SYNTHESIS OF ACRYLATES AND METHACRYLATES FROM COAL-DERIVED
SYNGAS

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ABSTRACT

Research Triangle Institute (RTI), Eastman Chemical Company, and Bechtel collectively are developing a novel process for the synthesis of methyl methacrylate (MMA) from coal-derived syngas, under a contract from the U.S. Department of Energy, Federal Energy Technology Center. This three-step process consists of synthesis of a propionate, its condensation with formaldehyde, and esterification of resulting methacrylic acid (MAA) with methanol to produce MMA. Eastman has focused on the propionate synthesis step. The resultant Mo catalysts work efficiently at much less severe conditions (170 °C and 30 atm) than the conventional Ni catalysts (270 °C and 180 atm). Bechtel has performed an extensive cost analysis which shows that Eastman's propionate synthesis step is competitive with other technologies to produce the anhydride. Eastman and Bechtel have also compared the RTI-Eastman-Bechtel three-step methanol route to five other process routes to MMA. The results show that the product MMA can be produced at 52¢/lb, for a 250 Mlb/year MMA plant, and this product cost is competitive to all other process routes to MMA, except propyne carbonylation. In the second step, RTI and Eastman have developed active and stable V-Si-P ternary metal oxide catalysts, Nb/SiO₂, and Ta/SiO₂ catalysts for condensation of propionic anhydride or propionic acid with formaldehyde. RTI has demonstrated a novel correlation among the catalyst acid-base properties, condensation reaction yield, and long-term catalyst performance. Eastman and Bechtel have used the RTI experimental results of a 20 percent Nb/SiO₂ catalyst, in terms of reactant conversions, MAA selectivities, and MAA yield, for their economic analysis. Current research focuses on enhancing the condensation reaction yields, a better understanding of the acid-base property correlation and enhancing the catalyst lifetime.

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LIST OF ACRONYMS

ACH	Acetone cyanohydrin
ASPEN	Advanced system for process engineering
DEK	Diethyl ketone
DME	Dimethyl ether
ESCA	Electron spectroscopy for chemical analysis
GC	Gas chromatograph
GC/FID	Gas chromatography/flame ionization detector
GC/MS	Gas chromatography/mass spectrometry
HCHO	Formaldehyde
HTHP	High-temperature, high-pressure
MGC	Mitsubishi Gas Chemical
MAA	Methacrylic acid
MMA	Methyl methacrylate
MP	Methyl propionate
MTBE	Methyl tert-butyl ether
NCSU	North Carolina State University
PA	Propionic acid
PAA	Propionic anhydride
ROI	Return on investment
SRI	Stanford Research Institute
SS	Stainless steel
SEM	Scanning electron microscope
RTI	Research Triangle Institute
STP	Standard temperature and pressure
TCD	Thermal conductivity detector
TEM	Transition electron microscope
XRD	X-ray diffraction
XRF	X-ray fluorescence

EXECUTIVE SUMMARY

Eastman has completed its experimental work in the generation of propionate derivatives. Over the last quarter, Eastman has primarily devoted its time to developing the economic model for the overall process. For the economic model, Eastman has compared the product value of the three-step methanol route to five other process routes to MMA, and the results show that for RTI-Eastman-Bechtel route, product MMA value of 52¢/lb for a 250 Mlb/year plant is competitive with each of the other process routes to MMA, except propyne carbonylation. Eastman has also developed several key invention reports as a part of its experimental research. Research Triangle Institute (RTI) is continuing to develop stable and selective catalysts for condensation of propionic anhydride or propionic acid with formaldehyde. A 20 percent Nb/SiO₂ catalyst has given the maximum methacrylic acid (MAA) yield at nominal operating conditions of 300 °C, 2 atm, 72:16:220 mmol/h propionic acid:formaldehyde:nitrogen, 5 g (16 to 25 mesh) catalyst charge. The performance of this catalyst in terms of reactant conversions, product selectivities, and MMA yield was the basis of Eastman-Bechtel cost comparison. The long-term deactivation study of this catalyst showed that it is at least three times as stable as the V-Si-P 1:10:2.8 and 10 percent Ta/SiO₂ catalyst, at nominally identical reaction conditions. All three catalysts deactivate primarily by coke deposition and are partially regenerable by oxidative regeneration. RTI and Eastman have filed a patent application on these novel Nb catalysts. RTI is continuing to synthesize more acid-base catalysts with a goal of developing a stable catalyst. Over the last quarter, RTI also prepared extended abstracts and slides for two presentations (one for Acid-Based Catalysis III in Rolduc, Germany, April 1997 and the other for XIII North American Meeting of the Catalysis Society, Chicago, IL, May 1997) and is currently preparing a manuscript for the Chemical Reaction Engineering VI Conference (Chemical Reactor Engineering for Sustainable Processes and Products, Banff, Alberta, Canada, June 8-13, 1997).

