

SYNTHESIS OF ACRYLATES AND METHACRYLATES FROM COAL-DERIVED SYNGAS

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AUTHORS: MAKARAND R. GOGATE AND JAMES J. SPIVEY
JOSEPH R. ZOELLER AND RICHARD D. COLBERG
GERALD N. CHOI
SAMUEL S. TAM

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RESEARCH TRIANGLE INSTITUTE
3040 CORNWALLIS ROAD
P O BOX 12194
RTP, NC 27709-2194

EASTMAN CHEMICAL COMPANY
KINGSPORT, TN 37662-5150

BECHTEL
SAN FRANCISCO, CA 94119-3965

BECHTEL
HOUSTON, TX 77252-2166

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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 (DOE/FETC). 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. Over the last quarter, RTI carried out activity tests on a pure (99 percent) Nb_2O_5 catalyst, received from Alfa Aesar, under the following experimental conditions: $T=300\text{ }^\circ\text{C}$; $P=4\text{ atm}$, $72:38:16:4:220\text{ mmol/h}$, $\text{PA:H}_2\text{O:HCHO:CH}_3\text{OH:N}_2$; 5-g catalyst charge. For the pure Nb_2O_5 material, the MAA yields (based on HCHO and PA) were at 8.8 and 1.5 percent, clearly inferior compared to those for a 10-percent $\text{Nb}_2\text{O}_5/\text{SiO}_2$ catalyst (20.1 and 4.5 percent). The X-ray diffraction (XRD) patterns of pure Nb_2O_5 and 20-percent $\text{Nb}_2\text{O}_5/\text{SiO}_2$ catalysts show that while pure Nb_2O_5 is very highly crystalline, SiO_2 support makes for an amorphous nature of the 20-percent $\text{Nb}_2\text{O}_5/\text{SiO}_2$ catalyst.

Over the last quarter, RTI also began research on the use of dimethyl ether (DME), product of methanol dehydrocondensation, as an alternate feedstock in MMA synthesis. As a result, formaldehyde is generated either externally or in situ, from DME, in the process envisaged in the contract extension. The initial work on the DME extension of the contract focuses on a tradeoff analysis that will include a preliminary economic analysis of the DME and formaldehyde routes and catalyst synthesis and testing for DME partial oxidation and condensation reactions. Literature guides exist for DME partial oxidation catalysts; however, there are no precedent studies on catalyst development for DME-methyl propionate (MP) condensation reactions, thereby making DME-MP reaction studies a challenge. The design of a fixed-bed microreactor system for DME feedstock studies was also finalized over the last quarter. The system is designed to be operated either in DME partial oxidation mode (for formaldehyde synthesis) or DME-MP condensation mode (for MMA synthesis).

TABLE OF CONTENTS

	Page
Disclaimer	i
Abstract	ii
List of Figures and Tables	iv
List of Acronyms	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 Feedstock Evaluation (RTI and Eastman)	4
Conclusions	5
1. Status	5
2. Forecast	7
References	7

LIST OF FIGURES

Number		Page
1	The RTI-Eastman-Bechtel three-step MMA process (with external formaldehyde feed)	1
2	Comparative XRD patterns for pure Nb ₂ O ₅ (labeled as calcined Nb) and 20% Nb/SiO ₂ (labeled as NbSiO ₂)	4
3	Reaction pathways for MMA synthesis	6
4	Proposed fix-bed microreactor system for DME feedstock studies	7

LIST OF TABLES

1	Comparison of Pure Nb ₂ O ₅ and 10% Nb ₂ O ₅ /SiO ₂ for Condensation Reactions	4
2	List of Possible Routes to MMA	6

LIST OF ACRONYMS

ACH	Acetone cyanohydrin
DME	Dimethyl ether
DOE	U.S. Department of Energy
FETC	Federal Energy Technology Center
HCHO	Formaldehyde
MAA	Methacrylic acid
MMA	Methyl methacrylate
MP	Methyl propionate
PA	Propionic acid
RTI	Research Triangle Institute
XRD	X-ray diffraction

EXECUTIVE SUMMARY

The Research Triangle Institute (RTI)-Eastman-Bechtel team is developing a novel process for the synthesis of methyl methacrylate (MMA) from coal-derived syngas. The three-step process consists of synthesis of a propionate from ethylene, carbon monoxide, and steam; its condensation with formaldehyde to produce methacrylic acid (MAA); and esterification of MAA with methanol to yield MMA. Preliminary economic analysis of the RTI three-step route shows that the process is cost-competitive with five other commercial or near-commercial technologies to make MMA. The results on process economics clearly warrant continued research on the RTI three-step process.

