1. CONTRACT OBJECTIVE:

To develop an oxidation/condensation route for synthesis of acrylates/methacrylates from syngas.

2. 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 completing the documentation and developing the potential extension of the oxidative condensation to dimethyl ether. Eastman has completed internal invention reports covering two patents and is working on the third with RTI which they expect to complete within the month. Bechtel has also completed its work on the cost analysis of the propionate synthesis work (Task 1). RTI is continuing to develop active and stable catalysts for the condensation of propionic acid and formaldehyde. A total of 74 acid-base catalysts have been tested so far. Two invention reports have been completed based on RTI and Eastman's work. A third invention report is currently being prepared for Eastman's review on a novel methodology of methyl propionate activation. RTI is continuing to synthesize more acid-base catalysts with a goal of developing a catalyst which exhibits stable activity over a 200 h test period. Over the last quarter, RTI has also completed its initial tests on the slurry reactor system.

3. STATUS:

Task 1. Propionate Synthesis (Eastman)

Over the last quarter, Eastman has devoted its time to completing documentation and developing the potential extension of the oxidative condensation to dimethyl ether. Eastman has completed two internal invention reports covering two key patents and is working on the third with RTI. Copies of the invention reports and the patents will be sent to DOE and RTI patent counsels when completed.

Task 1. Propionate Synthesis (Bechtel)

Bechtel has essentially completed its effort on a preliminary process design and economics to produce...
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propionic anhydride via ethylene carbonylation. A sensitivity study of its cost on the overall MMA process will need to be investigated at a later day.

Task 2. Condensation Catalysis (RTI/Eastman)

Task 2 (Condensation Catalysis) is nearly complete. [Work on Task 2 is continuing only in support of the slurry reactor testing (Task 3).]

Task 2 has the objective of developing heterogeneous catalysts for the condensation of formaldehyde with various propionates. In addition to tests on the condensation reaction alone, runs were also made in the fixed bed microreactor to test the “one step methanol” route to MMA, in which methanol, oxygen, and propionic acid are fed to the reactor to produce MMA. Although we produced MMA, the yields were low (4%), and MAA was also produced (around 9% yield of MAA).

The remaining work (as envisioned in the current project under Task 3) will focus on the “one-step methanol” route to MMA in the slurry reactor, where the kinetics in this backmixed system are different than in the plug flow microreactor. We have made two successful runs in the slurry reactor, and the results are encouraging, and are currently in the process of preparing a patent application for this process.

DME Extension:

This work, which we expect to begin in November, will focus on two routes to MMA using DME as an intermediate. In what has been identified as Route 1, methyl propionate reacts with formaldehyde (from the partial oxidation of DME) and DME to form MMA in one reactor. [An alternative to accomplish the same reactions would be to feed methanol, propionic acid, DME, and oxygen to the reactor, in effect generating the methyl propionate in-situ. It is unclear if this would work, but could be tested.] RTI will develop catalysts for both the partial oxidation of DME and the condensation of DME with methyl propionate. [We plan, with DOE approval, to reverse the order of Tasks 2.1 and 2.2 in the work plan for the extension since the condensation catalysts for the methyl propionate will likely take more time to develop, and are more critical to the overall effort.] In Route 2, propionic acid reacts with externally generated formaldehyde to produce methacrylic acid, which is then esterified with methanol to produce MMA. For Route 2, there are no new catalysts needed.

Technical issues:

Including the DME routes, we are now pursuing three possibilities for MMA synthesis: the “one step methanol route”, and the two DME-based processes: Route 1 and Route 2 above. We identified several technical issues that we will address in our experiments to fully evaluate these alternatives:

1. Use of formalin. Formalin is an aqueous solution of formaldehyde which is much less expensive than other forms of formaldehyde that are produced industrially. If we are unable to produce formaldehyde in-situ, the processes we are contemplating can still be competitive, especially if this
inexpensive form of formaldehyde can be used. To test this, we will run experiments using formalin in the fixed bed and slurry reactor tests to see if it affects the yield and perhaps minimizes deactivation (which we believe is the major issue to be addressed in the development of condensation catalysts).

