
PRODUCTION OF JET FUEL USING BIOCHEMCAT

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LIST OF ACRONYMS

AA	Acetic acid
BSEL	Bioproducts Sciences and Engineering Laboratory
GGE	Gallons Gasoline Equivalents
LBM	Lignocellulosic Biomass
NARA	Northwest Advanced Renewables Alliance
TS	Total Solids
VFA	Volatile Fatty Acids
WSU	Washington State University
WEx	Wet Explosion

EXECUTIVE SUMMARY

WSU-BSEL has worked in parallel with Gevo to investigate the production of jet fuels from the woody biomass using a proprietary BioChemCat process. The BioChemCat process is a new way to produce more biofuels from the biomass at a significantly lower cost. The overall objective of the BioChemCat project was to demonstrate the conversion of pretreated LBM using an innovative mixed culture fermentation technology capable of producing a wide range of VFAs from all sugars present in LBM. The VFAs were separated and converted to hydrocarbon biofuel through catalytic upgrading. By continuously removing VFAs as they are produced (extractive fermentation), we were able to recover the VFAs while both eliminating the need for pH adjustment and increasing the fermentation productivity. The recovered VFAs were then esterified and upgraded to hydrocarbon fuels through a parallel series of hydrogenolysis/decarboxylation and dehydration reactions.

LBM consists of cellulose enclosed within sheets of hemicellulose and lignin bound to each other through carbon-carbon linkages. These linkages are usually harder to break contributing to the recalcitrance of the biomass and hence, various thermochemical and biochemical methods have been developed to break these linkages and allow easy access of the cellulose fraction for enzymatic action. When compared to existing pretreatment methods, WEx, which is a combination of wet oxidation using oxygen addition to cause selective oxidative damage to the biomass combined with steam explosion, has shown greater ability to open and solubilize LBM. This pretreatment process has been demonstrated in pilot scale (1 ton TS/hr) in the pilot plant facility operated by the PI (Birgitte Ahring).

In the BioChemCat process, this pretreated LBM was anaerobically fermented using mixed microbial consortia obtained from the cow rumen. The temperature and pH of the fermentation was controlled to optimize VFA production. It was found that C-2 (acetic) and C-3 (propionic/lactic) acids were predominantly produced from

the anaerobic fermentation of the biomass hydrolysate with CO₂ and traces of H₂ produced in the headspace. These VFAs were then preferentially extracted from the fermentation broth using two different “green” separation techniques – supercritical carbon dioxide extraction and ion-exchange resins. Traditional techniques for VFA extraction from the fermentation broth involve the use of strong mineral acids which result in salts left behind as low-value waste. The current techniques produced minimal waste and showed high extraction efficiencies after optimization.

The extracted VFAs were then esterified using ethanol in an acidic environment to produce VFA esters, which were taken into the vapor phase during reactive distillation. These VFA esters were then allowed to flow through a packed catalyst bed to convert VFA ethyl ester to alcohols (C-2 to ethanol and C-3 to propanol/iso-propanol). These alcohols were then converted to jet fuels using slight modifications to the existing ATJ process. The catalysis work was done in conjunction with PNNL combinatorial catalyst laboratory.

We demonstrated a yield of 54% of VFAs as acetic acid equivalents (0.54 g/g LBM) from LBM (10% solids) corresponding to approximately 80 gge/dry ton-LBM. In comparison, producing the same hydrocarbon fuel from cellulosic ethanol would result in only 47 gge. We were also able to demonstrate, using techno-economic analysis, that we can produce drop-in biofuels for an estimated selling price of \$3.50 - \$4.00 per gge or lower with an estimated feedstock (LBM) cost of \$60 per dry ton. Based on the reaction mechanisms, a VFA yield of 54% can theoretically be obtained from conversion of dry LBM. Based on this project, we found that it was possible to further improve VFA yields and the techno-economic analysis indicated that the single greatest impact on process economics (other than feedstock costs) was the catalytic upgrading of VFAs.

INTRODUCTION

The production of transportation fuels from renewable resources is part of a significant effort by the U.S. Department of Energy to reduce dependence on foreign supplies of petroleum and to reduce greenhouse gas emissions. The production of ethanol from corn has developed to supply a significant fraction of the domestic transportation fuel use; however, concerns over the use of food grains to produce fuel and limitations of ethanol as a fuel have led to development of technologies to utilize non-food biomass resources as feedstock and also to produce fuel higher grade fuel products that can serve as drop-in replacement for existing petroleum-based hydrocarbon fuels. While many alternative pathways are also being investigated to convert biomass to both alcohols and hydrocarbon fuels, BioChemCat process is based upon anaerobic fermentation of pretreated biomass to VFAs followed by upgrading of the VFAs to hydrocarbon fuels. The primary steps in the BioChemCat process are shown in Figure BCC-intro.1.

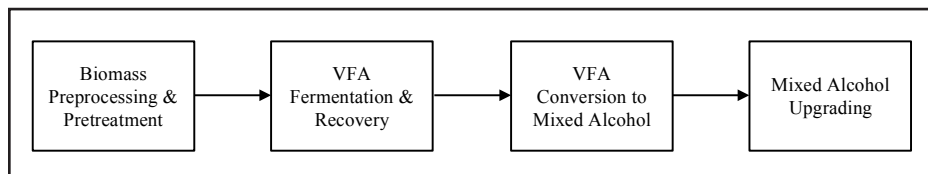


Figure BCC-intro.1. Process steps in the BioChemCat process.

In this process, the LBM obtained from the NARA feedstock group is pretreated with wet explosion pretreatment at conditions optimized for the different feedstocks for maximum biomass depolymerization followed by anaerobic fermentation using a microbial culture to produce VFAs. LBM contain recalcitrant fractions such as crystalline cellulose and lignin, which are only converted to a minor degree under anaerobic conditions. While traditional fermentations to ethanol and butanol require maximum conversion of cellulose and hemicellulose to the counterpart C5 and C6 sugar monomers, the VFA fermentation can work well with sugar oligomers, which remove the necessity for enzymatic hydrolysis. The enzymes usually contribute to approximately 10% of the biorefinery operating costs and the removal of the hydrolysis step can result in significant cost savings in the process.

Although the concept of producing biofuels using VFAs as the platform molecules is not new, the BioChemCat approach represents a major new development. Several major advantages to the new AcidoFuels VFA platform, include: 1) an efficient, effective WEx treatment that improves biomass availability for fermentation; 2) an approach that can utilize virtually any type of biomass, 3) it uses a robust mixed microbial culture for fermenting the biomass into VFAs which does not require sterility and produces high yields with high productivity, and 4) a more efficient separation process that allows for continuous recovery of VFAs, among other benefits. This will help ensure that the BioChemCat process avoid the limitations of other similar approaches.

The optimization of the four primary steps of the BioChemCat process shown in Figure BCC-intro.1 to get maximum jet fuel yield at low process costs is the primary goal of this project. These steps are based upon existing technologies, some technologies with improvements to enhance the yields and other technologies integrated in a new manner, with the goal of improving the economics of biomass conversion to hydrocarbon fuels. The techno-economic evaluation was conducted, using both experimental data from this program and process data from literature to provide insights into the benefits and risks of the BioChemCat process. A baseline reaction scheme based on the current state-of-art that also incorporates the fundamental aspects of the BioChemCat process for jet fuel synthesis from biomass is shown in Figure BCC-intro.2.

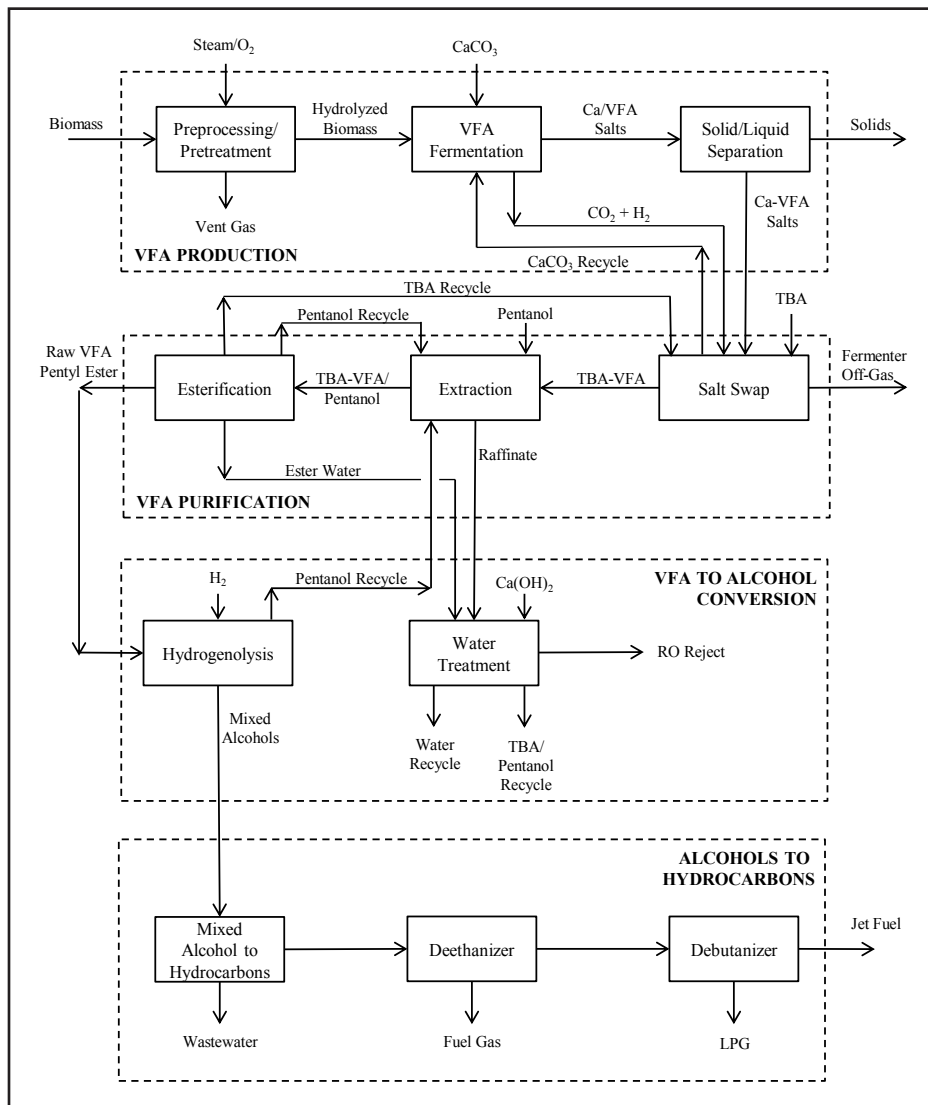


Figure BCC-intro.2. Block diagram for hydrocarbon fuel synthesis from VFA fermentation