INTRODUCTION

The most widely practiced commercial technology for the synthesis of methacrylic acid (MAA) and methyl methacrylate (MMA) is the acetone cyanohydrin (ACH) process (Figure 1). The ACH process requires handling of large quantities of extremely toxic and hazardous hydrogen cyanide and generates copious amounts of ammonium sulfate wastes which are either discarded or reclaimed at substantial cost. The ACH technology is currently environmentally and economically untenable for any new expansions, primarily because of the cost of either disposing or regenerating the bisulfate waste.

There is a strong drive within the chemical industry for a replacement process for MMA synthesis (Gogate et al., 1996a; Spivey et al., 1995a; Spivey et al., 1996). There is a particular interest in the process that is not petroleum-based, but rather based on domestically produced coal-based syngas. The processes based on C_2 -carbonylation shown in Figure 2 are commercially attractive technologies for MMA manufacture (Spivey et al., 1995a, 1995b; McKetta, 1989). Each of these four processes goes through a propionate intermediate, which is condensed with formaldehyde to produce either MAA (Processes [I] and [II]) or a mixture of MAA and MMA (Processes [III] and [IV]). (Note that in Process [III] formaldehyde is produced by partial oxidation of methanol, which also esterifies the resulting MAA to MMA.) The water produced in the partial oxidation reaction hydrolyzes a portion of the propionic anhydride (PAA) to form propionic acid (PA) which is recycled. The Research Triangle Institute (RTI)-Eastman process (Process [III]) is comprised of the following steps:

Step 1: Propionate synthesis from ethylene (1) and ethylene plus propionic acid (2)

Step 2: Condensation of propionate with formaldehyde

Figure 1. Schematic of the ACH process.

Figure 2. C₂-carbonylation technologies for MMA manufacture.

Step 3: Esterification with methanol

In this proposed process for MMA manufacture, Step 1 is commercially practiced by Eastman Chemical Company and Step 3 is a known art. Step 2, however, presents a challenge for successful commercial demonstration of the process. This condensation step is composed of two separate condensation reactions ([3] and [4]) which give the overall stoichiometry shown in Reaction (5).

As stated earlier, the first two steps represent the key technical challenges for a successful commercial demonstration of this process. These have been the focus of the RTI-Eastman-Bechtel team research effort.

The first step, propionate synthesis, is focused on two tasks:

- Development of a homogeneous catalyst for propionate synthesis, and
- Preliminary design and economic analysis.

The second step, condensation of formaldehyde with the propionate, is also focused on two tasks:

- Development of acid-base catalyst for condensation reaction, and
- Development of combined methanol partial oxidation-condensation catalyst for one-step MMA synthesis.

The progress toward achieving these goals has been addressed in the following sections.

RESULTS AND DISCUSSION

Task 1. Propionate Synthesis (Eastman and Bechtel)

Over the last quarter, Eastman has developed an economic model for the overall process and also devoted its time to developing the potential extension of the oxidative condensation scheme to dimethyl ether (DME) as the feedstock (instead of methanol).

In order to develop an economic model for the RTI-Eastman-Bechtel three-step HOPr/MeOH-based process, Eastman examined the product value of the RTI-Eastman route and compared it to five other commercial (or potentially commercial) technologies for MMA manufacture. (Note that the RTI-Eastman route is syngas-based.) These five other technologies used for comparison in this economic analysis are:

- Conventional ACH-based process (Rohm & Haas),
- New Mitsubishi Gas Chemical (MGC) ACH-based process,
- *i*-butylene oxidation process (Lucky, Japan Methacrylic),
- *t*-butanol oxidation process (Kyodo, Mitsubishi Rayon), and
- Propyne carbonylation (Shell, ICI).

