Final Scientific/Technical Report

Project Title: Development of an Economic and Efficient Biodiesel Production Process
Award Number: EE0003128

Recipient: University of North Carolina at Pembroke
Project Location: University of North Carolina at Pembroke, Pembroke, NC 28372 and North Carolina Agricultural and Technical State University, Greensboro, NC 27411

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3. Executive Summary:

The Biofuels Team at The University of North Carolina at Pembroke and North Carolina A&T State University carried out a joint research project aimed at developing an efficient process to produce biodiesel. In this project, the team developed and tested various types of homogeneous and heterogeneous catalysts which could replace the conventionally used soluble potassium hydroxide catalyst which, traditionally, must be separated and disposed of at the end of the process. As a result of this screening, the homogeneous catalyst choline hydroxide was identified as a potential replacement for the traditional catalyst used in this process, potassium hydroxide, due to its decreased corrosiveness and toxicity.

A large number of heterogeneous catalysts were produced and tested in order to determine the scaffold, ion type and ion concentration which would produce optimum yield of biodiesel. The catalyst with 12% calcium on Zeolite β was identified as being highly effective and optimal reaction conditions were identified. Furthermore, a packed bed reactor utilizing this type of catalyst was designed, constructed and tested in order to further optimize the process.

An economic analysis of the viability of the project showed that the cost of an independent farmer to produce the fuelstock required to produce biodiesel exceeds the cost of petroleum diesel under current conditions and that therefore without incentives, farmers would not be able to benefit economically from producing their own fuel.

An educational website on biodiesel production and analysis was produced and a laboratory experiment demonstrating the production of biodiesel was developed and implemented into the Organic Chemistry II laboratory curriculum at UNCP. Five workshops for local farmers and agricultural agents were held in order to inform the broader community about the various fuelstock available, their cultivation and the process and advantages of biodiesel use and production.

This project fits both Universities' goals in the Biofuels Research Initiative, since it uses an alternative fuelstock: namely canola. The outcomes of this project may eventually aid in reducing the state's consumption of corn and soybean, which are important food crops. The project will also encourage regional farmers to grow alternative crops for biofuel production. The success of this project has contributed towards the development of Robeson County, an economically disadvantaged region. Additionally it should be noted that Robeson County serves a large Native American population. Therefore, training and engaging this minority group in the energy industry was an important accomplishment.

4. Accomplishment of Goals and Objectives:

Goal – The goal of this Biofuels project was to develop a cost-effective protocol for biodiesel production utilizing locally grown oil-seed fuelstocks such as soybean and canola.

Objectives – Two objectives will guide this *Biofuels Project*:

(1) Develop and validate a cost-effective protocol for biodiesel production from vegetable oils.

a. Develop a catalyst to improve the conversion of vegetable oils to biodiesel
b. Improve the efficiency economic feasibility and automation

c. Develop and test a bench-scale biodiesel reactor, increase public awareness and farmer's know-how of the biodiesel fuel production and use
d. Produce various catalysts, characterize and test them to determine their efficiency
e. Produce research data and advance scientific knowledge

(2) Develop Biodiesel Education and Training.

a. Develop outreach strategies and resources for training farmers and promoting biodiesel technology
b. Develop an advanced and up-to-date energy lab at UNCP
c. Educate and train students
d. Develop energy courses, and establish energy research for undergraduate and graduate students, teach and train the local community including the farmers

Goals achievement

- Found optimum conditions for production of biodiesel from seed oil using the new catalyst developed by NC A&T
- Designed and constructed prototype reactors to demonstrate process to farmers and potential industrial partners
- Developed a website on Alternative/Renewable Energy to inform local agricultural community
- Completed an economic analysis of the process allowing farmers to understand initial investments required and potential advantages from biodiesel production

Although originally only a heterogeneous catalyst was to be developed by Dr. Shahbazi's group at NC-A&T, the investigators at UNCP decided to pursue a parallel path to screen homogeneous catalysts and optimize conditions for the use of the chosen catalyst. As a result, choline hydroxide was identified as an effective catalyst for transesterification of oil with methanol to generate biodiesel. Conditions which give the highest yield of biodiesel under a variety of conditions were also developed. Additionally, a reactor consisting of a heating mantle and condenser was designed, assembled and tested.

NC-A&T's efforts lead to the synthesis, testing and characterization of a number of heterogeneous catalysts ultimately leading to the selection of 12% Ca on a Zeolite β. Optimal conditions for use of this catalyst in a packed-bed column were also developed. The reactor for heterogeneous catalysis using the Ca on Zeolite β was designed assembled and tested in order to determine optimal reaction conditions.

An economic analysis of the costs of growing canola or other fuelstock crops, grinding the seeds to obtain the oil, initial purchase of reactor and consumables such as methanol and basic catalyst shows that it is not currently economically feasible for farmers to grow their own fuel, however there are other models under which this model could be sustainable. As such, no reactor or catalyst cost reduction could overcome this problem, and the cost to produce a gallon of biodiesel by independent farmers was found to be in excess of the cost of buying it, there were shown to be no savings for a farm producing their own renewable fuel as compared to purchasing it.

While originally the BFT had envisioned designed a course on biodiesel and other renewable and alternative energy production with the implementation of that course into the UNCP curriculum, within the first year of the project, we decided that limiting the information to only students at UNCP would cut out a major constituency in the community at large. Therefore, in lieu of the development of a course, an educational website was developed in order to inform all constituencies about biodiesel production.

A laboratory experiment for the Organic Chemistry II laboratory demonstrating the production of biodiesel from oil and methanol using ChOH was developed. The farming community was informed about the various fuelstock options and their cultivation through a number of workshops for local agricultural community. One biodiesel producer in Robeson county has been established and rapeseed, a fuelstock crop, is now being cultivating in the local area.

All reporting requirements were fulfilled.

5. Project Activities:

A. Catalyst Development

Screening the catalyst (A.1)

Previous research work by the members of the Biofuels Teams (BFT) at the University of North Carolina at Pembroke (UNCP) and North Carolina Agricultural and Technical State University (NC A&T) has allowed for identification of a series of organic molecules that will be efficient catalysts for the synthesis of biodiesel. These compounds should be:

- basic,
- nonvolatile,
- stable at temperatures below 60 ºC, and
- easy to incorporate in a solid matrix

Using these criteria, a variety of solid acid and base catalysts from selected catalyst libraries were identified and screened for their potential use in heterogeneous catalyst development. These libraries were identified through literature searches within the published data.

Homogeneous catalysis

In addition, several homogeneous have been screened for their use in the production of biodiesel. Moderately volatile amine bases such as diethyl amine and morpholine have shown successful outcomes but excesses of these catalysts and longer reaction times are required for excellent yields (<95%) to be achieved. The solid phase catalyst calcium hydroxyapatite shows relatively low conversion rates. A heterogeneous catalyst derived from morpholine showed low % conversion and leached from the solid support during the course of the reaction and so showed little promise.

Use of tetramethylammonium hydroxide (TMAH) under a variety of reaction conditions has been found to be successful, even at room temperature. Further screening indicated the choline hydroxide (CHOH) had numerous advantages including being less corrosive and having fewer problems in disposal since choline is a nutrient additive and not harmful. As a result choline hydroxide was the focus of our optimization efforts.

Heterogeneous process

Several heterogeneous catalysts have been screened for their use in the production of biodiesel. Calcium on Zeolite Y and sulfated Zirconia have been shown to be efficient catalysts for the conversion of fresh oil to biodiesel. Further optimization of reaction conditions, including a study of water tolerance, solvent, temperature and catalyst loading is needed.

Following the screening of the active catalyst components and supporting materials, the heterogeneous catalyst complexes will be synthesized. This type of catalyst will have some advantage over the traditional processes: absence of catalyst in the biodiesel and the glycerol by-product.

Our approach in the design of multifunctional catalysts is to develop heterogeneous acid/base catalysts which integrate the typically incompatible esterification and transesterification catalysts into a single reaction system for one-step biodiesel synthesis. The following three kinds of catalysts will be explored.

Layered double hydroxides (LDHs) will be synthesized based on the compounds whose general formal is $[[M^{2+}_{(1-x)}M^{3+}_{x}(OH)_2]^{x+}(A)_{x/n}{}^{n-}]$. Acid/base properties of LDHs will be controlled through the variation of the types and nature of the isomorphous substituted cations in the inner structure and the anions in the interlayer.

Zirconium- and Titanium-Based Compounds: Acidic zirconium silicate zeolites (i.e., Zr-zeolite-beta, Zr-TUD-1, and Zr-MCM-41), with oxides and Mg^{+2} and Ca^{+2} cations as basic promoters will be synthesized. Similarly structured basic titanosilicate, mesoporous zeolites, with oxides and Zr^{4+} and Sn^{4+} cations as acidic promoters will be synthesized. Compounds of the general formula $M(n\text{-butoxide})_{4-x}(maltolate)_x$ (where M is Ti or Zr) will also be synthesized. These compounds will be tested for their effectiveness as acid/base catalysts for the esterification and transesterification reactions.

