

DOE/PC/94065--T2

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**SYNTHESIS OF ACRYLATES AND METHACRYLATES
FROM COAL-DERIVED SYNGAS**

Quarterly Technical Progress Report

Submitted to

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Executive Summary

Task 1-Synthesis of Propionates

The objective of this Task is to develop the technology for the synthesis of low-cost propionates. These propionates are the basic feedstock for the subsequent reaction with formaldehyde to produce the target molecule, methyl methacrylate (MMA).

Eastman has explored several possible routes to the propionates and has concluded that the most promising is the synthesis of propionic anhydride from the reaction of propionic acid from and ethylene (and also hydrogen in some cases). The main advantage of the anhydride over the acid is that its subsequent reaction with formaldehyde does not produce water, which can lead to undesired byproducts. Bechtel is carrying out a cost analysis of the Eastman route to the anhydride to determine if it is *potentially* competitive with commercially practiced routes to the same molecule. The answer is expected next quarter.

Task 2-Condensation Catalysis

The objective of this Task is to develop catalysts for the condensation of the propionate (propionic anhydride is our target molecule) with formaldehyde. This reaction produces methacrylic acid (MAA), which would then be reacted with methanol to produce MMA in the slurry reactor. [The reaction of MAA and methanol is well understood and is not a technical barrier for the MMA synthesis.]

We have synthesized a wide range of catalysts and the results show that there is substantial byproduct formation, including 3-pentanone and some propionic acid. Our results show the highest yields of MAA using an alkalized alumina (1%Na/ γ -Al₂O₃). [Quantitative yields of methacrylic acid will be calculated when work is complete on the analytical system, which involves some new methods designed to improve the number of tests that can be carried out in a given time.]

Although the condensation of *propionic acid* with formaldehyde is well studied in the literature, little is reported on the condensation of the *anhydride*. Although it is likely that the same general types of acid/base catalysts that promote the acid condensation will also promote that of the anhydride, the strength and balance of the acid and base sites is likely to be different. We plan to explore the relationship of the catalyst properties and MMA yields using the Altamira system, due to be delivered this next quarter.

TASK 1: Synthesis of Propionates

Objective: The development of technology for the low cost generation of propionate feedstocks

STATUS

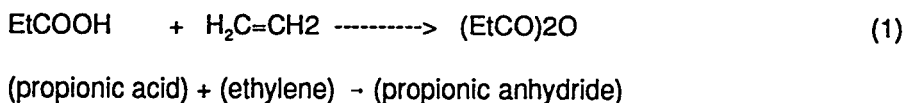
Propionate Costs (Bechtel)

Bechtel is carrying out a preliminary design/economic comparison of competitive methacrylic acid (MAA) and methyl methacrylate (MMA) technologies. A copy of the 1991 Chem Systems report on methacrylic acid/methacrylates was purchased and reviewed to provide a baseline comparison of existing MAA and MMA processes. Benchmark routes with which to compare our proposed syngas-based MMA synthesis via propionate in-situ oxidation/condensation include the commercial acetone/cynaohydrin process and the BASF process.

MMA production economics will be assessed on a consistent (1995) basis. Although the Chem Systems report contains production cost of various competitive MMA processes, it does not provide adequate process design details from which Bechtel can bring these costs up to date. We have recommended to DOE/PETC to purchase a copy of the 1993 SRI Process Economic Report on methacrylic acid and methacrylates. This SRI report will provide the in-depth process design information, with detailed PFD and equipment listing, that is needed to develop realistic costs.

Propionate synthesis (Eastman)

The first step in the generation of methacrylates, which is the key goal of this proposal, is the generation of the requisite propionyl moiety. Eastman Chemical Company's objective in Task 1 is to study methods for the generation of this propionyl moiety. Particular emphasis is placed upon the development of a new proprietary catalyst for this process which may replace existing catalysts that are based upon either expensive Pt group metals (i.e. Rh) or highly toxic nickel carbonyl. Eastman's initial focus has been the development of a propionic anhydride process based on the following conversion:



The process is also amenable to the production of propionic acid and its esters using similar chemistry. [Hydrogen is added as a reactant, in addition to propionic acid and ethylene, in some experiments.]