In the VFA production step, biomass is prepared for thermal hydrolysis by size reductions along with cleaning to remove rocks, stones, metals, and other contaminants. The pretreated biomass is thermally hydrolyzed in the wet oxidation/steam explosion reactor, then diluted with water and fed into the non-sterile, mixed-culture fermentation reactor along with nutrients and calcium carbonate for pH control. VFAs produced in the fermenter are separated from the fermentation solids as soluble calcium salts and pass with the clarified broth into the purification step.

Purification of the VFAs can be traditionally accomplished by a salt-swapping process. In this process, the clarified broth will be contacted with the complexing agent tributylamine (TBA) and carbon dioxide in the vent gas from the fermenter, resulting in the formation of an acid-amine complex and a solid precipitate of calcium carbonate. The TBA-VFA complex will then be extracted from the aqueous phase into n-pentanol and passes on the VFA to alcohol conversion step. Other separation methods were also studied such as supercritical carbon dioxide extraction and ion exchange resins. The primary goal of the optimized separation technology is the economic and efficient separation of the VFAs from the fermentation broth for further catalytic upgrading with minimal waste production.

In the first step of the alcohol conversion, a reactive distillation will be used to esterify the VFAs with the alcohol. During this step, the acid-amine/resin complex will be split with the amines/ion exchange resin recycled to the previous step. The ester product will then be hydrogenated to yield mixed alcohols from the VFAs and pentanol or the alcohol used for the esterification will be recycled. Distillation will be used to separate the mixed alcohol product from the recycle stream, and the mixed alcohol stream continues on to produce the hydrocarbons.

In the alcohol to hydrocarbon step, the mixed alcohols are catalytically converted to hydrocarbon fuel using catalytic dehydration and oligomerization (using Zeolite ZSM-5 catalyst). The primary product is jet-fuel range hydrocarbons along with some LPG and fuel gas, which are used in the process to generate steam.

The overall objective of the project was to demonstrate the technical feasibility of the BioChemCat project to produce jet fuels at low prices through optimization of the different steps shown in Figure BCC-intro.2. The tasks assigned to fulfill these project objectives are: 1) Co-culture optimization for high production yield and productivity of VFAs from pretreated biomass hydrolysate; and 2) Catalysis of platform molecules into jet fuel. The first task will be separated into two different parts focusing on optimization of the anaerobic fermentation of the pretreated biomass and the separation of VFAs from the fermentation broth for further catalytic upgrading.

TASK 1: CO-CULTURE OPTIMIZATION OF HIGH PRODUCTION YIELD AND PRODUCTIVITY OF VFAS FROM PRETREATED BIOMASS HYDROLYSATE

Task Objective

Traditionally, monocultures have been used in biorefineries to selectively produce platform molecules (such as acetic acid using *Moorella thermoacetica*) from pretreated biomass hydrolysate. However, these monocultures require high sterility conditions and the accompanying high capital and operating costs to maintain such conditions throughout the fermentation played a significant role in the overall process economics. However, in the BioChemCat project, we have used a robust mixed microbial culture that can work under low sterile conditions and produce a mixture of VFAs at high yields and productivities comparable with that using the bacterial monocultures. The primary task objective of the task is to optimize the fermentation conditions such as pH and temperature to facilitate maximum VFA yields from the pretreated biomass hydrolysate. This task is split into two parts: 1) optimization of the anaerobic fermentation to maximize VFA yield; and 2) separation of the VFAs from the fermentation broth using “green” and clean technologies.

Methodology

Fermentations in fed-batch mode has been run on both FS-01, FS-03 and FS-10, which were pretreated using the WEx method and then further fermented (10% TS) using 2% corn steep liquor as the only supplement. The WEx pretreatment of the woody biomass was made less severe to effectively obtain greater amount of sugar oligomers which was found to be an effective feed for the microbial culture. The anaerobic fermentation was done in a 5 L lab reactor at temperatures of 37 °C and 50 °C with pH varying between 5.5 and 6.5.

Apart from the separation process discussed in the block diagram shown in Figure BCC-intro.2, two other “green” separation technologies were tested for the extraction of VFAs from the fermentation broth.

Supercritical Fluid Extraction

A process schematic of the high-pressure carbon dioxide extraction equipment used for testing is shown in Figure BCC-1.1. The pH of the fermentation broth was adjusted to 2.5-3.0 using one molar sulfuric acid in order to precipitate proteins and acidify carboxylic acid-salts. This acidified rumen liquid was then centrifuged at 7000 rpm for 10 minutes.

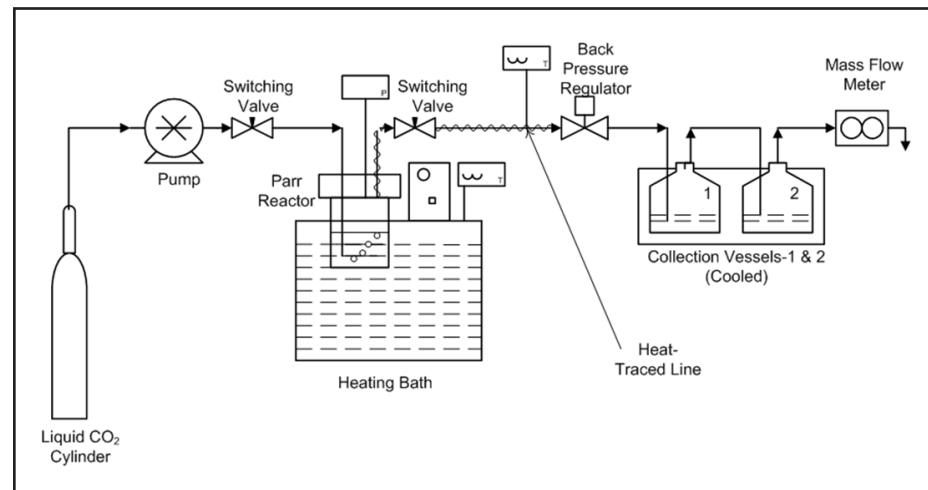


Figure BCC-1.1. Process schematic for the pressurized CO₂ extraction of acetic acid from aqueous solution or fermentation broth

Fifteen mL of pure acetic acid solution (or VFA fermentation broth) was added to a 50 mL Parr vessel, which was subsequently sealed, and placed in a temperature-controlled water bath. With all the inlet and outlet valves on the vessel closed, liquid carbon dioxide was allowed to flow through an SFT-10 supercritical pump and was pressurized to a desired set point (10.3-17.2 MPa); a Peltier-type cooling system (-10°C) was used to ensure carbon dioxide was maintained in its liquid form for efficient pumping purposes.

Afterward, the inlet valve to the Parr vessel was opened and liquid carbon dioxide was allowed to fill the vessel until desired pressure was reached. After the desired pressure was reached in the reactor, the outlet valve was opened to allow carbon dioxide-acetic acid mixture to flow through a back-pressure regulator and into the collection vessels. The outlet flow rate and the reactor pressure were maintained throughout the experiment by controlling the backpressure regulator, while constant pressure was maintained by the pump itself. The backpressure regulator was used to control the flow of carbon dioxide through the system at the set temperature and pressure, which was measured using this mass flow meter.

The line at the outlet of the extraction vessel and the back-pressure regulator were heat traced and were maintained at 65-70°C for all experiments. The actual temperatures inside the Parr vessel (maximum temperature = 350 °C) and on the backpressure regulator were measured throughout the experiment (± 0.5 °C) and controlled using in-house constructed temperature control devices composed of

Automation Direct Solo4848 controllers and J-type thermocouples. The extraction temperature was varied between 25 and 50 °C while the extraction time was varied between 1 and 5 hours.

After flowing through the back-pressure regulator, and expansion to near-atmospheric pressure, depressurized carbon dioxide was bubbled through two collection flasks (250 mL bottles) connected in series which contained 40 mL of 50/50 (v/v) ethanol/water maintained at 4-5°C in an ice bath. The collection flasks were used to “scrub” extracted acetic acid from the depressurized carbon dioxide solvent. The “scrubbed” carbon dioxide was then allowed to flow through a mass flow meter.