A basic catalyst, Calcium on Zeolite Y was prepared using wetness impregnation method. Fifty (50) g of Zeolite Y is calcined at 400 ^{o}C for 4 h followed by cooling in room temperature for 6 h. Five (5) cc solution of Calcium Nitrate is loaded onto Zeolite Y. The resulting product is vacuum dried at 100 ^{o}C for 4 h. The final product is calcined at 500 ^{o}C for 5 h and then cooled down at room temperature for 18 h.

The second catalyst, sulphated Zirconia, was prepared using solvent free method. Zirconylchloride Octahydrate ($ZrClO_2.8H_2O$) is mixed with Ammonium sulphate ($(NH_4)_2SO_4$) with the molar ratio of 1:6, the two powders were grounded at room temperature for 30 minutes, then the powder mixture was left at room temperature for 18 hours. Finally, the product was calcined at 600 ^{o}C under air, for 5 hours.

This method is preferred in preparing catalysts because no solvent is used, which would make this catalyst environmental friendly during the biodiesel reaction. Also this catalyst is considered to be acidic in nature which would have more conversion due to the Bronsted acidic sites, as well as avoidance of saponification during the biodiesel reaction. However it is well known that acidic catalysts would require more activation energy than those that are basic in nature. The BET showed the surface area of Sulphated Zirconia is rather limited. However the effectiveness of Bronsted acidic sites would enhance this catalyst's chances.

Ca on Al-MCM-41 was also synthesized using the following procedure**:** Commercial 3% Al incorporated MCM-41 was purchased from ACS Materials and was used as support to prepare 10 wt% Ca on Al-MCM-41 catalyst. An aqueous solution of calcium nitrate was added dropwise with stirring to the MCM-41 support until the consistency of a gum was achieved after which it was stirred for an additional 20 minutes and dried at 60ºC. The remaining calcium nitrate solution was then added and the catalyst was dried at 100ºC overnight. Calcination was carried out at 450°C for 3h in air atmosphere to produce the final 10wt% Ca on Al-MCM-41 catalyst.

Using zeolite-β, zeolite-Y, Al-MCM-41 and alumina as supports, different amounts of Ca (5, 7, 10, 12 and 15 wt%) were loaded by incipient wetness impregnation method. In a typical synthesis, aqueous solution of required amount of calcium nitrate was added dropwise to the dried support material and stirred manually until a gel was obtained. Then, the Ca loaded material was dried at 80°C overnight before calcination at 450-500°C for 5h in air to decompose the calcium nitrate.

The commercial zeolite-β obtained from Zeolyst was calcined at 450ºC for 5hrs in air to remove any adsorbed gases and moisture. Using calcined zeolite-β as catalyst support, different amounts of Ca (5, 7, 10, 12 and 15 wt%) were loaded by the incipient wetness impregnation method. In a typical synthesis, an aqueous solution of the required amount of calcium nitrate was added dropwise to the dried support material and stirred manually until a gel formed. Then, the Ca loaded material was dried at 80°C overnight and calcined at 500°C for 5h in air to decompose the calcium nitrate, resulting in nanoparticles of CaO over the zeolite-β support. In order to study the promotional effect of K or Na on Ca-zeolite-β, catalysts with trace amounts of K or Na are prepared under similar conditions and their performance will be tested in future, targeting for higher oil conversion.

Zeolite β loaded with optimized Ca content (10 and 12 wt%) and promoted with trace amounts (1 and 2 wt%) of K and Na were synthesized by impregnation method. Before the impregnation, the commercial zeolite-β powder was calcined at 450ºC for 5hrs in air to remove any adsorbed gases and moisture. Using calcined zeolite-β as catalyst support, aqueous solution of required amount of calcium nitrate along with K or Na precursor was added drop wise and mixed well to get uniform dispersion. The addition and mixing were continued until to get a gel. Then, the Ca loaded material was dried at 80°C overnight and calcined at 500°C for 5h in air to decompose the metal precursors, resulting nanoparticles of K or Na promoted Ca over the zeolite-β support.

The aluminum content, responsible for acidity in zeolites, in zeolite-β is considered as one of the important factor in controlling the activity of Ca/zeolite-β catalyst in transesterification reaction. Hence, post-treatment attempts were made to decrease the aluminum content in zeolite-β by treating with oxalic acid. Zeolite-β was treated with different concentration of oxalic acid for a definite period of time in order to remove the aluminum from the framework of zeolites. Hence, the acidity of zeolite-β is decreased and

the decrease in acidity is increase with increasing the concentration of oxalic acid. Using these modified zeolite-β, 12 wt% Ca catalysts will be prepared and catalytic activity will be tested to see the effect of aluminum removal on the transesterification activity.

Testing of the catalysts

The heterogeneous catalysts which were synthesized by NC A&T previously are under the following screening protocol:

Transesterification reaction:

500 ml Methanol and 0.7g of prepared Ca-Y was mixed in a tube for 20 minutes to prepare methoxide. Meanwhile, 100ml of soybean oil was heated to 55ºC while stirred at 400 rpm. Methoxide was added to the oil at a stable temperature of 55° C and kept stirring at 400 rpm. The mixture continued to be stirred at 55ºC for 1.5 hours while being stirred at 400 rpm to ensure a complete reaction. Excess methanol was used to ensure the presence of adequate methanol to carry out the transesterification process to completion.

Packed bed reactor:

2g of catalyst diluted with SiC was packed in the reactor and fixed into the reaction set up. The transesterification reaction was carried out over the catalyst by passing a mixture of waste cooking oil and methanol at 80°C under a pressure of 100 psi. The products obtained at different time intervals were analyzed using gas chromatograph following the European Standard EN 14103:2003.

Separation procedures:

The product mixture was placed in a separatory funnel and was allowed to separate at room temperature for 10 hours. Two layers were formed; the top layer consisted of biodiesel and bottom layer of glycerol. The bottom layer was removed and a small amount (0.3 ml) of acetic acid was used to wash the biodiesel in order to remove the undesired salts. The product was centrifuged for 20 minutes at 1400 rpm and allowed to settle and filtered with 0.2 mm filter paper to remove all of the suspended residuals.

Analytical measurements and the results:

The two standard methods of ASTM D6584 as well as EN1413 were used by the GC to obtain accurate results. The total methylester content in the biodiesel produced by the Ca-Y was found to be 94.98% which equals a 94.98% conversion rate from soybean oil to biodiesel. In addition, the ASTM D6584 was used to measure the glycerol, mono, di, triglycerides, and total glycerol (free + bound) percentages which, was found to be 0.02%, 0.01% 0.04%, 0.00%, and 0.03%, respectively. This data shows that a high transesterification reaction for the triglycerides has been achieved.

Furthermore, the total methylester content in the biodiesel produced by the sulfated zirconium (SZ) was found to be 89.14% which equals a 89.14% conversion rate from soybean oil to biodiesel. In addition, the ASTM D6584 was used to measure the glycerol, mono, di, triglycerides, and total glycerol (free + bound) percentages which, was found to be 0.00%, 0.35% 0.2%, 0.04%, and 0.12%, respectively. This data shows that the transesterification rate for this catalyst is low and the amount of mono- and di-glycerides remaining in the biodiesel is high (0.35% and 0.2%, respectively). This problem can be eliminated by increasing the reaction time from the current 1.5 hour to 2.5 hours. Therefore, among the two catalysts tested under the current condition, Ca on zeolite Y is most effective.

Catalyst characterization (A.3)

A BET instrument was used to characterize the calcium-on-Zeolite Y catalyst. BET allows for determination of surface area, pore size, and pore volume of the catalyst. The results show that the surface area of this catalyst is 534 m^2/ g. The surface area of the catalyst was determined by embedding a code in the BET software, while the pore size and pore distribution was calculated using Excel program, plotting the pore width (Å) versus desorption of nitrogen on the catalyst surface. This analysis has revealed that the pores are well distributed within 50 to 200 Angstrom.

Calcium on Zeolite Y and sulfated Zirconia which were synthesized last year were characterized using Brunauer, Emmett and Teller (BET) Instrument. This characterization will quantify physical parameters

such as surface area. Pore-volume and pore-size, which are used as indicators to determine the catalyst's potential effectiveness, need to be calculated from the surface area values.

First, a liquid nitrogen cell was weighted before loading the catalyst then the catalyst was placed inside the cell to degas the sample for 3 hours. Then it was removed and placed inside a liquid nitrogen cell to study the adsorption of nitrogen onto the catalyst which would provide a surface area scanning of the catalyst as well as pore size, pores distributions and pore volume. Finally the liquid nitrogen cell was weighed again. The results showed that the surface area of Ca on Zeolite Y was 534 m^2/ g. The pore volume of this catalyst was calculated to be in the range between 181.97 CC/g to 184.92 CC/g and they are uniformly distributed throughout the catalyst.

