

***CHARACTERIZATION AND CPDM MODELING OF VOLATILE FATTY  
ACID FERMENTATION WITH COTTON GIN TRASH AND CHICKEN  
MANURE AS SUBSTRATES***

A Senior Thesis

By

Joseph Han

1997-98 University Undergraduate Research Fellow  
Texas A&M University

Group: Engineering I

**Characterization and CPDM Modeling of Volatile Fatty Acid  
Fermentation with Cotton Gin Trash and Chicken Manure as  
Substrates**

by

Joseph H. Han

Submitted to the  
Office of Honors Programs and Academic Scholarships,  
Texas A&M University  
in partial fulfillment of the requirements for

1997-98 UNIVERSITY UNDERGRADUATE RESEARCH FELLOWS PROGRAM

Approved as to style and content by:



Mark T. Holtzapple, Advisor  
Department of Chemical Engineering



Susanna Finnell, Executive Director  
Honors Programs and Academic Scholarships

April 16, 1998  
Fellows Group: Engineering I

## Acknowledgments

I would like to express my thanks to Dr. Mark Holtzapple for giving me to opportunity to work on his research team. A “leap of faith” is often necessary to trust an undergraduate to do quality research. I would also like to thank Kyle Ross, Susan Burdick, and Vincent Chang who helped me with the immense learning curve in the laboratory. I would like to express my gratitude to the student workers without whom much of the work would never get done.

I would also like to express my appreciation to Dr. Edward Funkhouser and the University Honors Program staff. Without the efforts of Dr. Funkhouser and the staff, many undergraduates would miss the opportunity to experience research.

I would also like to thank Mr. Randy Marek for his help when something needed to be built or fixed.

## Table of Contents

Acknowledgments.....	ii
Table of Contents .....	iii
List of Figures .....	vi
List of Tables .....	vii
Abstract .....	1
Introduction.....	2
Factors Affecting Product Yields.....	5
Reactors.....	5
Residence Time.....	7
pH of the Solution.....	8
Methanogenesis.....	9
Oxygen Contamination .....	9
Substrate selection/ratio .....	10
Temperature .....	11
Modeling Using the CPDM Method.....	11
Experiments .....	13
Diffusion of Oxygen Through Reactor Walls.....	13
Batch Municipal Solid Waste/Sewage Sludge.....	13
Municipal Solid Waste / Sewage Sludge, Batch Reactor A .....	13
Municipal Solid Waste / Sewage Sludge, Batch Reactor B.....	15
Batch Cotton Gin Trash / Chicken Manure .....	15
Cotton Gin Trash / Chicken Manure, Batch Reactor 90 g solids/L .....	16

Cotton Gin Trash / Chicken Manure, Batch Reactor 200 g solids/L .....	17
Cotton Gin Trash / Chicken Manure, Batch Reactor 300 g solids/L .....	18
Cotton Gin Trash / Chicken Manure, Batch Reactor 350 g solids/L .....	19
CPDM Modeling using GT / CM Batch Data .....	20
CPDM Modeling Using Initial Data Points .....	20
CPDM Modeling Using All Data Points .....	24
Countercurrent Cotton Gin Trash/Chicken Manure.....	25
Results and Conclusions .....	27
Literature Cited .....	29
Appendix .....	30
A. Full Data Sets .....	30
Municipal Solid Waste / Sewage Sludge, Batch Reactor A .....	30
Cotton Gin Trash / Chicken Manure, 90 g solids/L.....	30
Cotton Gin Trash / Chicken Manure, 200 g solids/L.....	31
Cotton Gin Trash / Chicken Manure, 300 g solids/L.....	31
Cotton Gin Trash / Chicken Manure, 350 g solids/L.....	31
Cotton Gin Trash / Chicken Manure, Countercurrent.....	32
B. CPDM Modeling with Initial Data Points .....	33
Specific Rate Parameter Determination .....	33
Batch Reactor Simulation .....	34
C. CPDM Modeling with All Data Points.....	37
Specific Rate Parameter Determination.....	37
Batch Reactor Simulation .....	38

D. Apparatus and Procedures.....	41
Reactors.....	41
Rolling Mechanism.....	41
Head Gas Measurement.....	42
Countercurrent Procedures.....	43
Liquid Product Characterization.....	44
E. Equipment Parts.....	46
F. Supplier Information.....	47

## List of Figures

Figure 1. Schematic of the MixAlco Process.....	3
Figure 2. Pathway for Rumen Digestion.....	4
Figure 3. Batch Reactor .....	6
Figure 4. Fed-batch Configuration.....	6
Figure 5. Countercurrent Configuration.....	7
Figure 6. MSW / SS Acid Concentration, Batch Reactor A.....	14
Figure 7. MSW / SS Acid Concentration, Batch Reactor B .....	15
Figure 8. GT / CM Acid Concentration, 90 g solids/L .....	16
Figure 9. GT / CM Acid Concentration, 200 g solids/L .....	17
Figure 10. GT / CM Acid Concentration, 300 g solids/L .....	18
Figure 11. GT / CM Acid Concentration, 350 g solids/L .....	19
Figure 12. Polynomial Fit, Batch Reactor 90 g solids/L.....	20
Figure 13. Polynomial Fit, Batch Reactor 200 g solids/L.....	21
Figure 14. Polynomial Fit, Batch Reactor 300 g solids/L.....	21
Figure 15. Polynomial Fit, Batch Reactor 350 g solids/L.....	22
Figure 16. Predicted Acid Concentration, 90 g solids/L.....	23
Figure 17. Predicted Acid Concentration, 200 g solids/L.....	23
Figure 18. Predicted Acid Concentration, 300 g solids/L.....	24
Figure 19. Predicted Acid Concentration, 350 g solids/L.....	24
Figure 20. GT / CM Acid Concentration, Countercurrent .....	26

## List of Tables

Table 1. Annual U.S. Waste Biomass Collected .....	2
Table 2. Substrate Combinations .....	10
Table 3. MSW / SS Acid Concentration, Batch Reactor A .....	14
Table 4. MSW / SS Acid Concentration, Batch Reactor B.....	15
Table 5. GT / CM Acid Concentration, 90 g solids/L.....	16
Table 6. GT / CM Acid Concentration, 200 g solids/L.....	17
Table 7. GT / CM Acid Concentration, 300 g solids/L.....	18
Table 8. GT / CM Acid Concentration, 350 g solids/L.....	19
Table 9. Specific Rate Parameters, Initial Data Points .....	22
Table 10. GT / CM Acid Concentration, Countercurrent .....	25



## Abstract

With literally tons of biomass produced annually, a process that uses this waste as a feedstock would help reduce the problem of disposal. The MixAlco process is one that does just that. It converts biomass through anaerobic fermentation into volatile fatty acids, mixed alcohols, and ketones. These products can be used as raw chemicals or as fuel for their heating value. The process must be implemented on an industrial scale in order to obtain significant amounts of the products.

The substrates evaluated in this study are municipal solid waste (MSW), sewage sludge (SS), cotton gin trash (GT), and chicken manure (CM). The product concentrations obtained from using MSW and SS as the substrate were low compared to those obtained with GT and CM. Maximum product concentrations when using GT and CM at a temperature of 55°C were 22 g of total acid/L with acetic acid constituting 78 % of the total acids.

The Continuum Particle Distribution Modeling (CPDM) method is also applied to data collected for batch reactions. The model can accurately predict acid concentrations when excessive decomposition of the acid is not occurring. However, when liquid residence times are extended and the products decompose, the model does not accurately predict the decreasing product concentrations.

## Introduction

Environmental concerns have increased dramatically in the past years. One concern is the amount of waste generated per year and how to dispose of the waste. Literally tons of waste biomass is produced annually. For example, data shown in Table 1 are estimates for annual biomass waste collected in the United States.

**Table 1. Annual U.S. Waste Biomass Collected**

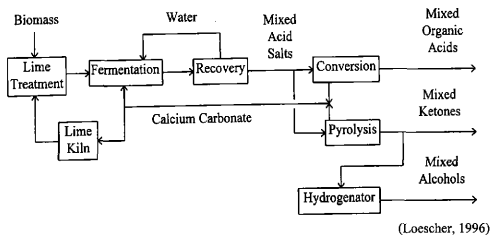
<b>Biomass Source</b>	<b>Dry Tons/Year (millions)</b>
Manure	174
Municipal Solid Waste	170
Crop Residues	64
Raw Sewage	60

(Chermisinoff et al., 1980)

The MixAlco process is a fermentation process that uses biomass waste as a raw material.

Anaerobic fermentation processes have been utilized for over a century (McCarty, 1982). Originally, the fermentation process treated municipal wastewater and the suspended organic material. The purpose of the anaerobic treatment was to aid in the disposal of the solid sludge. The process decomposed the material to carbon dioxide and methane. Even in 1895, the value of the decomposition products was recognized (McCarty, 1982). Donald Cameron of Exeter, England utilized the methane from the process for heating and lighting at the treating facility.

The MixAlco process is different from earlier processes in that value is placed on products other than methane. A schematic of the MixAlco process is shown in Figure 1.