After extraction was complete, the solution remaining in the vessel and those in the collection flasks were recovered by washing with known volume of water (in order to ensure complete dissolution of any excess acid) and the final volume of the recovered solution was measured. Concentration of acetic acid in the solution left after extraction was measured using both HPLC and gas chromatography (GC) while the recovered solutions were only measured using GC due to high ethanol content and its interference with the HPLC procedure as discussed in the next section.

Ion Exchange Resin

In this separation platform, the VFAs were removed using Amberlite IRA-67 from the fermentation broth as soon as it was produced with the primary objective of increasing VFA yields and microbial productivity. Preliminary column experiments were done using model C3-acid solution passing through a fixed bed of Amberlite IRA-67 (18 cm length x 1 cm i.d.) at different flow rates. It should be noted that Amberlite IRA-67 has a microporous gel structure with ammonium free base cat ion that binds with the lactate ion from the solution to facilitate extraction. Figure BCC-1.2 shows a schematic of the process equipment used for extractive fermentation processes.

The fermentation system was set using the microbial culture inoculated into the pretreated biomass hydrolysate followed by degassing of the headspace with N₂/CO₂ mixture to simulate anaerobic conditions. Initial batch experiments were done by connecting caustic soda as a base to control the pH of the anaerobic fermentation. The pH of the fermentation is initially controlled using 5N NaOH solution until the concentration of C-3 acid-salt in the fermenter is around 20 g/L (which is yet to be optimized). The pH control and C-3 acid separation is then changed to resin flask usually after the first feeding between 24 and 36 hours.

Extractive fermentation was done by replacing the base addition line connected to the fermenter with a dual-pump system intermittently running at 21.6 ± 0.4 mL/min between the fermenter and an insulated 250 mL working volume stirred flask. The resin flask initially containing 100 mL of water and was loaded with 120.0 ± 0.3 g of IRA-67 resin and set atop a hot plate operating at $45 \pm 3^\circ\text{C}$ stirred at 90 ± 10 rpm. Incoming broth was discharged at mid bed height and removed by suctioning from

a small volume liquid head above a mesh net at the top of the resin bed where the resin had settled. It should be noted that the recirculation pumps were operated through a decrease in the pH of the fermenter allowing the broth to flow through the ion exchange resin bed to eventually regulate the pH inside the fermenter to set point through adsorption of the C-3 acid onto the ion exchange resin. The fermenter was fed continuously until the recirculation pumps were running continuously due to the inability of the ion exchange resin to regulate pH of the fermenter due to saturation with C-3 acid.

After extractive fermentation, the VFA-saturated resin was washed and regenerated by the following scheme to determine total lactic acid productivity of system:

- 1) Resin was removed from flask, filtered to remove remaining interstitial broth, washed with water and filtered again. Vacuum filtration was performed using a Buchner funnel over a wetted piece of filter paper.
- 2) Filtered resin was transferred to a beaker by removing the bulk of the resin from the funnel and washing the residual resin out with water.
- 3) 100 mL (0.58 BV) of 2.5 N NaOH was added to the water-resin mixture and allowed to sit overnight at room temperature. This process was repeated twice, where the effluent VFA concentration in the resultant liquor was found to be less than or equal to 3 g/L.

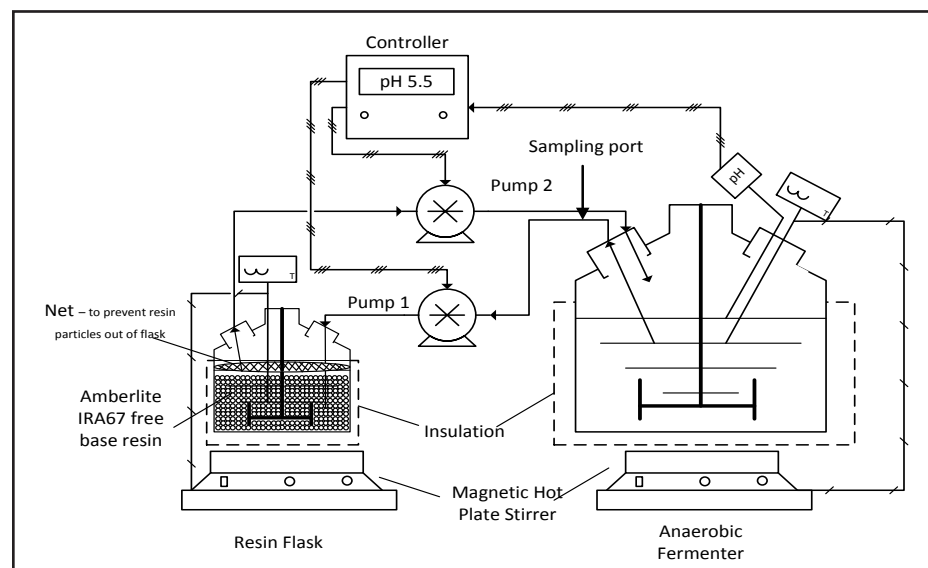


Figure BCC-1.2. Process schematic of the system used for batch cultivation of a lactic acid producing culture including extractive fermentation of lactic acid

Results and Discussion

Two different temperature conditions were primarily tested for the anaerobic fermentation of pretreated biomass hydrolysate to produce VFAs: 1) 37 °C (or mesophilic); and 2) 50 °C (or thermophilic). The results at these varied conditions indicated that the microbial culture can be effectively tuned to selectively produce different VFAs by controlling temperature and pH conditions.

Under thermophilic conditions, our maximum yield was found to be around 0.52 g/g sugar equivalents in the pretreated biomass (Figure BCC-1.3a) with an average yield of around 45 g VFA (acetic acid equivalents) per 100g of biomass or 28g VFA per 100g of woody materials. As can be seen in Figure BCC-1.3b, it was found that at these conditions, predominantly C-3 acids composed of propionic, isopropionic and lactic acids were preferably produced by the bacterial culture from pretreated biomass hydrolysate.

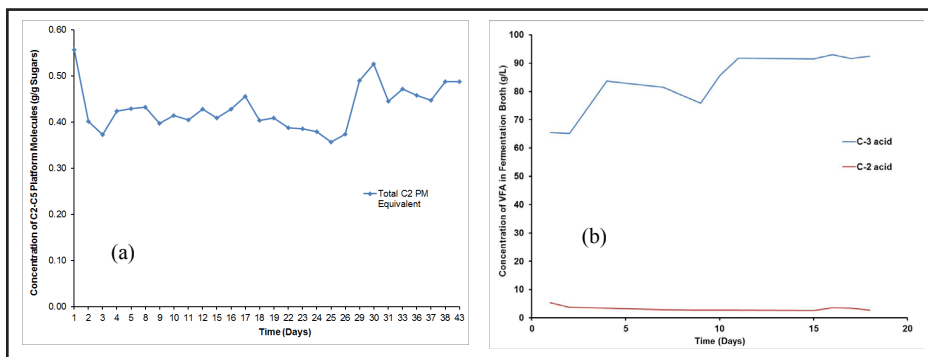


Figure BCC-1.3. Anaerobic fermentation of WEx biomass hydrolysate at thermophilic conditions (50 °C, pH 5.5): (a) Total VFA produced; (b) individual concentration of organic acids produced

Under mesophilic conditions, our maximum yield was found to increase to 72g of VFA as acetic acid equivalents per 100 g of sugar equivalents in the pretreated biomass. On an average, we obtained around 54g of VFA (acetic acid equivalents) per 100g of biomass sugar or 33g VFA per 100g of woody materials. The main VFAs obtained in the fermentation were C-2-4 and C-7 acids. It was found that greater amount of C-7 acid was produced by pretreated biomass when compared with similar fermentation done using non-pretreated biomass as feed. It can be seen from Figure BCC-1.4 that under optimized conditions, the anaerobic fermentation was capable of producing more than 0.5 wt% of VFA per gram of biomass sugars or 0.35 wt% VFA per gram of biomass.

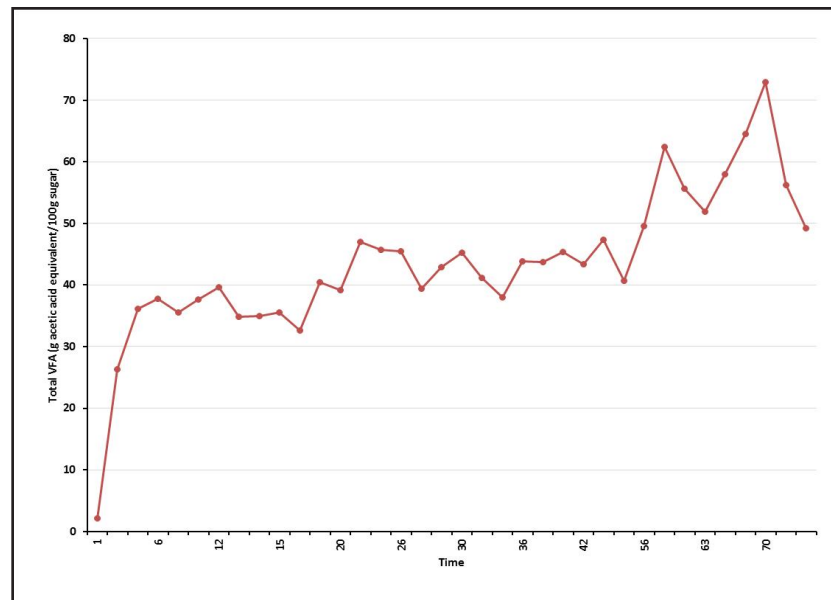


Figure BCC-1.4. Total VFA as acetic acid equivalents as a function of time (days) obtained in a continuous mesophilic anaerobic fermentation of WEx biomass using a mixed bacterial culture