On the other hand, the surface area of Sulfated Ziconium (SZ) was found to be small (100 m^2/g). However, the pore volume and pore distribution were sufficient enough for the conversion of oil to biodiesel inside the effective Bronsted acidic sites of this catalyst. The pore volume for SZ catalyst was found to be in the range between 1.58 CC/g to 3.55 CC/g and they are uniformly distributed throughout the catalyst.

Sulfated zironia was prepared via a solvent-free method. It has been tested as a heterogeneous acidic catalyst in the transesterification of used vegetable oil to biodiesel fuel. It is more favorable than acidic heterogeneous catalysts because of its lower corrosiveness.

The characterization process was initiated by placing a sample of the sulfated zirconia catalyst inside the cell to degas for 3 hours. Then the sample was removed and placed inside a liquid nitrogen cell to study the adsorption of Nitrogen on the catalyst. The BET testing method allows for determination of surface area, pore size, and pore volume of the catalyst. The results show that the surface area of this catalyst is 110 m^2/ g. The surface area of the catalyst was determined by embedding a code in the BET software, while the pore size and pore distribution was calculated using Excel program, by plotting the pore width (Å) versus desorption of nitrogen on the catalyst surface. This analysis has revealed that the pores are well distributed within 20 to 100 Angstrom.

The textural characteristics of commercial 3% Al-MCM-41 were analyzed by N_2 physisorption method. It showed larger surface area of 858 m^2/g and the average pore size distribution around 3nm, which indicates the good quality of the MCM-41 sample.

The X-ray diffraction patterns of Ca loaded zeolite-β catalysts were recorded to measure the dispersion and particle size of the Ca/CaO particles on the zeolite support. Figure 1 shows the XRD patterns of catalysts with different amount of Ca along with zeolite-β with same pretreatments. The XRD patterns do not show any peaks for Ca/CaO and only peaks corresponding to zeolite structure appeared in all the catalyst samples. This indicates that the Ca/CaO particles are below the detection limit of the XRD instruments (generally below 5 nm) and no larger particles are formed during the calcination. Generally, the peaks for Ca/CaO appear in between the two theta values of 30 and 70º.

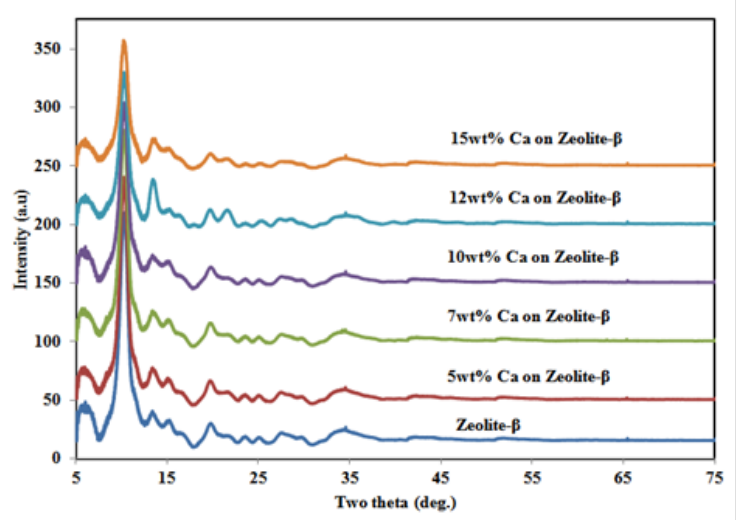


Figure 1. XRD Patterns of different amount of Ca loaded zeolite-β along with plain zeolite-β

Installation of the Micromeritics physisorption/chemisorption instrument allowed for the characterization of the prepared catalysts by N2 physisorption, temperature programmed reduction and acidity/basicity of the catalysts.

Characterization of basicity of Ca loaded zeolite-β catalysts by temperature programmed desorption of CO_2 in Micromeritics ASAP 2920 analyzer. The basicity of the Ca-zeolite Y catalyst was studied by temperature programmed desorption using CO_2 as probe molecule. Catalyst (200 mg) powder was pretreated under a helium stream at 500ºC (10C/min, 50 ml/min) to remove the adsorbents on the surface of the catalyst. Then, the temperature was decreased to 45ºC and the flow of pure CO_2 (25ml/min) was subsequently introduced into the sample for 30 min. Then, the flow was switched to He (100 ml/min) for 1h to remove the physisorbed CO_2 molecules on the surface of catalysts. The temperature programmed desorption of CO_2 was carried out between 45 and 800ºC at a heating rate of 5ºC/min in a He flow and the CO_2 was detected by TCD, after passing through ice trap to eliminate any trace of water.
The plots of temperature programmed desorption of CO_2 over zeolite-β loaded with different amount of calcium are shown in Figure 2. All the catalysts showed desorption bands at different temperature ranges indicating that the catalysts have basic sites with varying strength. A medium intensity peak is appeared around 90ºC representing the basic sites with lower strength while a low intensity broad peak appeared around 300ºC representing the basic sites with moderate strength. The basic sites with stronger strength are represented by high intensity desorption peak around 510ºC. The area under each peak is directly related to the number of basic sites and hence Ca loaded zeolite-β catalysts have more number of basic sites with higher strength, which could catalyze the transesterification of heavier oil molecules. When comparing the Ca content, the intensity of all three peaks increases with increasing Ca content up to 12 wt% indicating that added Ca particles are well dispersed over the zeolite support. When the Ca content is further increased to 15 wt%, a significant fall in the intensity of all three peaks is noted. Further, a high intensity desorption peak around 725ºC is observed. It is due to desorption of CO_2 molecules adsorbed on bulk Ca particles or Ca particles with very high basicity. Since the activity of 15 wt% Ca on zeolite-β catalyst in transesterification of waste cooking oil was significantly low compared to catalyst with 12 wt% Ca, it is strongly believed that the high temperature desorption peak from catalyst with 15wt% Ca is due to the formation of bulk Ca particles. The excess loading (15 wt%) of Ca leads to the formation of larger particles, which could be less active in transesterification reaction. This study indicates that 12 wt% Ca covers the surface of zeolite-β and show better activity and further increase in Ca content leads to formation of bulk Ca particles and hence lesser catalytic activity in transesterification.

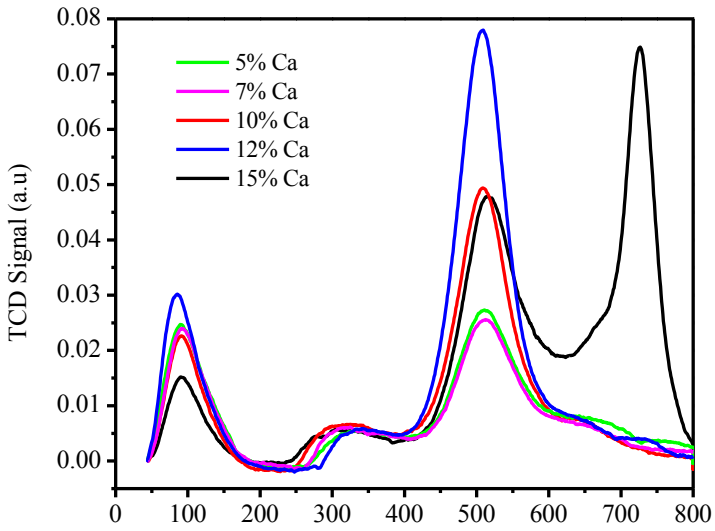


Figure 2. Temperature programmed desorption of CO_2 profiles of zeolite-β catalysts with varying Ca content revealing the strength of basic sites.

A.GN.1 Selection of the Catalyst

Homogeneous process

Choline hydroxide was selected as the catalyst which was used for reaction optimization for the homogenous process.

Heterogeneous process

Based on the previous studies, we selected zeolite-β as support for Ca-based catalysts for the transesterification of waste cooking oil. Optimization the Ca content over the zeolite-β for higher conversion of waste cooking oil at the temperature of 90 ºC and pressure of around 100-200 psi lead to the selection of a 12% Ca loading.

B. Process Optimization

Pretreatment of Fuelstock

- The conversion of the fuel stock is diminished by the presence of free fatty acids (FFA). Fuels stocks such as used vegetable oil and fat contain a high concentration of FFA. As a result additional catalyst must be added, increasing the mass of catalyst by a factor of 5. Due to the high cost of catalyst, a more efficient procedure involves the pretreatment of the fuel stock. Several pretreatment methods were developed.

- One method is to mix the oil with the glycerin layer from a previous reaction, heating gently. This method presents the disadvantage that a delay is required for the separation of layers.

- Another method is the treatment of the fuel stock with sodium sulfate and heating at 40-50 °C. The purification of the oil is then achieved by filtration over silica gel.

- Finally the last method is to treat the oil with sulfuric acid, and reflux for 2 hours. The oil needs purification by separation of the layers and filtration over silica gel. During this process, a conversion of 20-30% of the oil to biodiesel was observed.