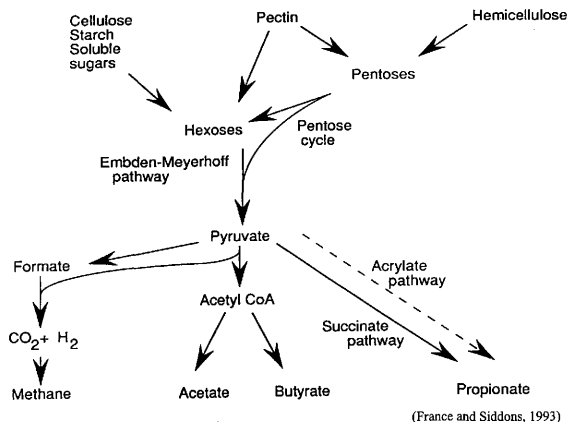


**Figure 1. Schematic of the MixAlco Process**

The MixAlco process is modeled after the fermentation that occurs within ruminant animals. Volatile fatty acids (VFA) are the products of microbial digestion in the rumen (France and Siddons, 1993). The fermentation produces principally acetic, propionic, and butyric acids. Higher acids are also produced in lesser amounts. These products can then be converted to their respective alcohol or ketone. The acid can be used in other processes, and the alcohol and ketone forms can be used for heating and fuel uses. Today, these products have a higher market value than methane.

Early studies placed biomass in the rumen of a fistulated steer. Because of evolution and natural selection, the microorganisms within the rumen are well suited to digest dietary carbohydrates. These carbohydrates consist of cellulose, hemicellulose, pectin, starch, and soluble sugars (France and Siddons, 1993). These substrates are first

degraded into their constituent sugars and then fermented to VFA. A representation of the pathway for the carbohydrates is shown in Figure 2.



**Figure 2. Pathway for Rumen Digestion**

Methanogenic bacteria in stagnant ponds and compost piles employ similar pathways (McCarthy, 1982).

The purpose of this study is to improve acid production from the MixAlco process. This process, once implemented on an industrial scale, could be used as a supplement to current energy sources. In order for the process to be economical, a minimum of 20 g of acid/L must be produced.

The production of acid depends on several variables. Reactor configuration, residence time, pH of the solution, methanogenesis, oxygen contamination, substrate

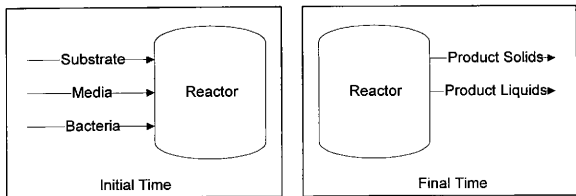
choice, and temperature all play roles in determining the acid concentration. It is difficult to determine exactly what role each factor plays; therefore, an empirical method will be used to model the system. The Continuum Particle Distribution Modeling (CPDM) method developed by Loescher (1996) will be used. Originally, the method was developed using mixed winter grass as the substrate. This study will extend the application of the modeling method to cotton gin trash and chicken manure.

### *Factors Affecting Product Yields*

#### Reactors

The reactors are an integral component of the MixAlco process. Not only are they the place where the decomposition occurs, but the reactor configuration is a variable in determining residence time for the liquids and solids. Three possible types of reactors are batch, fed-bath, and countercurrent.

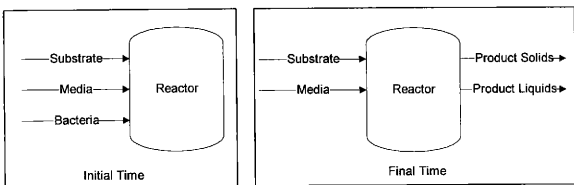
The batch configuration employs one reactor. The reactor is initially loaded with the substrate and media and inoculated with the bacteria. At the conclusion of the digestion, the product solids and product liquids are removed and characterized. This configuration is shown in Figure 3.



**Figure 3. Batch Reactor**

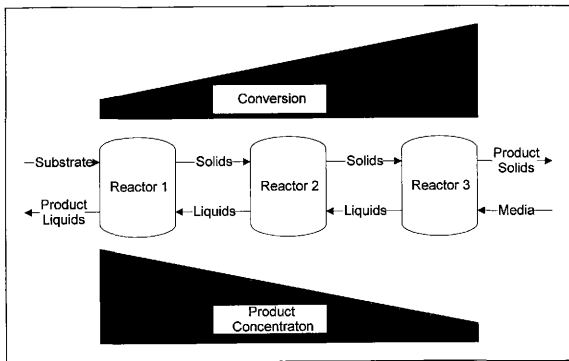
Samples may be removed periodically from the system to determine the extent of the reaction.

The fed-batch configuration also employs only one reactor. Similar to the batch configuration, the reactor is initially loaded with the substrate, media, and bacteria. However, at a future time, the product solids and product liquids are removed, and new substrate is added. Also fresh media is added; however, the fermentation microorganisms are allowed to reproduce naturally and sustain their population. This configuration is shown in Figure 4.



**Figure 4. Fed-batch Configuration**

The countercurrent configuration employs multiple reactors. The solids are transferred from one reactor to the next while the liquids are transferred between the reactors in opposite order. This movement is best illustrated in Figure 5.



(Loescher, 1996)

### Figure 5. Countercurrent Configuration

This configuration is most representative of what would occur on an industrial scale. However, because of the increased residence time, the system takes several weeks to attain steady state.

#### Residence Time

The residence time is how long either solids or liquids remain in the system. If solids residence time is increased, then digestion will increase. However, in order to

accommodate the increased solid residence time, larger reactor capacity must be available. The increased digestion improves yields and efficiency of the process; however, increased costs are associated with the larger reactor.

Liquid residence time determines the final concentration of acids in the product liquid. By decreasing liquid residence time, the media is circulated through the system at a faster rate, and product acids do not accumulate in the media. The increased rate requires a greater amount of fresh media to be introduced into the system and makes it more difficult to recover the volatile fatty acids from the product liquid because of the low final concentration. Again, a trade-off exists between improved production and costs.

#### pH of the Solution

The pH of the media affects production in two ways. Lower pH's indicate the presence of acids produced from the biomass degradation. With the presence of the acids, the bacteria may be inhibited from further digesting the biomass.

However, a low pH aids production by limiting methanogenesis (Zehnder et al., 1982). In the degradation of biomass, methane is produced by the reduction of VFA's. By preventing this final step, more of the products from the reaction are kept in the VFA form rather than methane and carbon dioxide.

These issues are acknowledged in this study by the use of two additional chemicals. Calcium carbonate,  $\text{CaCO}_3$ , is added to the system to convert the product acids to their respective salt forms. This conversion prevents inhibition. Urea,  $\text{CH}_4\text{N}_2\text{O}$ ,



is added to control the pH of the solution and to provide a nitrogen source for protein synthesis.

### Methanogenesis

As stated earlier, methane is an undesired product from the biological digestion pathway. To control the production of methane, iodoform,  $\text{CHI}_3$ , is added to the system. Because of the similar structure to methane, iodoform is thought to occupy the active sites where methane is produced. By limiting this production, products of the decomposition are kept in a more desirable form.

To make the addition of iodoform easier, a solution of 2% by weight in ethanol is used. The target concentrations of iodoform in solution when added to the reactor is 5 ppm. For batch reactors, the iodoform is added once when the reaction is started. For fed-batch and countercurrent reactors, iodoform is added to each reactor whenever new substrate is added or products are transferred.

### Oxygen Contamination

Because the MixAlco process is based on anaerobic fermentation, oxygen would limit production of VFA's. The contamination of oxygen is limited during handling by using nitrogen gas to purge the reactors during product transfer. Also, once the transfer is complete, a nitrogen blanket is placed in the reactor.

Additionally, the liquid media contains an oxygen scavenger. Cysteine sulfide is added to the media before use to trap any oxygen molecules that may diffuse into the media.

#### Substrate selection/ratio

Feedstock to the MixAlco process is usually a combination of two substrates. One substrate is chosen for its carbohydrate content, and a complement is added as nutrients for the bacteria. Two such combinations are shown in the table below.

**Table 2. Substrate Combinations**

<b>Combination</b>	<b>Cellulose Source</b>	<b>Nutrient Source</b>
#1	Municipal Solid Waste (MSW)	Sewage Sludge (SS)
#2	Cotton Gin Trash (GT)	Chicken Manure (CM)

These substrates can contain an extensive lignin network that limits enzymatic access the carbohydrates. By pretreating the substrate with lime,  $\text{Ca}(\text{OH})_2$ , many beneficial results are obtained (Chang). Most notably, an increase of both available sites and surface area for enzymatic degradation increases acid production.

The ratio of the two substrates in each combination can affect the acid production rate. A ratio between 80:20 to 60:40 for cellulose source to nutrient source is used (Rapier, 1995).

### Temperature

Temperature affects the rate at which bacteria digests the substrate. Several temperature ranges exist. Mesophilic is usually defined as ranging from 35°C to 45°C. Thermophilic temperatures are usually 55°C to 65°C. A higher temperature increases the production rate; however, the higher temperature also increases the rate at which the product acids are reduced to carbon dioxide. The experiments in this study were conducted at a temperature of 55°C.

### *Modeling Using the CPDM Method*

The kinetics of a reaction describe the rate at which the reaction occurs. For the MixAlco process, the kinetics would describe the rate at which acids are produced. The surface area of particles has an effect on reaction kinetics; however, because of digestion, the surface area changes. This method assumes a “continuum particle” which represents real particles of different diameters.