The conventional ACH-based processes, *i*-butylene oxidation and *t*-butanol oxidation, are commercial processes and the new Mitsubishi Gas Chemical process will be commercial in the near term. The propyne carbonylation process is patented by Shell and the patent rights have been acquired by ICI (reported recently in *Chemical and Engineering News*, February 1997, p. 12). The comparison is made for capital cost, production cost (or product value), and sensitivity of capital cost and product value to capacity. A consistent basis of 250 Mlb/year is used for economic estimates; for the propyne carbonylation process 100 Mlb/year capacity is assumed. A schematic of RTI-Eastman-Bechtel route to MMA is shown in Figure 3.

The general economic approach for comparison included a Stanford Research Institute (SRI) report (SRI, 1993) as a starting point for the RTI-Eastman-Bechtel three-step HOPr/MeOH-based process, and subsequently modifying SRI's material balance, reactor size, and equipment design to reflect RTI's fixed-bed reactor performance (conversion and selectivity) on a 20 percent Nb/Si catalyst at nominal operating conditions of 300 °C, 2 atm, 72:16:220 mmol/h of propionic acid:formaldehyde:nitrogen, 5 g catalyst (8 to 20 mesh or 0.7- to 1.1-mm size fraction). Eastman

Figure 3. Eastman/RTI/Bechtel three-step HOPr/MeOH-based MMA process (with external formaldehyde feed).

assumed that the reaction kinetics is first order in formaldehyde to eliminate the effect of nitrogen (used in excess as a diluent) and the large stoichiometric excess of HOPr. The raw material costs were updated. For comparison with five conventional routes currently used commercially to produce MMA, a ChemSystems report (ChemSystems, 1996) on these commercial routes was used.

The product value comparison for the RTI-Eastman-Bechtel HOPr/MeOH route with five commercial routes is shown in Figure 4. The comparison is made on a consistent basis (250 Mlb/year, 10 percent return on investment ([ROI])). The product value comparison shows that the RTI three-step process at 52¢/lb MMA is competitive with all commercial technologies for MMA manufacture, except propyne carbonylation (at 44¢/lb). However, the propyne carbonylation technology suffers from limited raw material supply and is not likely to be a commercial technology in the United States. Both the conventional ACH and MGC ACH-based process (at 73¢/lb and 70¢/lb MMA, respectively) cost more than the RTI three-step route, and so does the *I*-butylene oxidation route (at 59¢/lb). In the United States, the *I*-butylene route is not likely to be commercial because of the raw material demands for methyl tert-butyl ether (MTBE) plants. *t*-Butanol oxidation process at 55¢/lb MMA appears quite competitive with the RTI three-step process, and, with the recent Air Products and Chemicals, Inc., research aimed at converting coal-derived syngas directly into *t*-butanol, this process needs to be investigated as a possible research prospect.

Figure 4. MMA processes, product value comparison (10% ROI).

The sensitivity study of different process parameters to MMA product value for the RTI three-step process was also examined in greater detail by Eastman; the results are shown in Figure 5. The results show that among the parameters examined, reaction rate (g MAA/kg cat·h), raw material price (formaldehyde, methanol, and ethylene) and MAA selectivity have a pronounced effect on the MMA product value. For example, at a nominal reaction rate of 200 g MAA/kg cat·h (of the current RTI catalyst 20 percent Nb/SiO₂, at the following experimental conditions: 300 °C, 2 atm, 72:16:220 mmol/h PA:HCHO: N₂, 5 g catalyst charge within the size fraction .7 to 1.1 mm), the MMA product value is 58¢/lb; however, at the reaction rate of 3,300 g MAA/kg cat·h (with assumptions: first-order reaction in propionic acid, first order in formaldehyde, no nitrogen diluent, PA/HCHO=1.5), the MMA product value is only ca. 50¢/lb. Thus, even with the current RTI catalyst (20 percent Nb/SiO₂ at the above experimental conditions), the RTI three-

Figure 5. RTI-Eastman-Bechtel three-step HOPr/MeOH-based MMA process-sensitivity study.

step process is cost-competitive with all other commercial technologies for MMA manufacture. It should be noted that the current RTI catalyst does deactivate (at nominal operating conditions of 300 °C, 2 atm, 72:16:220 mmol/h propionic acid:formaldehyde:nitrogen), the activity loss is about 64 percent over a 180-h period; the sensitivity of the number of reactors on the MMA product value is minimal. The base reaction rate is considered to be 1,400 g MAA/kg cat·h (with assumptions: first-order reaction in formaldehyde, zero order in PA, PA/HCHO=1.5, and no nitrogen).