- The last two methods present the disadvantage that additional reagents are needed, which increases the cost of the procedure. None of these methods were successful in eliminating

the free fatty acids to a concentration equal to that of the pure oil. For this reason the oils were then filtered over a column of basic alumina to reduce the amount of free fatty acids present. The most efficient method is the use of the glycerin layer from the previous reaction. In this way no additional compounds need to be employed.

- In order to be able to utilize a variety of fuels stocks with the homogeneous catalyst TMAH, conditions needed to be determined for use with water fuel stock containing high concentrations of water and free fatty acids. A variety of pretreatment methods with different fuel stock were developed and tested in order to allow us to remove water and free fatty acids prior to its conversion to biodiesel. A different approach to using TMAH as a catalyst in the reaction of waste oil containing large amounts of FFA requires a five-fold increase in the amount of catalyst to be used. Due to the high cost of catalyst, it was determined to be more cost-effective to remove the FFA and water from the fuel stock prior to the reaction by pre-treatment. Several pretreatment methods were developed:

- Mixing the oil with the glycerin layer from a previous reaction and heating gently.

- Treatment of the fuel stock with sodium sulfate and heating at 40-50 °C followed by filtration over silica gel.

- Treatment of the oil with sulfuric acid and heating at reflux for 2 hours followed by separation of the layers and filtration over silica gel. During this process, a conversion of 20-30% of the oil to biodiesel was observed.

- The last two methods present the disadvantage that additional reagents are needed, which increases the cost of the procedure. None of these methods were successful in eliminating the free fatty acids to a concentration equal to that of the pure oil. For this reason the oils were then filtered over a column of basic alumina to reduce the amount of free fatty acids present. The most efficient method is the use of the glycerin layer from the previous reaction. In this way no additional compounds need to be employed.

a. Homogeneous Catalyst Process

The UNCP BFT optimized reactions for two phase transfer catalysts. TMAH (tetramethylammonium hydroxide) and ChOH (Choline Hydroxide). The **TMAH catalyst is more efficient, requiring 8.4% moles of catalyst/moles of oil**. The **second catalyst (ChOH) is less efficient (9.9% moles of catalyst/moles of oil),** but the second catalyst has a lower cost, and has the advantage that it is less toxic. For used vegetable oil (UVO) an increased amount of catalyst is required.

For TMAH the reaction has been found to be complete in 20 hours at room temperature and less than 1 hour at 55-60ºC. We have also cut by more than half the amount of methanol required for complete reaction. Stirring rate and method have been found to be important in efficient completion of the reaction.

Two methods which streamline the washing process have been developed. Following the reaction, self-washing with glycerol byproduct have been found to draw out many impurities in the reaction mixture. Also, by injecting 5% water into the reaction at completion, the reaction is halted and the reaction mixture requires less water washes and results in lower amounts of soap.

Scale-up

Several experiments were conducted aimed at successfully increasing the scale upon which the conversion of oil to biodiesel can be successfully carried out in the presence of tetramethylammonium hydroxide (TMAH) and excess methanol. Early attempts to increase the scale of the biodiesel production indicate to us that additional reaction times will be necessary due to the longer time necessary to heat the reaction mixture at reflux. For a reaction volume of 250 mL, the reflux time should be increased to 1.5 hours and for a volume of 500 mL the reaction

time should increase to 2 hours. This time increase may not be necessary if the final reactor will be equipped with better heating and mixing accessories.

Characterization of biodiesel produced

Installation of the Liquid Chromatograph-Mass Spectrometer is complete and all of the BFT faculty members and research student assistants have been trained on its use. Furthermore, a new Gas Chromatograph which was explicitly designed for biodiesel analysis has been ordered. In conjunction, these two instruments will allow us to fully characterize the biodiesel produced in our experiments using EN and ASTM standard protocols.

The new Gas Chromatograph was received and installed during this quarter. It has been calibrated and tested. Training of the BFT faculty has taken place. This will allow us to begin testing the fuel to verify that the quality of the fuel is in agreement with the ASTM and EN standards. Initially the fuel was tested by ^{1}H NMR. This method is fast but not sensitive enough to see low percentage of glycerin still present. Recently we acquired an LC-MS, and we were able to detect mono-, and di-glycerides still present in our sample. In order ensure better conversion, we will increase the reaction time.

A study was conducted as to the usefulness of injecting water into the reaction mixture near the end of the reaction phase. During the last five minutes of the reaction, water equal to a mass of 5% to the original oil mixture was injected into the reaction. As a result, the glycerol byproduct separated out in less than 30 minutes. Also, the glycerol mass was about 20% greater than the regular method with no prewash. This is after accounting for the mass of the injected water. LCMS studies also indicated that more catalyst and glycerides were removed with the prewash method. This helps to reduce the time and materials needed in the final purification of the biofuel.

Scaling up the process

Early attempts to scale-up the process indicate that longer reaction times will be necessary due to the longer time necessary to heat the reaction mixture at reflux. For a reaction volume of 250 mL the reflux time should be increased to 1.5 hours and for a volume of 500 mL the reaction time should increase to 2 hours. This time increase may not be necessary in the final reactor if is equipped with better heating and mixing accessories.

b. Heterogeneous Catalyst Process

NCAT (North Carolina A&T State University) studied different acidic supports such as zeolite-Y, zeolite-β, alumina, and MCM-41 to provide a substrate for a Ca catalyst. Transesterification of vegetable and waste cooking oil in batch and continuous process was studied. A comparison of different substrates and Ca concentrations determined that 10wt% Ca on Zeolite-β gave the best conversion and would be used in optimization studies.

S.No	Catalyst	Temperature (°C) / Reactor	Conversion (Total ester content) (%)	Linolenic acid M.E content (%)
1	5wt%Ca-5wt%Mg on Zeolite Y	80 – batch	80.5	5.2
2	10wt% Ca on 3% Al-MCM-41	80 - batch	82.6	5.4
3	10wt% Ca on Zeolite Y	80 – batch	81.8	5.3
4	10wt% Ca on alumina	80 – continuous	83.8	5.1
5	10wt% Ca on alumina	80 – continuous	78.1	5.2
6	10wt% Ca on Zeolite-β	80 – continuous	84.3	5.0

7	10% Mg on Zeolite Y	80 – batch	53.8	5.4

Details of a batch process.

Biodiesel was produced in batch process with sulfated zirconia according to the following protocol:

1. Prepare methoxide by mixing 500 mL methanol and 0.7g of catalyst in a tube for 20 minutes;
2. Place stir bar gently inside the beaker, pour 100 ml of soybean oil into beaker, place the oil onto stir/hot plate;
3. Set hot plate to 55ºC, and stir to 400 rpm, allow oil to reach reaction temperature, the hot plate will bring the temperature to 55ºC; (this is below the evaporation temperature of methanol which is 64ºC). We want to run the reaction at a temperature below the evaporation temperature of methanol.
4. Add the methoxide to oil when the temperature has stabilized at 50ºC and keep stirring at 400 rpm.
5. Run the reaction for 1.5 hrs.

A high amount of methanol is used in these reactions, because a portion of methanol will start evaporating at 55^{o}C and only about 20% will stay in the system to complete the transesterification process. In addition, the batch reactor with magnetic mixing is to ensure both uniform and constant concentrations alcohol and catalyst during the reaction process. While alcohol has only polar group in its molecule, the oil has both polar and non-polar groups. Thus, it requires a continuous mixing of the two liquids to enhance their reaction. Mixing in these experiments was achieved with a stirrer bar operated at 400 rpm.

Reaction rates have been studied as a function of temperature, reaction time, and the molar ratio between oil and methanol. Optimization experiments were conducted over a range of temperatures from 303 K to 333 K with 10K intervals, and three molar ratios of oil to methanol (1:3, 1:5, and 1:12). At the uniform isothermal conditon of 333 K the optimum conversion rate of 88.7% was achieved within 90 minutes. The optimum molar ratio between the oil and methanol mix was determined to be 1:3.
Details of a flow process.

In order to evaluate the performance of the prepared catalysts, 2g of catalyst diluted with SiC was packed in the reactor and fixed into the reaction set up. The transesterification reaction was carried out over the catalyst by passing a mixture of waste cooking oil and methanol at 90°C under a pressure of 100-200 psi. The products obtained at different time intervals were analyzed using gas chromatograph following the European Standard EN 14103:2003 method. It was found that the oil conversion increased with increasing Ca loading over zeolite-β. Among the catalysts studied under identical experimental conditions, 10wt% Ca on zeolite-β showed 91% oil conversion with 4.7% free fatty acid content at 90ºC. Catalysts with 5 and 7 wt% Ca showed lesser oil conversion under similar experimental conditions.