Process Description. Typically, the catalytic reaction is performed at a pressure of 400-1000psig using a gas mixture consisting of ethylene and carbon monoxide which contains 5-10% hydrogen to maintain the catalyst and operates satisfactorily in the temperature range of 140-200°C.

The reaction has been observed to run at rates as high as 5-6 moles/L-h. However, at these high rates, the reaction is mass transfer limited with the existing equipment. Most reactions in this study are run at slower reaction rates (typically in the range of 0.6 to 2.5 moles/L-h) to avoid these complications. In the batch processes used to study this process, the ratio of propionic acid to catalyst is typically in the range of 300-1200:1 and demonstrates linear production rates until conversions of 75-85% are achieved, at which time the reaction rate decreases.

Summary of Results. This quarter, Eastman has made progress toward this goal in the following areas:

- a. refining the kinetic model
- b. conducting key model reactions to probe free radical behavior

- c. in-situ infrared studies of the catalyst components
- d. assisted Bechtel in arriving at a preliminary process design.

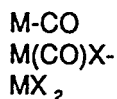
a) *Kinetic Modeling.* Eastman has been actively expanding the range of kinetic models for the propionyl process. These expanded models are still not complete, but Eastman has made several observations that are revealing. They have verified the ½ order dependence upon ethyl iodide [a homogeneous catalyst for reaction (1) above], and zero order dependencies upon ethylene and hydrogen (beyond small minimum requirements). Eastman has also observed some anomalous results with regard to the metal component. It appears that the reaction order with respect to the metal component is dependent upon the level of iodide salt. These results need to be reproduced and expanded, but imply competing pathways with differing rate limiting steps. Expanded studies on the iodide salt level and CO pressure are already underway and Eastman intends to investigate the metal catalyst anomaly further in the coming quarter.

b) *Reactions to probe free radical behavior.* Over the last quarter, Eastman examined several reactions to probe the mechanism of its propionyl catalyst. These studies are important in minimizing the cost of the propionyl synthesis, and therefore of the MMA. Typical methylcyclopentanyl radical forming probes failed since isomerization of the olefinic-halide substrates was more rapid than the free radical initiation process. However, benzyl bromide provided a very good probe. Using stoichiometric quantities of M(CO)X and benzyl bromide in diglyme and in the absence of added CO, Eastman obtained bibenzyl as the major product (from radical coupling) but equally important, significant quantities of phenylacetates, particularly benzyl phenylacetate and PhCH₂CO₂CH₂CH₂OCH₂CH₂CH₂CH₂CH₃ (from reaction with solvent). (Products determined by GC-MS, quantification underway.)

The presence of bibenzyl indicates that there are free radicals generated (as suspected earlier based on the isolation of 3,4-hexanedione derived products in the propionyl process), but the presence of phenylacetates indicates that the free radicals may (and probably do) subsequently interact with the metal carbonyl complexes. This probe serves to indicate that carbonylation of the radical likely occurs by subsequent attachment to a metal carbonyl, not by direct carbonylation of the free radical as initially proposed since benzyl radicals are known to be refractory to direct carbonylation. Eastman will be looking at several similarly probes in the near future.

This observation and the kinetics (particularly the metal anomaly) will lead to some revisions (but not dramatic changes) in the earlier proposed mechanisms. These mechanistic proposals are being tested for mathematical consistency.

c) *In-Situ Spectroscopic Probes.* Last quarter, Eastman reported results of its in-situ infrared spectroscopic probes which indicated the simultaneous presence of the following three catalyst phases under reaction conditions:



where M = Catalyst and X = an anionic component. Further studies indicate that the dominant phases, M-CO and M-X⁻, are in equilibrium with each other as indicated in reaction (2) below.



Over the last quarter, Eastman has obtained an initial estimate of the equilibrium constant for reaction (2) [K = ca. 240-260] to use in clarifying rate expressions. Further work is planned to ensure that this equilibrium constant is correct.

d) *Design/Cost Estimation of Commercial Reactor System (with Bechtel.)* In addition to reaction rate and effluent data, Eastman has exchanged an information it had developed outside this contract pertinent to the best (most economical) reactor design. Although details of this information are subject to secrecy agreement (since they were developed prior to the granting of this contract), the conclusions were shared with Bechtel to assist in minimizing the time required for their assessment of the propionyl portion of the economic appraisal and to allow them to focus their efforts quickly.

