

Report Title:

Synthesis of Methyl Methacrylate from Coal-derived Syngas

Report Type:

QUARTERLY

Reporting Period Start Date: 04/01/1999 End Date: 06/30/1999

Principal Author(s): Makarand R. Gogate and James J. Spivey
Jospeh R. Zoeller and Richard D. Colberg
Gerald N. Choi

Report Issue Date: 07/19/1999

DOE Award No.: DE- AC22 -94PC94065--19

Submitting
Organization(s)

Research Triangle Institute
3040 Cornwallis Road P.O. Box 12194
RTP, NC 27709-2194

(1)

Name & Address

Eastman Chemical Company
Kingsport, TN 37662-5150

(2)

Bechtel
San Francisco, CA 94119-3965

(3)

(4)

(5)

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, nor assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

Research Triangle Institute (RTI), Eastman Chemical Company, and Bechtel collectively are developing a novel three-step process for the synthesis of methyl methacrylate (MMA) from coal-derived syngas that consists of the steps of synthesis of a propionate, its condensation with formaldehyde to form methacrylic acid (MAA), and esterification of MAA with methanol to produce MMA. The research team has completed the research on the three-step methanol-based route to MMA. Under an extension to the original contract, we are currently evaluating a new DME-based process for MMA. The key research need for DME route is to develop catalysts for DME partial oxidation reactions and DME condensation reactions.

During the April-June quarter(04-06/99) the first in-situ formaldehyde generation from DME and condensation with methyl propionate is demonstrated and the results are summarized. The supported niobium catalyst shows better condensation activity, but supported tungsten catalyst has higher formaldehyde selectivity. The project team has also completed a 200-hour long term test of PA-HCHO condensation over 30% Nb₂O₅/SiO₂. Three activity cycles and two regeneration cycles were carried out. 30% Nb₂O₅/SiO₂ showed similar MAA yields as 10% Nb₂O₅/SiO₂ at 300°C. However, the deactivation appears to be slower with 30% Nb₂O₅/SiO₂ than 10% Nb₂O₅/SiO₂.

An detailed economic analysis of PA-HCHO condensation process for a 250 million lb/yr MMA plant is currently studied by Bechtel. Using the Amoco data-based azeotropic distillation model as the basis, an ASPEN flow sheet model was constructed to simulate the 'formaldehyde and propionic acid condensation' processing section based on RTI's design data. The RTI MAA effluent azeotropic distillation column was found to be much more difficult to converge. The presence of non-condensable gases along with the byproduct DEK (both of which were not presented in Amoco's data) appear to the culprits.

TABLE OF CONTENTS

	Page
Disclaimer	i
Abstract	ii
List of Figures	iv
List of Abbreviations	v
Executive Summary	vi
Introduction	1
Results and Discussion	2
Task 1. Propionate Synthesis (Eastman and Bechtel)	2
Task 2. Condensation Catalysis (RTI)	2
Task 3. Slurry Reactor Studies (RTI and Eastman)	3
Task 4. DME Cost Estimation Study (Bechtel and Eastman)	3
Task 5. DME Condensation Study (RTI and Eastman)	6
Conclusions	8
1. Status	8
2. Forecast	9
References	9

LIST OF FIGURE

Number		Page
1	The RTI-Eastman-Bechtel Three-Step MMA process.	1
2	Long term reaction-regeneration cycle study of PA-HCHO condensation on a 30%Nb ₂ O ₅ /SiO ₂ catalyst	2
3	External Formaldehyde\Propionic Acid Condensation Route to MMA.	3

LIST OF TABLE

Number		Page
1	DME partial oxidation and in-situ condensation with methyl propionate.	7

LIST OF ABBREVIATIONS

ACH	Acetone cyanohydrin
DME	Dimethyl ether
DOE	U.S. Department of Energy
ESCA	Electron spectroscopy for chemical analysis
MAA	Methacrylic acid
MMA	Methyl methacrylate
MP	Methyl propionate
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