Optimization of Ca content:

In order to optimize the Ca content over zeolite-β for transesterification of waste cooking oil, we carried out the transesterification reaction in a trickle bed continuous flow reactor using zeolite-β loaded with different amounts of Ca. The oil : methanol ratio was 1 : 10 and flow rate was 5 ml/min for all the reactions. Figure 1 shows the effect of Ca content on the conversion of oil to esters at different temperatures. The oil conversion is increased with increasing Ca content up to 12 wt% and catalyst with 15wt% Ca showed a slight fall in activity at all the temperatures studied. When increasing the reaction temperature from 80 to 100 ºC, a significant increase in oil conversion is observed independent of Ca content. Hence, catalyst with 12 wt% Ca was selected as optimum for the higher activity of transesterification of waste cooking oil.

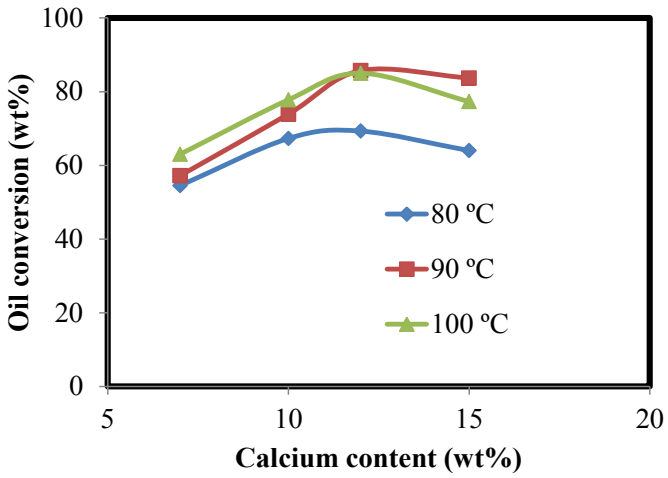


Figure 1. Effect of calcium content in Ca/zeolite-β on oil conversion at different temperatures.

Optimization of Pressure

The transesterification reaction was carried out over 10 and 12 wt% Ca on zeolite-β at different pressures and the activity results are presented in Figure 2. It was found that an increase in reaction pressure increased the activity significantly. But, higher pressure (around 400 psi) was found to decrease the activity of both 10 and 12 wt% Ca loaded catalysts significantly.

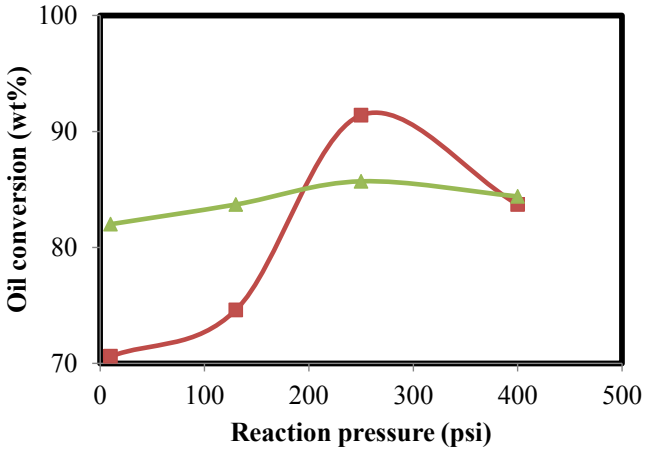


Figure 2. Effect of reaction pressure on oil conversion at 90 ºC over 10 and 12 wt% Ca on zeolite-β catalysts.

Optimization of Flow Rate:

In order to optimize the process for continuous production of biodiesel, the transesterification of waste cooking oil was carried out at different flow rates and oil to methanol mole ratio over 12 wt% Ca on zeolite-β catalyst at previously optimized reaction conditions (temperature: 100ºC; pressure: 250psi). For optimizing the feed flow rate, transesterification experiments were carried out at the flow rate of 2, 4, 6, 8 and 10 ml/min over 2g of catalyst bed at 100ºC. The oil conversion was monitored and shown in Figure 2. It was found that the oil conversion is higher at lower flow rate and decreased with increasing the flow rate. Flow rate in between 4 and 6ml/min is showing moderate level of oil conversion under the experimental conditions studied. At moderate level of flow, the activity of the catalyst is stabilized, which could be used for large scale applications.

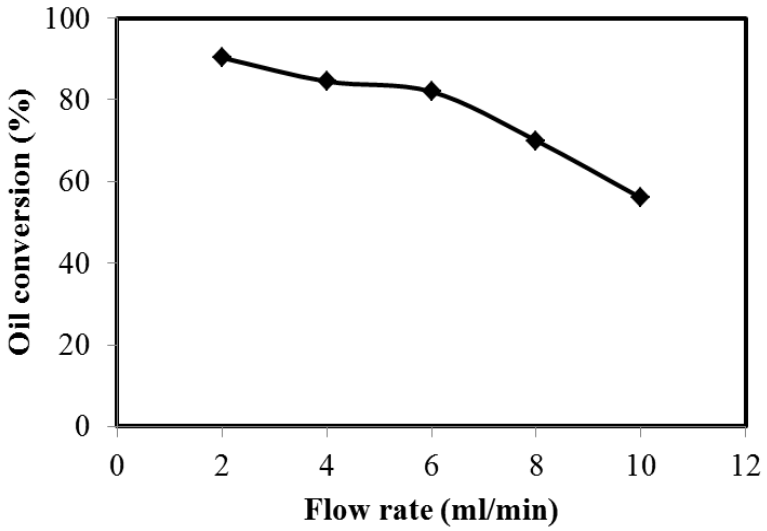


Figure 2. Effect of feed flow rate on the oil conversion over 12 wt% Ca/zeolite-β catalyst (Conditions: Temperature - 100ºC; Pressure – 250 psi)

Further, the effect of oil : methanol ratio on oil conversion was studied by monitoring the activity of the catalyst using the feed material with different oil : methanol ratio. Figure 3 represents the oil conversion of 12 wt% Ca/zeolite-β under the oil to methanol ratio from 1:3 to 1:20. It was found that the oil to methanol ratio of 10 and 12 showed moderate level of oil conversion. Hence, the oil to methanol ratio in the range of 10-12 is found to be optimum even though the higher ratios showed better oil conversion. It is clear from the activity studies that excess methanol in the reactant favors oil conversion and hence the biodiesel production.

Optimization of Methanol Content:

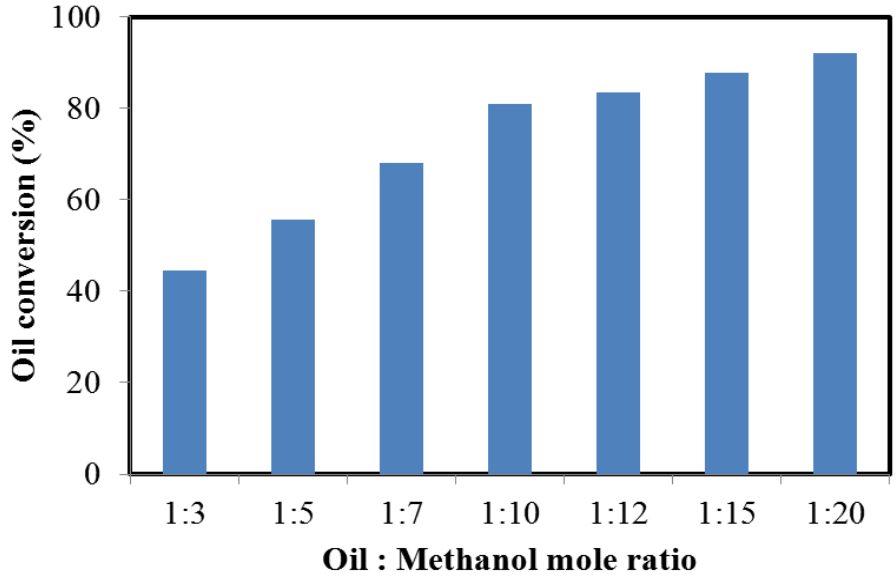


Figure 3. Effect of oil : methanol ratio on the oil conversion over 12 wt% Ca/zeolite-β (conditions: temperature – 100 ºC, pressure – 250 psi, flow rate – 5 ml/min).

Based on the studies, we found that zeolite-β is more suitable support to 12 wt% Ca catalyst for transesterification of waste cooking oil. Other experimental conditions such as temperature (100 ºC),

pressure (250 psi), flow rate (4-6 ml/min/2g of catalyst), oil : methanol mole ratio (10-12) were optimized for the continuous production of biodiesel by transesterification process using waste cooking oil.

C. Prototype Reactor Design

Original Hypothesis

The original goal of the project was the creation on an efficient biodiesel reactor. For this purpose the original design was a reactor that has a heterogeneous catalyst that can be recovered, and thus more efficient then a homogeneous catalyst that it is lost after reaction. Other advantages of using the heterogeneous catalyst is that the catalyst is less corrosive and the reactor can be build using less expensive materials, and the separation procedure can be simplified avoid the formation of soapy water, thus allowing a more efficient method for the synthesis of biodiesel.

Following the first peer-review meeting in January 2011, at the beginning of the project, the reviewers suggested developing equally a procedure for homogenous catalysis for comparison purposes. Following this advice our team decided to use a phase transfer catalyst, that cannot be recovered but present equally the advantage of simplifying the purification method and being less corrosive.