2. Kinetics of the condensation reactions. Because the economics that will be done by Bechtel will include tradeoffs that may affect the concentrations and temperatures of the reactors, we need to develop power law expressions for the condensation reactions (is water an inhibitor?? what is the affect of acid concentration??). We will do some limited tests to develop this data.

3. Catalysts for the one-step route. Our initial tests were made using a physical mixture of an Fe/Mo (for partial oxidation of methanol to formaldehyde) and a V-Si-P (for the condensation) catalyst. Because there is ample precedent for metal migration from one catalyst to another in these liquid systems, we would prefer to use one catalyst that performs both functions. We will thus test the Group 5 catalysts for this one-step route, though we do not envision a substantial effort to develop a completely new catalyst for this purpose.

4. Material balances for the condensation runs. Comprehensive material balances are not carried out routinely for the condensation runs. We need to repeat selected runs to account for any unreacted formaldehyde in the exit gas, since this would affect the economics. In particular, selected runs from the M₁-series of catalysts will be repeated (10% M₄/SiO₂ and 20% M₄/SiO₂), with the sodium sulfite method for formaldehyde. Currently, we are also developing another chromatographic technique for formaldehyde based on a Chromosorb 107 Deactiglas column.

Task 3. Slurry Reactor Studies (RTI/Eastman)

Over the last quarter, RTI has demonstrated the operation of the slurry reactor testing, in addition to pressure testing and operation with a few candidate slurry fluids. NCSU has completed the testing of a few candidate fluids like decalin and tetralin, and continue to test additional liquids.

Two runs were carried out in the slurry reactor system, which showed that both methyl methacrylate and methacrylic acid could be co-produced in the slurry reactor, although the product analysis was a medley of at least 40 other peaks as well. Although the selectivity to methacrylates is poor, we feel that these results are patentable and therefore have given these results in rather general terms.

4. FORECAST

RTI

1. Carry out fixed bed experiments according to the following priority:

1. Experiments with Formalin and Propionic Acid with 5, 10, and 20% M₁/SiO₂ Catalyst. We currently conduct the experiments at 300 °C, 2 atm, 5 g cat charge, 72:16:220 mmol/h PA:HCHO:Nitrogen. 16 mmol/h is 0.48 g HCHO per hour which is 1.297 g Formalin per hour
(37% w/w HCHO). This corresponds to 16 mmol/h HCHO: 4 mmol/h CH₂OH and 38 mmol/h H₂O. 72 mmol/h PA equals 5.33 g/h PA. The reactor feed rate then would be 6.627 g/h.

2. **Long-term activity check on M₁/SiO₂ catalyst with the formalin system.** We will preferably do a long-term run on the 10% M₁/SiO₂ system, since we already have a long-term activity result, and we can then isolate the effect of steam.

3. **Reaction Orders and Activation Energies.** This will need a concerted effort. We will use a 8-20 mesh 10% M₁/SiO₂ catalyst. The variables will be T, P, and partial pressures of PA, HCHO, and nitrogen. A two-level, five factor experimental design will lead to 2^5 experiments = 32 experiments + 1 CP run = 33 experiments. We will do a one-quarter fraction, which will result in 8 runs + one CP run = 9 runs. + some non-design runs to get the T effect and an accurate estimation of activation energy.

4. **Experiments with Acetic Acid on M₁/SiO₂ Catalysts.** With the set of five M₁/SiO₂ catalysts, we will test each of them at nominally identical conditions of 300 °C, 2 atm, 5 g cat charge, 72:16:220 mmol/h AA:HCHO:Nitrogen. This will give us a side-by-side comparison among acetic acid and propionic acid.

2. Prepare patent disclosure on methyl propionate activation under the working title “Conversion of Methyl Esters to Unsaturated Acids and Their Esters” (this could include, for example, the conversion of methyl acetate to acrylic acid).

3. Set up tentative dates in December for a meeting of the project team with DOE.

4. Prepare annual report for review by Bechtel and Eastman.

**Eastman**

1. Provide Bechtel with data on acid cost for Route 2 cost analysis. Bechtel will assume for an effect of acid concentration on rates for Route 2 but can substitute RTI data once tests are done.
2. Provide Bechtel with data on methyl propionate rates as part of the cost analysis for Route 1.

**Bechtel**

1. Begin tradeoff analysis (starting with Route 1) once DME extension is in place.

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