Based on these results, further experiments were done with wet-exploded biomass at different solids loading using the mixed microbial consortia and it was found that the VFA titer increased from 22.8g/L at 2.5% total solids to as high as 40.8g/L at 5% total solids at mesophilic conditions. In these studies, the wet exploded biomass was supplemented with 2wt% corn steep liquor as a nutrient source and preliminary results indicated that there was no significant effect of the carbon content in corn steep liquor on the VFA yields. The study indicated that while acetic acid was predominantly produced during these fermentations, there was significantly lesser amount of acetic acid produced at 5% total solids loading when compared to that at 2.5% total solids loading (Figure BCC-1.5). It was hypothesized that the difference in mass balance between the anaerobic fermentations at the different solids loading could be due to an increased methanogenic activity at 5% total solids, which led to conversion of the excess acetic acid further to methane. The mass balance also indicated that the lignin-carbohydrate ratio in the wet-exploded biomass increased from 0.88 to 2.68 at 5% total solids while it increased from 0.82 to only 1.75 at 2.5% total solids indicating significant carbohydrate consumption at the lower solids loading. This was directly translated to around 5.09g VFA (C-2 to C-4 acids) produced per g of carbohydrate in the wet exploded biomass at 2.5% total solids while there was only 3.17g VFA produced per g carbohydrate at 5% total solids. Hence, even though higher VFA titer was obtained at 5% total solids, the study indicated that a higher amount of VFA was produced per g of the biomass sugars (after wet explosion pretreatment) at the lower (2.5%) total solids loading.

The VFAs produced in these processes have been separated from the fermentation broth using different separation methodologies discussed previously.

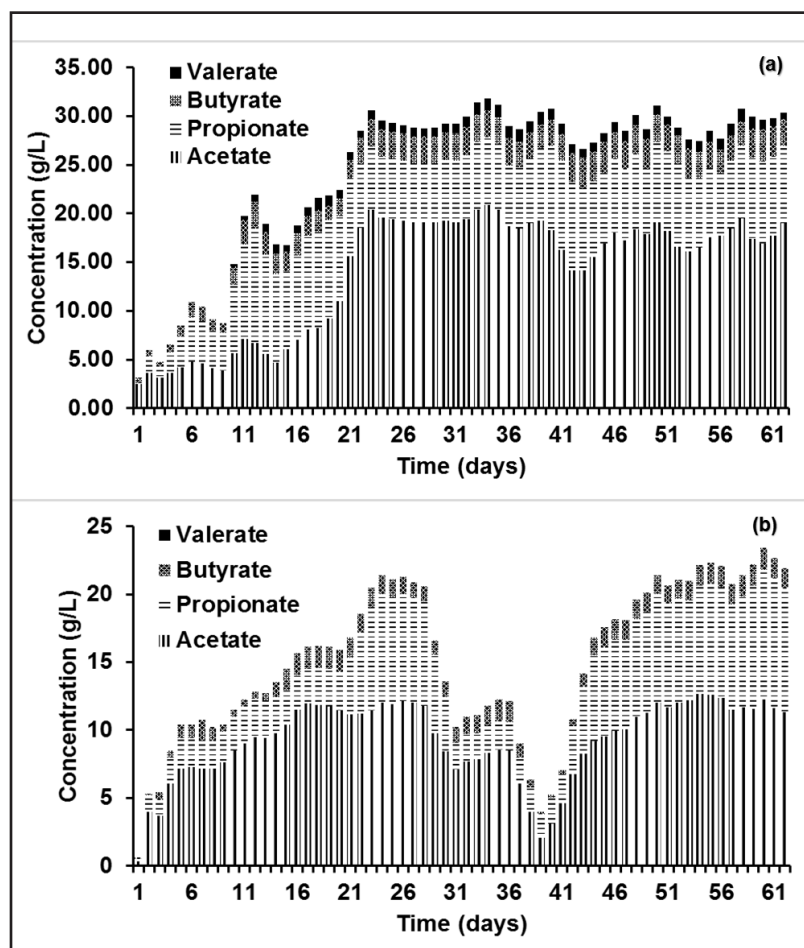


Figure BCC-1.5. Concentrations of individual VFAs (g/L) produced from rumen fermentation of wet exploded biomass at (a) 2.5% TS; and (b) 5% TS. The decrease in VFA's between day 26 and 40 was due to problems with the feed pump.

Supercritical Fluid Extraction

Initial experiments were done using different concentrations of acetic acid dissolved in water as feedstock to study and predict the extraction efficiency of pressurized CO_2 . The solvency behavior of pressurized CO_2 towards acetic acid solution was studied in the form of two variables: (a) % AA extracted referring to the total amount of acetic acid extracted from the solution; and (b) solvent utilization efficiency which is the mass of acetic acid extracted per gram of CO_2 through the system. Regression studies were done using temperature (25-50 °C), AA concentra-

tion (4.65-92.4 g/L), solvent flow rate (0.68-2.06 g CO_2 /min), residence or extraction time (1-5 hours) and pressure (1500-2500 psi).

The regression studies indicated that an optimal extraction efficiency of 92.5% can be achieved at the highest initial concentration (92.4 g/L), highest solvent flow rate (2.03 g/min), and highest extraction time (5 hrs) used, with pressure and temperature being 45°C and 2150 psi (14.5 MPa). The maximum predicted value of solvent utilization efficiency by the regression model was 6.97 mg acid/ g carbon dioxide at 0.73 g CO_2 /min solvent flow, 45°C, 2500 psi (17.2 MPa), initial acid concentration of 92.4 g/L and an extraction time of 1 hour, where equilibrium mass driving force gradient was the greatest.

The results from the statistical model were confirmed through dynamic flow experiments done as a function of extraction time between 1 and 6 hours at 35°C temperature, 1500 psi (10.3 MPa), 2.03 g CO_2 /min solvent flow rate and 85.8 g/L initial acetic acid concentration. The percentage acetic acid extracted and solvent utilization efficiency are shown in Figure BCC-1.6. It can be seen that there is an acceptable correlation between the observed and the predicted results for the tested experimental conditions, however some inconsistencies are present, most likely due to the more complex behavior than the quadratic polynomial used by the statistical model.

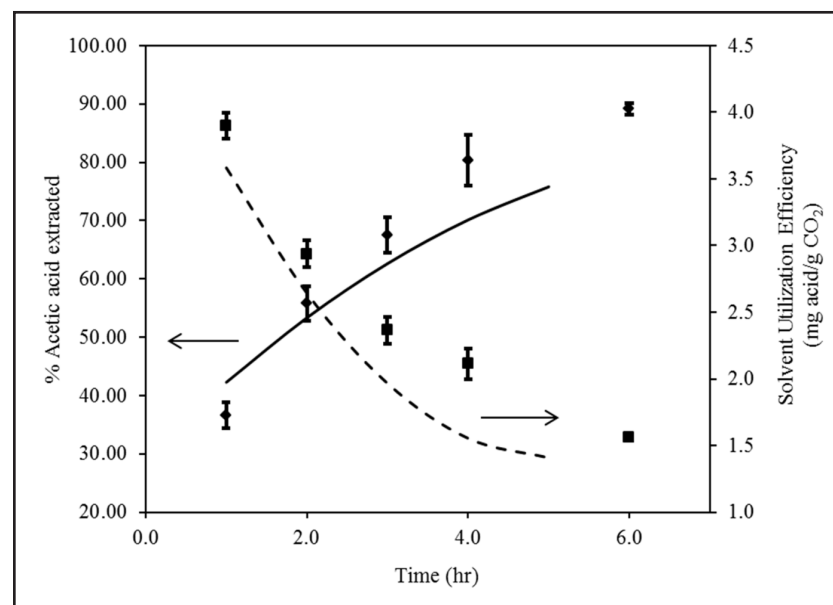


Figure BCC-1.6. Comparison of dynamic confirmation experimental results with the response surface model fit to the optimization data at 1500 psi (10.3 MPa), 35°C, 85.8 g/L initial acetic acid concentration, and 2.03 g/min solvent flow rate. Lines indicate statistical model and points indicate experimental results for percentage acetic acid extracted (— model, ◆ data), and solvent utilization efficiency (--- model, ■ data).

In order to understand the physical nature of the results obtained from the dynamic flow experiments, a mass transfer model was derived assuming well-mixed bulk phases transferring acetic acid at bubble interfaces using a two-film linear driving force mass transfer model. A volumetric mass transfer coefficient based on the equations given in the theoretical section was determined to be $2.848 \pm 0.001 \text{ hr}^{-1}$, with a sum of residuals square (SRS) value of 14.91. Compared to data obtained, the statistical model from the optimization study yielded a SRS of 345.89, indicating the dynamic mass transfer model is more accurate. This is expected, as the statistical model fits an equation, which has no physical meaning, while the dynamic mass transfer model is tailored to convective mass transfer phenomena observed.

The following conditions were selected to extract VFAs from fermentation broth for comparison with the model solution: 50°C temperature, 2500 psi (17.2 MPa) pressure, 1.95 g CO₂/min average solvent flow rate and total extraction time of 1 hour. The fermentation broth was spiked with different acetic acid concentrations for testing purposes while maintaining same pH throughout. The percentage acetic acid extracted from the fermentation broth using supercritical CO₂ under the aforementioned conditions is given along with the model predictions in Figure BCC-1.7. All the extractions performed on rumen fluid samples using supercritical CO₂ were performed in duplicate and the respective standard deviations are given in the figure.