EXECUTIVE SUMMARY

Research Triangle Institute (RTI), Eastman Chemical Company, and Bechtel collectively are developing a novel three-step process for the synthesis of methyl methacrylate (MMA) from coal-derived syngas that consists of the steps of synthesis of a propionate, its condensation with formaldehyde to form methacrylic acid (MAA), and esterification of MAA with methanol to produce MMA. The research team has completed the research on the three-step methanol-based route to MMA. Under an extension to the original contract, we are currently evaluating a new DME-based process for MMA. The key research need for DME route is to develop catalysts for DME partial oxidation reactions and DME condensation reactions.

During the April-June quarter(04-06/99) the first in-situ formaldehyde generation from DME and condensation with methyl propionate is demonstrated and the results are summarized. The supported niobium catalyst shows better condensation activity, but supported tungsten catalyst has higher formaldehyde selectivity. The project team has also completed a 200-hour long term test of PA-HCHO condensation over 30% Nb₂O₅/SiO₂. Three activity cycles and two regeneration cycles were carried out. 30% Nb₂O₅/SiO₂ showed similar MAA yields as 10% Nb₂O₅/SiO₂ at 300°C. However, the deactivation appears to be slower with 30% Nb₂O₅/SiO₂ than 10% Nb₂O₅/SiO₂.

An detailed economic analysis of PA-HCHO condensation process for a 250 million lb/yr MMA plant is currently studied by Bechtel. Using the Amoco data-based azeotropic distillation model as the basis, an ASPEN flow sheet model was constructed to simulate the 'formaldehyde and propionic acid condensation' processing section based on RTI's design data. The RTI MAA effluent azeotropic distillation column was found to be much more difficult to converge. The presence of non-condensable gases along with the byproduct DEK (both of which were not presented in Amoco's data) appear to the culprits.

INTRODUCTION

The most widely practiced commercial technology for the synthesis of methacrylic acid (MAA) and methyl methacrylate (MMA) is the acetone cyanohydrin (ACH) process. The ACH process requires handling of large quantities of extremely toxic and hazardous hydrogen cyanide and generates copious amounts of ammonium sulfate wastes that 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.[1-4] The Research Triangle Institute (RTI)-Eastman-Bechtel research team is developing a novel three-step process for synthesis of methyl methacrylate from coal-derived

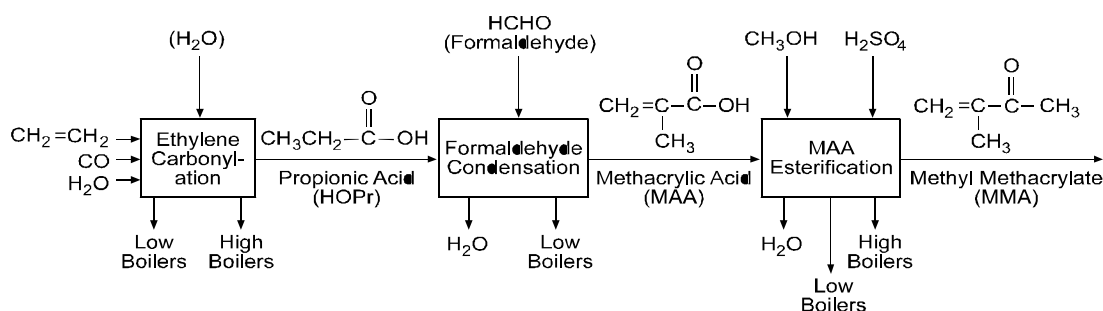


Figure 1. The RTI-Eastman-Bechtel three-step MMA process (with external formaldehyde feed).

syngas. This three-step process is shown schematically in Figure 1. In this process for MMA manufacture, Steps 1 (ethylene carbonylation) and 2 (formaldehyde condensation), present challenges for successful commercial demonstration of the process. Step 3 (MAA esterification) is a known art.