PLANS FOR NEXT QUARTER

During next quarter, emphasis will be focused on 1) developing a conceptual design for the synthesis of propionic anhydride based on Eastman's catalytic process of C2 = carboxylation, and 2) evaluating its economics with existing technology. Eastman is in the process of transmitting the necessary design data to Bechtel.

TASK 2: Condensation Catalysis

Objective: The development of an experimental database for the rapid condensation of formaldehyde, or its derivatives, with acetates and propionates.

STATUS

The following was accomplished in the previous quarter:

- (1) Synthesis of condensation catalysts active for methacrylic acid synthesis.
- (2) Characterization of condensation catalysts.
- (3) Experimental testing of the condensation catalysts on the bench-scale microreactor system.

Synthesis of Condensation Catalysts

The synthesis of condensation catalysts was carried out in accordance with the protocol laid out in the Technical Proposal. A summary of this protocol has also been given below:

TABLE I. Summary of Condensation Catalysts for MAA Synthesis

Catalyst Group	Support	Additive(s)
A	Alumina	Alkali metals
B	Aluminosilicates	Alkali and alkaline earth metals
C	Silica	Alkali metals
D	Titania	$V_2O_5 + P_2O_5$
E	Silica	$V_2O_5 + P_2O_5$
F	Silica	Ta, W, Nb
G	Magnesia	MnO

The catalysts from groups A, B, C, and G were prepared by the incipient wetness technique, in which a required amount of support (usually 10 g) was weighed out and the amount of water needed to achieve incipient wetness and the amount of additive need to achieve a 1% catalyst loading were determined. The resulting wet mixture was dried at 100 °C for 24 h and then calcined at 600° C again for 24 h. Na catalysts were calcined at 400 °C.

The catalysts from groups E were prepared by the co-precipitation (gel precipitation for Ti-based catalysts) method. For example, a V-Ti-P catalyst with an atomic ratio of 1:2:6 was prepared as follows, following the procedure of Ai (*Applied Catalysis*, 54 (1989) pp. 29-36): Titanium chloride (usually 20 mL) was added dropwise to chilled water (ca. 500 mL). After the solution was diluted with ca. 2000 mL of water, dilute aqueous ammonia was added to precipitate the titanium hydroxide (final pH = 8-9). The precipitate was washed about 10 times with water by decantation and then filtered. Ammonium metavanadate (ca. 9.7 g) was added to about 50 mL of lactic acid and the mixture was warmed slowly, resulting in a clear-blue solution of VO^{2+} . The titanium hydroxide gel and 57 g of 85% phosphoric acid were mixed while being stirred, to give a thick, white gel. Thereafter, this gel was mixed with the clear-blue VO^{2+} solution and excess water was evaporated by vigorous stirring in hot air current. The blue cake was evaporated again by gradually raising the temperature in an oven

from 50 to 200 °C for 6 h. The resulting solid was calcined at 300 °C for 6 h and finally again at 450°C for 6 h in a stream of air.

The catalysts from group D (the V-Si-P catalysts) were also prepared following the procedures of Ai (*Bull. Chem. Soc. Jpn.*, 63 (1990) pp. 1217-1220; *J. Catal.*, 124 (1990) pp. 293-296).

Characterization of Condensation Catalysts

The synthesized catalysts have been analyzed for metal content by an inductively coupled plasma - optical emission spectrometry (ICP-OES) analysis. The catalysts were first dissolved in HNO₃/HCl/HF by microwave heating and then subjected to ICP-OES. The results have been summarized in Table III. The legends of the catalysts in the ICP-OES have been summarized in Table II.

TABLE II. Catalyst ID for the ICP-OES table

Catalyst #	ICP-OES ID	Catalyst (atomic ratio)
01	mo1	Na / Al ₂ O ₃ (1%)
02	mo2	Mn / MgO (1%)
03	mo3	V-Ti-P (3-1-3)
04	dup	V-Ti-P (3-1-3)
05	mo4	Na / SiO ₂ -Al ₂ O ₃ (1%)
06	mo5	Ca / SiO ₂ -Al ₂ O ₃ (1%)
07	mo6	V-Ti-P (1-6-6)
08	dup	V-Ti-P (1-6-6)
09	mo7	V-Si-P (1-12-2.8, 30% SiO ₂)
10	mo8	V-Ti-P (1-2-6)
11	mo9	V-Ti-P (1-2-2)
12	m10	V-Si-P (1-10-2.8, 25% SiO ₂)
13	m11	V-Si-P (1-10-2.8, 30% SiO ₂)
14	srm	std ref matl (qc)

The catalysts are also being analyzed for surface area and pore size distribution, as well as by x-ray diffraction analysis, to determine the composition of active phases in the catalysts. The results on these are awaited. We are also awaiting the Altamira system, which will further enable us to relate the acid-base properties of these catalysts to the product yield and selectivity.