Approached used

Homogeneous reactor design

As mentioned earlier the choice for a homogeneous catalyst was a phase transfer catalyst. The advantage of these catalysts is that is less corrosive, is used in smaller concentration because the phase transfer proprieties allow a better mixing of the polar and nonpolar media, and also the purification of the fuel will be easier. The disadvantage of this process is that the catalyst cannot be recovered. After screening two catalysts were the most promising choline hydroxide (ChOH) and tetramethyl ammonium hydroxide (TMAH).

Following the procedure optimization, a crude lab-scale prototype reactor has been constructed. In terms of further optimization of the reactor, we have determined that the reactor type will be a batch reactor and should be equipped with an efficient heating and mixing system. Additionally the reactor should contain:

(1) Mixing container –for pretreatment
(2) Filtering column – for pretreatment and purification
(3) Separatory container
(4) Distillation column – for methanol recovery

The bench-scale prototype was assembled. The following picture shows the bench top reactor. The components are a three neck flask, were the reactants are mixed and take place the reaction and a distill head equipped with a condenser that allows the recovery of methanol. The reactor is heated using a mantle that allows effective the stirring of the reaction mixture.

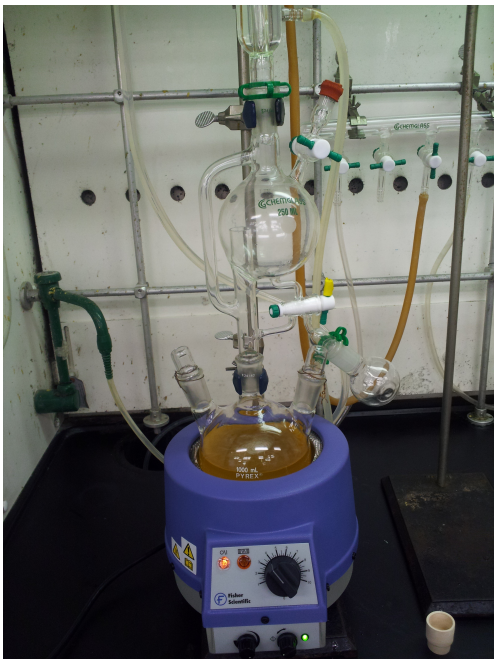


Figure 1

Heterogeneous catalyst process

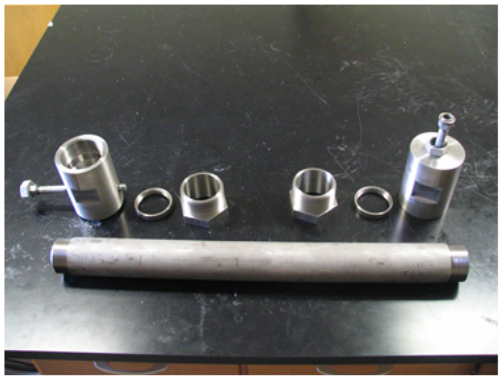
The catalyst of choice for the heterogeneous process is a Zeolite. This catalyst present the advantage that has an acidic and basic catalytic surface that allow the simultaneous conversion of both the glycerides and free fatty acids (FFA), thus increasing the conversion. After screening and procedure development the catalyst that was selected is Calcium on Zeolite β (Ca-β).

A plug-flow reactor has been designed to operate inside a Thermo Scientific Lindberg tube furnace. Furnace will maintain a steady temperature inside the stainless steel reactor. A NI Labview-based data acquisition unit will be used to record the reaction temperature, pressure and flow rate. Below are some specifications of the above reactor:

(1) Type: Plug flow reactor (PFR)
(2) Materials: stainless steel
(3) Dimensions: 2” in diameter x 25” in length
(4) Effective reactor volume: 1 liter
(5) Maximum flow rate: 250 ml/min or ~4 Gal/h

The **Figure 2** shows the various components of the PFR rector.

Various Components of the PFR



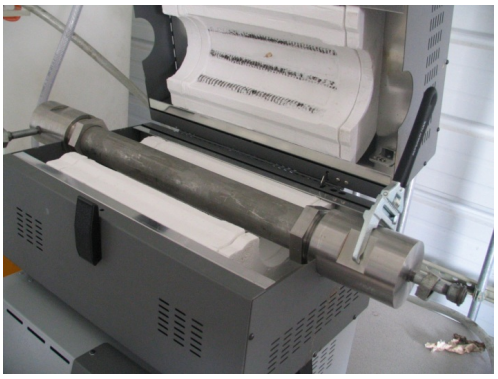


Figure 2

Results: problems encountered and departure from planned methodology

Homogeneous bench top-reactor

The homogeneous bench top reactor was tested and the results are presented in the **Table 1**. The reaction conditions for **Expt. 1** were developed in our lab. Despite the good conversion, using a large excess of methanol (28 equivalents) will increase the reaction cost due to the fact that the methanol distillation will consume a lot of energy and time. A more cost-effective procedure could use an increased amount of catalyst, (**Expt. 2** and **3**) and less methanol (6 equivalents). Optimization of conditions is ongoing.

A variation of **Expt. 4** was describe in the literature (Weidner et al., 2011), and the large amount of catalyst necessary for the reaction raises the cost of the process, despite that the fact that no distillation of the excess methanol is necessary. **Expt. 5** demonstrates that significantly less catalyst can be used since this reaction has a high conversion rate, meeting the ASTM D6584 standard of containing less than 0.24% free and total glycerin, however, it used substantially less catalyst than **Expt. 4**. The optimization conditions are still under study.

Expt. 6 is the standard procedure using KOH and was performed for the purpose of comparison. We can see that using pre-treated used vegetable oil (**Expt. 1 vs. 2**) requires the addition of a larger quantity of catalyst. Because used vegetable oil is a fuel stock that is more likely to be used by the farmers, work is underway to determining the relation between the acid value of the oil (calculated by titration) and the amount of additional catalyst necessary for the reaction.

By comparing **Expts. 7-9**, we can determine that it is not an advantage to mix the two phase transfer catalysts. **Expt 10** show that the same amount of KOH and phase transfer catalyst, in this case TMAH, can be used instead.

Table. 1. Reactions conditions and results

Expt.	Type of oil	Moles of oil[1]	Moles of MeOH	Catalyst used	Mole % catalyst[2]	% Conversion (m/m%)[3]	Percent Weight[4]
1	Pure canola	0.27	7.5	TMAH	1%	99.15%	97%
2	Used	0.49	2.81	TMAH	4%	74.62%	92%

	vegetable						
3	Used vegetable	0.49	2.81	ChOH	5%	83.20%	91%
4	Pure soybean	0.49	2.81	ChOH	17%	98.77%	94%
5	Pure vegetable	0.49	2.81	ChOH	10%	98.05%	89%
6	Pure vegetable	0.49	2.81	KOH	13%	99.2%	86%
7	Pure soybean	0.49	2.81	TMAH & ChOH	2% & 2%	79.85%	78%
8	Pure soybean	0.49	2.81	TMAH	3%	76.11%	89%
9	Pure soybean	0.49	2.81	ChOH	5%	85.98%	93%
10	Used vegetable	0.49	2.81	KOH & TMAH	4% & 1%	75.58%	90%
11	Used vegetable	0.49	2.81	KOH	13%	95.99%	99%

1. Moles of oil is approximate since different fatty acids will give different molar masses.
2. Relative to moles of oil.
3. From GC-FID data
4. % by mass biodiesel isolated to mass of oil reacted

Heterogeneous PFR reactor

Process optimization of Ca-β in PBR system

The process is designed to optimize the thermal operating conditions as well as the optimum molar ratio effect for the transesterification reaction in a continuous system. The first heat exchanger will heat up the feed (to the targeted temperature) before sending it to the PBR, while the second heat exchanger will cool down the PBR output. The second heat exchanger is designed to entrap the evaporated method as all of the targeted temperatures are above the boiling point of methanol. The PBR dimensions are designed to be:

1) The diameter is 2 inches (5.08 cm).
2) The length is 25 inches.
3) The effective length is 20 inches (50.08 cm).
4) The effective volume is 1029.63 ml (1 Liter).

The PBR reactor will be filled with 5 inches of glass fiber, 18.68 g of Ca-β, glass pits and silicon Carbide. The loaded amounts of silicon carbide and glass pits are based on the reactor's free volume calculations. The process will be scaled down in which the specified amount of loaded catalyst matches the targeted oil to methanol molar ratios. Silicon carbide is chemically an inert compound; however, it plays a crucial role in facilitating the transesterification process. Silicon carbide as well as the glass pits will inhibit the pressure build-up inside the PBR reactor.

The loaded glass fiber mesh size will be chosen according to the size of nanoscaled Ca-β. The catalyst will go through molecular sieving before loading to the rector. This will ensure that, all of the catalyst will be entrapped by the glass fiber inside the reactor.