To utilize this method, the acid concentrations are converted to acetic equivalent units. This unit is based on the reducing power of the acids produced by the MixAlco process. From these data, a best-fit curve is found. The data is fit to the equation:

$$[\text{AceticEquivalent}] = a \cdot t^{0.1} + b \cdot t^{0.3}$$

The exponents, 0.1 and 0.3, are chosen arbitrarily to give a good fit to the data.

The equation derived from the curve fit is then differentiated to give the rate of acid production. The rate is then fit using a least squares method with respect to six parameters, a, b, c, d, e, and f, given by the form:

$$\text{SpecificRate} = \frac{a \cdot (1 - x)^d}{1 + b \cdot x^e + c \cdot [\text{AceticEquivalent}]^f}.$$

In the above equation, x represents the percent conversion of the solids. From this specific rate, given certain initial conditions and reactor configuration, the acid production can be predicted.

For a complete description of the CPDM method, see Loescher (1996).

## Experiments

### *Diffusion of Oxygen Through Reactor Walls*

A concern exists that as the reactors age, their structure degrades and allows oxygen to diffuse into the system from the atmosphere. In order to determine the extent of diffusion, if any, of oxygen through the reactors, 100 mL of media was placed in a new reactor. The standard procedure of adding a nitrogen blanket to the reactor was performed. This reactor was placed in experimental conditions (55°C), and the head gas composition was monitored. By analyzing the head gas, no appreciable change in the composition occurred. Even after being exposed to the experimental conditions for three months, the head gas composition remained constant. Thus, degradation of the reactors is not a cause for oxygen contamination.

### *Batch Municipal Solid Waste/Sewage Sludge*

Municipal solid waste and sewage sludge were used as the substrate for a series of batch reactors. These reactors were to be used to later inoculate a countercurrent reaction utilizing these substrates.

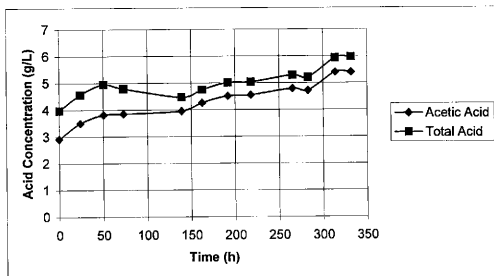
### Municipal Solid Waste / Sewage Sludge, Batch Reactor A

This study used municipal solid waste and sewage sludge as the substrate. Both products were pretreated with lime as suggested by Chang. Solids loading was 75 g/L.

and the volume of the reactor was 0.30 L. The ratio of municipal solid waste to sewage sludge was 80 to 20. Acid production is shown in the table below.

**Table 3. MSW / SS Acid Concentration, Batch Reactor A**

Time (h)	Acetic Acid (g/L)	Total Acid (g/L)
0	2.909	3.966
24	3.498	4.561
51	3.825	4.954
73	3.851	4.789
139	3.957	4.464
163	4.262	4.743
192	4.516	5.014
218	4.553	5.039
266	4.787	5.285
283	4.713	5.203
314	5.396	5.931
332	5.396	5.961



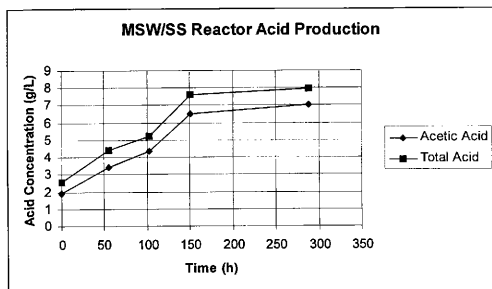
**Figure 6. MSW / SS Acid Concentration, Batch Reactor A**

Municipal Solid Waste / Sewage Sludge, Batch Reactor B

This study had the same initial loading as Reactor A.

**Table 4. MSW / SS Acid Concentration, Batch Reactor B**

Time (h)	Acetic Acid (g/L)	Total Acid (g/L)
0	1.927	2.551
55	3.434	4.428
103	4.328	5.223
151	6.527	7.595
289	7.032	7.927



**Figure 7. MSW / SS Acid Concentration, Batch Reactor B**

***Batch Cotton Gin Trash / Chicken Manure***

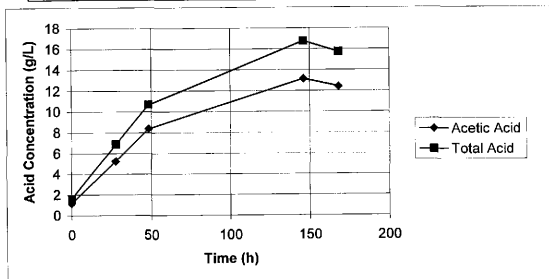
Because the acid production from using municipal solid waste and sewage sludge was much lower than the economic limit, studies were then focused on using cotton gin trash and chicken manure as the substrate.

Cotton Gin Trash / Chicken Manure, Batch Reactor 90 g solids/L

This reactor uses cotton gin trash and chicken manure in a batch reactor configuration. Both substrates were pretreated with lime. To the 0.20 L reactor,  $\text{CaCO}_3$ , 2%  $\text{CHI}_3$  in ethanol, and urea were added at 2 g, 40  $\mu\text{L}$ , and 0.15 g respectively when the reaction was started. The solids loading was 90 g solids/L, and the ratio of gin trash to chicken manure was 60 to 40. The acid concentrations are shown in the table below.

**Table 5. GT / CM Acid Concentration, 90 g solids/L**

Time (h)	Acetic Acid (g/L)	Total Acid (g/L)	Total Acetic Equivalents (g/L)
0	1.175	1.599	1.899
28	5.259	6.891	7.953
48	8.399	10.701	12.133
146	13.161	16.754	18.969
168	12.418	15.718	17.773



**Figure 8. GT / CM Acid Concentration, 90 g solids/L**

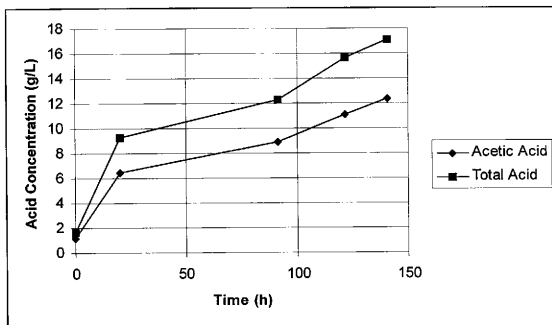


Cotton Gin Trash / Chicken Manure, Batch Reactor 200 g solids/L

This reactor was similar to the reactor with 90 g solids/L initial loading, the difference being that the initial solids loading for this reactor was 200 g solids/L for a reactor volume of 0.20 L. Acid concentrations are shown in the table below.

**Table 6. GT / CM Acid Concentration, 200 g solids/L**

Time (h)	Acetic Acid (g/L)	Total Acid (g/L)	Total Acetic Equivalents (g/L)
0	1.175	1.599	1.899
20	6.497	9.231	10.875
92	8.872	12.274	14.226
122	11.081	15.604	18.223
141	12.385	17.079	19.810



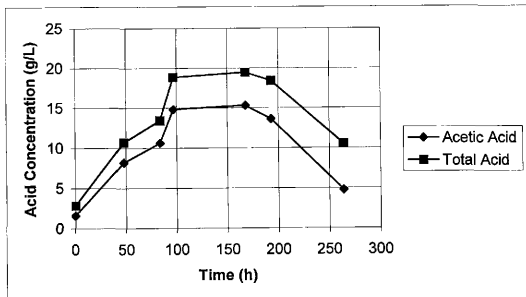
**Figure 9. GT / CM Acid Concentration, 200 g solids/L**

Cotton Gin Trash / Chicken Manure, Batch Reactor 300 g solids/L

This reactor is similar to the previous reactors except for the initial solids loading of 300 g/L for a reactor volume of 0.20 L. The acid concentrations are shown below.

**Table 7. GT / CM Acid Concentration, 300 g solids/L**

Time (h)	Acetic Acid (g/L)	Total Acid (g/L)	Total Acetic Equivalents (g/L)
0	1.615	2.845	3.589
48	8.214	10.707	12.333
84	10.629	13.452	15.272
97	14.822	18.849	21.444
168	15.299	19.451	22.177
193	13.615	18.401	21.455
264	4.784	10.514	14.152



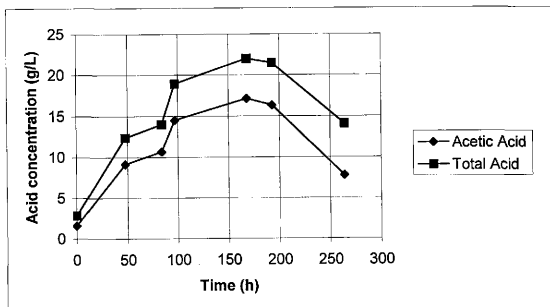
**Figure 10. GT / CM Acid Concentration, 300 g solids/L**

Cotton Gin Trash / Chicken Manure, Batch Reactor 350 g solids/L

This reactor had an initial solids loading of 350 g/L. The acid concentrations are shown below.

