

ABSTRACT

JAIRAM, SUGUNA. Synthesis of Solid Base and Acid Catalysts from Agricultural Residues For Use in Fatty Acid Methyl Esters (FAMES) Production. (Under the direction of Dr. Praveen Kolar).

The goal of this research was to produce biodiesel, a mixture of fatty acid methyl esters (FAMES), facilitated by green catalysts, synthesized from agricultural waste material. The objectives were to test KI impregnated oyster shells as base catalyst and sulfonated tobacco char as acid catalyst for the production of FAMES from soybean and synthetic waste oils respectively. The catalysts were synthesized using wet impregnation of KI and H_2SO_4 respectively, followed by calcination. Surface characterization was performed for the catalysts using the techniques of Scanning Electron Microscopy (SEM), Electron Dispersive Spectroscopy (EDS), X-Ray Diffraction (XRD), Brunaur-Emmett-Teller surface area estimation (BET) and Surface acidity. The catalysts were separately tested in batch configurations; the KI impregnated oyster shell on virgin soybean oil; and H_2SO_4 impregnated carbonized tobacco stalk on oleic acid (Free Fatty Acid) esterification. Results indicated that 86% conversion was achieved through base catalysis in a batch reactor under best suited conditions of 50 °C, 1:10 oil to methanol ratio, 1 g catalyst loading, at 3 mmol/g impregnation of KI on calcined oyster shells. Reactions went to near completion with nearly 98% conversion through acid catalysis of oleic acid in methanol under the conditions of 6 h soaking of carbon in concentrated H_2SO_4 , 4 h reaction time, 60 °C and 1:24 FFA to methanol ratio, with a 1 g catalyst loading. These were then combined in a continuous, sequential flow reactor to convert waste oil with high FFA content into biodiesel. The kinetics of both the catalysts was studied in both schemes and reusability or longevity test was conducted to

establish durability of the catalysts Considering the impact of tobacco production in the state of North Carolina, and the growing aquaculture industry in the eastern states of the United States, the results presented in this research could have significant and positive economic impact.

Synthesis of Solid Base and Acid Catalysts from Agricultural Residues For Use in Fatty Acid
Methyl Esters (FAMES) Production

by
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A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the degree of
Master of Science

Biological and Agricultural Engineering

Raleigh, North Carolina

2011

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DEDICATION

I dedicate this work to my family and friends back in India, who have supported me through every walk of my life and my friends here in Raleigh who have made this my second home.

BIOGRAPHY

Suguna was born on the 22nd of February, 1988 in Hyderabad, India. She moved to Chennai when she was 12 and completed her schooling there. She then pursued her B.Tech in Biotechnology at SASTRA University and developed an interest for research in bio-fuels. Immediately after receiving her degree in June 2009, she moved to the US to pursue her graduate studies. She started working at the Biological and Agricultural Engineering department at North Carolina State University in Aug 2009 and is moving to University of Florida, Gainesville to do her doctoral studies in the Agricultural and Biological Engineering department in the Fall of 2011.

ACKNOWLEDGMENTS

There are a lot of people I would like to thank for their help, support and guidance through my 2 years of research at NCSU. Foremost, my parents who have taken an active interest in my work and have read every paper, article and manuscript I have written for every course! Their support is paramount in any form of success I achieve.

I would like to thank Dr. Praveen Kolar, for his continuous guidance, through every one of the numerous roadblocks through this project. I would also like to thank Dr. Ratna Sharma and Dr. Osborne for being on my committee and for their constant feed-back. My gratitude for the completion of my work is extended to the Environmental Analysis Lab in the department, Dr. Roger McFeeters and Mr. Seth Fornea of USDA-ARS for help with biodiesel analysis, Chuck Mooney and Roberto Garcia for catalyst surface characterization, Dr. Jack Davis for help with density-viscosity studies; and North Carolina Agricultural Research Service for providing funding for this research.

My heartfelt thanks goes out to all my friends at Raleigh; specifically, Vikram Palagummi and Sameer Suresh my coffee buddies, Kiran Kumar Ramesh for our awesome weekly rituals, Aditya Sreenivas Balu for the music, Aditya Ravi, for being my dad away from home, Giridhar Murlidharan for always being my vent out punch-bag and Veronica Mbaneme, for all the help on and off work. Lastly, I would like to acknowledge the Global Village Coffee House, for helping me beat the stress associated with every pitfall I have faced through the course of my studies at NCSU.