It can be seen from Figure BCC-1.7, that there was no statistically significant difference (as indicated by a simple student's t-test) in the percentage acetic acid extracted from fermentation broth (31% AA extracted at 4.46 g/L initial concentration) until the initial concentration of acetic acid was greater than 15 g/L (29.6% AA extracted). The percentage acetic acid extracted increased with an increase in the initial acetic acid concentration above 15 g/L until around 50 g/L when it slightly decreased with increasing concentrations. This trend was significantly different to that obtained using the statistical model, although as acid concentration increased, differences diminished. The observable differences between the model prediction and experimental results pertaining to acetic acid extraction from the rumen fluid with low initial concentrations can be attributed to the presence of small concentrations of propionic and butyric acid in the cow rumen fluid (around 1.49 g/L and 1.22 g/L respectively). The presence of propionic and butyric acid along with other un-characterized acidic components in the fermentation broth also affected the extraction of acetic acid at low concentrations as indicated by the higher standard error bars for the first experimental data point in Figure BCC-1.7. However, with an increase in the concentration of acetic acid in the fermentation broth, the equilibrium started to shift towards general trend for supercritical carbon dioxide extraction of acetic acid with lesser variations in the experimental data.

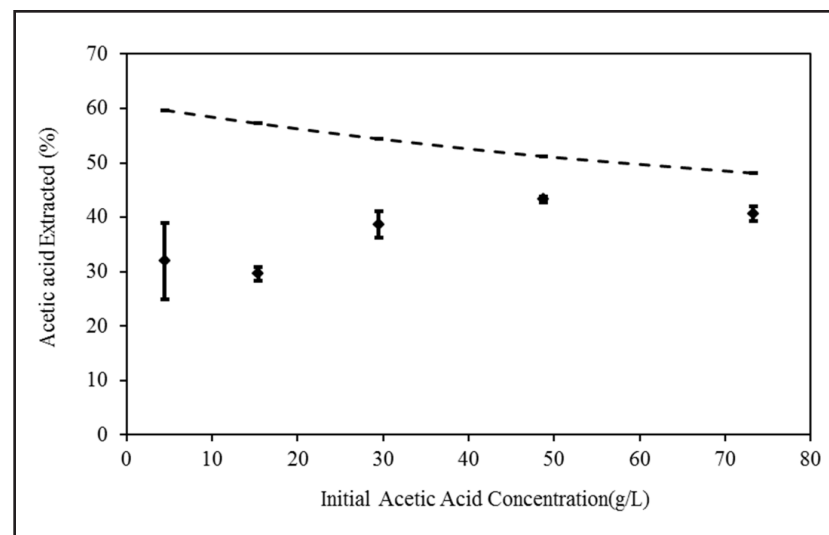


Figure BCC-1.7. Percentage acetic acid extracted from rumen fluid and model prediction versus initial concentration of acid at 50°C, 2500 psi (17.2 MPa), 1.95 g/min flow rate, and 1 hour extraction time (— model, ◆ data).

While the extraction of volatile fatty acids using pressurized carbon dioxide has shown close to 92% recovery of acetic acid at the optimized conditions, the technology at its current stage can be considered expensive due to the compression requirements for carbon dioxide. However, these costs can be mitigated by further optimizing the conditions and also through carbon dioxide serving as a carrier or solvent for these volatile fatty acids as it progresses further into catalytic upgrading to convert to jet fuels. With carbon dioxide as a solvent for the acids in catalytic upgrading, the need for other solvents such as organic or hydro-alcoholic solvents and any acid-base reaction resulting in waste production can be avoided.

Ion Exchange Resin

When compared with supercritical carbon dioxide technology, ion exchange resin as a cost-effective alternative extraction methodology will be studied and optimized for the extraction of the volatile fatty acids from fermentation broth. Unlike in the case of supercritical carbon dioxide extraction where negligible amount of studies were available in literature, the ion exchange extraction of volatile fatty acids has been studied for the last 20 years but has not been successfully optimized for actual extraction from fermentation broth. Literature review revealed that the use of a weak-base ion exchange resin can help achieve greater extraction of the volatile fatty acids while requiring lower amounts of a strong base such as sodium hydroxide or ammonium hydroxide to elute the acid from the resin.

Figure BCC-1.8 shows the time course of glucose, xylose, and lactic acid for the batch versus extractive fermentation. The control/batch fermentation was able to

perform at similar productivity as that of the extractive fermentation, until concentration of the C-3 acids reached around 20 g/L, the point at which the glucose uptake rate slowed rapidly. Despite the drop in glucose consumption rate in the control fermentation, the culture seems to be able to consume xylose at the same rate as the extractive fermentation, albeit somewhat slower than glucose. Overall, the productivity of the extractive fermentation process as calculated using equation 5 (0.329 g/L/hr) was found to be 1.31-fold greater than that of the control (0.252 g/L/hr), likely due to the fermentation operating below the level of product inhibition of its production.

Further studies were done to test the stability of the ion-exchange resin, a total of 11 complete resin loadings were done over the time of the experiment. Each resin loading included the saturation of the resin with the VFA during extractive fermentation followed by desorption of the VFAs from the resin using base and re-loading the resin back into the resin flask. To determine whether the reuse sequence had an effect on the VFA loadings, a one-factor analysis of variance with replicates was performed. Results showed that within 95% confidence interval, the reuse sequence did not have an effect of the ability for the resin to load C-3 acids, but it did have an effect on acetic acid binding. The standard error for the fed-batch and extractive fermentation was found to be less than 2%. The overall change in acetic acid resin binding capacity versus reuse sequence was on average a 4.9 % drop per reuse cycle from the initial loading. It can be assumed that this change could be due to a loss or blockage of active sites by heavy organics or free ions present in the hydrolysate. If a certain quantity of sites were further lost for the binding of C-3 acids to the resin during recirculation of the fermentation broth, since lactic is a stronger acid than acetic, it is expected that the result would be less available active sites for acetic acid binding.

Conclusions

The results indicated that maximum VFA yield (around 0.54g/g biomass sugars or 0.33g/g dry biomass) could be obtained from the WEx pretreated biomass hydrolysate using the robust microbial culture under mesophilic conditions of 37 °C and pH 6.5. No enzymatic hydrolysis was done prior to anaerobic fermentation contributing to the low cost of the BioChemCat process. The microbial culture favored sugar oligomers as feed versus the C5 and C6 monomers to produce VFAs.

Supercritical CO₂ extraction of VFAs from the fermentation broth has never been tested before under dynamic flow conditions and the work carried out in this project is first of its kind. While pressurized CO₂ showed greater affinity towards C-3 and C-4 acids when compared to acetic acid, the studies did indicate extraction efficiency of around 92% at optimized conditions. However, the concentration-time profile indicated that the extraction rate decreased at around 2.5 hours mainly due to decrease in the concentration of acetic acid in the solution. However, the total amount of CO₂ required for the maximal extraction of acetic acid from the fermentation broth and the accompanying compression requirements contributed to the failure of economic feasibility of the process when compared to the current state-of-art.

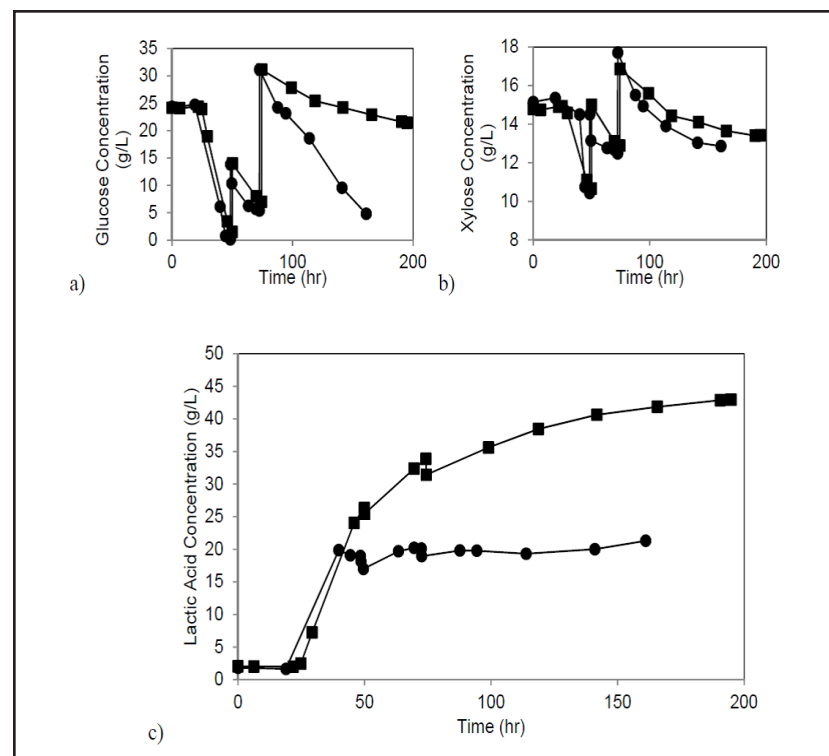


Figure BCC 1.8. Time-course concentrations of a) glucose, b) xylose, and c) lactic acid in fed-batch and fed batch cultures with extractive fermentation operated at pH 5.5 and 50°C using the SMC and Amberlite™ IRA-67 ion exchange (IX) resin. Ion exchange extractive fermentation, ●, control fed-batch fermentation, ■. Note: once the resin system was put online in the extractive fermentation, the rapid concentration drop is due to dilution of the system with water from the resin flask.