**Table 8. GT / CM Acid Concentration, 350 g solids/L**

Time (h)	Acetic Acid (g/L)	Total Acid (g/L)	Total Acetic Equivalents (g/L)
0	1.615	2.845	3.589
48	9.137	12.370	14.479
84	10.674	13.987	16.128
97	14.502	18.917	21.764
168	17.120	21.984	25.057
193	16.335	21.441	24.688
264	7.770	14.082	18.076



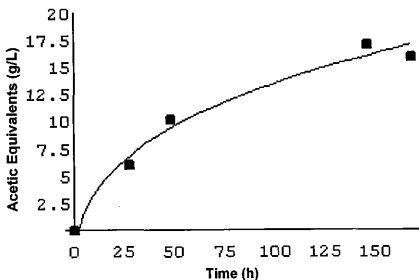
**Figure 11. GT / CM Acid Concentration, 350 g solids/L**

### ***CPDM Modeling using GT / CM Batch Data***

The above data shows a decreasing acid concentration after a seven-day residence time. The degradation of the acid at the higher temperature probably causes this reduction. Even though  $\text{CHI}_3$  was added to deter reduction of the product acids to methane, the initial addition to the reactor is apparently only effective for seven days. Because of this decreasing concentration, two models were created. One discards data after the fifth data point. The second model uses all data collected.

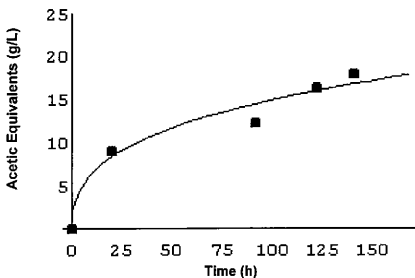
### **CPDM Modeling Using Initial Data Points**

The polynomial fit for the first five data points are each initial solids loading is shown below.



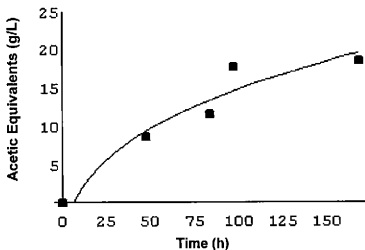
$$[\text{AceticEquivalent}](\text{g/L}) = -7.28428 \cdot t(\text{h})^{0.1} + 6.27428 \cdot t(\text{h})^{0.3}$$

**Figure 12. Polynomial Fit, Batch Reactor 90 g solids/L**



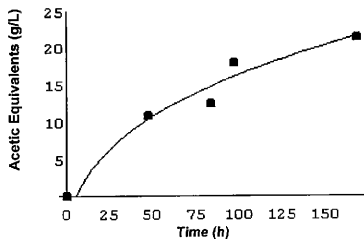
$$[\text{AceticEquivalent}](\text{g/L}) = -226121 \cdot t(\text{h})^{0.1} + 4.63803 \cdot t(\text{h})^{0.3}$$

**Figure 13. Polynomial Fit, Batch Reactor 200 g solids/L**



$$[\text{AceticEquivalent}](\text{g/L}) = -12.5402 \cdot t(\text{h})^{0.1} + 8.71143 \cdot t(\text{h})^{0.3}$$

**Figure 14. Polynomial Fit, Batch Reactor 300 g solids/L**



$$[\text{AceticEquivalent}](\text{g/L}) = -13.3039 \cdot t(\text{h})^{0.1} + 9.41714 \cdot t(\text{h})^{0.3}$$

**Figure 15. Polynomial Fit, Batch Reactor 350 g solids/L**

Based on the above data, the parameters for the specific rate equation are shown in the table below.

**Table 9. Specific Rate Parameters, Initial Data Points**

Parameter	Value
a	0.79 h <sup>-1</sup>
b	1.00
c	10.63 (g/L) <sup>-1.99</sup>
d	-3.36
e	1.05
f	1.99

Based on these parameters, the model predicts the acid concentrations shown in the following figures.

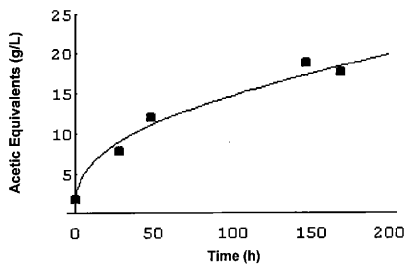


Figure 16. Predicted Acid Concentration, 90 g solids/L

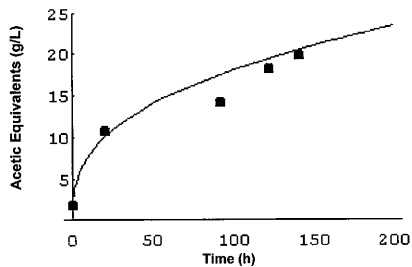


Figure 17. Predicted Acid Concentration, 200 g solids/L

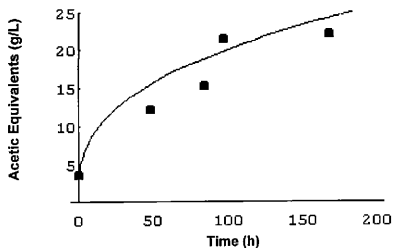


Figure 18. Predicted Acid Concentration, 300 g solids/L

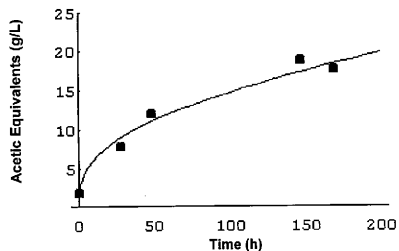


Figure 19. Predicted Acid Concentration, 350 g solids/L

CPDM Modeling Using All Data Points

The results from the modeling using all data point can be found in Appendix C.

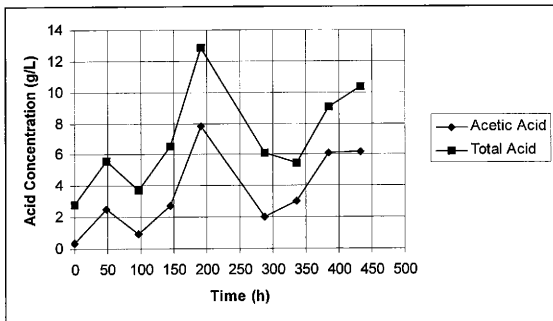


***Countercurrent Cotton Gin Trash/Chicken Manure***

Three reactors were operated in a countercurrent process. The procedure is listed Appendix D. The solids loading for the set of reactors is 288 g/L. This value was determined by drying a sample to determine the water content. Then the fraction of solids was multiplied by the kept weight in each reactor to determine the solids loading. Though the reactors have been operating countercurrently, recently discovered differences in interpretations of the procedure have prevented the system from attaining steady state. The procedure states that the reactors should be centrifuged before the contents are moved countercurrently. Another method of transfer prescribes two successive centrifuge and transfer procedures. This alternate method will result in a different liquid residence time, upon which the model is dependent. The data below show the transient state of the system.

**Table 10. GT / CM Acid Concentration, Countercurrent**

<b>Time (h)</b>	<b>Acetic Acid (g/L)</b>	<b>Total Acid (g/L)</b>	<b>Total Acetic Equivalents (g/L)</b>
0	0.326	2.796	4.066
48	2.486	5.611	7.363
96	0.963	3.709	5.288
144	2.727	6.498	8.737
192	7.828	12.833	15.898
288	1.995	6.112	8.649
336	2.997	5.480	7.016
384	6.103	9.076	10.859
432	6.162	10.312	12.843



**Figure 20. GT / CM Acid Concentration, Countercurrent**

Therefore, data are not available to compare against the modeling done with the batch systems.

## Results and Conclusions

The bacteria cultures produce acids from the gin trash and chicken manure substrate in greater amounts than municipal solid waste and sewage sludge at thermophilic conditions. However, these acids quickly decompose because of the higher temperatures. In order to maximize acid production, liquid residence times should be limited to seven days. With limited liquid residence times, the acids will be removed from the system before degradation begins to offset new acid production. An alternative to shorter residence times would be periodic addition of iodoform to the system. Data indicates that iodoform inhibits the reduction of product acids to methane initially; however, by continuously adding iodoform, the effectiveness may be extended beyond seven days.

Reactor failure was a factor in limited data collected. Due to safety concerns, glass containers are not used. The polypropylene reactor bottles quickly deform when placed under pressure at elevated temperatures. Not only is there gas produced from the reaction, but because of the thermophilic temperatures, the gas law predicts a higher pressure for a given volume. Though experiments show that diffusion is not a concern with these reactors, pressure cannot be allowed to build up. The reactors must be vented daily to minimize pressure. Further studies should be done to determine the effect of creating a vacuum within the container before returning the reactor to the air bath. With less initial gas in the reactor, the pressure should increase at a slower rate.

Also, as expected, a higher initial solids loading leads to higher acid concentrations. The CPDM method when applied to cotton gin trash and chicken manure accurately predicts acid production. More data should be taken in further studies

to better refine the model. Also, the countercurrent system should be allowed to reach steady state in order to verify the model against experimental data.

The model was extended to data for multiple reactors with different numbers of data points. The *Mathematica* input files are listed in the Appendix B and Appendix C. The inputs files for the model utilizing All Data Points include revisions to handle data sets with different numbers of data points.

In conclusion, the data collected by this study indicates that an industrial scale process using cotton gin trash and chicken manure as the substrate for the MixAlco process could be economical.