TABLE II. Characterization of Condensation Catalysts by ICP-OES
(all compositions in µg/g unless noted)

	mo1	mo2	mo3	dup l	mo4	mo5	mo6	dupl	mo7	mo8	mo9	m10	m1 1	srm
Al	54.3 %	436	136	<10 0	6.17 %	6.13 %	<10 0	<10 0	124	346	156	357 0	155 0	6.13 %
B	<5	25.8	<5	<5	<5	27.1	<5	<5	<5	<5	<5	5.2	16. 1	113
Ba	3.3	<2	6.6	8.0	5.1	4.8	2.3	<2	3.9	7.0	44.0	9.8	19. 0	398
Be	<1	<1	<1	<1	<1	<1	<1	<1	3.2	3.2	1.0	1.4	1.1	7.1
Cl	3.3	<2.5	<2.5	4.5	2.7	<2. 5	<2. 5	<2. 5	2.7	<2. 5	<2. 5	<2. 5	<2. 5	6.2
Ca	432	175 0	193 0	938	246	1.18 %	199 0	127 0	49.9	809	119 0	200 0	327 0	2.67 %
Cr	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	130
Cu	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	75.8
Fe	145	141	567	197	370	546	249	59.6	151	582	81.6	710	330 0	4.09 %
Pb	156	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	28.8	<25	183
Mg	34.7	15.6 %	612	139	55.5	191	301	141	51.7	129	185	455	944	1.21 %
Mn	<4	662 0	19.9	10. 3	5.0	9.6	18.6	14.7	4.5	19.1	84.3	21.5	81. 5	584
Mo	<30	<30	60.0	77. 8	<30	<30	<30	<30	<30	36.2	<30	<30	<30	<30
Na	1.30 %	<10 0	224	135	953 0	407	270	128	1.08 %	184	180	256 0	1.0 7%	566 0
Ni	19.7	29.4	<15	<15	15.3	59.5	<15	<15	<15	<15	<15	<15	<15	53.6
P	<75	<75	16.5 %	16. 4%	<75	<75	18.6 %	17.1 %	7.85 %	28.5 %	18.4 %	8.21 %	8.8 3%	110 0
Si	141 0	946 0	<10 0	213	29.0 %	33.1 %	124 0	149	27.2 %	213 0	<10 0	25.7 %	25. 0%	24.7 %
Sr	4.6	3.6	11.7	7.7	5.4	9.0	9.3	4.9	3.1	15.6	94.1	14.8	31. 9	131
Ti	276	196	7.22 %	7.3 3%	93.2	693	23.9 %	21.8 %	206	6.79 %	19.7 %	145	<75	304 0

Zn	41.3	149	<15	<15	44.3	111 0	<15	<15	25.6	145	<15	<15	16. 4	445
V	70.9	84.6	30.6 %	30. 5%	101	<10	4.65 %	4.24 %	5.01 %	10.2 %	12.2 %	5.33 %	5.7 9%	48.0

Experimental Testing of Condensation Catalysts

The testing of these catalysts was carried out in a bench-scale fixed-bed microreactor system, currently fully operational at RTI. First, four blank runs were carried to elucidate the thermal and possibly the reactor wall effects on the reactants. The results from these blank runs have been summarized below:

Run #1

Feed: ca. 6 mL/h pure propionic anhydride
Diluent: ca. 60 mL/h (NTP) nitrogen
Preheater: 400 °C
Reactor: 400 °C
Pressure: 20 psi
Catalyst: no catalyst

Feed liquid analyzed by GC/MS => pac (?, tr, 358,611); pan (17,291,641)

Product liquid analyzed by GC/MS => 3-p (?, tr, 432,400); pac (2,832,793); pan (11,594,595)