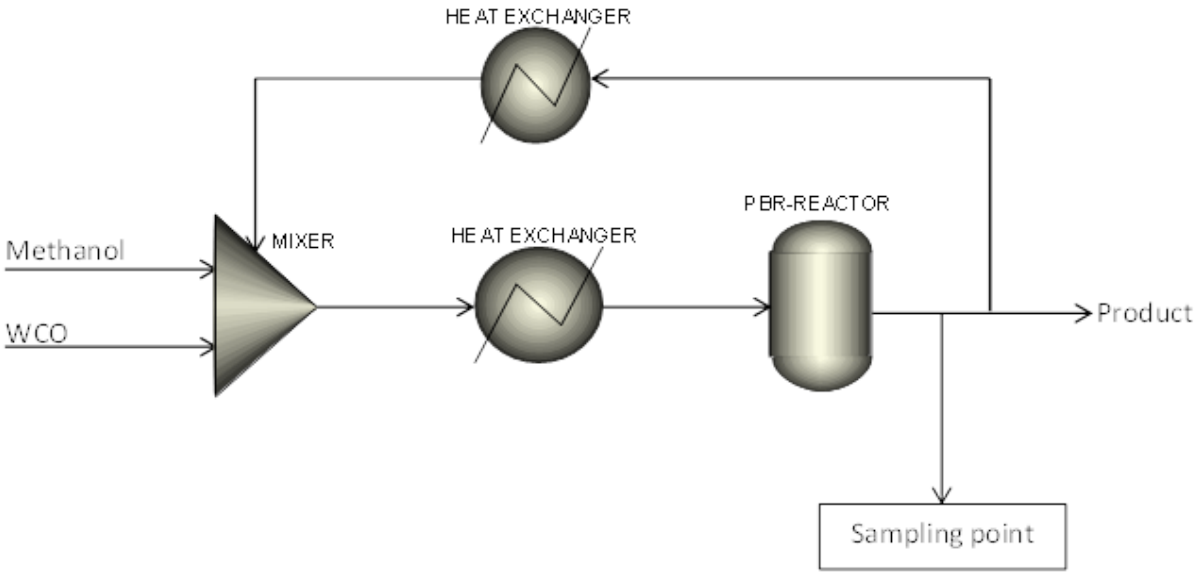


Figure 3:
Process Flow Diagram of the Transesterification Reaction in a Packed-Bed Reactor

Experiment design

The molar ratio of oil to methanol will be manipulated by varying the flow rates of methanol and oil in the feed line. The analysis will be with respect to the conversion and the yield calculations. When the analysis is finalized, the output should be the optimum temperature, optimum oil to methanol molar ratio and the lifetime of Ca-β catalyst

Table 2- Matrix of Experimental Conditions

Experiment #	Temperature	Molar ratio	Conversion
1	T1	M1	-
2	T1	M2	-
3	T1	M3	-
4	T2	M1	-
5	T2	M2	-
6	T2	M3	-
7	T3	M1	-
8	T3	M2	-
9	T3	M3	-
10	T1	M1	-
11	T2	M1	-
12	T3	M1	-
13	T1	M2	-
14	T2	M2	-
15	T3	M2	-
16	T1	M3	-
17	T2	M3	-
18	T3	M3	-

Notes:

T1 = 70 ^{o} C M1 = 1:3

T2 = 90 ^{o}C M2 = 1:5

T3 = 120 ^{o}C M3 = 1:10

Results and discussion

The results will be expressed in the terms of the temperature as well the molar ratio effects. The process is fully optimized; those optimization conditions are used to record the life time of the catalyst. The resulting life time is related to the previously mentioned loading of Calcium on Zeolite β.

Table 3- Effect of Oil/Methanol Molar ratio on Transesterification Rate

Experiment #	Temperature	Molar ratio	Conversion
1	T1 (70 ^{o})	M1 (1:3)	55.1
2	T1 (70 ^{o})	M2 (1:5)	59
3	T1 (70 ^{o})	M3 (1:10)	64.1
4	T2 (90 ^{o})	M1 (1:3)	63.1
5	T2 (90 ^{o})	M2 (1:5)	74.6
6	T2 (90 ^{o})	M3 (1:10)	80
7	T3 (120 ^{o})	M1 (1:3)	76.9
8	T3 (120 ^{o})	M2 (1:5)	79.1
9	T3 (120 ^{o})	M3 (1:10)	85.2

In these 9 experiments, the molar ratio effect is recorded by manipulating the flow rates of waste cooking oil and methanol in the input line. The results show that, in experiment 6 and 9, where the molar ratios of oil to methanol were 1:10, higher conversion rates of FFA into methyl-esters are recorded (80 % and 85.2 %). From these experimental data we can conclude that for the specified Ca-β composition, the best molar ratio under the specified temperature conditions is 1:10.

Table 4- Effect of temperature on Transesterification Rate

Experiment #	Temperature	Molar ratio	Conversion
10	T1	M1	55.3
11	T2	M1	62.8
12	T3	M1	76.6
13	T1	M2	58.8
14	T2	M2	74.3
15	T3	M2	79.4
16	T1	M3	64.2
17	T2	M3	80.2
18	T3	M3	84.9

The experiments ranging from 10 to 18 are specifically targeting the temperature effect on the continuous process in PBR. Experiments 17 and 18 showed higher conversion percentages compared to the rest. This will lead to a major fact that, the activation energy of this catalyst is between 90 ^{0} C and 120^{0} C. These obtained results can be used and proved by using Arrhenius law in kinetics to further determine this reaction rate as well as the reaction constant.

The set of experiments ranging from 10 to 18 (the temperature effect table) , these experiments have been used in replicate to the sets ranging from 1 to 9. The replication of those two different sets has been done to study the reproducibility of the resulting data as well as studying the temperature effect.

Table 5- Life time of Ca-β Catalyst

Sample #	Time (h)	Conversion (w%)
1	12	72.2
2	24	85.18
3	48	85.2
4	72	85.1
5	84	63.4

Also, in this study, the life time of Ca-β is detected. Samples were collected on different time intervals and the corresponding conversion percentages as well as the yield was recorded. The time interval was a sample/12h. The five experimenters of the catalyst life time were run after the process being optimized. The catalyst retained the conversion efficiency when exposed to a re-calcination step at 500^{O} C for 5 hours.

Conclusion: assessment of the impact of variations on project results.

Homogeneous bench top-reactor

Concerning the optimization reaction conditions, further work is necessary to identify the most efficient and cost effective method. Although, the high cost of ChOH and TMAH catalysts compared to potassium hydroxide presently prevent the widespread use of the method described, possible increased demand for these compounds could lower their prices, thus making this method a viable alternative.

Heterogeneous PFR reactor

With respect to the heterogeneous process several conclusions can be drawn. Calcium on Zeolite β showed higher surface area of 534 m^2/g. the porosimeteric analysis of this catalyst lays under the mesoporous range. The optimum conditions related to the calcium loading on Zeolite β is 120 ^{o}C as the temperate condition and 1:10 as the molar ratio of oil to methanol. The optimum temperature represents the activation energy of this catalyst under the given inputs. Further analysis has been done to record the life time of the catalyst. The catalyst maintained the same conversion efficiency for 72 h. It has experimentally been shown that, after 72 h, the active sites along the catalyst surface were blocked due to the mass transfer related issues. However, the active sites on Ca-β were recovered by re-calcinating the catalyst at 500 ^{o}C for 5-hours.

This procedure it is more expensive then the homogeneous catalyst process. The catalyst it is not commercially available, and the synthesis method is expensive and complex. Another issue is the blockage of active sites after 72h. The recovery process requires a powerful oven and a large consumption of energy. Despite these problems the efficiency of the process can be improved if private companies decide to produce this catalyst in larger quantities and in using a cost efficient synthesis.

D. Economic Analysis

The Economic Analysis does the feasibility study of producing biodiesel using feedstock. The goal of the analysis is to see whether there will be energy cost savings for famers to have a small scale biodiesel production. We use a simple model where farmers grow feedstock and use it to produce biodiesel to fuel their farming vehicles. The analysis considers various costs in the process of making biodiesel, the fuel production per year and the market price of diesel.

D.1 Determine the cost to produce one gallon of biodiesel

The total production costs are divided into two parts: operation costs and fixed costs. The operation costs include costs of feedstock (costs of growing and crushing canola seeds), costs of methanol, costs of catalyst and other costs (insurance, tax, etc.). The fixed costs include costs of reactor and refining equipment and the investment in the building and the land.