## Literature Cited

- Chang, V. S., B. Burr, and M. T. Holtzapple, *Lime Pretreatment of Switchgrass*, Manuscript, Chemical Engineering Department, Texas A&M University.
- Cheremisinoff, N. P., P. N. Cheremisinoff, and F. Ellerbusch, *Biomass: Applications, Technology, and Production*, Marcel Dekker, New York (1980).
- France, J. and R. C. Siddons, "Volatile Fatty Acid Production," in *Quantitative Aspects of Ruminant Digestion and Metabolism*, J. M. Forbes and J. France, eds., CAB International, Wallingford, UK (1993).
- Loescher, M. E., "Volatile Fatty Acid Fermentation of Biomass and Kinetic Modeling Using the CPDM Method", PhD Dissertation, Texas A&M University, College Station, TX (1996).
- McCarty, P. L., "One Hundred Years of Anaerobic Treatment," in *Anaerobic Digestion 1981*, D. E. Hughes, D. A. Stafford, B. I. Wheatley, W. Baader, G. Lettinga, E. J. Nyns, W. Verstraete, and R. L. Wentworth, eds., Elsevier Biomedical, Amsterdam (1982).
- Rapier, C. R., "Volatile Fatty Acid Fermentation of Lime-treated Biomass by Rumen Microorganisms", MS thesis, Texas A&M University, College Station, TX (1995).
- Zehnder, A. J. B., K. Ingvorsen, and T. Marti, "Microbiology of Methane Bacteria," in *Anaerobic Digestion 1981*, D. E. Hughes, D. A. Stafford, B. I. Wheatley, W. Baader, G. Lettinga, E. J. Nyns, W. Verstraete, and R. L. Wentworth, eds., Elsevier Biomedical, Amsterdam (1982).

## Appendix

### A. Full Data Sets

All acid concentrations given in (g/L).

#### Municipal Solid Waste / Sewage Sludge, Batch Reactor A

Time (h)	Acetic	Propionic	Butyric	Valeric	Other	Total	AcEq
0	2.909	0.412	0.240	0.145	0.260	3.966	4.722
24	3.498	0.460	0.273	0.183	0.147	4.561	5.270
51	3.825	0.483	0.304	0.186	0.155	4.954	5.707
73	3.851	0.384	0.276	0.154	0.124	4.789	5.417
139	3.957	0.156	0.211	0.103	0.037	4.464	4.813
163	4.262	0.149	0.214	0.102	0.016	4.743	5.067
192	4.516	0.135	0.225	0.115	0.023	5.014	5.359
218	4.553	0.116	0.227	0.117	0.026	5.039	5.384
266	4.787	0.107	0.230	0.133	0.027	5.285	5.644
283	4.713	0.098	0.226	0.126	0.039	5.203	5.563
314	5.396	0.054	0.251	0.155	0.075	5.931	6.359
332	5.396	0.063	0.260	0.167	0.075	5.961	6.410

#### Municipal Solid Waste / Sewage Sludge, Batch Reactor B

Time (h)	Acetic	Propionic	Butyric	Valeric	Other	Total	AcEq
0	1.927	0.242	0.234	0.122	0.025	2.551	2.956
55	3.434	0.360	0.362	0.228	0.043	4.428	5.089
103	4.328	0.314	0.349	0.184	0.048	5.223	5.820
151	6.527	0.381	0.398	0.193	0.096	7.595	8.321
289	7.032	0.251	0.388	0.203	0.052	7.927	8.548

#### Cotton Gin Trash / Chicken Manure, 90 g solids/L

Time (h)	Acetic	Propionic	Butyric	Valeric	Other	Total	AcEq
0	1.175	0.093	0.204	0.113	0.014	1.599	1.899
28	5.259	0.570	0.752	0.257	0.053	6.891	7.953
48	8.399	0.924	1.061	0.272	0.046	10.701	12.133
146	13.161	1.473	1.665	0.388	0.067	16.754	18.969
168	12.418	1.303	1.551	0.379	0.067	15.718	17.773

Cotton Gin Trash / Chicken Manure, 200 g solids/L

Time (h)	Acetic	Propionic	Butyric	Valeric	Other	Total	AcEq
0	1.175	0.093	0.204	0.113	0.014	1.599	1.899
20	6.497	1.304	1.033	0.346	0.052	9.231	10.875
92	8.872	1.855	1.179	0.311	0.058	12.274	14.226
122	11.081	2.385	1.631	0.444	0.063	15.604	18.223
141	12.385	2.453	1.684	0.493	0.064	17.079	19.810

Cotton Gin Trash / Chicken Manure, 300 g solids/L

Time (h)	Acetic	Propionic	Butyric	Valeric	Other	Total	AcEq
0	1.615	0.644	0.373	0.125	0.087	2.845	3.589
48	8.214	0.872	0.502	0.065	0.082	9.734	12.333
84	10.629	0.997	0.586	0.064	0.080	12.356	15.272
97	14.822	1.307	0.901	0.115	0.072	17.217	21.444
168	15.299	1.142	1.014	0.123	0.067	17.645	22.177
193	13.615	1.580	1.077	0.142	0.063	16.478	21.455
264	4.784	1.958	1.262	0.180	0.068	8.251	14.152

Cotton Gin Trash / Chicken Manure, 350 g solids/L

Time (h)	Acetic	Propionic	Butyric	Valeric	Other	Total	AcEq
0	1.615	0.644	0.373	0.125	0.087	2.845	3.589
48	9.137	1.089	1.715	0.176	0.253	12.370	14.479
84	10.674	1.102	1.809	0.220	0.184	13.987	16.128
97	14.502	1.444	2.462	0.284	0.225	18.917	21.764
168	17.120	1.660	2.728	0.348	0.127	21.984	25.057
193	16.335	1.759	2.775	0.374	0.198	21.441	24.688
264	7.770	2.218	3.418	0.441	0.236	14.082	18.076

Cotton Gin Trash / Chicken Manure, Countercurrent

<b>Time (h)</b>	<b>Acetic</b>	<b>Propionic</b>	<b>Butyric</b>	<b>Valeric</b>	<b>Other</b>	<b>Total</b>	<b>AcEq</b>
0	0.326	2.009	0.079	0.269	0.113	2.796	4.066
48	2.486	2.095	0.474	0.394	0.162	5.611	7.363
96	0.963	1.711	0.563	0.279	0.194	3.709	5.288
144	2.727	2.202	0.747	0.571	0.250	6.498	8.737
192	7.828	2.446	1.651	0.616	0.292	12.833	15.898
288	1.995	1.856	1.598	0.487	0.176	6.112	8.649
336	2.997	1.161	0.905	0.252	0.164	5.480	7.016
384	6.103	1.515	1.051	0.220	0.185	9.076	10.859
432	6.162	1.915	1.701	0.307	0.226	10.312	12.843



## B. CPDM Modeling with Initial Data Points

### Specific Rate Parameter Determination

```

so=0.8
datapts=5
aceqtot={1.899,7.953,12.133,18.969,17.773,
1.899,10.875,14.226,18.223,19.810,
3.589,12.333,15.272,21.444,22.177,
3.589,14.479,16.128,21.764,25.057};
nos={ 90,0,90,0,90,0,90,0,
200,200,200,200,200,
300,300,300,300,300,
350,350,350,350,350};
rts={ 0,0,27.8,48.3,146.3,168.3,
0,0,20.3,91.7,122.0,140.7,
0,0,48.0,84.0,97.0,168.0,
0,0,48.0,84.0,97.0,168.0};

aceq=Table[aceqtot[[i]]-aceqtot[[Quotient[i-1,datapts] datapts +1]],{i,1,datapts*4}]

intr1=f->Fit[Table[{rts[[x]],aceq[[x]]},{x,datapts*0+1,datapts*0+datapts}],{x^0.1,x^0.3},x]
pfit1=Plot[fv./intr1,{x,1,rts[[datapts]]}]
plist1=ListPlot[Table[{rts[[x]],aceq[[x]]},{x,datapts*1}],Prolog->{PointSize[0.02],RGBColor[0,0,0]}]
Show[pfit1,plist1,Prolog->{PointSize[0.02],RGBColor[0,0,0]},PlotRange->{0,25}]

intr2=f->Fit[Table[{rts[[x]],aceq[[x]]},{x,datapts*1+1,datapts*1+datapts}],{x^0.1,x^0.3},x]
pfit2=Plot[fv./intr2,{x,1,rts[[datapts]]}]
plist2=ListPlot[Table[{rts[[x]],aceq[[x]]},{x,datapts*1+1,datapts*1+datapts}],Prolog-
->{PointSize[0.02],RGBColor[0,0,0]}]
Show[pfit2,plist2,Prolog->{PointSize[0.02],RGBColor[0,0,0]},PlotRange->{0,25}]

intr3=f->Fit[Table[{rts[[x]],aceq[[x]]},{x,datapts*2+1,datapts*2+datapts}],{x^0.1,x^0.3},x]
pfit3=Plot[fv./intr3,{x,1,rts[[datapts]]}]
plist3=ListPlot[Table[{rts[[x]],aceq[[x]]},{x,datapts*2+1,datapts*2+datapts}],Prolog-
->{PointSize[0.02],RGBColor[0,0,0]}]
Show[pfit3,plist3,Prolog->{PointSize[0.02],RGBColor[0,0,0]},PlotRange->{0,25}]

intr4=f->Fit[Table[{rts[[x]],aceq[[x]]},{x,datapts*3+1,datapts*3+datapts}],{x^0.1,x^0.3},x]
pfit4=Plot[fv./intr4,{x,1,rts[[datapts]]}]
plist4=ListPlot[Table[{rts[[x]],aceq[[x]]},{x,datapts*3+1,datapts*3+datapts}],Prolog-
->{PointSize[0.02],RGBColor[0,0,0]}]
Show[pfit4,plist4,Prolog->{PointSize[0.02],RGBColor[0,0,0]},PlotRange->{0,25}];

cutoff=0
rate=Table[1/nos[[idx]] D[fv./intr1,x]/x->rts[[idx]],{idx,datapts*0+2,datapts*0+datapts-cutoff}];
AppendTo[rate,Table[1/nos[[idx]] D[fv./intr2,x]/x->rts[[idx]],{idx,datapts*1+2,datapts*1+datapts-
cutoff}]];
AppendTo[rate,Table[1/nos[[idx]] D[fv./intr3,x]/x->rts[[idx]],{idx,datapts*2+2,datapts*2+datapts-
cutoff}]];