Over the last quarter, RTI carried out activity tests on a pure Nb_2O_5 catalyst and compared the MAA yields (based on HCHO and PA) to 10 percent $\text{Nb}_2\text{O}_5/\text{SiO}_2$ catalyst. At nominally identical experimental conditions, the pure Nb_2O_5 catalyst gives about one-half the yields of a 10-percent $\text{Nb}_2\text{O}_5/\text{SiO}_2$ catalyst. It therefore appears that the $\text{Nb}_2\text{O}_5/\text{SiO}_2$ catalyst system is still definitely the preferred one for formaldehyde condensation reactions. In a further attempt to cut costs, the RTI-Eastman-Bechtel team is investigating a dimethyl ether (DME)-based process for MMA synthesis. In the envisaged process, formaldehyde required for condensation reaction is generated from DME partial oxidation, either in situ or externally. Methyl propionate (MP) is used as a propionyl source, instead of propionic acid. The DME-MP system selectively produces MMA and does not require costly acid-ester-water separation, which negatively affects process economics. Initial work on the DME route focuses on tradeoff analysis which includes preliminary economic analysis of the DME route and the original RTI route, as well as DME-MP condensation reaction studies.

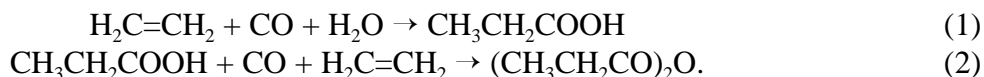
RTI also finalized the design of a fixed-bed microreactor system for DME feedstock studies. The system is designed to be operated either in a DME partial oxidation mode (for formaldehyde synthesis) or DME-MP condensation mode (for MMA synthesis).

INTRODUCTION

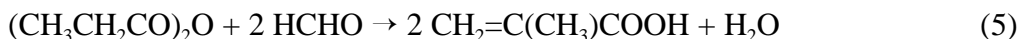
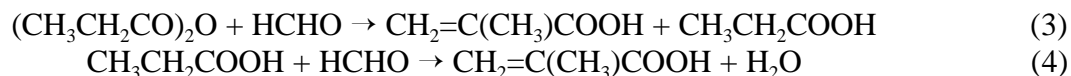
The most widely practiced commercial technology for the synthesis of methacrylic acid (MAA) and methyl methacrylate (MMA) is the acetone cyanohydrin (ACH) process. The ACH process requires handling of large quantities of extremely toxic and hazardous hydrogen cyanide and generates copious amounts of 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., 1996a, 1997a, 1997b; Spivey et al., 1995, 1996). There is a particular interest in the process that is not petroleum-based, but rather based on domestically produced coal-based syngas. The Research Triangle Institute (RTI)-Eastman-Bechtel three-step process (shown schematically in Figure 1) 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



Step 3: Esterification with methanol

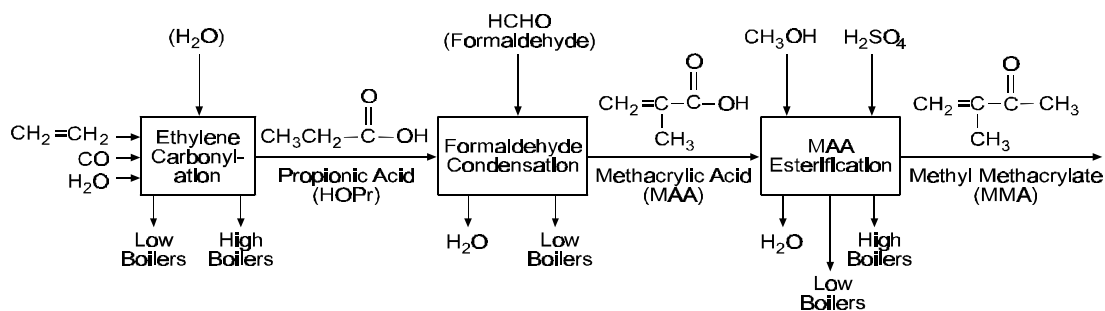
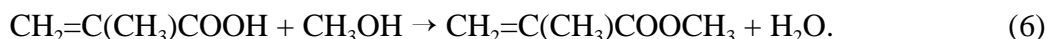