The three-step methanol route has been investigated by the RTI-Eastman-Bechtel research team. For investigation purposes, the scope of work was divided into three tasks. Task 1 focused on the synthesis of a propionate from ethylene, CO, and steam, Task 2 focused on the condensation of the propionate with formaldehyde, and Task 3 focused on the one-step oxidative condensation in a slurry reactor. Due to a promising economic evaluation of the three-step process, where propionate synthesis, condensation, and esterification are carried out in separate reactors, the development of one-step MMA process in a slurry reactor (Task 3), was de-emphasized, for now. Upon conclusion of the original contract, the RTI-Eastman-Bechtel research team undertook the development of a DME-based process to MMA, as an extension to the three tasks of the original contract. This add-on task is now called as Task 4 and Task 5, and termed as DME Cost Estimation Study and DME Condensation Study, respectively.

Under this extension, the RTI-Eastman-Bechtel research team is studying the use of DME, instead of methanol, to generate formaldehyde, either externally or in situ. Methyl propionate (MP) is used as the propionyl source, instead of PA. The DME-based route can produce MMA

in one step, and is possibly a cost-effective alternative to the methanol-based route.

RESULTS AND DISCUSSION

Task 1. Propionate Synthesis (Eastman and Bechtel)

Eastman and Bechtel have completed the experimental work and economic analysis for the overall process, and have completed their responsibilities per the statement of work for the original contract.

Task 2. PA-HCHO Condensation Catalysis (RTI)

During the month of June, RTI has carried out a long-term continuous condensation of formaldehyde with propionic acid with regeneration over 30% Nb₂O₅/SiO₂ at 300°C. Three activity and two regeneration cycles have been completed. The total time on stream, not including the time for regenerations, for the reaction is about 200 hours. The results are summarized in Figure 2. The results show that 30% Nb₂O₅/SiO₂ deactivates slowly with time but can be regenerated to its original activity with 2% O₂ in nitrogen over night like 10% Nb₂O₅/SiO₂ at 400°C. For example, the second activity cycle decreases from the initial activity of 32.5% yield down to 27.1% yield of MAA over 73 hours. After the 2nd regeneration, the activity was brought back to 32.4% yield of MAA followed by slow deactivation which resulted in 28.9% yield after about 72 hours. The yield of MAA over 30% Nb₂O₅/SiO₂ is similar to the yield over 10% Nb₂O₅/SiO₂, but the deactivation over 30% Nb₂O₅/SiO₂ appears to be slower than the deactivation over 10% Nb₂O₅/SiO₂. The reason for the slower deactivation is not clear at this

