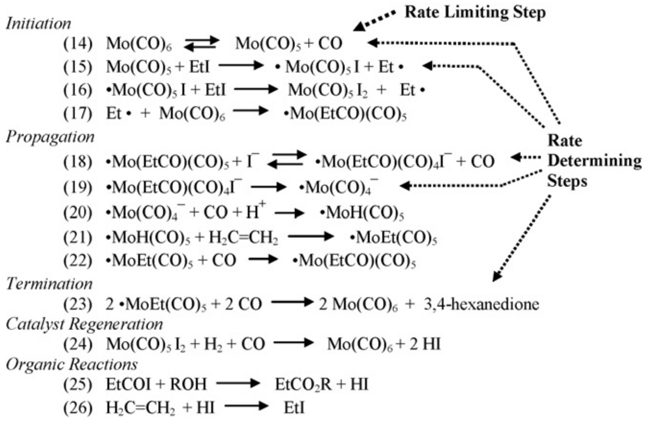

**Fig. 12.** Proposed mechanism for the carbonylation of ethylene using a $Mo(CO)_6$ catalyst.

$$H_2C{=}CH_2 + CO + ROH \rightarrow CH_3CH_2CO_2R \tag{13}$$

$$R{=}Me, H, CH_3CH_2C({=}O){-}$$

The process was unique in several ways. While it was the first example of a chromium group metal proven to be useful in a carbonylation, the preponderance of evidence indicates that it proceeds via a unique organometallic free radical mechanism as shown in Fig. 12.

Like any radical process, the reaction sequence had the classical steps of initiation, propagation, and termination associated with a radical process. Like most radical processes, it had a rate-limiting initiation step, but like most radical reactions, it also had subsequent rate determining steps which reflect how long the radical chain is maintained. (It is important to distinguish between a rate-limiting step, which reflects the slowest step in a process, and rate determining steps, which consists of any step which ultimately affects the rate of the reaction.)

The proposed mechanism agreed well with the kinetics. Using the steady state approximation, the mechanism in Fig. 12 resulted in following rate equation:

$$\text{Rate} = k_{\text{obs}}\frac{[\text{EtI}]^{1/2}[\text{Mo(CO)}_6]^{1/2}[\text{I}^-]}{(K_{\text{m1}}[P_{\text{CO}}] + [\text{EtI}])^{1/2}(K_{\text{m2}}[P_{\text{CO}}] + 1)}$$

where $k_{\text{obs}} = (k_{18}k_{14}{}^{1/2})/k_{23}{}^{1/2}$; $K_{\text{m1}} = k_{-14}/k_{15}$; $K_{\text{m2}} = k_{-18}/k_{19}$. As shown in Table 1, a comparison of the expected rate dependencies and the observed rate dependencies shows that there was a good agreement between the observed kinetics and those expected if the proposed mechanism is operative. (The hydrogen component did not enter the kinetics once there is sufficient hydrogen to permit the reduction of Mo(II) to Mo(0) as shown in Eq. (24).)

In organic chemistry, reactions orders of 1/2 or 3/2 are normally indicative of a free radical reaction. However, there was additional supporting evidence for a radical process, specifically:

- The reaction was ineffective for carbonylations that normally proceed via nucleophilic processes such carbonylations utilizing methyl iodide or benzyl bromide.

**Table 1**
Comparison of expected and observed rate behaviors for the Mo catalyzed carbonylation of ethylene.

| Component | Expected order | Observed order |
|---|---|---|
| $P_{CO}$ | −1 to −1.5 | −1.2 (varies with [EtI]) |
| Mo | 0.5 | 0.6 |
| $I^-$ | 1 | 1.0 |
| EtI | Complex form should fit:<br>$(C_1[EtI]^{1/2})/(C_2 + [EtI])^{1/2}$ | Conforms to:<br>$(C_1[EtI]^{1/2})/(C_2 + [EtI])^{1/2}$ |
| $H_2C{=}CH_2$ | 0 | 0 |

- The reaction was inhibited by radical scavengers or other metals.
- Low levels of coupled products (3,4-hexanedione and its derivatives) were detected in the product mixture.
- There was literature precedent for the generation of radicals from alkyl halides and zerovalent Mo species via an electron transfer process [25,26].
- The catalyst composition was subsequently demonstrated to induce another free radical process [27] (benzyl ether fragmentation).

Further, there was evidence that reaction (15) proceeded via an inner sphere electron transfer process as shown below:

$$Mo(CO)_5 + EtI \rightarrow {}^{\bullet}Mo(CO)_5{}^{+} + EtI^{\bullet -} \qquad (27)$$

$$EtI^{\bullet -} \rightarrow Et^{\bullet} + I^{-} \qquad (28)$$

$$^{\bullet}Mo(CO)_5{}^{+} + I^{-} \rightarrow {}^{\bullet}Mo(CO)_5I \qquad (29)$$

The resultant $^{\bullet}Mo(CO)_5$ I species was expected to undergo additional, more rapid, electron transfer with EtI.) Supporting evidence for the electron transfer process was as follows:

- The radical behavior mentioned above.
- The literature precedent demonstrating that Mo(0) species interact with alkyl halides via an electron transfer process (also described above).
- There was no dependence upon the nature of the halide used. The same rate is observed when EtBr and a bromide salt are substituted for EtI and an iodide salt. (This is characteristic of an electron transfer process.)
- As expected with an electron transfer process, the reaction was markedly accelerated by the addition of a polar aprotic solvent [28].

The belief that this is an inner sphere process was based on the observation that the rate-limiting step was the dissociation of CO from $Mo(CO)_6$ and the fact that the reaction could be inhibited by large excesses of weak ligands, such as water. Both observations were indicative of the requirement for a vacant coordination site and would imply an inner sphere process.