```

```
AppendTo[rate,Table[1/nos[[idx]] D[ft/.intr4,x]/.x->rts[[idx]],{idx,datapts*3+2,datapts*3+datapts-
cutoff}]];

```

```
rate=Flatten[rate];

```

```
xes=Table[If[(aceq[[idx]]/so/nos[[idx]])>1,0.999,(aceq[[idx]]/so/(nos[[idx]])),{idx,datapts*0+2,datapts*0
+datapts-cutoff}]];
AppendTo[xes,Table[If[(aceq[[idx]]/so/nos[[idx]])>1,0.999,(aceq[[idx]]/so/(nos[[idx]])),{idx,datapts*1+2,
datapts*1+datapts-cutoff}]];
AppendTo[xes,Table[If[(aceq[[idx]]/so/nos[[idx]])>1,0.999,(aceq[[idx]]/so/(nos[[idx]])),{idx,datapts*2+2,
datapts*2+datapts-cutoff}]];
AppendTo[xes,Table[If[(aceq[[idx]]/so/nos[[idx]])>1,0.999,(aceq[[idx]]/so/(nos[[idx]])),{idx,datapts*3+2,
datapts*3+datapts-cutoff}]];
xes=Flatten[xes];

```

```
aces=Table[aceqtot[[idx]],{idx,datapts*0+2,datapts*0+datapts-cutoff}]];
AppendTo[aces,Table[aceqtot[[idx]],{idx,datapts*1+2,datapts*1+datapts-cutoff}]];
AppendTo[aces,Table[aceqtot[[idx]],{idx,datapts*2+2,datapts*2+datapts-cutoff}]];
AppendTo[aces,Table[aceqtot[[idx]],{idx,datapts*3+2,datapts*3+datapts-cutoff}]];
aces=Flatten[aces];

```

```
rmodel[x_,ac_]:=a(1-x)^d/(1+b(x)^e+c ac^f)

```

```
fit=FindMinimum[Sum[(rate[[idx]]-rmodel[xes[[idx]],aces[[idx]]]^2,{idx,1,(datapts-1-
cutoff)*4}],{a,3,0,30},{b,1,-100,100},{c,10,-1000,1000},{e,1.05,0,1000},{f,1.2,0,1000},{d,1.2,-
50,1000},MaxIterations->100000]

```

```
totalerr=Sum[rate[[idx]]^2,{idx,1,(datapts-1-cutoff)*4}]

```

```
pctfit=100-(fit[[1])/totalerr)*100

```

```
rmodel[x,ac]/.fit[[2]]

```

```
Plot3D[rmodel[x,ac]/.fit[[2]],{x,0,95},{ac,0,20},ViewPoint->{2.442,5.268,1.970},PlotRange-
>{0,0.25},PlotPoints->40]

```

### Batch Reactor Simulation

```
so=0.8

```

```
rmodel[x_,ac_]:=a(1-x)^d/(1+b(x)^e+c ac^f)
rmodel[x,ac]

```

```
fit={1.75877 10E-7 , {a -> 0.793308, b -> 1.00032, c -> 10.6326, e -> 1.04829,
f -> 1.99275, d -> -3.36335}}
```

```
datapts=5

```

```
aceqtot={1.899,7.953,12.133,18.969,17.773,
1.899,10.875,14.226,18.223,19.810,
3.589,12.333,15.272,21.444,22.177,
3.589,14.479,16.128,21.764,25.057};
nos={ 90.0,90.0,90.0,90.0,90.0,
200,200,200,200,200,
```

```

300,300,300,300,300,
350,350,350,350,350);
rts={ 0.0,27.8,48.3,146.3,168.3,
0.0,20.3,91.7,122.0,140.7,
0.0,48.0,84.0,97.0,168.0,
0.0,48.0,84.0,97.0,168.0};

run=1;
nos[[(run-1)*datapts+1]]
aceqtot[[(run-1)*datapts+1]]

nos[[(run-1)*datapts+1]] rmodel[(aceqtot[[(run-1)*datapts+1]]-aceqtot[[(run-1)*datapts+1]])/
(so nos[[(run-1)*datapts+1]]), aceqtot[[(run-1)*datapts+1]]]/.fit[2]]

ans=NDSolve[{ acid'[t]==nos[[(run-1)*datapts+1]] rmodel[(acid[t]-aceqtot[[(run-1)*datapts+1]])/
(so nos[[(run-1)*datapts+1]]), acid[t]]/.fit[2]], acid[0]==aceqtot[[(run-1)*datapts+1]],
acid[t],{t,0,200}]

p1=Plot[acid[t]/.ans,{t,0,200},PlotRange->{0,25}]
p1dat=ListPlot[Table[{rts[[(run-1)*datapts+i]],aceqtot[[(run-1)*datapts+i]]},{i,1,datapts}]
Show [p1,p1dat,Prolog->{PointSize[0.02],RGBColor[0,0,0]},PlotRange->{0,25}]

run=2;
nos[[(run-1)*datapts+1]]
aceqtot[[(run-1)*datapts+1]]

nos[[(run-1)*datapts+1]] rmodel[(aceqtot[[(run-1)*datapts+1]]-aceqtot[[(run-1)*datapts+1]])/
(so nos[[(run-1)*datapts+1]]), aceqtot[[(run-1)*datapts+1]]]/.fit[2]]

ans=NDSolve[{ acid'[t]==nos[[(run-1)*datapts+1]] rmodel[(acid[t]-aceqtot[[(run-1)*datapts+1]])/
(so nos[[(run-1)*datapts+1]]), acid[t]]/.fit[2]], acid[0]==aceqtot[[(run-1)*datapts+1]],
acid[t],{t,0,200}]

p2=Plot[acid[t]/.ans,{t,0,200},PlotRange->{0,25}]
p2dat=ListPlot[Table[{rts[[(run-1)*datapts+i]],aceqtot[[(run-1)*datapts+i]]},{i,1,datapts}]
Show [p2,p2dat,Prolog->{PointSize[0.02],RGBColor[0,0,0]},PlotRange->{0,25}]

run=3;
nos[[(run-1)*datapts+1]]
aceqtot[[(run-1)*datapts+1]]

nos[[(run-1)*datapts+1]] rmodel[(aceqtot[[(run-1)*datapts+1]]-aceqtot[[(run-1)*datapts+1]])/
(so nos[[(run-1)*datapts+1]]), aceqtot[[(run-1)*datapts+1]]]/.fit[2]]

ans=NDSolve[{ acid'[t]==nos[[(run-1)*datapts+1]] rmodel[(acid[t]-aceqtot[[(run-1)*datapts+1]])/
(so nos[[(run-1)*datapts+1]]), acid[t]]/.fit[2]], acid[0]==aceqtot[[(run-1)*datapts+1]],
acid[t],{t,0,200}]

p3=Plot[acid[t]/.ans,{t,0,200},PlotRange->{0,25}]

```

```

p3dat=ListPlot[Table[{rts[(run-1)*datapts+i],aceqtot[(run-1)*datapts+i]}, {i,1,datapts}]]
Show [p3,p3dat,Prolog->{PointSize[0.02],RGBColor[0,0,0]},PlotRange->{0,25}]

run=4;
nos[(run-1)*datapts+1]
aceqtot[(run-1)*datapts+1]

nos[(run-1)*datapts+1] rmodel[(aceqtot[(run-1)*datapts+1]-aceqtot[(run-1)*datapts+1]]/
(so nos[(run-1)*datapts+1]), aceqtot[(run-1)*datapts+1]]/.fit[2]]

ans=NDSolve[{ acid[t]==nos[(run-1)*datapts+1] rmodel[(acid[t]-aceqtot[(run-1)*datapts+1]]/
(so nos[(run-1)*datapts+1]), acid[t]/.fit[2]], acid[0]==aceqtot[(run-1)*datapts+1]},
acid[t],{t,0,200}]

p4=Plot[acid[t]/.ans,{t,0,200},PlotRange->{0,25}]
p4dat=ListPlot[Table[{rts[(run-1)*datapts+i],aceqtot[(run-1)*datapts+i]}, {i,1,datapts}]]
Show [p1,p1dat,Prolog->{PointSize[0.02],RGBColor[0,0,0]},PlotRange->{0,25}]