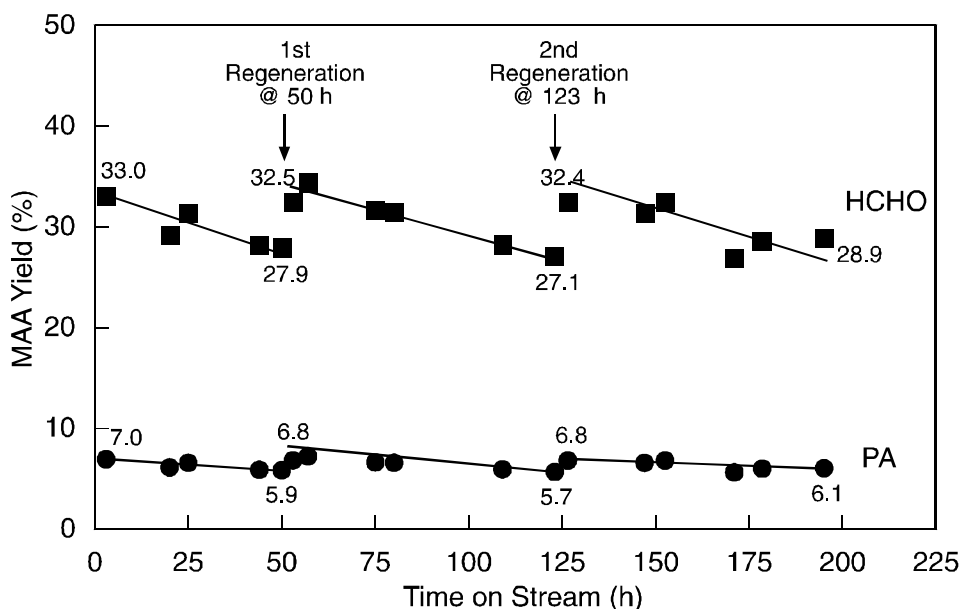


Figure
reactio

regeneration cycle study of PA-HCHO condensation on a 30%Nb₂O₅/SiO₂ catalyst.

point. Possibly, the higher Nb loading has contributed to the stability of the 30% Nb₂O₅/SiO₂

2. Long term
n-

catalyst for PA-HCHO condensation. We will further analyze the reaction by-products such as DEK, CO, and CO₂ to investigate the possible explanation.

Task 3. Slurry Reactor Studies (RTI and Eastman)

Based on Eastman's economic analysis, the RTI three-step route to MMA, based on a vapor phase condensation reactor, appears commercially promising. The slurry reactor technology will therefore be revisited after the partial oxidation of DME and in-situ condensation with methyl propionate.

Task 4. DME Cost Estimation Study(Bechtel and Eastman)

Bechtel is continuing with the development of a conceptual design and economic analysis for the syngas-based methyl methacrylate (MMA) synthesis via 'externally generated' formaldehyde (HCHO) vapor-phase condensation with propionic acid (HOPr). The design is based on RTI's experimental data of HCHO and HOPr condensation reaction using niobium oxide catalysts, and it is for a plant to produce 250 million lb/yr of MMA. US Gulf Coast basis for capital equipment, raw material and utilities, and operating labor cost will be assumed. Results will be benchmarked with the MMA synthesis process economic analyses reported by SRI [5].

Figure 3 shows the overall process for the current design under consideration.

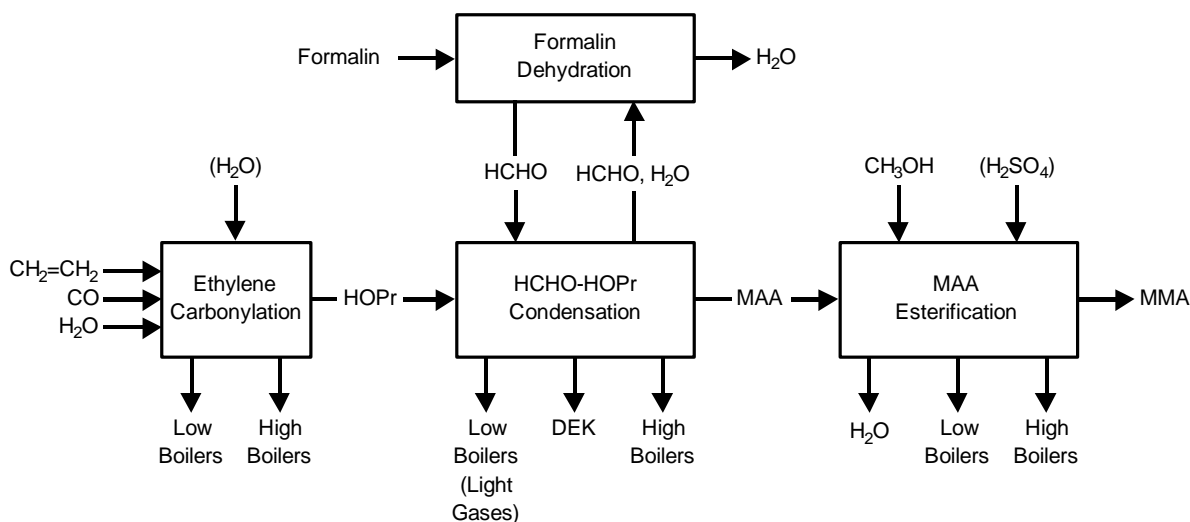


Figure 3: External Formaldehyde/Propionic Acid Condensation Route to MMA

The plant consists of four separate processing sections: Formalin dehydration; Ethylene carbonylation; Formaldehyde/propionic acid condensation and MAA esterification.