Figure 1. The RTI-Eastman-Bechtel three-step MMA process (with external formaldehyde feed).

In this proposed process for MMA manufacture, Step 3 is a known art. Steps 1 and 2, however, present a challenge for successful commercial demonstration of the process. The condensation step (Step 2) is composed of two separate condensation reactions ([3] and [4]) that 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, focuses on two tasks:

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

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

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

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

RESULTS AND DISCUSSION

Task 1. Propionate Synthesis (Eastman and Bechtel)

Eastman has completed the experimental work and economic analysis for the overall process. The results have been well covered in earlier reports. Based on Eastman's economic analysis, the RTI-Eastman-Bechtel three-step process is cost-competitive with five other commercial or near-commercial technologies for MMA manufacture.

Detailed results on the economic analysis have been given in earlier reports. The product value comparison for the RTI-Eastman-Bechtel three-step route with five other MMA routes shows that the RTI three-step process at 52¢/lb MMA is competitive with all other technologies for MMA manufacture, except propyne carbonylation (at 44¢/lb). These encouraging economic results clearly warrant further research on the RTI three-step process.

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 (Gogate et al., 1997a, 1997b). The catalyst development effort at RTI has focused on developing an active, selective, and stable 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 effective condensation catalysts. 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 has been demonstrated to be the most superior.

Over the last quarter, RTI carried out activity tests on a pure Nb₂O₅ catalyst (Alfa Aesar). The as-received catalyst was calcined at 350 °C for 4 h and at 450 °C for 6 h, in a forced-air convection oven. The catalyst was sieved into a 0.7- to 1.1-mm size fraction for condensation tests. The catalyst (5-g portion) was tested at the following conditions:

- T = 300 °C
- P = 4 atm
- W = 5 g
- F = 72:38:16:4:220 mmol/h, PA:H₂O:HCHO:CH₃OH:N₂O.

The results, summarized in Table 1, show that pure Nb₂O₅ is not as effective as a 10-percent Nb₂O₅/SiO₂, under formalin conditions.

The comparative X-ray diffraction (XRD) patterns of pure Nb₂O₅ and a 20-percent Nb₂O₅/SiO₂ are shown in Figure 2. The pure Nb₂O₅ shows sharp, well-defined peaks, indicating a highly ordered crystal structure with large crystallites of Nb₂O₅, while the 20-percent Nb₂O₅/SiO₂ shows a more broad, amorphous pattern, likely due to amorphous nature of the silica support. The finer crystallites of Nb₂O₅ may also contribute to an increased activity of the 20-percent (and 10-percent) Nb₂O₅/SiO₂ catalysts compared to pure Nb₂O₅. The pure Nb₂O₅ catalyst is currently being characterized for its physical and chemical properties to further understand the activity differences between these two catalysts. A patent application has been filed by RTI-Eastman researchers on the niobium catalyst (Gogate et al., 1996b).

Based on the Eastman-Bechtel economic analysis (presented in Task 1), the sensitivity of the reaction rate (g MAA/g cat·h) of condensation step and the deactivation of condensation catalyst have the most significant impact on the MMA product value. Current research at RTI has therefore focused on:

- improving the reaction rate (from the current value of about 200 g MAA/g cat·h)
- enhancing the catalyst life on-stream, for the current 10 percent Nb₂O₅/SiO₂ catalyst. This catalyst deactivates from an initial MAA yield of 58 percent (based on HCHO) to 31 percent over 180 h under trioxane conditions, at 300 °C, 2 atm, 72:16:220 mmol/h, PA:HCHO:nitrogen.