Weak base ion exchange resins, such as Amberlite IRA-67, have been previously used to extract various organic acids from the fermentation broth but have not been successfully optimized for extractive fermentations. Through the designed process, it was found that the pH of the fermentation broth was successfully controlled while continuously extracting the VFAs from the fermentation broth. The microbial productivity of the anaerobic fermentation was also considerably increased and the resin was found to be stable over long period of extraction through regular washing intervals. The ion exchange resin while little expensive when compared to the current state-of-art (tertiary amines), has shown great potential and the technical and economic feasibility of the process can be significantly increased through further optimization of the designed process.

TASK 2: CATALYSIS OF PLATFORM MOLECULES INTO JET FUEL

Task Objective

In this task, the separated VFAs are esterified through reactive distillation followed by hydrogenolysis of the VFA esters to produce alcohols. The alcohols are then treated with zeolite catalyst using the traditional alcohol-to-jet fuel process with experimental conditions slightly modified based on the average carbon number of the alcohol mixture (obtained from hydrogenolysis) to produce jet fuels. The hydrogenolysis was tested for the VFAs obtained from both mesophilic (mostly C-2 or acetic acid) and thermophilic conditions (mostly C-3 acid) separately.

Methodology

The entrained water was first separated from the extracted VFA solution in a gravity liquid-liquid separation vessel. The dewatered extract was then esterified using methanol/pentanol as alcoholic solvent to form the VFA ester. Different acidic conditions were tested for effective esterification of the VFAs including auto-catalyzed, CO₂-assisted, acidic ion exchange resin-assisted and mineral acid-assisted esterification. The reaction temperature (30-75 °C), reaction time (1-6 hrs), alcohol-VFA ratio (1:1 to 10:1) and catalyst to VFA ratio (0.1:1 to 1.5:1) were initially varied to determine the optimal conditions for effective esterification. Initial studies were performed to study the kinetics and optimize conditions for acid-catalyzed esterification of C-3 acid to its methyl ester. These kinetic measurements were designed using a central composite response surface experimental design and performed in 2mL Eppendorf tubes in jacketed and heated stirrers. The stirring speed was maintained at 800 rpm for all the experiments. The CO₂-catalyzed esterification experiments alone were performed at 65 °C and 2500 psi pressure for comparison purposes using a heated Parr vessel fitted with liquid CO₂ pump and backpressure regulator.

The VFA mixtures were also fed to a reactive distillation column where the alcoholic solvent contacted the VFAs at 175 °C and 3 bar pressure to emulate the baseline reaction scheme. The water was removed overhead along with the substantial solvent. The overhead in the distillation column was cooled and the alcoholic solvent separated for recycle, while the water phase continues on for any prior treatment. In case of the tertiary amines used in separation of VFAs from the fermentation broth, the VFA esters were separated from the amines using a vacuum distillation column and the amines can be recycled for separation step. The data from this process was directly used in techno-economic assessment studies discussed in Task 3 of this report.

The VFA esters were then hydrogenated with an excess of hydrogen over catalyst at temperatures around or above 200 °C and pressures around 10-13 bar to produce alcohols. In case of acetic acid intermediate, CuO/ZnO catalyst was used with ethanol as the final product. Studies were also done using Co/SiO₂ and similar other

catalysts to produce propanol/isopropanol mixture from C-3 acids obtained from anaerobic fermentation under thermophilic conditions. The experiments were done using a tubular reactor as shown in Figure BCC-2.1.

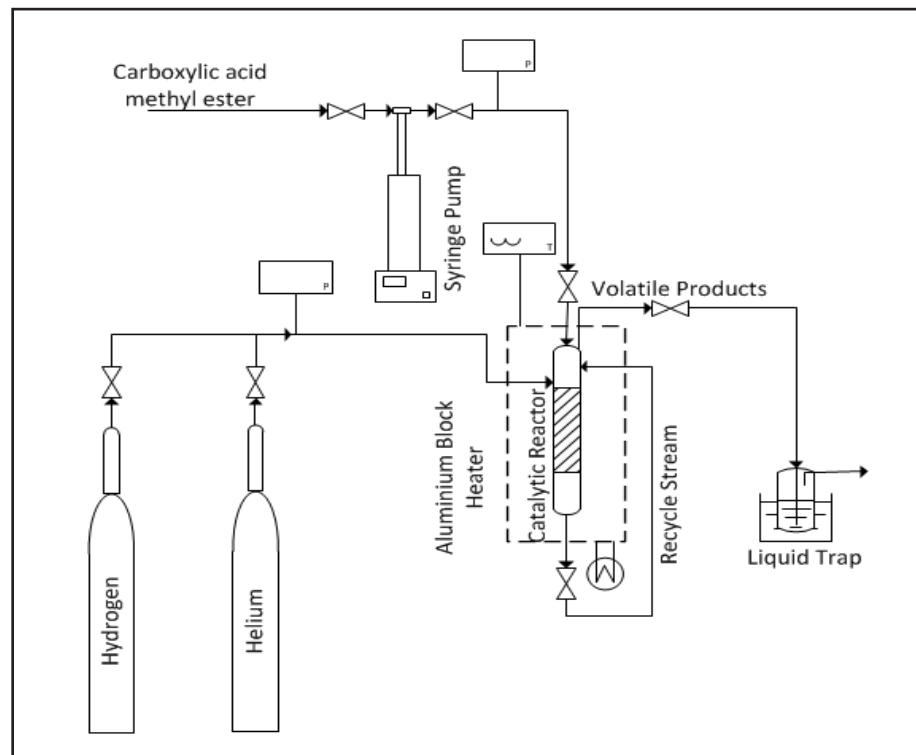


Figure BCC-2.1. Process schematic of catalytic vapor-phase hydrogenation of VFAs to alcohols

The alcohols could then be distilled to separate product from the solvent and then fed at vapor phase to another catalytic reactor packed with zeolite catalyst at about 300-400 °C and pressure of 20-25 bar to produce jet fuel components.

Results and Discussion

Predominant acid-catalyzed esterification processes has using sulfuric acid as the catalyst for efficient conversion of the carboxylic acid to its methyl or ethyl ester. However, it has been found that ethyl esters have the tendency to form azeotropes with the carboxylic acids and water, thereby, making their separation through distillation difficult. So, our study focused on the conversion of the carboxylic acid to its methyl ester through acid-catalyzed and reactive esterification processes.

Under comparable conditions, the % C-3 acid conversion as a function of reaction time is shown in Figure BCC-2.2. It can be seen that the sulfuric acid-catalyzed esterification process was found to yield the best conversions. However, a sulfuric acid-C3 acid ratio of 1.5:1 is unrealistic for a catalytic system due to corrosion effects. It can be seen from Figure BCC-2.2 that amberlyst 15-catalyzed esterification process yielded molar conversions similar to that catalyzed using sulfuric acid. However, a strong acid or base is used to elute the methyl ester from the resin making the process undesirable. The autocatalyzed and carbonic acid-catalyzed esterification processes yielded similar results indicating negligible effect of carbon dioxide under the specified temperature and pressure conditions on the esterification of the acid using methanol. Further optimization of the process variables needs to be performed to better understand the kinetics of the esterification process and yield better molar conversions.

Figure BCC-2.3 shows the effect of reaction time and temperature on the conversion of 20 wt% C-3 acid solution at Methanol-C3 acid ratio or 10:1 and catalyst-C3 acid ratio of 1:1 (catalyst-sulfuric acid). It can be seen from Figure BCC-2.3 that the % molar conversion increases significantly with reaction time (around 60% at 1 hour to around 85% at 6 hours) at low temperatures (around 30 °C). However, this increase in the molar conversion is less at the higher temperatures (around 75 °C) where the molar conversion was around 85% when time = 1 hour and 91% when time = 6 hours.

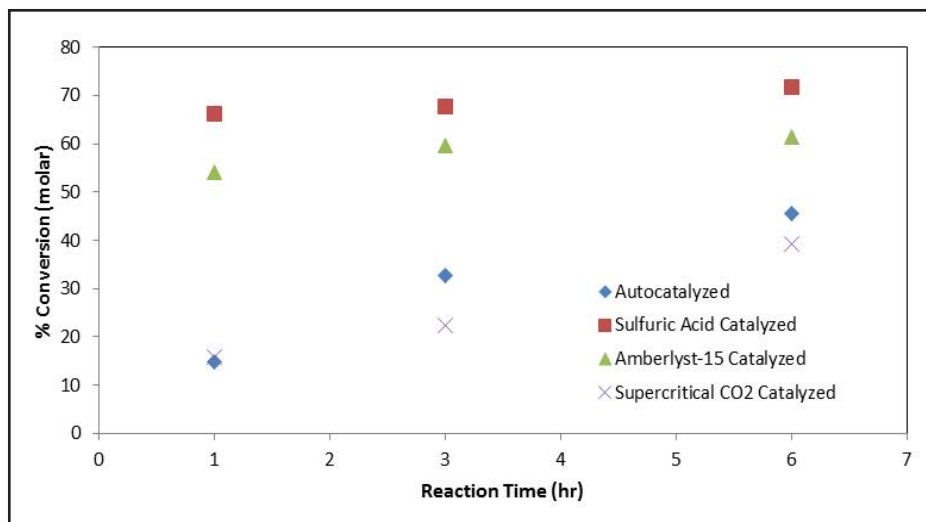


Figure BCC-2.2. Comparison of conversions at 20 wt% C-3 acid feedstock, 10:1 methanol to C-3 acid molar ratio, 0.1:1 catalyst eq charge to C-3 acid ratio (for amberlyst-15- and sulfuric acid-catalyzed), and 75 °C reaction time (65 °C for CO₂).