Design Basis and Background Information:

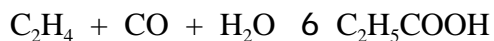
A brief description of each processing section, its design bases and assumption employed (particularly those of RTI's data of formaldehyde/propionic acid condensation reaction) are as follows:

1) Formalin Dehydration -

This plant has an objective to produce an anhydrous formaldehyde stream from industrially available formalin (~ 40 wt% formaldehyde in water) for the vapor condensation reaction with propionic acid. The project team agreed that a design as described in SRI's PEP #11D [56] can be adopted for the current study. It involves reacting the purchased formalin feed with 2-ethylhexanol to form a hemiacetal intermediate. The hemiacetal is then dehydrated via fractionation; the water is distilled overhead, along with any light by-products in the recycled formaldehyde solution from the condensation reaction, and discarded. The hemiacetal is then thermally decomposed into anhydrous formaldehyde vapor and 2-ethylhexanol for recycle. The anhydrous formaldehyde is sent on to the propionic acid condensation reactor.

2) Ethylene Carbonylation -

In this plant, ethylene (C₂H₄) is carbonylated with CO (from a CO-riched syngas from coal gasification) and water to produce propionic acid (HOPr) in according to the reaction –

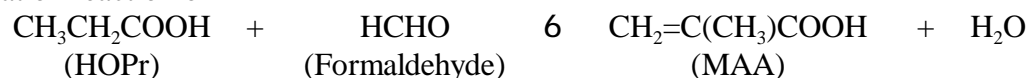


The reaction takes place in the presence of molybdenum hexacarbonyl [Mo(CO)₆] catalyst. The overall process scheme is very similar to that of C₂H₄ carbonylation with HOPr to make propionic anhydrous – a process Bechtel had carried out a design\ economics analysis earlier in the program. The plant produces a liquid HOPr stream which has to be heat exchanged before feeding it to the HCHO\HOPr reactor.

The project team agreed that the 'ethylene carbonylation to propionic acid' design needs not to be replicated. Eastman will furnish sufficient information for estimating the cost of the propionic acid as feedstock for the current analysis.

3) Formaldehyde and Propionic Acid Condensation –

The process design of this section represents the bulk of the current Bechtel efforts. RTI's experimental data serves as the design basis. In this section, the formaldehyde and propionic acid vapor condensation reaction of



is carried out via a fixed-bed reactor filled with niobium oxide catalyst supported on silica (Nb₂O₅:SiO₂). Two reactors are to be designed in parallel: one on stream while the other is kept on standby after regeneration. Based on RTI's catalyst deactivation study, it is assumed that the Nb₂O₅:SiO₂ catalyst can be regenerated by 2% O₂ in N₂ at 400 °C [6] with negligible decrease in reaction rate, conversion and selectivity over time. The overall plant design is based on RTI data of the 20% Nb₂O₅:SiO₂ formulation. Agreed upon design conditions, data and assumptions are as follows:

A. Vapor-phase reactor operating conditions:

- 300 °C
- 15 to 30 psig

B. Feed ratio

- 2:1 molar ratio of HOPr:HCHO with no nitrogen dilution

C. Conversion and production rate

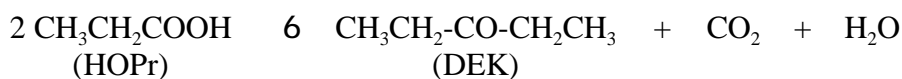
- 45% based HCHO (22.5% based on HOPr)
- 2 moles MAA/(liter catalyst-hr) [6]