The RTI-Eastman-Bechtel three-step process consisting of external formaldehyde generation, condensation of formaldehyde with propionic acid, and external esterification of MAA, thus appears competitive with all the other commercial technologies for MMA manufacture. To make these economic assertions more sound, a few knowledge gaps including catalyst deactivation, intrinsic reaction kinetics, and formaldehyde generation and recovery need to be addressed.

Task 2. Condensation Catalysis (RTI)

The condensation of formaldehyde with propionic acid is a synthetic route to MAA and MMA. The reaction is considered to be acid-base catalyzed and a representative mechanism is shown in Figure 6 (Gogate et al., 1997). The catalyst development effort at RTI has focused on developing a stable, selective, and active condensation catalyst for this reaction. As a result of screening over 80 potential catalytic materials, group V metals including vanadium, niobium, and tantalum have been shown to be quite effective condensation catalysts. The economic analysis presented in Task 1 above (carried out by Eastman and Bechtel) was based on the performance of a 20 percent Nb/SiO₂ catalyst, in terms of formaldehyde and propionic acid conversions and MAA selectivity,

at nominal operating conditions of 300 °C, 2 atm, mole flow rates of propionic acid: formaldehyde:nitrogen 72:16:200 mmol/h, 5 g catalyst charge (0.7- to 1.1-mm size fraction), and a volume hourly space velocity of 1,080 cm³/g cat·h. A patent application has been filed by RTI-Eastman researchers on the niobium catalyst (Gogate et al., 1996b).

Figure 6. Representative mechanism for propionic acid and formaldehyde.

The catalyst performance of niobium catalysts with different loadings of niobium on silica support are shown in Table 1. The results show that the catalyst comprised of 20 percent Nb/SiO₂ is the most active catalyst. As a comparison, the performance of the V-Si-P 1:10:2.8 catalyst is also given in Table 1 (this catalyst was the most active from the vanadium group). The long-term deactivation of a 10 percent Nb/SiO₂, V-Si-P 1:10:2.8, and 10 percent Ta/SiO₂ is shown in Figure 7. Note that, although a 20 percent Nb/SiO₂ catalyst was the most active, a 10 percent Nb/SiO₂ was chosen for the long-term activity run primarily because the two other catalysts consist of approximately 10 percent metal loadings. The results of the long-term deactivation run showed that the 10 percent Nb/SiO₂ is the most active and stable catalyst, on a normalized MAA yield basis. Recall that the long-term experiment with the 10 percent Nb/SiO₂ catalyst is carried out with propionic acid as the feed for condensation, with 5 g catalyst charge (a nominal space velocity of 1,080 cm³/g cat·h. The experiments with the V-Si-P 1:10:2.8 catalyst

Table 1. Nb-Si Catalysts for Condensation Reactions^a

Nb-Si ^b Catalyst (atomic ratio)	Surface area (m ² /g)	Surface acidity (μmol [NH ₃]/g) ^c	q-Ratio	MAA yield (/HCHO)	MAA yield (/PA)
1:99 (1%)	110.9	14.9	0.763	22.9	4.91
2:98 (2%)	100.3	23.2	0.655	NA ^d	NA
5:95 (5%)	119.1	28.6	0.801	58.2	12.7
10:90 (10%)	86.5	27.3	0.806	58.6	12.5
20:80 (20%)	NA	34.8	0.746	71.0	15.2
V-Si-P (1:10:2.8) (comparison)	96.5	150.8	0.444	47.0	10.1

^a Reaction conditions: T = 300 °C, P = 2 atm (30 psi in-house nitrogen), mole flow rates of propionic acid formaldehyde:nitrogen ~ 72:16:220 mmol/h, 5 g catalyst charge, ~ 1,080 cm³/g cat·h.

^b Nb₂F₅ and Nalco 1034A colloidal silica, atomic ratio represents ratios of starting precursors.

^c Measured by NH₃-adsorption at 50 °C.

^d NA = Not available.

Experimental Conditions V-Si-P, Ta-Si

For V-Si-P, Ta-Si: 300 °C, 2 atm, 15 g cat. charge, 41:17:220 mmol/h

PAA:HCHO:Nitrogen, 290 cm³/g cat·h

For Nb/Si: 300 °C, 2 atm, 5 g cat. charge, 72:16:220 mmol/h

PA:HCHO:Nitrogen, 1080 cm³/g cat·h

Figure 7. Long-term activity check on V-Si-P 1:10:2.8, 10% Ta-Si, and 10% Nb-Si catalysts.

and the 10 percent Ta/SiO₂ are carried out with propionic anhydride as the feed, with a 15-g catalyst charge (a space velocity of ca. 290 cm³/g cat·h).