```

## C. CPDM Modeling with All Data Points

### Specific Rate Parameter Determination

```

so=0.8
datapts=7
aceqtot={1.899,7.953,12.133,18.969,17.773,0,0,
1.899,10.875,14.226,18.223,19.810,0,0,
3.589,12.333,15.272,21.444,22.177,21.455,14.152,
3.589,14.479,16.128,21.764,25.057,24.688,18.076};
nos={ 90,90,0,90,0,90,0,90,0,90,0,
200,200,200,200,200,200,200,
300,300,300,300,300,300,300,
350,350,350,350,350,350,350};
rts={ 0,0,27.8,48.3,146.3,168.3,0,0,
0,0,20.3,91.7,122.0,140.7,0,0,
0,0,48.0,84.0,97.0,168.0,193.0,264.0,
0,0,48.0,84.0,97.0,168.0,193.0,264.0};

aceq=Table[aceqtot[[i]]-aceqtot[[Quotient[i-1,datapts] datapts +1]],{i,1,datapts*4}]

intr1=ft->Fit[Table[{rts[[x]],aceq[[x]]},{x,datapts*0+1,datapts*0+datapts-2}],
{x^0.1,x^0.3},x]
pfit1=Plot[ft/.intr1,{x,1,rts[[datapts*0+datapts-2]]}]
plist1=ListPlot[Table[{rts[[x]],aceq[[x]]},{x,datapts*1-2}],{PointSize[0.02],
RGBColor[0,0,0]}]
Show[pfit1,plist1,Prolog->{PointSize[0.02],RGBColor[0,0,0]},PlotRange->{-10,20}]

intr2=ft->Fit[Table[{rts[[x]],aceq[[x]]},{x,datapts*1+1,datapts*1+datapts-2}],
{x^0.1,x^0.3},x]
pfit2=Plot[ft/.intr2,{x,1,rts[[datapts*1+datapts-2]]}]
plist2=ListPlot[Table[{rts[[x]],aceq[[x]]},{x,datapts*1+1,datapts*1+datapts-2}],
Prolog->{PointSize[0.02],RGBColor[0,0,0]}]
Show[pfit2,plist2,Prolog->{PointSize[0.02],RGBColor[0,0,0]},PlotRange->{-10,20}]

intr3=ft->Fit[Table[{rts[[x]],aceq[[x]]},{x,datapts*2+1,datapts*2+datapts}],
{x^0.1,x^0.3},x]
pfit3=Plot[ft/.intr3,{x,1,rts[[datapts*2+datapts]]}]
plist3=ListPlot[Table[{rts[[x]],aceq[[x]]},{x,datapts*2+1,datapts*2+datapts}],
Prolog->{PointSize[0.02],RGBColor[0,0,0]}]
Show[pfit3,plist3,Prolog->{PointSize[0.02],RGBColor[0,0,0]},PlotRange->{-10,20}]

intr4=ft->Fit[Table[{rts[[x]],aceq[[x]]},{x,datapts*3+1,datapts*3+datapts}],
{x^0.1,x^0.3},x]
pfit4=Plot[ft/.intr4,{x,1,rts[[datapts*3+datapts]]}]
plist4=ListPlot[Table[{rts[[x]],aceq[[x]]},{x,datapts*3+1,datapts*3+datapts}],
Prolog->{PointSize[0.02],RGBColor[0,0,0]}]
Show[pfit4,plist4,Prolog->{PointSize[0.02],RGBColor[0,0,0]},PlotRange->{-10,20}]

```

```

cutoff=0
rate=Table[1/nos[[idx]] D[fv.intr1,x]/.x->rts[[idx]],{idx,datapts*0+2,datapts*0+
datapts-cutoff-2}];
AppendTo[rate,Table[1/nos[[idx]] D[fv.intr2,x]/.x->rts[[idx]],{idx,datapts*1+2,
datapts*1+datapts-cutoff-2}];
AppendTo[rate,Table[1/nos[[idx]] D[fv.intr3,x]/.x->rts[[idx]],{idx,datapts*2+2,
datapts*2+datapts-cutoff}];
AppendTo[rate,Table[1/nos[[idx]] D[fv.intr4,x]/.x->rts[[idx]],{idx,datapts*3+2,
datapts*3+datapts-cutoff}];
rate=Flatten[rate];

xes=Table[If[(aceq[[idx]]/so/nos[[idx]])>1,0.999,(aceq[[idx]])/so/(nos[[idx]])],
{idx,datapts*0+2,datapts*0+datapts-cutoff-2}];
AppendTo[xes,Table[If[(aceq[[idx]]/so/nos[[idx]])>1,0.999,(aceq[[idx]])/so/
(nos[[idx]])],{idx,datapts*1+2,datapts*1+datapts-cutoff-2}];
AppendTo[xes,Table[If[(aceq[[idx]]/so/nos[[idx]])>1,0.999,(aceq[[idx]])/so/
(nos[[idx]])],{idx,datapts*2+2,datapts*2+datapts-cutoff}];
AppendTo[xes,Table[If[(aceq[[idx]]/so/nos[[idx]])>1,0.999,(aceq[[idx]])/so/
(nos[[idx]])],{idx,datapts*3+2,datapts*3+datapts-cutoff}];
xes=Flatten[xes];

aces=Table[aceqtot[[idx]],{idx,datapts*0+2,datapts*0+datapts-cutoff-2}];
AppendTo[aces,Table[aceqtot[[idx]],{idx,datapts*1+2,datapts*1+datapts-cutoff-2}];
AppendTo[aces,Table[aceqtot[[idx]],{idx,datapts*2+2,datapts*2+datapts-cutoff}];
AppendTo[aces,Table[aceqtot[[idx]],{idx,datapts*3+2,datapts*3+datapts-cutoff}];
aces=Flatten[aces];

rmodel[x_ac_]:=a(1-x)^d/(1+b(x)^e+c ac^f)

fit=FindMinimum[
Sum[(rate[[idx]]-rmodel[xes[[idx]],aces[[idx]])]^2,
{idx,1,(datapts-1-cutoff)*4-(2)*2}],
{a,3,0,50},{b,5,-100,100},{c,10,-1000,1000},
{e,1.5,0,1000},{f,1.8,0,1000},{d,1,-10,1000},MaxIterations->100000]

totalerr=Sum[rate[[idx]]^2,{idx,1,(datapts-1-cutoff)*4-(2)*2}]

pctfit=100-(fit[[1]]/totalerr)*100

rmodel[x_ac]/.fit[[2]]

Plot3D[rmodel[x_ac]/.fit[[2]],{x,0,.95},{ac,0,20},ViewPoint->{2.442,5.268,1.970},
PlotRange->{0,1},PlotPoints->40]

```

### Batch Reactor Simulation

```

so=0.8
rmodel[x_ac_]:=a(1-x)^d/(1+b(x)^e+c ac^f)
rmodel[x_ac]

fit= {2.05831 10^-7 ,{a-> 4.95245, b-> 4.99923, c-> 9.44343,
e-> 1.50789, f-> 3.10472, d-> -8.64968}}

```

```

fit= {2.56243 10E-7, {a -> 4.1404, b -> 4.99923, c -> 9.97744,
e -> 1.50701, f -> 3.01889, d -> -8.82503}}

datapts=7

aceqtot={1.899,7.953,12.133,18.969,17.773,0,0,
1.899,10.875,14.226,18.223,19.810,0,0,
3.589,12.333,15.272,21.444,22.177,21.455,14.152,
3.589,14.479,16.128,21.764,25.057,24.688,18.076};
nos={
90.0,90.0,90.0,90.0,90.0,90.0,90.0,
200,200,200,200,200,200,200,
300,300,300,300,300,300,300,
350,350,350,350,350,350,350};
rts={
0,0,27.8,48.3,146.3,168.3,0,0,
0,0,20.3,91.7,122.0,140.7,0,0,
0,0,48.0,84.0,97.0,168.0,193.0,264.0,
0,0,48.0,84.0,97.0,168.0,193.0,264.0};

run=1;
nos[[(run-1)*datapts+1]]
aceqtot[[(run-1)*datapts+1]]

nos[[(run-1)*datapts+1]] rmodel[(aceqtot[[(run-1)*datapts+1]]-aceqtot[[(run-1)*
*datapts+1]])/(so nos[[(run-1)*datapts+1]]), aceqtot[[(run-1)*
datapts+1]]]/.fit[[2]]

ans=NDSolve[{ acid[t]==nos[[(run-1)*datapts+1]] rmodel[(acid[t]-aceqtot[[(run-1)*
datapts+1]])/(so nos[[(run-1)*datapts+1]]), acid[t]]/.fit[[2]],
acid[0]==aceqtot[[(run-1)*datapts+1]]], acid[t],{t,0,200}]

p1=Plot[acid[t]/.ans,{t,0,200},PlotRange->{0,25}]
p1dat=ListPlot[Table[{rts[[(run-1)*datapts+i]],aceqtot[[(run-1)*datapts+i]]},
{i,1,datapts-2}]]
Show[p1,p1dat,Prolog->{PointSize[0.02],RGBColor[0,0,0]},PlotRange->{0,25}]

run=2;
nos[[(run-1)*datapts+1]]
aceqtot[[(run-1)*datapts+1]]

nos[[(run-1)*datapts+1]] rmodel[(aceqtot[[(run-1)*datapts+1]]-aceqtot[[(run-1)
*datapts+1]])/(so nos[[(run-1)*datapts+1]]), aceqtot[[(run-1)*
datapts+1]]]/.fit[[2]]

ans=NDSolve[{ acid[t]==nos[[(run-1)*datapts+1]] rmodel[(acid[t]-aceqtot[[(run-1)*
datapts+1]])/(so nos[[(run-1)*datapts+1]]), acid[t]]/.fit[[2]],
acid[0]==aceqtot[[(run-1)*datapts+1]]], acid[t],{t,0,200}]

p2=Plot[acid[t]/.ans,{t,0,200},PlotRange->{0,25}]
p2dat=ListPlot[Table[{rts[[(run-1)*datapts+i]],aceqtot[[(run-1)*datapts+i]]},