D. Selectivity

<u>HCHO Selectivity</u>		<u>HOPr Selectivity</u>	
- to MAA [6]	70%	- to MAA [6]	75%
- to DEK (dimethy ketone)	None	- to DEK	5%
- to coke and light ends	25%	- to coke and light ends	15%
- to heavy boilers	5%	- to heavy boilers	5%

The above data suggests the following reaction loss:

- DEK Formation



- Unidentified Losses

HOPr 6 HOPr losses due to coke and light gases

HCHO 6 HCHO losses due to coke and light gases

HOPr 6 HOPr losses due to heavy boilers

HCHO 6 HCHO losses due to heavy boilers

E. Catalyst life

- One year

It is anticipated that MAA product separation will be a challenge. The Reactor effluent contains the main product, MAA; byproducts of H₂O, DEK and CO₂; unconverted HCHO and HOPr reactants, along with both the light end and heavy boiler byproducts which we will treat as inerts. Both MAA and HOPr form azeotropes with water and both azeotropes have a boiling point of ~212 °F. Furthermore, it is well know that HCHO, in the presence of water, reacts with water to form hydrate of methylene glycol which itself tends to polymerize to poly(oxmethylen glycols) [HO-(CH₂O)_n-H]. Its VLE also exhibits a binary HCHO\H₂O azeotropic behavior having a boiling point of also 212 °F. In addition, the byproduct DEK also forms a heterogenous azeotrope with water. All of the above will contribute to the MAA product separation difficulties.

Our objective is to produce a water-free stream of MAA with minimum residual HOPr to send on to esterification. This is a ‘water management’ problem involving distillation separation of multiple binary water-based azeotropes.

4) MAA Esterification -

The project team agreed that the design of this section should be based on a “standard” MAA esterification process as described in SRI [5]. It was also agreed that this design can be capacity factored for our current study.

Bechtel has been focussing primary on the formaldehyde\propionic acid condensation effluent separation process design and simulation. Specifically, the process scheme proposed and patented by Amoco [7] to separate a reaction mixture containing MAA, HCOH, HOPr and water using azeotropic distillation was investigated and simulated. In their patent, Amoco had shown that when using an organic solvent (nC_7) as an entrainer to form a heterogeneous azeotrope with water (which has a boiling point lower than that of the MAA\H₂O, HOPr\H₂O binary homogeneous azeotrope pairs), water can be removed from the mixture as an overhead nC_7 \H₂O\HCOH stream and a nearly anhydrous MAA and HOPr stream can be produced from the bottom of the column. A sidedraw stream containing mostly HOPr and HCOH can be recovered and upon further separation, recycled as feeds. The nC_7 \H₂O overhead is condensed and phase separated. The upper organic (nC_7) layer is returned to the column as reflux. The aqueous lower layer is recycled for recovery of HCHO.

The Amoco azeotropic distillation process was simulated using ASPEN with reasonable success: a water-free MAA and HOPr bottom stream was produced, and a sidedraw stream containing mostly of HCHO and HOPr (with small amount of MAA and H₂O which tends to associate with HCHO) was recovered. Column was operated\simulated at a reasonable temperature (< 310 °F) and pressure (~ atmospheric) conditions as to avoid potential MAA polymerization. Amoco cited in their patent that this is required and a suitable inhibitor needs to be added to the mixture to prevent MAA polymerization. The azeotropic distillation was simulated using ASPEN Plus as a three-phase Radfrac model, using an UNIQUAC activity coefficient model, a FMEH20 package to predict the VLE behavior of formaldehyde and water mixture, and customized Newton\Azeotrope convergence algorithm.

Using the Amoco data-based azeotropic distillation model as the basis, an ASPEN flow sheet model was constructed to simulate the ‘formaldehyde and propionic acid condensation’ processing section based on RTI’s design data. The RTI MAA effluent azeotropic distillation column was found to be much more difficult to converge. The presence of non-condensable gases along with the byproduct DEK (both of which were not presented in Amoco’s data) appear to be the culprits. Work is in progress.