Because the Nb/Si series of catalysts looked more promising in relation to the V/Si/P or Ta/Si catalysts, a detailed material balance was developed for the 1, 5, 10, and 20 percent Nb/Si catalysts. The results are shown in Table 2 and include the feed and product makeup for the Nb/Si catalysts. These results are important in quantifying the chemical conversions for reactants and MAA selectivities. For the Nb/Si catalysts, these parameters are summarized in Table 3. It is clear that the MAA selectivities based on both formaldehyde and propionic acid exceed 95 percent, and conversion of formaldehyde is greatest at 78 percent for the 20 percent Nb/Si catalyst. These values were used by Eastman in its preliminary economic analysis (presented in Task 1).

Based on the RTI, Eastman, and Bechtel meeting on October 24, 1996, it was suggested that formalin be evaluated as an alternate feedstock to trioxane. Formalin, an inexpensive source of formaldehyde, is readily available and consists of a solution of 37 wt% formaldehyde in water, with about 8 to 10 percent methanol as a stabilizer. The fixed-bed microreactor system was modified extensively for use with formalin, with the addition of an ice bath and impinger. Isopropanol was used as a solvent for at least seven reaction species, including formaldehyde,

Table 2. Condensation Reactions of Niobium on Silica Catalysts

Ex. No.	Nb-Si Atomic Ratio	Reactor Feed (mmol)		Reactor Product (mmol)				
		EtCOOH	HCHO	EtCOOH	HCHO	MAA	DEK	CO ₂ +CO
1	1:99	186.0	40.0	176.0	30.4	9.20	0.20	0.31
2	5:95	186.0	40.0	159.0	14.5	23.3	0.21	0.42
3	10:90	186.0	40.0	159.0	15.0	23.5	0.28	0.48
4	20:80	186.0	40.0	154.0	8.5	28.4	0.38	0.52

Table 3. Conversions and Chemical Selectivities

Ex. No.	Nb-Si Atomic Ratio	Conversion (%)		MAA Selectivity (%)		MAA Yield (%)	
		HCHO	PA	HCHO	PA	HCHO	PA
1	1:99	24.0	5.37	93.5	92.0	23.0	4.90
2	5:95	63.8	14.52	91.2	86.2	58.2	12.5
3	10:90	62.4	14.52	94.0	87.0	58.7	12.6
4	20:80	78.8	17.20	90.0	88.8	71.0	15.2

water, methanol, propionic acid, diethyl ketone, methacrylic acid, and methyl propionate. A tedlar bag was used for fixed-gas analysis, including CO, CO₂, and N₂. The reaction system is shown in Figure 8.

The analysis of the multicomponent mixture comprised of formaldehyde (HCHO), H₂O, CH₃OH, PA, methyl propionate (MP), MAA, MMA, and diethyl ketone (DEK) was carried out using a 1/8" OD × 6' stainless steel (SS) 316 packed column with 80/100 mesh poropak[®] T, with an HP 5890 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD), with helium carrier at 29.9 mL/min at 30 °C, and column head pressure of ca. 35 psig at 30 °C.

The nominal molar flow rates of propionic acid, formaldehyde, and nitrogen were kept identical for comparison between trioxane and formalin. Thus, while the nominal molar flow rates for PA:HCHO:N₂ were at 72:16:220 mmol/h for trioxane feed, the reactant feeds for the formalin case were PA:HCHO:H₂O:CH₃OH:N₂ = 72:16:38:4:220 mmol/h. The experiments were carried out

Figure 8. Fixed-bed reactor system for formalin as the source of formaldehyde.

with a 10 percent Nb/SiO₂ catalyst (0.7- to 1.1-mm size fraction), at 300 °C, 2 atm, and in a fixed-bed microreactor system (Figure 8).