Run #2

Feed: ca. 6 mL/h pure propionic acid
Diluent: ca. 60 mL/h (NTP) nitrogen
Preheater: 400 °C
Reactor: 400 °C
Pressure: 20 psi
Catalyst: no catalyst

Feed liquid analyzed by GC/MS => pac (12,196,195)

Product liquid analyzed by GC/MS => pac (12,456,569)

Run #3

Feed: ca. 6 mL/h 1,3,5, trioxane in propionic anhydride
(20:80 (w/w))
Diluent: ca. 60 mL/h (NTP) nitrogen
Preheater: 400 °C
Reactor: 400 °C
Pressure: 20 psi
Catalyst: no catalyst

Feed liquid analyzed by GC/MS => to (3,518,263); pan (13,183,224)

Product liquid analyzed by GC/MS => to (630, 949, tr); pac (3,869,775); pan (8,562,349)

Run #4

Feed: ca. 6 mL/h 1,3,5, trioxane in propionic acid
Diluent: ca. 60 mL/h (NTP) nitrogen
Preheater: 400 °C
Reactor: 400 °C
Pressure: 20 psi
Catalyst: no catalyst

Feed liquid analyzed by GC/MS => to (2,435,114); pac (7,542,663)
Product liquid analyzed by GC/MS => pac (12,470,569); pan (302,099, tr)

After these blank runs were completed, actual experimental runs were commenced. The results from three of these have been summarized below:

Run #5

Feed: ca. 12 mL/h 1,3,5, trioxane in propionic acid
Diluent: ca. 60 mL/h (NTP) nitrogen
Preheater: 400 °C
Reactor: 400 °C
Pressure: 20 psi
Catalyst: 1% (w/w) Na/Al₂O₃

Feed liquid analyzed by GC/MS => to (3,108,541); pac (9,564,848)
Product liquid analyzed by GC/MS => 3-p (496,585, ?); pac (8,592,413); maa (1,284,834)

Run #6

Feed: ca. 6 mL/h 1,3,5, trioxane in propionic acid
Diluent: ca. 60 mL/h (NTP) nitrogen
Preheater: 400 °C
Reactor: 400 °C
Pressure: 20 psi
Catalyst: 1% (w/w) Na/Al₂O₃

Product liquid analyzed by GC/MS => 3-p (5,131,456, ?); pac (4,076,102); maa (711,402)

Run #7

Feed: ca. 6 mL/h 1,3,5, trioxane in propionic anhydride
Diluent: ca. 60 mL/h (NTP) nitrogen
Preheater: 400 °C
Reactor: 400 °C
Pressure: 20 psi
Catalyst: 1% (w/w) Na/Al₂O₃

Product analyzed by GC/MS => 3-p (5,725,345, ?); pac (4,380,232); maa (456,106)

We are currently further improving our GC and GC/MS system, in order to be able to estimate the products on a quantitative basis. At this juncture, we have qualitatively confirmed the presence of methacrylic acid in the product, particularly when trioxane is fed with propionic acid over our catalysts.