Task 5. DME Condensation Study(RTI and Eastman)

In-situ formaldehyde generation and condensation with methyl propionate were tested over supported niobium and tungsten catalysts at 320 and 340°C. This is the first demonstration of MMA synthesis directly from DME, oxygen and methyl propionate in one single reactor. The results are summarized in Table 1. As shown in Table 1, the 10%Nb/SiO₂ is active for oxidation of DME. However, the formation of formaldehyde is not very selective. The conversion of DME at 320°C is 32.0% with 5.1% selectivity to formaldehyde. The conversion increases to 39.5% when temperature is increased to 340°C while the selectivity decreases to 2.5%. When partial oxidation of DME combines with in-situ condensation with methyl propionate(MP) the results are quite different. The conversion of DME decreases in the presence of MP from 32.0%

to 16.1% at 320°C with MP conversion of 17.6%. It indicates that DME competes with MP for reaction with oxygen. When the reaction temperature increases from 320°C to 340°C the conversion of DME further decreases to 9.9% and the conversion of MP increases to 27.4%. In the case of DME, the conversion includes the oxidation of DME to formaldehyde, a partial

Table 1. DME partial oxidation and in-situ condensation with methyl propionate.

	Catalyst	T(°C)	Conversion(%)		Selectivity(%)		
			DME	MP	MMA	MAA	HCHO
DME Partial oxidation	10%Nb/SiO ₂	320	32.0	NA	NA	NA	5.1
DME Partial oxidation	10%Nb/SiO ₂	340	39.5	NA	NA	NA	2.5
In-situ condensation	10%Nb/SiO ₂	320	16.1	17.6	36.3	3.6	19.2
In-situ condensation	10%Nb/SiO ₂	340	9.9	27.4	99.6	8.4	22.6
DME Partial oxidation	10%W/SiO ₂	340	30.7	NA	NA	NA	20.0
In-situ condensation	10%W/SiO ₂	340	9.5	13.6	14.1	5.5	148.5

DME:MP:O₂:N₂=5:63:5:210 mmol/h.

Selectivity calculation is based on DME consumption.

oxidation product, and CO₂, a complete oxidation product. For MP, the conversion includes the direct oxidation to CO_x, reverse esterification, and condensation with formaldehyde.

The selectivities to MMA, MAA and formaldehyde are calculated based on the consumption of DME. The MMA selectivity increases from 36.3% to 99.6% when temperature increases from 320°C to 340°C. The MAA selectivities are 3.6% and 8.4% at 320°C and 340°C, respectively. The selectivities to formaldehyde, possibly generated both from DME and methanol obtained from the hydrolysis of MP, are 19.2% and 22.6% at 320°C and 340°C, respectively. It may seem odd that the sum of selectivity to MMA, MAA, formaldehyde is exceeding 100%. However, methanol is an extra source for formaldehyde formation besides DME. Methanol can be produced via the hydrolysis of MP as mentioned earlier. We have no way to determine what portion of formaldehyde generated is from DME or methanol at this point and therefore don't know what portion of MMA or MAA is obtained directly from partial oxidation of DME and in-situ condensation with MP.

10% W/SiO₂ was also tested for partial oxidation and in-situ condensation with MP. The reactions are carried out at 340°C and the results are also included in Table 1. The conversion of DME over 10% W/SiO₂ is lower than the conversion over 10%Nb/SiO₂, but the selectivity is higher. Conversion and selectivity are 30.7% and 20.0% over 10%W/SiO₂, respectively. The conversion of DME drops significantly to 9.5% in the presence of MP at 340°C with relatively

lower MMA(14.1%) and MAA(5.5%) selectivity, but with extremely high selectivity to formaldehyde(148.5%). Again, the formaldehyde formation may come from both DME and methanol partial oxidation. Although the supported tungsten catalyst shows less activity for MMA and MAA formation than the supported niobium catalyst, it results in better formaldehyde selectivity in the presence or absence of MP. The results suggest that we need to further improve the activity and selectivity of the reaction. Using supported tungsten catalyst for partial oxidation of DME to formaldehyde followed by condensation over supported niobium catalyst may be an effective approach to improve the process.