The comparison between trioxane and formalin as the feedstock is shown in Table 4. The results clearly show that both the initial yield of MAA and the long-term performance for trioxane is superior to that of formalin. Thus, while the initial MAA yield was 58.6 percent based on charged HCHO for trioxane, this value was only 22.5 percent for formalin. Over a 180 h reaction test, the MAA yield decreased from 58.6 percent to 21.1 percent for trioxane, while the 10 percent Nb/SiO₂ catalyst deactivated to almost trace MAA after the same test, in the presence of formalin. The results of the long-term activity test for formalin, in terms of MAA yields (based on HCHO and PA) as a function of time are shown in Figure 9. The material balance of each of the data points was carefully checked and is also included in Figure 9. The average carbon balance for this experimental set is ca. 92 percent, which indicates a good mass accountability. One surprising trend was the increased CO formation rates with formalin as the feed, shown in Figure 10. While the initial rate of CO is only at 0.15 mmol/g cat·h, the CO and MAA formation rate nearly

Table 4. Comparison of Formaldehyde Feedstocks^a

	MAA Yield/HCHO			MAA Yield/PA		
	Initial	40 h	180 h	Initial	40 h	180 h
Trioxane ^b	58.6	51.2	21.1	12.5	9.9	4.6
Formalin ^c	22.5	10.1	tr ^d	4.92	2.2	tr

^aT = 300 °C, P = 2 atm, 10% Nb/SiO₂ catalyst 8-20 mesh (0.7-1.1 mm).

^bTrioxane feed makeup: 72:16:220 mmol/h; PA:HCHO:N₂.

^cFormalin feed makeup: 72:16:38:4:220 mmol/h; PA:HCHO:H₂O:CH₃OH:N₂.

^dtr = trace amount.

Experimental Conditions: T = 300 °C, P = 2 atm, 5 g 8-20 mesh (0.7-1.1 mm) Nb/SiO₂ catalyst, feed makeup = 72:16:38:4:220 mmol propionic acid: formaldehyde:water:methanol:nitrogen.

Figure 9. Results of long-term activity test with 10% Nb/SiO₂ catalyst-MAA yields.

becomes comparable after only about 50 h of reaction time. While the mechanism for increased CO formation with formalin is not yet completely understood, it can be speculated that the CO formation occurs via HCHO decomposition, and the presence of methanol and water in the feed alter the oxidation state of niobium. For a simplistic niobium compound such as Nb₂O₅, the oxidation state is 5⁺, and this oxidation state may revert to a lower number, in the presence of possible reductants. The catalyst performance in the presence of water vapor is also demonstrated to be inferior in earlier reaction studies (Ai, 1988, 1990).

From these comparative experiments, it can be inferred that trioxane is a more feasible feedstock for vapor phase condensation reactions. Further work will therefore focus on this feedstock alone and also on quantifying the effects of water and methanol on the niobium catalysts; interactions among niobium, silicon, and oxygen in the catalyst matrix; identification of oxidation states of niobium as a function of on-stream time; and a better evaluation of catalyst stability with and without the presence of oxygen.

Task 3—Slurry Reactor Studies (RTI and Eastman)

Based on the RTI, Eastman, and Bechtel meeting at RTI on October 24, 1996, it was decided to deemphasize the in situ oxidative condensation of methanol with propionic acid, in the presence of oxygen. Eastman's assertion that the three-step methanol route consisting of external

Experimental Conditions: T = 300 °C, P = 2 atm, 5 g 8-20 mesh (0.7-1.1 mm)
 Nb/SiO₂ catalyst, feed makeup = 72:16:38:4:220 mmol propionic acid:
 formaldehyde:water:methanol:nitrogen.

Figure 10. Results of long-term activity test with 10% Nb/SiO₂ catalyst-MAA and CO rates.

formaldehyde generation, condensation of formaldehyde with propionic acid, and external esterification of MAA is likely to be cost-competitive with existing technologies for MMA manufacture was the basis for this decision. Eastman recently completed a detailed economic evaluation of the RTI three-step process and the results have been included under Task 1, in this report. Based on these results, the in situ slurry reactor process development was deemphasized in favor of the more attractive RTI three-step route. The results included in the following paragraphs are RTI's research on slurry reactor studies in the last two quarters. The slurry reactor technology will likely be revisited at the end of the DME extension of this contract (slated for completion on March 31, 1999).

The third task focuses on the in situ condensation catalysis of methanol, oxygen, and PA in a slurry reactor. RTI has designed, assembled, and constructed a high-temperature, high-pressure (HTHP) slurry reactor system for Task 3. The heart of the system is a 50-mL stirred autoclave from Autoclave Engineers (Erie, Pennsylvania). The system can be operated up to 400 °C, 100 atm, 40 wt% catalyst slurry ratios, and impeller speeds of up to 2,000 rpm. The system is capable of handling up to four gaseous feeds (flow rates of up to 200 mL [standard temperature and pressure (STP)]/min), controlled by Brooks electronic mass flow controllers, and two liquid feeds (flow rates of up to 360 mL [STP]/h) controlled by a Duplex ThermoSeparation Products MiniPump. These features are adequate for the proposed work. The feed and product section instrumentation of the system is sketched in Figures 11 and 12. The entire unit is sketched in Figure 13.