Task 3. Slurry Reactor Studies (RTI and Eastman)

Currently, the RTI-Eastman-Bechtel research team has decided to deemphasize the in situ oxidative condensation of methanol with propionic acid (PA), in the presence of oxygen. Eastman's assertion that the three-step methanol route consisting of external formaldehyde

Table 1. Comparison of Pure Nb₂O₅ and 10% Nb₂O₅/SiO₂ for Condensation Reactions^a

	MAA yield/HCHO (%)	MAA yield/PA (%)
Pure Nb ₂ O ₅	8.8	1.56
10% Nb ₂ O ₅ /SiO ₂	22.5	4.92

^aT = 300 °C, P = 4 atm, feed makeup: 72:38:16:4:220 mmol/h, PA:H₂O:HCHO:CH₃OH:N₂.

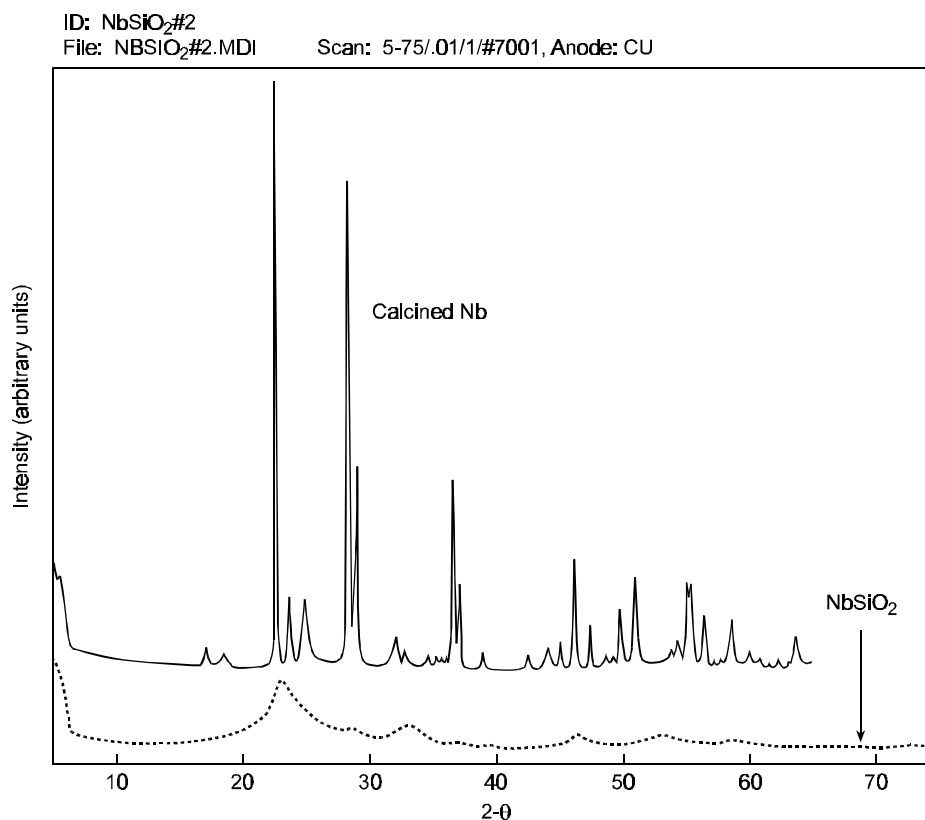


Figure 2. Comparative XRD patterns for pure Nb₂O₅ (labeled as calcined Nb) and 20% Nb/SiO₂ (labeled as NbSiO₂).

generation, condensation of formaldehyde with PA, and external esterification of MAA is likely to be cost-competitive with existing technologies for MMA manufacture was the basis for this decision. Based on Eastman's economic analysis, the in situ slurry reactor process development was deemphasized in favor of the more attractive RTI three-step route. It is likely that the slurry reactor technology be revisited at the end of the dimethyl ether (DME) extension of this contract (slated for completion on March 31, 1999).