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1. Introduction

Since the Industrial revolution in the 19th century, there has been a race towards industrialization and mechanization and a trend for increased energy utilization. As a result of this, the global industry now faces a dual problem; one of a fuel crisis and one of ecological damage. The rapid growth in the industrial sector over the last century has scarred the ecosystem and has depleted majority of the non-renewable sources of energy. The International Energy Agency (IEA) [1] has released a world energy outlook, 2009 fact sheet which paints a rather bleak but unfortunately real picture regarding the energy situation worldwide. In the report, the IEA predicted a 40% increased energy demand as compared to 2007 by 2020 and a 70% increased demand by 2030. Although it is projected that the natural oil reserves will serve this increased demand till 2030, it will have a profound effect on the environment and could lead to dire consequences on public health due to poor air quality and pollution, especially in developing countries. This would be due to a higher margin in their energy demand. Additionally, majority of fuel used by both developed and developing nations is not indigenous. This leads to a dependency on the oil suppliers and could lead to political conflicts [2]. Economically, as a large portion of the easily accessible sources of fuel are depleted, the remaining sources are becoming more expensive to extract. Although new oil reserves have been found in the arctic, which accounts for about 13% of the world's undiscovered oil and 30% of its undiscovered natural gas, extraction at such harsh climatic conditions are estimated to be very expensive [3]. This new find has also created significant political combat between Canada, USA and Russia for ownership of the oil proving the stress

here is not only economical and environmental but also political. To overcome this stress on both the environment and world economics, it is necessary to reduce the dependence on this finite source of energy.

In view of this, stringent environmental regulations have been enforced to control emissions and improve the existing situation. Efforts are being made in every field to reduce the percentage dependence on fossil fuels to meet the growing energy needs. Renewable sources are being developed world wide to combat increasing fuel prices, greenhouse gas emission and wide spread ecological pollution.

2. Biomass - a resource for energy production.

Biomass as a source for energy has been under focus recently due to ready availability, local production of feed stock, usability of waste products as alternative feedstock, and reduced emissions from hence produced bio-fuels. The National Renewable Energy Laboratory (NREL) recognizes largely two forms of bio based fuels; bio-ethanol and bio-diesel. The focus of this work will be on biodiesel.

2.1 Biodiesel: Origin, usage and advantages

The exploratory production of biodiesel from vegetable oil stemmed from the initial idea of using vegetable oil directly as a fuel. It is documented that the original idea in the building of the diesel engine was to use vegetable oil as an alternate fuel [4]. The advantages of vegetable oil as fuel sources are the inherent heat content (80% of diesel fuel), renewability and ready availability [5]. The first diesel engine built and displayed at the Paris Exhibition

in 1900 was made with the intention of using vegetable oil as fuel. Peanut oil was used at the exhibition to demonstrate that oil can be used as an alternate fuel. However, this had some major drawbacks. The high viscosity of the oil would lead to poor atomization of fuel in the combustion chamber which would result in operational problems and engine deposits.

Among several methods, transesterification of oil was one of the proposed methods for the reduction of viscosity of the oil based fuel. Transesterification of oil is the reaction of oil with an organic alcohol (usually methanol) in the presence of a catalyst to produce fatty acid methyl (alkyl) esters and glycerol. The mixture of fatty acid methyl esters hence produced is known as biodiesel.

Biodiesel is a naturally oxygenated, cleaner fuel replacement to petroleum diesel produced by the transesterification of triglycerides such as used and refined vegetable oils, grease and fat. Bio-diesel has a large number of advantages. It is safe, renewable, non-toxic, biodegradable [4] and has a lower concentration of sulfur compounds [6]. Biodiesel can be transported using existing pipelines for fuel transport and can also directly be used in the existing diesel engines [7]. According to a study conducted by Sheehan et al in 1998 for the usage of biodiesel in urban buses, [8] tail pipe emissions of particulates from busses that use biodiesel were reported to reduce by 68%. Additionally, tailpipe emissions of SO_x are eliminated.