The unique mechanism had some interesting consequences. First, while ethylene was one of the key reactants, it did not enter the rate equation and was irrelevant to the kinetics once there is sufficient ethylene to overcome mass transfer. Second, the reaction, unlike many carbonylations, is inversely dependent on CO and the reaction accelerates as the partial pressure of CO is decreased. There is a limit since the reaction will proceed so fast at low pressure that the CO ligands are cannibalized and Mo precipitates. As a consequence, this reaction was destined to be one of the lowest pressure processes for ethylene carbonylation. Further, unlike many other catalysts which proceed via nucleophilic processes, the Mo catalyst is useful for the generation of methyl propionate and propionic anhydride. (Prior catalysts co-produced acetic acid when attempting to generate methyl propionate and when attempting to generate propionic anhydride, the reactions were product inhibited and, as a consequence, could only proceed at low conversion.)

The key to make this process work was, that by generating a radical and subsequently capturing the radical with zerovalent $Mo(CO)_6$ (reaction (17)), the normally kinetically inert 18-$e^-$ electron $Mo(CO)_6$ was converted to a 17-$e^-$ electron Mo(I) species which could never be coordinatively satisfied. As a consequence, the ligand exchanges and additions required for active catalysis became very rapid as the Mo species rapidly shuttled between 17-$e^-$ electron and 19-$e^-$ electron species. (The exchange of ligands in 17-$e^-$ and 19-$e^-$ Mo species often occurs at diffusion limited rates.)

With a superior ethylene carbonylation in place, attention was turned to the condensation of formaldehyde with propionic acid ($EtCO_2H$) or its derivatives. The catalyst used for the condensation was a niobium oxide on silica catalyst [21,24,29] and the optimal catalysts were found to have a Nb/Si ratio between 1:9 and 1:4, representing a 10–20 wt.% Nb loading. The niobium oxide–silica catalysts used in this process are amphoteric catalysts and both selectivities and lifetimes were found to be optimal when the relative ratio of weak acid/base sites to strong acid/base sites, a condition met by the 10–20 wt.% Nb on silica catalysts.

Since the Mo catalyst could readily generate methyl propionate, propionic acid, and propionic anhydride, all three were tested in the process. Condensation of formaldehyde with propionic acid provided the highest rates and selectivities, although propionic anhydride was nearly as useful. However, the condensation of formaldehyde with methyl propionate was less selective and not as fast. As a consequence, the study focused on the condensation of propionic acid with formaldehyde.

In practice, the 10–20% Nb on silica catalyst was operated using a 4:1 excess of propionic acid: formaldehyde. The reaction was co-fed with nitrogen as a diluent (propionic acid:formaldehyde:nitrogen ratio = 4:1:12; 1100 $cm^3/(g_{cat}\,h)$) and operated at 300 °C and 2 atm pressure. When operated in this mode, the conversion of formaldehyde was 75% and conversion of propionic acid was 16%. Selectivities were very good. (93–97% based on formaldehyde consumed and 97–99% based on propionic acid consumed.) The primary by-products observed were carbon monoxide (from formaldehyde), carbon dioxide, and diethyl ketone. (The later two products come from decarboxylative condensation of propionic acid with itself.)

The primary mode of deactivation was reduction of $Nb_2O_5$ to less active (or inactive) $Nb_2O_3$ by formaldehyde as shown in reaction (30), a process that also accounts for the carbon monoxide co-product. A slower, secondary mode of deactivation was carbonization of the surface. As a consequence, the catalyst required periodic reactivation with air to reoxidize Nb(III) to Nb(V) and to combust the carbon residues.

$$(1/2)Nb_2O_5 + H_2C{=}O \rightarrow (1/2)Nb_2O_3 + CO + H_2O \qquad (30)$$

The attainment of a synthesis gas based process for methacrylic acid represented a safer and less polluting process by eliminating the use of hydrogen cyanide and by eliminating the associated ammonium bisulfate waste stream. The process was surprisingly competitive and the synthetic pathway has been implemented by Davy-Lucite [30], although they use different catalysts than those used in the Eastman Chemical Company – Research Triangle Institute process, which verifies the commercial viability of this approach.

## 6. Conclusions

As these three processes indicate, it is feasible to displace large scale organic chemicals currently produced from natural gas or natural gas liquids with coal-based synthesis gas. As natural gas becomes increasingly more expensive relative to more abundant coal and as the United States seeks a hydrogen-based economy and energy independence, Eastman Chemical Company believes that coal gasification should play a critical role in the transition and continues to research improved gasification and chemical generation using coal as a feedstock. Improvements in coal gasification that Eastman Chemical Company has made over the course of its 24+ years of gasifier operation demonstrates that coal gasification is a clean process with the potential of allowing access to energy with reduced greenhouse gases since the gasification process also permits ready sequestration of $CO_2$ as a part of its operation. Consistent with this belief, Eastman Chemical Company has announced plans to construct gasifiers and operate associated chemicals production in additional locations [31–33]. These announcements represent new locations for Eastman Chemical Company, express confidence in the technology for chemical production, and demonstrate that the advantages are not unique to their Kingsport, TN site.

In a parallel to the petrochemical industry, where large scale oil refineries directed primarily toward fuel production for transportation and heating gave birth to a dependent petrochemical industry, one can easily envision an analogous emergence of a “coal chemical” industry wherein widespread, large scale coal gasification units dedicated primarily to the production of electrical power and transportation fuels would provide the economies of scale for the synthesis gas feedstocks that can make chemicals from coal a widespread alternative to most of the chemical processes now dependent upon natural gas components and petroleum resources.

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