Figure 11. RTI-Eastman slurry reactor system—feed section instrumentation.

The work thus far has focused on using decalin as the slurry fluid, based on tests conducted at North Carolina State University (NCSU), under the guidance of Prof. Roberts. The nominal reaction conditions chosen for the first two tests were: 20 mL decalin, 1 g catalyst charge (Fe/Mo + V/Si/P), 300 °C, 20 atm, 500 rpm, and 150:150:200:200 mmol/h propionic acid:methanol:nitrogen:oxygen. The initial results have proven that MMA and MAA can be coproduced in one single slurry reactor, although the product indicates that there are at least 40 other species present in the condensate. Some of these products may have been formed due to the thermal or chemical degradation of the slurry fluid (decalin) itself and can be obviated by carefully altering the reaction conditions. A more comprehensive gas chromatography/mass spectrometry (GC/MS) analysis for molecular identification of these products is under way. Further tests will focus on slightly less severe conditions and even lower catalyst slurry ratios. A GC analysis of the initial product from the slurry reactor is shown in Figure 14.

Task 4. DME Feedstock Evaluation (RTI and Eastman)

The current RTI-Eastman-Bechtel research on MMA synthesis uses methanol to generate formaldehyde in the external formaldehyde generation step. This formaldehyde is subsequently

Figure 12. RTI-Eastman slurry reactor system—product section instrumentation.

Figure 13. RTI-Eastman slurry reactor system—flow diagram.

Experimental Conditions:

20 mL Decalin, 1 g cat. charge (Fe/Mo + V-Si-P),
 300 °C, 20 atm, 500 rpm,
 150:150:200:200 mmol/h PA: CH₃OH:N₂:O₂
 (~11.2 mL/h: 4.8 mL/h: 100mL/min: 100 mL/min)

Figure 14. Gas chromatograph/flame ionization detector (GC/FID) product analysis from slurry reactor run 101896.

condensed with propionic acid, and the resulting MAA is externally esterified with methanol to form MMA.

An extension to this approach was proposed by the RTI-Eastman-Bechtel team, which extends this research and evaluates the use of DME rather than methanol as the formaldehyde precursor. With three formaldehyde sources (MeOH oxidation, external formaldehyde, and MeOH dehydrogenation), two methyl sources (methanol and DME), and three propionate feedstocks (propionic acid, propionic anhydride, and methyl propionate), there are a total of 18 cases of different possible routes to MMA. These are summarized in Table 5. Based on a detailed reaction pathway analysis, shown in Figure 15, Cases 3 and 17 are selected for further studies including reaction studies and tradeoff analysis. Case 3 is the current RTI three-step methanol route, with external formaldehyde generation step and an external esterification step. The detailed reaction stoichiometry for Case 3 is shown in Figure 16.

Case 17 is the DME feedstock with methyl propionate, with methanol oxidation as a source for formaldehyde. Detailed stoichiometry for Case 17 is shown in Figure 17.

The current RTI-Eastman-Bechtel three-step route is termed as Route ② (Case 3) and the DME-based route is termed as Route ① (Case 17), for tradeoff analysis. A detailed economic analysis carried out by Eastman and Bechtel has shown that the RTI three-step route to MMA (Route ②)

is cost-competitive with all commercial technologies. The results have been included here in Task 1. Bechtel and Eastman propose to carry out a similar analysis for Route ① to demonstrate and

Case	Me feedstock	Pr feedstock	Formaldehyde source
1	MeOH	HOPr	MeOH dehydrogenation
2			MeOH oxidation
•3			External formaldehyde
4		Pr ₂ O	MeOH dehydrogenation MeOH
5			Oxidation
6			External formaldehyde
7		MeOPr	MeOH dehydrogenation
8			MeOH oxidation
9			External formaldehyde
10	DME	HOPr	MeOH dehydrogenation
11			MeOH oxidation
12			External formaldehyde
13		Pr ₂ O	MeOH dehydrogenation
14			MeOH oxidation
15			External formaldehyde
16		MeOPr	MeOH dehydrogenation
•17			MeOH oxidation
18			External formaldehyde

Figure 15. Reaction pathways for MMA synthesis (Routes ① and ② denote the selected pathways for tradeoff analysis).