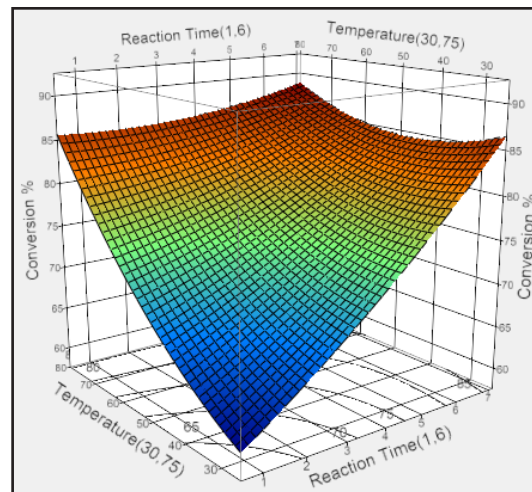


Figure BCC-2.3. The effect of reaction time (1-6hrs) and temperature (30-75 °C) on the conversion of the C-3 acid at initial concentration of 20wt% to methyl ester at 10:1 methanol-acid molar ratio, and 1:1 catalyst-acid molar ratio.

Initial studies on the catalytic hydrogenation of VFAs were done using cobalt catalyst impregnated in silica as catalyst. Preliminary investigation indicates that in the conversion reaction scheme where dehydration mechanisms are important, **silica may not be the most effective support**, as there are many other much more acidic supports available with comparable surface area shown to be appropriate for propylene glycol dehydration. According to the ammonia temperature programmed desorption (TPD) results from investigation of various supports (Figure BCC-2.4), a high Si/Al ratio HZSM-5 support is highly capable of dehydration reactions due to a strong affinity for protons (stronger acid-base bonds). An issue with selection of a support based solely on these values is that if a support is too acidic, coke will form, deactivating catalyst. Therefore, a combination of effective hydrogenation/hydrogenolysis metal must be combined with an appropriately acidic support in order to catalyze the one-pot synthesis of VFAs to alcohols. From these investigations, the main aim of our work is to investigate the production of mixed alcohols from VFAs by understanding the role of catalyst support acidity in the conversion reaction.

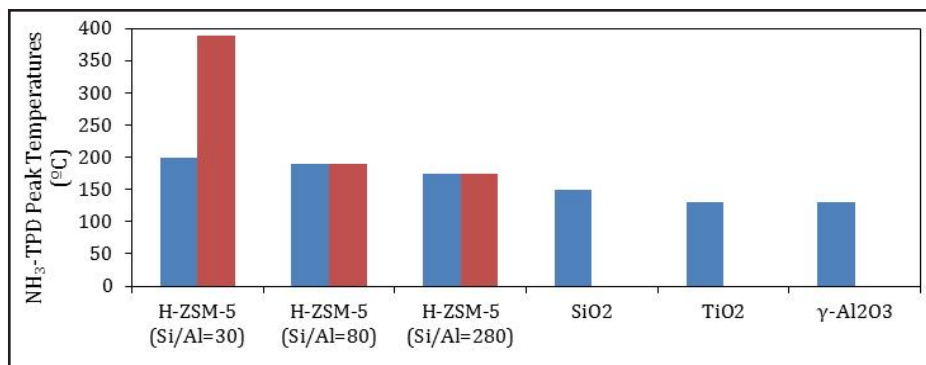


Figure BCC-2.4. Average desorption temperatures for ammonia bound to various acidity catalysts supports.

In order to gather data to understand and optimize dehydrations reactions in this conversion scheme, we plan to first study the conversion and yield of using VFA methyl and ethyl esters (specifically C-2 and C-3 acids which were predominantly produced in the anaerobic fermentation) with a 10 wt% cobalt on fumed silica catalyst at the to-date reported best conditions for propanol production, as well as different weight loading of this catalyst on varying acidity of supports such as cobalt on carbon black, amorphous silica, γ-alumina, acidic zeolite (HZSM-5, varying Si/Al ratios), and titania to promote changes in catalyst dehydration ability. To screen all of these catalysts, small batch reactions were used.

Preliminary experiments done using liquid phase hydrogenation of acetic acid using Pt-Rh catalyst on silica had indicated a catalyst conversion of not higher than 50% for a maximum selectivity greater than 90% towards ethanol production. This decreased conversion was found to be due to the conversion of acetic acid to ethyl acetate at higher concentrations of ethanol produced. This work was not a part of the USDA-NARA initiative and was primarily used to justify our decision to consider vapor phase hydrogenation of the methyl or ethyl ester of the VFAs to produce mixed alcohols. Further studies are currently being done to optimize and characterize the catalyst for effective vapor-phase hydrogenation to produce alcohols. Preliminary studies have indicated that temperatures above 200 °C and pressures below 1 MPa are best conditions to test and optimized effective catalytic hydrogenation of VFAs to alcohols, which can be further dehydrated and oligomerized in the presence of a zeolite catalyst to produce jet fuels.

Conclusions

Initial studies on the kinetic measurements of different acids used to catalyze esterification of VFAs indicated abnormally high values of mineral acids (catalyst to VFA ratio of 1.5:1) required for optimal esterification. However, these acidic conditions were uncommon for scale-up purposes (also affects capital costs due to high corrosion at strong acidic conditions) and further studies indicated that reactive distillation was a better option for maximum esterification efficiency with minimal losses.

Different catalysts have been used for preliminary studies in catalytic hydrogenation of VFA esters to alcohols. While alcohol yields as high as 90% has been seen in these preliminary studies, there is still further requirement for catalyst screening to improve efficiencies. The data obtained for catalytic hydrogenolysis of acetic acid ester to produce ethanol has been used for techno-economic assessment and data provided in the appendix section of this report.

Furthermore, techno-economic analysis was conducted for the conversion of cellulosic biomass to hydrocarbon fuels by the BioChemCat process through collaboration with CleanVantage, LLC and the estimated selling price for the hydrocarbon fuel was found to be \$3.92 per gallon. (Please see Appendix for further details).

NARA OUTPUTS

- Ahring, B.K. 2012. Panel Meeting and Presentation at NARA 2012 Annual Meeting, Missoula, MT, Sept 13-14, 2012.
- Ahring, B.K., Rana, D. and Teller, P., 2012, Wet explosion pretreatment of different feedstocks and its potential for producing biofuels. Pacific Rim Summit on Industrial Biotechnology and Bioenergy, Vancouver. Oct 10-12.
- Ahring, B.K. 2012. New development for production of hydrocarbon biofuels. Frontier in Biorefining. St. Simon Island, Georgia. Oct 30-Nov 2.
- Garrett, B., Srinivas, K. and Ahring, B. K., 2014, Design and optimization of a semi-continuous high pressure carbon dioxide extraction system for acetic acid, ***Journal of Supercritical Fluids***, 95, pp. 243-251.
- Garrett, B., Srinivas, K., and Ahring, B. K., 2015, Performance and stability of Amberlite™ IRA-67 ion exchange resin to extract lactic acid and maintain pH during homolactic fermentation of sugars from pretreated corn stover, ***Biochemical Engineering Journal***, 109, pp. 162-169.
- Murali, N. Fernandez, S. & Ahring, B. K. (2017). Fermentation of wet-exploded corn stover for the production of volatile fatty acids. ***Bioresource Technology***, vol. 227, pp. 197-204.

NARA OUTCOMES

The BioChemCat project as discussed in this report has shown great potential to produce hydrocarbon fuels at a competitive price when compared to the current state-of-art. The advantages of the BioChemCat process have been enumerated earlier in this report. The anaerobic fermentation of the WEx pretreated lignocellulosic biomass sugars to produce VFAs has been extensively optimized in the present study. However, some preliminary studies have indicated that further optimization could result in maximum conversion of other components present in the biomass. These preliminary studies were primarily focused on the anaerobic digestion of these lignin components using the robust microbial culture to produce methane and the work has been published in Bioresource Technology (Ahring et al., 2015) and has received significant attention among the scientific community. However, subsequent studies have indicated that through control of the fermentation conditions, the robust microbial culture can be encouraged to consume these recalcitrant biomass fractions (such as lignin) to effectively increase VFA production and further experimentation in this direction can significantly enhance techno-economics of the BioChemCat process (Murali et al., 2017).