Considering these advantages, the usability of biodiesel in an engine has been explored and the concept of a blend fuel came into being, wherein a blend of biodiesel and petroleum diesel are used in existing diesel engines.

Although biodiesel can directly be used in existing engines, its high solvation property leads to its contamination as it dissolves residues in the fuel tank and fuel line. These can cause clogging in the fuel filter so either a change would be necessary in the engine design would be to replace or increase the size of the filters [9] or a biodiesel blend may be used. B20 is a common blend of 20% biodiesel with 80% petroleum diesel which is being marketed to be used directly in existing engines. The government of the United States, in an effort to promote the usage and production of this clean fuel, has introduced initiative for both the consumer and producer in the direction of promoting biodiesel. Blends of B20 and above qualify for alternative fuel credits under the Energy Policy Act of 1992. Also, production facilities are entitled to a reduction in state and federal tax based on their contribution towards the usage of biodiesel (1% for a large scale facility and 0.1% for a smaller facility) [10].

3. Bio-diesel production process:

Biodiesel is a combination of Fatty Acid Methyl Esters (FAME) that is formed on transesterification of tri glycerides. Transesterification, (also called alcoholysis) is a reaction between fat or oil with alcohol to form esters and glycerol.

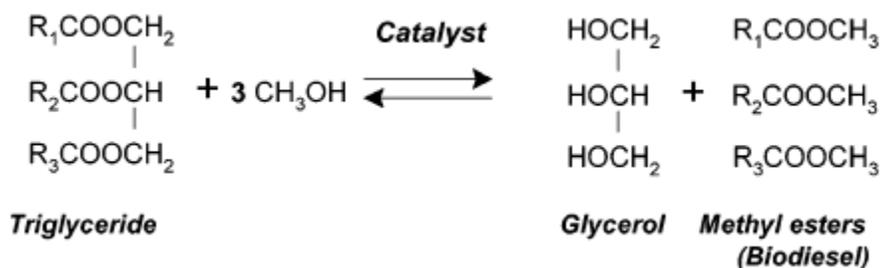


Figure 1: Reaction scheme for transesterification of oil to biodiesel using methanol and catalyst. One mole of triglyceride reacts with three moles of methanol to produce one mole each of methyl esters and glycerol.

Since it is a reversible reaction, excess alcohol is added to ensure the forward reaction is favored. Methanol and ethanol are preferred alcohols used in this reaction. This is due to their low cost, polarity, small size of carbon chain and solubility in KOH and NaOH [11] which are widely used as catalysts. This reaction may proceed through acid, base or enzyme catalyzed schemes or the supercritical methanol scheme.

3.1 Homogeneous catalysts

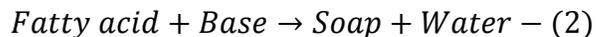
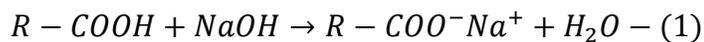
In this scheme, the oil, methanol and catalyst are in the liquid phase. Although oil is immiscible in the alcohol, it is general practice to use a catalyst that is soluble in the alcohol to reduce inter phase mass transfer limitations.

3.1.1 Acid catalyzed scheme:

In this process, an acidic group is used to aid the transesterification process. Acid catalysis for transesterification has been studied and it has been documented that these reactions require large amounts of methanol, high reaction temperature and a long reaction time.

Despite these, this scheme is generally the choice when the oil source is a waste or used oil with high Free Fatty Acid (FFA) content, generally greater than 1% [12].

When FFA content is high, on addition of the alcohol, soap formation occurs, which hinders the biodiesel production and contaminates the product in addition to reducing the activity of the catalyst. Soap is the salt of a fatty acid and is known for its ability to adhere to both organic and inorganic groups.



Equation 1 and 2: Formation of soap in the presence of free fatty acid. This is the side reaction that reduces biodiesel yield in the presence of free fatty acids and water in the feed oil.

From the above scheme, it is clear that along with soap, water is also formed, the presence of which in fuels reduces its efficiency.