Figure 16. Case 3: MeOH feedstock/HOPr feedstock/external formaldehyde – Route ②.

evaluate its economic merit. Finally, the RTI-Eastman-Bechtel team proposes to develop Route ① DME-based process in a slurry reactor.

At the present time, the research is continuing on three fronts:

1. Tradeoff analysis of Route ①,
2. DME-to formaldehyde reaction studies and identification of promising catalysts, and
3. Catalysts for DME-MP condensation.

Figure 17. Case 17: DME feedstock / MeOPr feedstock / MeOH oxidation – Route ①.

CONCLUSIONS

1. Status

Task 1 (Propionate Synthesis) is complete. Task 2 (Condensation Catalysis) is nearly complete. The work on Task 2 is continuing in support of Task 3 (Slurry Reactor Studies) which is under way. In Task 1, Eastman and Bechtel have carried out a preliminary economic evaluation of the RTI three-step methanol process consisting of external formaldehyde generation, condensation of formaldehyde with propionic acid, and external esterification of resulting methacrylic acid with methanol to form MMA. The results show that for a 250 Mlb/year product and 10 percent rate of return on investment, the product value of RTI-Eastman-Bechtél three-step route is at 52¢/lb and

is cost-competitive with all technologies for MMA manufacture, except propyne carbonylation, which suffers from limited raw material supply. Based on this economic analysis, the RTI-Eastman experimental program on Task 3 (Slurry Reactor Studies) was somewhat deemphasized, in favor of the experimental campaign for the DME extension. In Task 2 (Condensation Catalysis), RTI research is currently focused on enhancing the catalyst stability of the niobium series of catalysts, based on the economic analysis. Initial experiments with cesium promotion of Nb/Si catalysts do not show any marked improvement in the catalyst life.

2. Forecast

Including the DME route, we are evaluating two possible routes to MMA. The three-step methanol route has already shown that it is cost-competitive with existing technologies for MMA manufacture, based on Eastman's economic analysis. The current research in the three-step methanol route is focused on the following:

- **Long-term catalyst activity**—effect of cesium promotion on catalyst life will be examined, and effects of steam and methanol on altering the oxidation state of niobium catalyst will be studied. Possible beneficial effects of oxygen co-feed to maintain the catalyst activity will also be studied.
- **Catalyst structure**—The structure of the niobium catalyst will be studied in greater detail, by scanning electron microscope/transition electron microscope/x-ray fluorescence (SEM/TEM/XRF). Possible active species of niobium and their oxidation states will be studied by x-ray diffraction (XRD) and electron spectroscopy for chemical analysis (ESCA). The deactivated catalysts will be characterized in more detail to elucidate the difference in physical and chemical properties of the fresh and deactivated catalysts.
- **Intrinsic kinetics**—Eastman's economic analysis assumed a first-order kinetics in formaldehyde. Detailed kinetics will have to be obtained for validating these assumptions. Activation energy, temperature, and concentration dependence of the MAA reaction rate will be determined. The MAA reaction rate is the single most important parameter affecting the MMA product value, based on Eastman's analysis.
- **Material balance on experimental runs**—Detailed material balances will be developed on all niobium and vanadium series of catalysts to obtain more accurate estimates of the formaldehyde and propionic acid conversions, MAA selectivities, MAA yields, and MAA reaction rates.

The DME extension of the current contract will begin formally on April 1, 1997. The initial research on the DME contract will focus on the following:

- **Tradeoff analysis**—The tradeoff analysis will include a detailed economic analysis of Route ① (DME route) and Route ② (methanol route) and will focus on material and energy balances, equipment design, and production cost estimates. Essentially, Bechtel will extend Eastman's work (reported in Task 1 of this report) and will prepare a detailed

advanced system for process engineering (ASPEN) modeling for comparative analysis between Route ① and Route ②.

- **Catalysts for DME partial oxidation**—Fixed-bed tests will be carried out on the partial oxidation of DME to formaldehyde. The initial focus will be on the WO_3 series of catalysts, reported to be promising for such reactions. We will also test classical methanol partial oxidation catalysts, based on the Ag/SiO_2 and FeMoO_3 systems.
- **Catalysts for methyl propionate condensation**—Fixed-bed tests will be carried out on the condensation of methyl propionate with DME/methanol and initially with externally generated formaldehyde. BASF has developed some promising methyl propionate catalysts, which will be the starting point of RTI research on propionate condensation reactions.

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