Report Title:

Synthesis of Methyl Methacrylate from Coal-derived Syngas

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DISCLAIMER

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.

Over the last quarter(January-March/99), in-situ formaldehyde generation and condensation with methyl propionate were tested over various catalysts and reaction conditions. The patent application is in preparation and the results are retained for future reports.

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1 The RTI-Eastman-Bechtel Three-Step MMA process. 1

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.

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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 (Gogate et al., 1997; Spivey et al., 1998, 1997a, 1997b). The Research Triangle Institute (RTI)-Eastman-Bechtel research team is developing a novel three-step process for synthesis of methyl

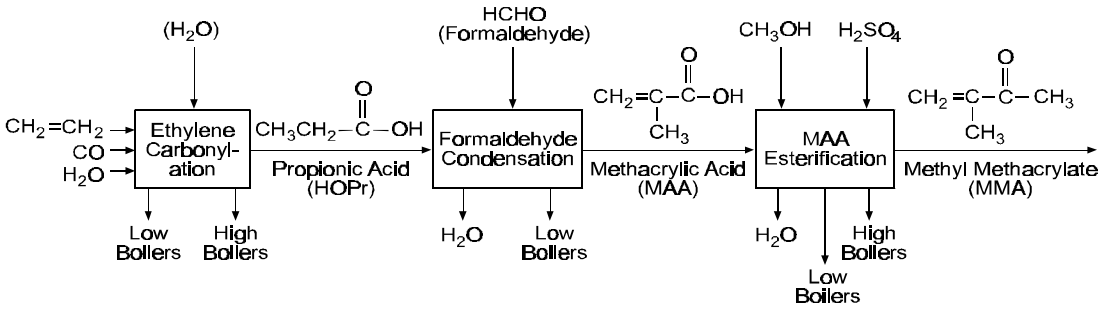

Figure 1. The RTI-Eastman-Bechtel three-step MMA process (with external formaldehyde feed).

methacrylate from coal-derived 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)

RTI has completed the condensation study of propionic acid and formaldehyde over various supported vanadium, niobium and tantalum catalysts.

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 and Eastman are carrying out the tradeoff analysis and preliminary plant/economics studies for the in-situ generation of formaldehyde and methyl propionate condensation with formaldehyde.

Task 5. DME Condensation Study(RTI and Eastman)

Over the last quarter(January-March/99), in-situ formaldehyde generation and condensation with methyl propionate were tested over various catalysts and reaction conditions. The obtained results are suitable for patent application and are retained for future reports. A patent application is in preparation.

CONCLUSIONS

1. Status

Tasks 1&2 are completed. Task 3 is on hold and will likely be revisited after the completion of DME extension. In Task 5, in-situ formaldehyde generation and condensation with methyl propionate and propionic acid were tested. The obtained results will be reported in the future reports. A paper titled “Catalytic synthesis of methacrylates over silica-supported niobium catalysts” was presented at the ACS National meeting at Anaheim, CA, March 20-26, 1999. A copy of the presentation is attached in Appendix A. A project meeting was also held in Anaheim.

Bechtel presented the preliminary economic analysis of the methacrylate synthesis process. A copy of the presentation is attached in Appendix B.

2. Forecast

We will continue testing the in-situ formaldehyde generation and condensation reaction over various potential catalysts. Bechtel will do an economic analysis according to the experimental results obtained.

REFERENCES

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Appendix A: Presentation by RTI at ACS National meeting at Anaheim, CA, March 20-26, 1999.

Appendix B: Presentation by Bechtel at the project meeting at Anaheim, March 23, 1999.