Task 4. DME Feedstock Evaluation (RTI and Eastman)

The DME extension of the current contract on synthesis of acrylates and methacrylates from coal-derived syngas began on April 1, 1997. This 2-year extension increases the period of performance to March 31, 1999, and focuses on studying the use of DME rather than methanol as a source of formaldehyde. Specifically, the original RTI-Eastman-Bechtel three-step route to MMA uses methanol to generate formaldehyde in the external formaldehyde generation step. This formaldehyde is subsequently condensed with PA, and the resulting MAA is externally esterified with methanol to form MMA. The DME extension of this contract will study the uses of DME to generate formaldehyde, either externally or in situ.

With three formaldehyde, three propionyl, and two methyl sources, there are a total of 18 different possible routes to MMA. These are summarized in Table 2. Based on a detailed reaction pathway analysis, shown in Figure 3, Cases 3 and 17 are selected for further studies. Case 3 is the original RTI three-step route with propionic acid as the propionyl source and an external formaldehyde source. This route is termed as the formaldehyde route. Case 17 is the MMA route of the extension to this contract, with MP as the propionyl source and DME/methanol partial oxidation as the formaldehyde source. This is termed as the DME route.

The RTI-Eastman-Bechtel three-step route (formaldehyde route) is cost-competitive with all commercial or near-commercial technologies to MMA manufacture. At the outset, a similar economic study will be carried out on the DME route to evaluate its economic merit. This study will be carried out primarily by Bechtel, with guidance from Eastman.

Over the last quarter, RTI has completed the design of a fixed-bed microreactor system for DME partial oxidation reaction and DME-MP condensation reaction studies. The schematic of the proposed reaction system is shown in Figure 4. Finally, the RTI-Eastman-Bechtel team proposes to demonstrate and develop the DME route in a three-phase slurry reactor.

CONCLUSIONS

1. Status

Task 1 (Propionate Synthesis) is complete. Task 2 (Condensation Catalysis) is nearly complete. The niobium catalysts resulting from Task 2 have proven to be active, selective, and stable for condensation reactions. Task 3 (Slurry Reactor Studies) is on hold and will likely be revisited during the DME extension (Task 4) of the current contract. Preliminary economic analysis of the RTI-Eastman-Bechtel three-step process compares very favorably with five other commercial or near-commercial technologies to produce MMA. These economic results clearly indicate the commercial viability of the RTI three-step process (formaldehyde route), and warrant continued research, particularly in the area of catalyst deactivation and in enhancing the reaction rate in condensation step. The DME route which is a subject of the 2-year extension to the original contract (which has studied the formaldehyde route) can be potentially even more cost-effective compared to the formaldehyde route. Current research on the DME route focuses on assembly and operation of a fixed-bed reactor system for DME partial oxidation reaction and identification of suitable catalyst systems for DME-MP condensation reactions.

Table 2. List of Possible Routes to MMA

Case	Me feedstock	Pr feedstock	Formaldehyde source
1	MeOH	HOPr	MeOH dehydrogenation
2			MeOH oxidation
•3			External formaldehyde
4		Pr ₂ O	MeOH dehydrogenation
5			MeOH 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