The mechanism for acid catalyzed transesterification is as follows:

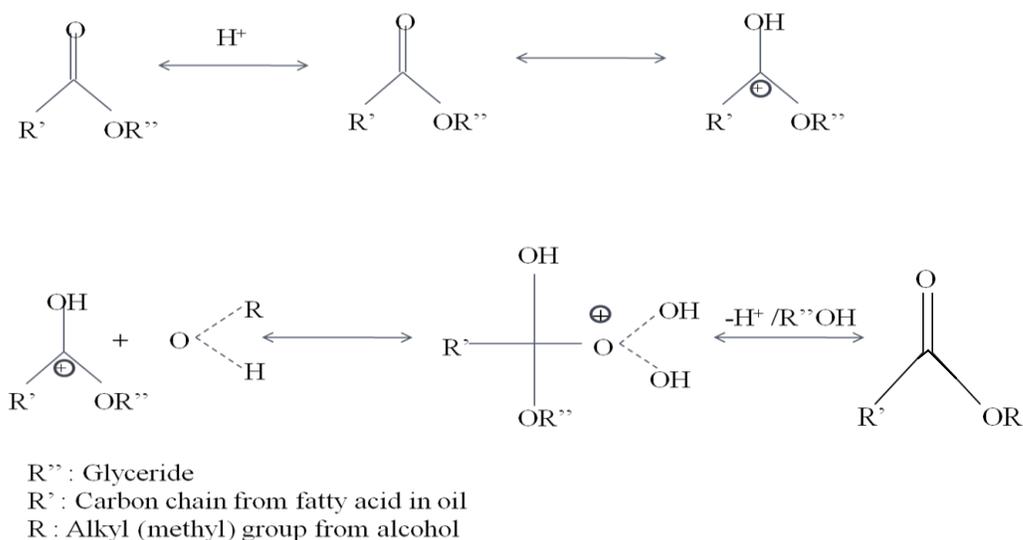


Figure 2: Mechanism for acid catalyzed reaction. Proton from the acid attacks the carbonyl group on the fatty acid forming an unstable intermediate with which the methanol reacts to produce the fatty acid methyl ester.

For a free fatty acid and methanol, the end product along with the methyl ester will be water.

A lot of research has been done on the usability of acids as catalysts. Though high conversion rates have been achieved in many tests, the oil to methanol ratio has been found to be alarmingly high. Values range from 1:30 at boiling point of methanol for a 69% conversion at 18 h [14], 1:74 to 1:250 at 80 °C [15], 1:100 at 64 °C with a heterogeneous catalyst, and at elevated temperatures of about 95 °C in 18 h, ratio was estimated at 30:1 for a reaction time of 6 h in a sample of trap grease that contained 50% free fatty acid [16]. The use of acid catalysis is still justified, being an economical option that can enable the usage of waste oil resources for the production of biodiesel.

3.1.2 Alkali catalyzed scheme:

In this process, a base is used to catalyze the transesterification process. The mechanism is as follows:

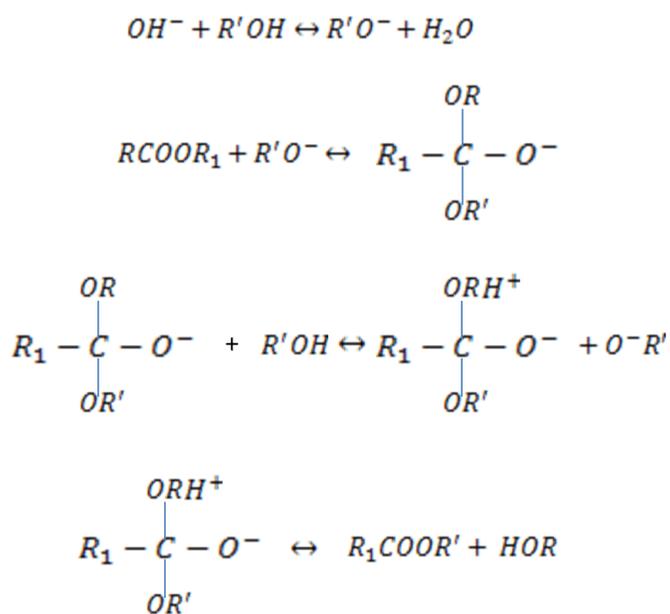


Figure 3: Mechanism for base catalyzed reaction. The hydroxyl group of the catalyst attacks the methanol molecule creating a carbanion (negatively charged carbon atom). This reacts with the triglyceride to produce the ester.