```

```

      {i,1,datapts-2}]]
Show[p2,p2dat,Prolog->{PointSize[0.02],RGBColor[0,0,0]},PlotRange->{0,25}]

run=3;
nos[[(run-1)*datapts+1]]
aceqtot[[(run-1)*datapts+1]]

nos[[(run-1)*datapts+1]] rmodel[(aceqtot[[(run-1)*datapts+1]]-aceqtot[[(run-1)*
*datapts+1]])/(so nos[[(run-1)*datapts+1]]), aceqtot[[(run-1)*
datapts+1]]]/.fit[2]]

ans=NDSolve[{ acid'[t]==nos[[(run-1)*datapts+1]] rmodel[(acid[t]-aceqtot[[(run-1)*
datapts+1]])/(so nos[[(run-1)*datapts+1]]), acid[t]]/.fit[2]],
acid[0]==aceqtot[[(run-1)*datapts+1]]}, acid[t],{t,0,300}]

p3=Plot[acid[t]/.ans,{t,0,300},PlotRange->{0,25}]
p3dat=ListPlot[Table[{rts[[(run-1)*datapts+i]],aceqtot[[(run-1)*datapts+i]]},
{i,1,datapts}]]
Show [p3,p3dat,Prolog->{PointSize[0.02],RGBColor[0,0,0]},PlotRange->{0,25}]

run=4;
nos[[(run-1)*datapts+1]]
aceqtot[[(run-1)*datapts+1]]

nos[[(run-1)*datapts+1]] rmodel[(aceqtot[[(run-1)*datapts+1]]-aceqtot[[(run-1)*
*datapts+1]])/(so nos[[(run-1)*datapts+1]]), aceqtot[[(run-1)*
datapts+1]]]/.fit[2]]

ans=NDSolve[{ acid'[t]==nos[[(run-1)*datapts+1]] rmodel[(acid[t]-aceqtot[[(run-1)*
datapts+1]])/(so nos[[(run-1)*datapts+1]]), acid[t]]/.fit[2]],
acid[0]==aceqtot[[(run-1)*datapts+1]]}, acid[t],{t,0,300}]

p4=Plot[acid[t]/.ans,{t,0,300},PlotRange->{0,25}]
p4dat=ListPlot[Table[{rts[[(run-1)*datapts+i]],aceqtot[[(run-1)*datapts+i]]},
{i,1,datapts}]]
Show [p4,p4dat,Prolog->{PointSize[0.02],RGBColor[0,0,0]},PlotRange->{0,25}]

```



#### *D. Apparatus and Procedures*

##### Reactors

The reactors consist of a 1000 mL Nalgene polypropylene carbonate bottle with the central portion of the cap removed. Quarter-inch stainless steel tubing is bent to act as a mixer when the reactor is rotated horizontally. The tubing is placed through #11 stopper near the outer edge. The stopper fits the mouth of the Nalgene bottle, and the cap secures the stopper in the bottle. Also, the stopper is cored in the middle to accept a modified test tube. This test tube which can accept a septum is cut and fire-polished, then flared on the cut side. A press-fit secures the test tube into the stopper. The septum in the test tube allows for gas removal and sampling from the reactor.

##### Rolling Mechanism

The rolling mechanism is contained within a New Brunswick Controlled Environment Incubator Shaker. An Omega CN76000 temperature controller allows for a constant temperature for the contents of the shaker. A 2-in aluminum frame holds pairs of bearings that are connected by ½-in stainless steel tubing. The stainless steel tubing is covered in flexible PVC tubing to provide better friction with the reactor. The stainless steel tubing is driven using a switch-controlled AC generator, pulley, and timing belt. The reactors are rotated by placing them horizontally on the tubing.

*Troubleshooting:*

1. If the stainless steel “handles” on the reactors are too long, then the reactor will tend to tilt over. This symptom can be fixed by placing another reactor with the two handles overlapping in the rolling mechanism. The two handles will balance the weight of the reactors and help prevent further tilting.
2. If the reactors become deformed from excessive pressure, there will not be enough contact area to rotate the reactors. The solution is to transfer the contents into a new bottle.
3. Replacement parts are listed in Appendix E.

Head Gas Measurement

The gas measurement device consists 2-L glass tubes with a tape measure attached. One end of the glass tube is placed in a pool of water. The other end has two outlets. One goes to a vacuum pump. The other end is attached to tubing at the end of which is a three-way syringe and hypodermic needle. The vacuum initially raises the level of the water in the tube. Then the needle is placed through the septum of the reactor, and the three-way needle is moved so that the reactor and glass tube are connected. The change in water level indicates how much gas was contained within the reactor initially.

*Troubleshooting*

1. If the water level is dropping slowly when three-way syringe is initially moved, then the problem is that the needle may be clogged. Move the three-

way syringe to connect the syringe and needle. Try pulling air and/or water through the needle into the syringe to remove any blockage.

2. If the water level will not remain constant when all openings are sealed, the system is leaking. There are several places where leaks can occur. The glass stopcock that controls the vacuum line may need additional vacuum grease. Remove the stopcock and regrease. Also, the three-way syringe may leak if particles are trapped between the rotating mechanism and housing. Try washing the syringe with water, and if that fails, replace the syringe.

#### Countercurrent Procedures

The three reactors (labeled as shown in Figure 5) are removed from the shaker and allowed to reach ambient temperatures. Then, gas measurement values are taken for each reactor. To prevent oxygen contamination, for all steps where the reactor is open, a nitrogen purge is placed inside of the reactor.

The stopper and associated apparatus are removed, and a complete cap is placed on each reactor. The reactors are then centrifuged for 10 minutes at 3500 rpm.

The liquid is then quantitatively removed from Reactor 1, and a liquid sample is drawn for product characterization. The reactor with solids is then weighed. Solids are quantitatively removed until the weight is 170 g. The following is then added: 8 g of chicken manure, 12 g of gin trash, 2 g of  $\text{CaCO}_3$ , 0.15 g of urea, and 40  $\mu\text{L}$  of  $\text{CHI}_3$ . The contents are mixed by hand, and the liquid from Reactor 2 is poured into Reactor 1. The stopper is then replaced, and the reactor capped.

Reactor 2 is then weighed. Again solids are removed until the target weight is reached. The target weight is 170 grams minus the mass of solids removed from reactor 1. Once the target mass has been reached, the solids removed from Reactor 1 are placed in Reactor 2. Similar amounts of  $\text{CaCO}_3$ , urea, and  $\text{CHI}_3$  are added to Reactor 2. The liquid from Reactor 3 is then poured into Reactor 2. The contents are mixed by hand, and the reactor is sealed.

Reactor 3 undergoes a similar procedure as Reactor 2; however, the solids removed from Reactor 3 are the product solids. These solids are collected and stored for characterization. Also, because there is not another reactor from which to pour liquid into reactor 3, 150 mL of fresh media is placed into Reactor 3.

#### Liquid Product Characterization

The product composition is determined with a Hewlett Packard 5890 Gas Chromatograph. Also attached is a Hewlett Packard 7673A Controller/Automatic Sampler to autoinject multiple samples. A Hewlett Packard 3396 Series II Integrator collects the output from the Gas Chromatograph for further analysis.

The complete procedure is listed in Appendix D of Loeschner (1996).

#### *Troubleshooting:*

1. If the GC gives the error message for "Loop Down," this message indicates that the communications loop between the different components of the GC setup is in error. One solution is to manually break the communication connection by unplugging the small black wire from one of the components.

Then upon reconnection of the communications wire, the components will automatically attempt to reconnect.

*E. Equipment Parts*

<b>Apparatus</b>		
<b>Description</b>	<b>Supplier</b>	<b>Part Number</b>
<b>Reactor</b>		
Bottle, 1000 mL	Nalgene	1000 mL PPCO
1/4" Stainless Steel Tubing	RP Supply	
<b>Rolling Mechanism</b>		
Fan Motor	Grainger	4M632
Bearings	McMaster-Carr	7930K13
AC Generators	McMaster-Carr	6142K53
Reducer Bushing	McMaster-Carr	6420K13
Set-screw coupling	McMaster-Carr	6412K14
1/2" Stainless steel tubing	RP Supply	
Pully	Motion Industries	16L050 X 1/2
Timing Belt	Motion Industries	124L050

***F. Supplier Information***

<b>Supplier</b>	<b>Address</b>	<b>Phone Number</b>
Bryan Livestock Commission Company	6095 E State Highway 21 Bryan, TX 77808-8641	(409) 778-0904
Grainger	7777 Parnell Houston, TX 77021	(713) 748-8280
McMaster-Carr Supply Company	P.O. Box 740100 Atlanta, GA 30374-0100	(404) 346-7000
Motion Industries, Inc.	1206 W. Wm. J. Bryan Parkway Bryan, TX 77803	(409) 779-8485
R. P. Supply	P. O. Box 19 Highway 21 East Kurten, TX 77862	(409) 589-3113
Southwood Valley Turf	3312 Texas Ave S College Station, TX 77845-0583	(409) 696-6443