We were able to find a Biodiesel Production Worksheet designed by Ontario Ministry of Agriculture, Food and Rural Affairs as our base model for our production cost analysis. The worksheet is designed for producers considering small scale oilseed processing and biodiesel production. The worksheet allows us to enter crop prices, equipment (and other capital) costs, operating costs and calculate the cash flow and income/expense. We are working with three separate worksheets: oilseed crushing worksheet, biodiesel production worksheet and income-expense cash-flow worksheet. In the oilseed crushing worksheet, we have different feed stock input so that we can compare their costs of production. Also, we compare two different crushing equipment with different crushing capacities. One piece of equipment is designed to crush 5 tons per day, while the other is designed to crush 10 tons per day. In the biodiesel production worksheet, we compare two different reactors with different capacities. One reactor is designed to process 40 gallons per batch, while the other reactor is designed to process 80 gallons per batch. In the income-expense cash-flow worksheet, we provide both cash flow financial analysis and income/expense economic analysis for two scenarios. In the first scenario, the smaller crushing equipment is used in conjunction with the smaller reactor. In the second scenario, the bigger crushing equipment is used in conjunction with the bigger reactor.

We have found that it is not economical for the farmers to produce biodiesel on their own. The result applies to both small-scale and large-scale reactors. The underlying reason is the high cost of raising feedstock. Without adding the cost of reactor, the cost of raising feedstock itself is $5.00 per gallon. Therefore, without compensating farmers' partial growing costs, it would be difficult to encourage local farmers to proceed with this model.

In order to make it economically feasible, potential remedies are 1) government subsidy, 2) double use of oil which means selling cooking oil and recovering the oil to make biodiesel, 3) a comprehensive economic model which integrates other industries such as agricultural, chemical, biofuel, energy industries etc.

D.2 an Alternative model

We have discovered the successful California-based 'Fryer to Fuel' program that converts local waste oil into biodiesel. To see the possibility to replicate that program in this region, we have started collaborative efforts with regional partners, including the Biofuels Center of North Carolina, the NC Southeast Economic Development Partnership, Robeson Community College, Indigenous Biosolutions, LLC. Also, we have contacted some local restaurants. Our findings show that many restaurants are interested in participating in such a program. If we were able to build such program, insufficient restaurant oil supply would not be a problem. Additionally, We arranged a meeting with STARWORKS, who showed interest in collaborating with UNCP and American Indian Solutions to utilize their existing biodiesel production facility. We also met American Indian Solutions, Inc. Currently, they are in the process of developing a collaboration.

E. Education and Outreach

Develop links with local farming community (E.1)

Dr. Tirla has corresponded with Red Birch, Piedmont Biofuels and a number of local county extension agents in planning the workshop. The county extension agents served as a "go-between" to help facilitate outreach to the local farmers who might have an interest in the proposed technology. Dr. Tirla also attended the "Forum on the Roadmap to Meeting the BioFuels Goals of the Renewable Fuels Standard by 2022" organized by the USDA held on Oct. 27, 2011 in Raleigh, NC. Participants included

the NC Biofuels Center, NCSU, NC Solar Center, Piedmont BioFuels, Novozymes, Triangle BioFuels and NC Farm Bureau federation.

Dr. Tirla has visited a number of local farms and one attendee of the workshop has decided to grow a test plot of canola and is networking with other farmers about the prospect of forming a biodiesel coop among the local agricultural community. Throughout the project, BFT members were available to the local farming community in order to answer questions on canola cultivation and biodiesel production. We were contacted by a local university and an area entrepreneur for input and collaboration.

Also, on March 20, 2011, two members of the BFT and two UNCP students toured the Piedmont Biofuels facility in Pittsboro, NC to explore a different business model for biodiesel production. Piedmont Biofuels uses mainly waste vegetable oil as its fuelstock.

On May 23, 2011, two members of the BFT visited the Red Birch Energy facility in Bassett, VA in order to tour their biodiesel production facility.

At the workshop on July 18th, 2011 we were able to meet a number of agricultural researchers from North Carolina State University. A number of farmers, agricultural extension agents and a representative from the NC Biotechnology Center, Randall Johnson, were in attendance.

Dr. John Mattox from Fayetteville State met with the BFT faculty during our weekly meeting on February 29, 2012. Dr. Mattox indicated his interest in collaborating with the BFT on future educational and community awareness activities on alternative energy. We hope that an annual joint UNCP/FSU symposium on regional initiatives in renewable energy will be developed in the near future.

The BFT faculty met twice with Eric Locklear of Indigenous Biosolutions. Mr. Locklear built a biodiesel production facility at the UNCP Business Incubator site at ComTech on the outskirts of Pembroke. The BFT consulted with Mr. Locklear on a number of issues related to the safety of his faculty and reactor choice and dry-wash resins. Both parties have benefited from the exchange and future collaborations with Mr. Locklear seem likely and promising.

As a result of our efforts to plan a meeting for local farmers in July 2011, we contacted and developed closer contacts with Mr. Jeff Riddle of TechCorps, a company that buys and processes rape seed for a variety of purposes. In addition, the BFT was introduced to some new members of the local farming community at these meetings.

Dr. Tirla met with a local farmer to discuss the promotion of the production and use of biodiesel among local farmers.

Dr. Tirla was contacted by Dr. Reginald Oxendine, an entrepreneur with non-profit who wants to assemble a reactor for conducting outreach and pilot for testing to demonstrate and encourage biodiesel production in the local area. Currently the BFT and Dr. Oxendine are looking for funding opportunities to be able to acquire this reactor.

Hold workshops for local farmers (E.1.DL.1)

The first workshop for local farmers was held on February 11, 2011. It was held at The Regional Center for Economic, Community, and Professional Development at The University of North Carolina at Pembroke at the Carolina Commerce and Technology Center. Participants included Red Birch, Piedmont Biofuels and a number of local county extension agents. A number of local farmers and extension agents attended and were given a chance to learn more about the process of producing biodiesel from a variety of perspective.

A workshop for the local agricultural community on the technical aspects related to planting, growing and harvesting canola was held on July 18, 2011. In consultation with the agricultural extension agents and

the Robeson County Farm Bureau, this workshop was held at the Robeson County Farm Bureau in Lumberton, NC. Two main goals of this workshop were to train local farmers about canola growth allowing more of them to grow the crop which might, in turn, facilitate the formation of a cooperative among local farmers. Speakers included: Earl Hendrix, a local canola farmer, Dr. Kim Tungate, Energy Crops Program Manager for the NC Solar Center, John Garner, an NC State Graduate Student studying canola cultivation, and Gary Sink of Red Birch Energy, a biodiesel producer. The workshop was well attended with several local farmers in attendance.

Two farmers meeting were held in the summer of 2012. On July 13' 2012 a meeting was held at the COMTech conference center in Pembroke, NC and on September 7, 2012 a meeting in the Regional Center furthered our connections with the local agricultural and fuelstock producers. The July meeting featured Jeff Riddle of Technology Crops International and Eric Locklear of Indigenous Biosolutions. The September meeting featured Jeff Riddle and a colleague from TechCrops. Jeff Riddle from TechCrops will be addressing the economics of rape seed production for biodiesel use, Eric Locklear will be relaying his experiences with setting up a biodiesel production facility, and Earl and Gary Hendrix, two local rapeseed growers will talk about cultivation of rapeseed as a fuelstock.

The final farmer's meeting was held July 12th, 2013. At this meeting held at the ComTech conference center, the BFT reviewed the finding so of the project, both scientific and economic.

Create outreach materials for farming community (E.2)
A trifold brochure was designed and printed and is now available at several locations at UNCP.

Develop material for course on Biofuel (E.4)
BFT members developed a website which will function as an educational tool for students and community members concerning all aspects of biodiesel production. The site http://www.uncp2.edu/biofuels/.

An organic chemistry laboratory experiment on the production and analysis of biodiesel produced by the reaction of vegetable oil and methanol with catalytic choline hydroxide was demonstrated to be successfully achievable by students.

In addition, student researchers from the BFT group presented research on reaction optimization and using IR to analyze biodiesel samples at one national, two regional and three local undergraduate research/chemistry conferences.

Demonstrate biofuel production at a local farm (E.3)
The large scale portable reactors which had previously been owned and supported by the university has been given away and so although the BFT looked for other opportunities to carry out this demonstration including conducting a large-scale test at the NC Biofuels Center in Oxford NC, ultimately it was impossible to purchase a large enough quantity of choline hydroxide for the reactor and so this demonstration was never achieved.

F. Project Management and Reporting

This quarterly reports as well as Financial Report SF-425 were submitted on/by Oct. 30th, 2010 January 30th, 2011, April 30th, 2011, July 30th, 2011, October 30th, 2011, January 30th, 2012, April 30th 2012, July 30th, 2012, October 30th, 2012, January 30th, 2013, April 30th, 2013, October 30th 2013, and January 30th, 2014.

6. a. Publications and presentations

1. Tirla; T. Dooling; S. Harrelson; R. Smith; D. Hunt*; C. McKee* "Using IR Spectroscopy to determine Biodiesel Conversion", *Journal of Undergraduate Chemistry Research*, **2013,** *12*, 83-85.

2. Communication at 2nd Annual World Congress on Bioenergy, Xi'an, China, April 22-28, **2012**.

3. Communication at the International Conference on Pollution and Environmental Remediation, ICPER'13, Toronto, Canada, July 15-17, **2013**.

b. Website produced
www.uncp2.edu/biofuels