Here, R-OH is a diglyceride, R₁ is a long chain alkyl group and R' the methyl group.

For an alkali catalyzed scheme, the system should be void of water as its presence can trigger off soap formation or saponification. Soap lowers biodiesel yield and renders separation of esters, glyceride and soap very difficult [11]. Alkali catalyzed process is industrially used for the preparation of biodiesel from virgin oil sources.

3.1.3 Supercritical methanol process

In this process, supercritical fluid conditions are enforced on methanol and hence, transesterification proceeds without the requirement of a catalyst. In the usage of waste oil however, ferric sulfate is used as catalyst for a two step process aided biodiesel production process. The ferric sulfate catalyses esterification of the free fatty acids and the transesterification process to produce FAME is followed at the supercritical conditions of methanol. This is at high temperatures of around 350 °C and oil to alcohol ratio ranging from 1:10 to 1:50 and 100 bar pressure. The yield is found in the range of 50 to 65% in the first 15 min [17].

Although the efficiency of this method is high, the conditions for the reaction are very harsh and energy consuming.

3.2 Enzyme catalyzed scheme

The move towards enzyme catalyzed transesterification was based on the difficulties faced in the recovery of the acid and base homogeneous catalysts and in purification of the same [18]. Also, an enzyme based reaction is a greener approach in any industrial process. Recent studies show that lipase enzymes can catalyze transesterification reactions and tolerates water content of oil thereby reducing soap formation as a by reaction [19]. Though the high cost of the enzymes is a major pitfall in this scheme, Nouredini et al., (2005) [20] concluded that immobilization is a viable option for effective reuse of the catalyst and purification of

products. Studies done on immobilized enzymes in various matrices have shown promising results. Immobilization on microporous polymerized matrix containing aldehyde groups was used to produce 97% yield from pure sunflower oil and 90.5% from waste oil in 10 h using a 1:10 oil to methanol ratio and 97% yield in a 12 h reaction using lipase immobilized in waste activated bleaching earth [19, 21].

3.3 Heterogeneous catalysis

Although homogeneous catalysts are easily obtained and give high yields, major disadvantages include high energy consumption, unwanted soap formation in the presence of water, separation of end products and recovery of alcohol [4]. Studies show that solid catalysts could prove a more economical and eco friendly alternative. In some cases, solid base catalysts can achieve conversion rates close to that from existing alkoxide systems [22]. The advantages of using heterogeneous catalysts include reusability of catalyst, insensitivity to water content and soap formation is prevented.

3.3.1 Solid acid catalysts

Homogeneous acid catalysts involve the usage of strong acids that could corrode equipment and pose handling issues. The use of heterogeneous catalysts could eliminate these problems. However, due to the presence of three different interaction phases, this system will pose additional mass transfer restrictions and could reduce reaction rates. In general, these solid catalysts are deemed satisfactory in esterification reactions if they are stable, have a large

number of strong catalytic sites, high surface hydrophobicity and high porosity. The porous structure of the catalyst is required such that the reagents can orient and react to form the product [22]. With the ability to manipulate these characteristics, zeolites have attracted attention. Zeolites can be produced with monitored pore sizes and acidic properties and with the incorporation of appropriate organic groups, can be made hydrophobic without affecting the acidic properties. Zeolites are microporous alumino-silicates. Unless modified, zeolites produce a low conversion rate of less than 10%. This could be due to diffusion limitations attributed to its bulkiness [23]. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio can be altered to control the acidity of the structure and pore size. Other options in solid acidic catalysts are sulfonated zirconia catalysts which are classified as super acidic compounds with reaction temperatures of about 140 to 160 °C but Kiss et al., (2005) [23] reported that catalyst lost about 90% of its activity after the first round which ruled out its reuse. Combinations of metal oxides of the type $(\text{Al}_2\text{O}_3)_X(\text{SnO})_Y(\text{ZnO})_Z$ have produced conversion percentages of about 80% in 4 h or reaction time [24]. Marciniuk et al., (2009) [13] documented a 95% conversion rate in 2 h using acidic lanthanum and aluminum diphosphates.