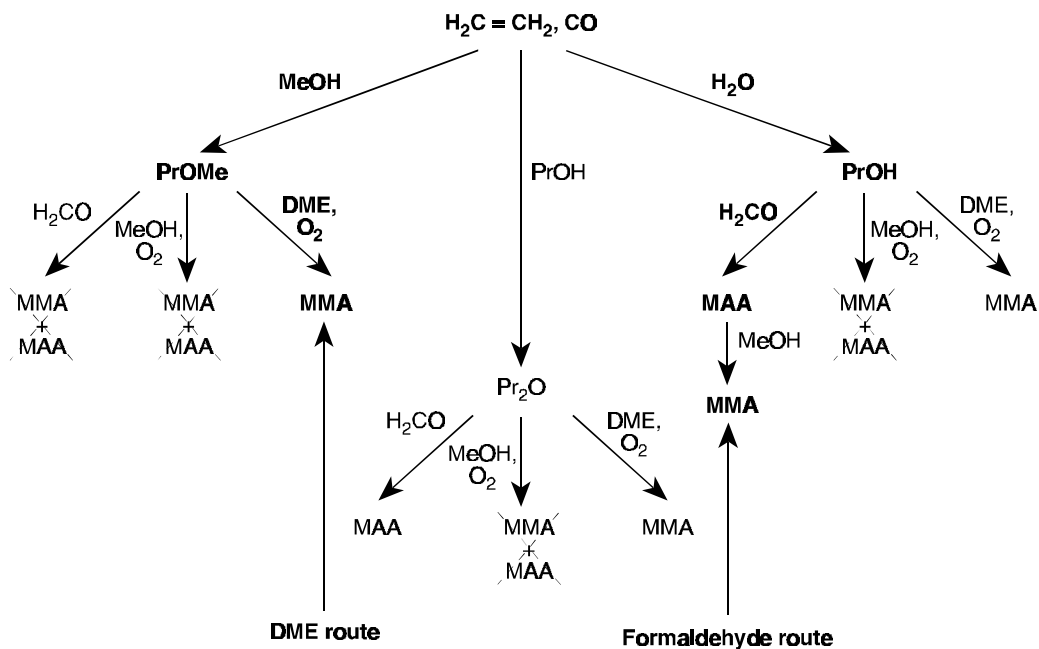


Figure 3. Reaction pathways for MMA synthesis.

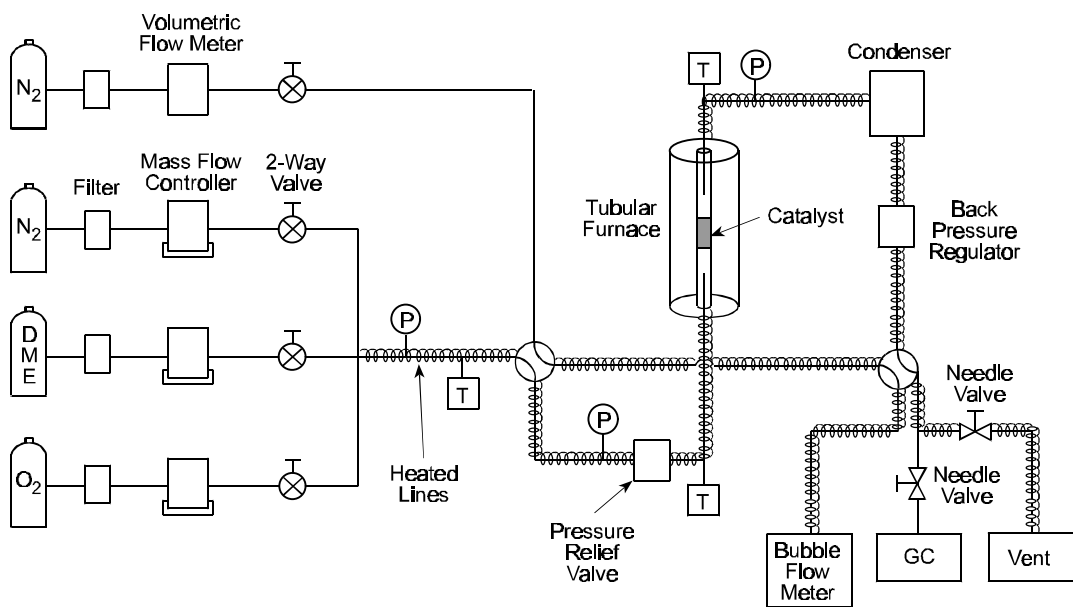


Figure 4. Proposed fixed-bed microreactor system for DME feedstock studies.

2. Forecast

Current and ongoing research on the RTI three-step methanol route focuses on the following:

- Identification of stable cations for Nb matrix
- Reaction kinetics, including reaction orders in formaldehyde, propionic acid, and activation energy of the reaction to validate Eastman's assumptions regarding reaction orders incorporated in their economic analysis.

The initial research on the DME extension of this contract will focus on the following:

- Tradeoff analysis—The tradeoff analysis will include a preliminary economic analysis of Route ① (DME route) and Route ② (methanol route) and will focus on material and energy balances, equipment design, and cost estimates.
- Catalyst synthesis for DME partial oxidation and condensation—Fixed-bed tests will be carried out on both the partial oxidation of DME to formaldehyde and condensation of MP with DME/methanol, initially with externally generated formaldehyde.

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