Summary of Condensation Catalysis Experimental Runs*

Run #	Feed	Catalyst	Product Analysis by GC/MS
1	pure pan, ca. 6 mL/h	-	3-p, pac, pan
2	pure pac, ca. 6 mL/h	-	pac
3	trioxane in pan, ca. 6 mL/h	-	to (?), pac, pan
4	trioxane in pac, ca. 6 mL/h	-	to (?), pac, pan
5	trioxane in pac, ca. 12 mL/h	1% Na / activated Al ₂ O ₃	pac, maa, no pan
6	trioxane in pac, ca. 6 mL/h	1% Na / activated Al ₂ O ₃	3-p (?), pac, maa, no pan
7	trioxane in pan, ca. 6 mL/h	1% Na / activated Al ₂ O ₃	3-p, pac, maa
8	trioxane in pan, ca. 6 mL/h	1% Mn / MgO	3-p (?), pac (FID)
9	trioxane in pan, ca. 6 mL/h	1% Ca / SiO ₂ - Al ₂ O ₃	3-p (?), pac
10	trioxane in pan, ca. 6 mL/h	1% Na / SiO ₂ - Al ₂ O ₃	3-p (?), pac
11	trioxane in pan, ca. 6 mL/h	V-Ti-P (1-2-6)	3-p (?), pac
12	trioxane in pan, ca. 6 mL/h	V-Ti-P (1-6-6)	3-p (?), pac (FID)
13	trioxane in pan, ca. 6 mL/h	V-Ti-P (1-2-2)	3-p (?), pac (FID)
14	trioxane in pan, ca. 6 mL/h	V-Ti-P (1-1/3-1)	3-p (?), pac (FID)
15	trioxane in pan, ca. 6 mL/h	V-Si-P (1-12-2.8)	3-p (?), pac, maa (*) (FID)
16	trioxane in pan, ca. 6 mL/h	V-Si-P (1-10-2.8, 25%)	run IP
17	trioxane in pan, ca. 6 mL/h	V-Si-P (1-10-10)	run IP
18	trioxane in pan, ca. 6 mL/h	V-Si-P (1-2.8-2.8)	run IP
19	trioxane in pan, ca. 6 mL/h	V-Si-P (1-10-2.8, 30%)	3-p (?), pac (FID)
20	trioxane in pan, ca. 6 mL/h	V-P (1-1.05)	catalyst in preparation

(*Note: Nominal Reaction Conditions: T = 400 °C, P = 20 psi, nitrogen flow = ca. 60 mL(NTP) / h; ? Products 3, 4, 6, 9, 10, 11 : Tentative ID only by GC/MS due to poor match quality; ? Products 8-15, 19 : Overlapping retention times with mma and to in the FID; * : Marginally above the detection limit in the FID)

Notes:

pan: propionic anhydride
pac: propionic acid
to: 1,3,5, trioxane
3-p: 3-pentanone
maa: methacrylic acid

Column: DB-624 fused silica capillary column
Oven T: 50 °C (1 min) ramp to 200 °C @ 20 °C/min
Injection: Split ratio 1:20 (1/20 μ L of 1 μ L)
Solvent: Toluene
Detector: FID/MSD
Carrier gas: Helium @ 4 mL/min (20 psi head pressure, with a post-column splitter).

Initial Findings from the Condensation Catalysis Runs

The initial observations from the condensation catalysis runs have been summarized below:

(1) When pure propionic anhydride alone is fed to the reactor, without any catalyst, the product condensate contains propionic anhydride and some propionic acid. When a mixture of trioxane along with propionic anhydride is fed to the reactor, without any catalyst, the product condensate contains propionic anhydride, propionic acid, and a solid white insoluble material. It does not dissolve in the product liquid mixture, even after heating while being stirred. This suggests that it is NOT trioxane, since trioxane is readily soluble in both propionic acid and propionic anhydride. Based on area % comparison, ca. 25% more of anhydride is converted to the acid, in presence of trioxane in the feed.

(2) When pure propionic acid alone is fed to the reactor, without any catalyst, the condensate contains pure propionic acid only. When a mixture of trioxane with acid is fed to the reactor, the condensate contains acid, tr 3-p, and again a solid insoluble white material, which does not dissolve.

(3) When trioxane is fed along with anhydride over a 1% $\text{NA/Al}_2\text{O}_3$ catalyst at 400 °C, the product condensate does not contain any insolubles. The product liquid is a mixture of propionic acid, tr propionic anhydride, and some methacrylic acid. When trioxane is fed along with acid over 1% $\text{NA/Al}_2\text{O}_3$ catalyst at 400 °C, the product liquid contains unreacted propionic acid, 3-p (?), and methacrylic acid. The area % count for methacrylic acid in the propionic acid feed case is more than the anhydride case.

PLANS FOR THE NEXT QUARTER

The following goals are set for the next quarter:

1. Complete physical characterization of the prepared catalysts (BET- N_2 surface area, pore size distribution and average pore volume, and active phases by x-ray diffraction).
2. Initiate chemical characterization of the prepared catalysts for acid-base properties (NH_3 -pyridine TPD for acidity and phenol- CO_2 TPD for basicity).
3. Continue synthesis and testing of V-Si-P catalysts with different atomic ratios and different silicas.
4. Relate the acid-base and catalyst physical properties to the methacrylic acid yield and selectivity and initiate identification of active and selective catalysts for methacrylic acid yield.
5. Begin design of the slurry reactor system.