FUTURE DEVELOPMENT

Further impetus should, however, be put on optimizing the separation technologies tested as a part of the BioChemCat project. These sustainable and “green” technologies are environmental-friendly and on optimization, can significantly replace the current state-of-art developed by Eggeman et al. (2005). Other separation technologies such as electrodialysis could also significantly increase VFA separation from the fermentation broth with little requirement for further purification before catalytic upgrading. The presence of any contaminants such as phenolic compounds or similar lignin products or microbial decomposition products from anaerobic fermentation can affect the esterification and hydrogenolysis of the VFAs. While the current state-of-art has been designed to operate efficiently with single VFA such as acetic acid, further optimization of the separation technology for a multi-component VFA mixture obtained from anaerobic fermentation is required. In such a case, the separation technologies studied as a part of this project have shown greater capabilities when compared to the current state-of-art and further optimization can significantly decrease the costs. The supercritical fluid extraction of VFAs from the fermentation broth indicated that there was a significant decrease in the extraction rate with decrease in concentration of the VFAs in the solution below a certain limit. Understanding the extraction dynamics, it is possible to increase extraction efficiency through counter-current continuous contact between the solvent and the fermentation broth where the VFA concentration does not fall below its limiting concentration. In case of the ion exchange resin, extractive fermentation was found to significantly enhance both the separation of the VFAs from the fermentation broth while increasing microbial productivity through continuous removal of the VFAs as soon as it was produced. However, Amberlite IRA-67 was selectively efficient for separating C-3 acids and selection of better weak base ion exchange resin could increase the process efficiency. As previously stated, the separation technologies studied as a part of the project has shown great promise to replace the current platform used in biorefineries and through recommended modifications, the techno-economics and hydrocarbon yield from the BioChemCat process can be improved.

The hydrocarbon yield can also be increased through proper selection and optimization of the hydrogenolysis catalysts used for conversion of the mixed VFAs to alcohols and significant focus has been recommended in this direction.

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APPENDIX

Techno-Economic Assessment of the BioChemCat Process

Objective: The purpose of this task is to estimate the techno-economics of hydrocarbon fuel production from biomass via the BioChemCat pathway. The conversion of biomass to platform molecules was modelled using optimized conversion efficiencies obtained from the experiments. The specific processes for the purification and catalytic upgrading of VFAs to hydrocarbons were selected based on the process's capability to be scaled-up for commercialization. As indicated previously, the techno-economics was done through collaboration with CleanVantage, LLC.

Methodology: A process simulation was developed for the BioChemCat process to convert biomass to hydrocarbon fuels in CHEMCAD 6.5 using parameters obtained from the experiments done as a part of this project as well as from literature sources. Given the resources for further optimization, the “green” separation processes such as supercritical fluid technology and ion exchange resins tested as a part of this project have the capability to be scale-up for demonstration. However, considering the current high cost requirements in the tested technologies, the techno-economic assessment used the VFA separation and conversion to mixed alcohols after the process described by Eggerman et al. (2005). The mixed alcohol-to-jet fuel synthesis was based upon the methanol to gas process modeled by Jones and Zhu (2009). The economic model was constructed based on the methodology adopted in Davis et al. (2013). The fixed operating costs were determined by estimating staffing levels and salaries for plant operation and supervision. A burden on 90% was applied for employee benefits and overhead costs. The maintenance costs and insurance/taxes were taken to be 2% and 0.7% respectively of the fixed capital investment.

Results and Discussion: Table BCC-app.1 gives an overview of the process performance determined from the modeling of the VFA fermentation to hydrocarbon fuel process.

Table BCC-app.1. Process Performance Overview

Production	
Biomass feed, dry basis	2000 ton/day
Yields (per dry metric ton feed)	
VFA (intermediate)	564 kg/metric ton
Mixed alcohol (intermediate)	139 gal/metric ton
Hydrocarbon fuel (final product)	81.5 gal/metric ton
Total hydrocarbon fuel product	53.6 million gal/y
Utilities	
Natural gas (hydrogen generation)	67 MJ/gal fuel
Natural gas (supplemental fuel for steam)	75 MJ/gal fuel
Electrical	8 MJ/gal fuel
Process Cooling	77 MJ/gal fuel
Water	5.7 gal/gal fuel
Wastewater	7.7 gal/gal fuel

The VFA fermentation pathway has potential advantage over the traditional sugar fermentation to alcohol due to the lower production of carbon dioxide and the simultaneous conversion of non-carbohydrate components to VFA (proteins, extractives, some lignin). Further optimization of the VFA fermentation pathway for greater carbohydrate conversion could achieve even higher yields. Ongoing work on the optimization of the alternate separation technologies aimed at continuously removing VFAs from the fermentation broth has demonstrated the potential for increasing the hydrocarbon product yield up to 99 gallons per dry metric ton of feedstock, which could further lower the minimum required selling price for the hydrocarbon fuel.

The discounted cash flow analysis found the minimum selling price for the hydrocarbon fuel at a 10% ROI to be \$3.917 per gallon. The breakdown of the primary cost components of the minimum selling price is shown in Table BCC-app.2. The primary components of the cost are seen to be the feedstock, natural gas, depreciation, and investor return. These four components together represent 73% of the minimum selling price.

As can be seen from Table BCC-app.2, most of the utility usage in the process is in the conversion of the VFA to the intermediate mixed alcohols (more than 95% of the natural gas, 90% of the cooling water). Steam requirements for the esterification reactions and distillations are substantial, requiring natural gas for steam generation to supplement the energy in the lignin residue and fuel gas by-product streams. A significant amount of natural gas is also required to produce the hydrogen necessary for the conversion of the VFA to alcohols.

Natural gas use is a significant operating cost that may be able to be significantly reduced by identifying alternative solvents and/or complexing agents that will result in lower energy requirements in the conversion of the VFA to alcohols. A substantial fraction of the natural gas is used to produce steam to drive the esterification reactions and distillations in this conversion. It must be noted that the separation and conversion processes modeled were based on data available for processes developed for a single acid product (acetic acid) rather than the mixed VFA product of the BioChemCat process. This resulted in less than optimum separation profiles in some of the process steps. Investigating and identifying different solvents or complexing agents with more optimal separation profiles for the mixed alcohol intermediate from the mixed VFA conversion could possibly reduce operating costs through supplemental fuel reduction and also capital costs through a reduction in the required boiler capacity.

The high-energy demands of the modeled separation and conversion processes also consume all the steam recovered from the combustion of the lignin residues. Combustion of the lignin residues in many biomass conversion plants is sufficient to supply the electrical needs of the plant and to export power to the grid. Reduction of the steam demand through optimization of the separation and conversion processes as described above could result in reduced electrical demand, or possibly even a revenue stream from excess production of electricity.

Capital costs could be significantly reduced by purchasing hydrogen rather than installing and operating a steam methane reformer for its production. Such a change would lower the capital expenditure by about \$100 million and would also eliminate half of the natural gas consumption. However, this change would also result in an increase in operating cost due to the purchase cost of the hydrogen (assumed at \$2/kg, which appeared to be at the low end of reported typical hydrogen costs). Modifying the discounted cash flow model to include the purchase of hydrogen rather than self-manufacture found very little change in the required selling price of the fuel product. Although capital costs could be reduced substantially by eliminating the hydrogen plant, the increased operating costs associated with the purchase of hydrogen off-set the economic benefits from the reduced capital.

The VFA conversion process (including the boiler) represents nearly 50% of the fixed capital expense for the process and could be a good target for capital cost reduction. In addition to investigating changes previously discussed to increase energy efficiency, alternative pathways for conversion could also be explored that could reduce complexity and cost of this part of the process.

From the TEA, it was found that the primary factors contributing to this selling price are:

1. The yield of hydrocarbon product is a primary contributor to the selling price of the fuel. Higher yields spread capital and operating costs over fewer gallons of product yielding a higher product cost per gallon. The projected yields in this study were relatively high (81.5 gal/metric ton dry biomass), but additional improvements may be possible to further increase the yield and to lower the cost of the product.
2. Capital costs for the overall system were relatively high, accounting for about 35% of the projected fuel-selling price (22% from ROI, 13% from depreciation). The most significant contributors to the capital cost were the hydrogen generation system and the biomass boiler for the lignin residues (about 43% of the installed equipment costs).
 - a. Purchase of hydrogen from an external source rather than generating internally would reduce capital costs but increase operating costs and did not have a significant effect on the projected selling price.
 - b. Further development and optimization of the separation and upgrading processes to lower energy demands could provide a significant reduction in both capital and operating costs.
3. Feedstock costs represent a significant fraction (22%) of the fuel-selling price, which can only be reduced significantly by increasing the yield of fuel per ton of feedstock.

Table BCC-app.2. Capital and Operating Cost Summary

CAPITAL COSTS	Millions of \$	% of Total PE
Purchased Equipment (PE)		
Preprocessing	\$12.3	7.7%
Pretreatment	\$19.9	12.4%
Fermentation and VFA Production	\$13.7	8.6%
VFA Purification	\$12.5	7.8%
VFA to Hydrocarbon Conversion	\$18.5	11.5%
Hydrogen Generation	\$29.2	18.2%
Steam Boiler System	\$40.1	25.0%
Utilities, Water Treatment, and Other Systems	\$14.3	8.9%
Total Purchased Equipment Cost	\$160.5	100.0%
Installation Costs	\$189.7	118.2%
Indirect Costs and Working Capital	\$234.9	146.4%
TOTAL CAPITAL INVESTMENT	\$585.1	364.5%
OPERATING COSTS	\$/gal	% of Total
Variable Operating Costs		
Feedstock	\$0.843	21.5%
Natural Gas	\$0.629	16.1%
Electricity	\$0.151	3.9%
Other Variable Costs	\$0.153	3.9%
Total Variable Operating Costs	\$1.776	45.4%
Fixed Operating Costs	\$0.388	9.9%
Cost of Production (Variable + Fixed)	\$2.164	55.3%
Other Costs		
Depreciation	\$0.516	13.2%
Average Income Tax	\$0.367	9.4%
Average ROI	\$0.870	22.2%
Total Other Costs	\$1.753	44.7%
MINIMUM SELLING PRICE AT 10% ROI	\$3.917	100.0%