Further improvement for partial oxidation of DME to formaldehyde followed by condensation with methyl propionate is on hold. Resources have been re-committed to PA-HCHO condensation over 30% Nb₂O₅/SiO₂.

CONCLUSIONS

1. Status

Task 1 is completed. In Task 2, we have completed a 200-h run of PA-HCHO condensation over 30%Nb/SiO₂. 30%Nb/SiO₂ showed similar condensation activity for MAA yield as 10%Nb/SiO₂. The deactivation rate of 30%Nb/SiO₂ is, however, slower than that of 10%Nb/SiO₂. We will further analyze the reaction by-product to investigate the causes of lower deactivation. Bechtel is continuing the economic analysis of the propionic acid-formaldehyde condensation work for Task 4. Using the Amoco data-based azeotropic distillation model as the basis, an ASPEN flow sheet model was constructed to simulate the 'formaldehyde and propionic acid condensation' processing section based on RTI's design data. The RTI MAA effluent azeotropic distillation column was found to be much more difficult to converge. The presence of non-condensable gases along with the byproduct DEK (both of which were not presented in Amoco's data) appear to be the culprits. Task 5, the first in-situ formaldehyde generation from DME and condensation with methyl propionate is demonstrated and the results are summarized. The supported niobium catalyst shows better condensation activity, but supported tungsten catalyst has higher formaldehyde selectivity. However, the overall yields to MMA and MAA are low over both catalysts. Further study on in-situ formaldehyde generation from DME and condensation with methyl propionate, is on hold.

A poster titled "Environmental Benign Synthesis of Methacrylates over Silica Supported Niobium Catalysts" was presented at the 16th North American Catalysis Society Meeting at Boston from May 31st to June 4th, 1999. A copy of the presentation was attached to the May monthly report.

2. Forecast

We will further analyze the reaction by-products from PA-HCHO condensation to investigate the causes of lower deactivation over 30%Nb/SiO₂. The economic analysis of the propionic acid-formaldehyde condensation work will continue through the end of September. Final report will be submitted after the completion of the project.

REFERENCES

1. Gogate, M.R., J.J. Spivey, J.R. Zoeller. 1997. "Synthesis of methyl methacrylate by vapor condensation of formaldehyde with propionate derivatives," *Catal. Today*, 36(3), pp. 243-255.
2. Spivey, J.J., M.R. Gogate, J.R. Zoeller, G.C. Tustin. 1998. U.S. Patent 5,710,328, "Synthesis of α -, β -unsaturated carboxylic acids and anhydrides," January 20.
3. Spivey, J.J., M. R. Gogate, J.R. Zoeller, R.D. Colberg. 1997. "Novel Catalysts for Environmentally Friendly Synthesis of Methyl Methacrylate," *Ind. Eng. Chem. Res.*, 36(11), pp. 4600-4608.
4. Spivey, J.J., M.R. Gogate, J.R. Zoeller, R.D. Colberg, S.S. Tam, G.N. Choi. 1997. "Environmentally Friendly Synthesis of Methyl Methacrylate from Coal-derived Syngas," in *Proceedings of International Chemical Congress - Fifth Chemical Congress of North America, Cancun, Mexico*.
5. SRI, *Methacrylic Acid and Esters*, PEP Report 11D, Chapter 8 (1993).
6. Based on data for 20% Nb₂O₅:SiO₂, 2.25:1 HOPr:HCHO at 300°C [RTI Presentation at Eastman (12/16/98)].
7. Process for Recovery of Methacrylic Acid; U S Patent 4,599,144 (1986)