Another category of complexes being investigated are heteropolyacids. There are very strong Bronstead acids and have high acidity, oxidizing ability and thermal stability. They can be used in both homogeneous and heterogeneous reaction, based on the nature of the compound. They can be made solid by their reaction with monovalent cations, to produce a salt [25]. Tungstophosphoric acids have been studied in this regard as homogeneous and

heterogeneous catalysts. In one particular study conducted in Liverpool, UK, the esterification of hexanoic acid was observed in both states if the catalyst. At 60 °C and atmospheric pressure, nearly 100% conversion was achieved in the homogeneous scheme after 6 h of reaction and 1:20 acid to methanol ratio. In the heterogeneous scheme, approximately 45% conversion was achieved on a 15% loading of the HPA on support. A major issue through this experiment was the high leaching of the acid component. However, they did report that the intrinsic catalytic activity in both schemes was much greater than conventional acid catalysts [26]. To overcome solubility in aqueous phase, Cesium was added in varying concentrations, improving the complex's stability during the reaction and increasing reaction rates [27] [28]. Reactions were carried out at 60 °C at approximately 1:30 fatty acid to methanol ratio for 6 h. Maximum conversion was achieved as 73% with high recyclability and very low leaching [29].

Another popular catalyst structure is the use of ion exchange resins. These are co-polymers of molecules like styrene, and sulfonic acid groups, grafted on benzene. The catalytic abilities of this polymer are dependent on its swelling capability, in order for the reactants to diffuse in, react and the product to diffuse out. For this to be achieved, the number of cross-links between the polymer chains should be low, but not too low so that the matrix loses its structural integrity. In the use of these catalysts, swelling is through soaking in typically ethanol and swelling time is also now a parameter, in catalyst reaction conditions [30]. These polymers, on supports like Nafion and Amberlyst have been used in both continuous and

batch systems and have showed ranges of conversion efficiencies from 46% to 100% when used under moderate conditions of 60 to 65 °C at methanol to oil/FFA ratio ranging from 1:6 to 1:12 [31-34] . It may be also noted that through these studies, it has been a consistent observation that reusability of these catalysts are high and above 10 cycles. However, the only major drawback was the loss of catalyst after 10-12 cycles due to breakdown of the matrix. Also, the anion exchange resin is more effective in conversion of glycerides to FAME than the cation exchange resin for esterification of FFA [32].

Activated carbon has also been explored as supports for acid groups for catalysis in biodiesel production. However, due to its inherent inertness, the deposition of acid groups is not very effective and leads to leaching. This is overcome by using cellulosic substrates for production of the carbon [35]. The nature of this material being highly porous, enables the deposition of active components on the surface and enables it high thermal and structural stability.

Activated carbon has also been used as a support for other acidic groups like heteropolyacids, metal complexes etc and has grown in popularity because it is easily available, inexpensive and is reliable over repeated usage. The disadvantage of all these works is the high temperature needed to ensure high reaction rates. This is why solid base catalysts have an edge over acidic catalysts.

3.3.2 Solid base catalysts:

The typical production method for biodiesel fuel is a base catalyzed process with a homogeneous catalyst usually NaOH or KOH. Biodiesel conversion rates are high and are

obtained at mild reaction conditions and a short reaction time [36]. However, the disadvantages of complicated downstream and inability to reuse the catalyst from the homogeneous scheme still persist. A large amount of research has been conducted using solid base catalysts. Although the reported reaction times are higher than those of the conventional methods, the reusability of catalyst and environmental benefits validate the use of these solid base catalysts. Alkali metal doped catalysts (Li, Na and K doped on CaO, MgO, Al₂O₃) were investigated for conversion rates by MacLeod et al., in 2008 [37]. They found that conversion was related to the basic activity of the catalyst. They found that MgO doped with Li gave conversion rates of up to 95% in 40 min. Their studies also show that doping of the metal oxide increases basic strength and calcination is not required. On doping, yields greater than 90% were achieved in a 3 h reaction time. Also, on reusing the catalysts, conversion rates did not drop significantly, however, the group encourages that further work be done on the catalysts to avoid dopant leaching in the industrial scale.

A research group led by Kawashima et al., (2008) [38] used catalysts that were made with one transition metal and one alkaline earth metal of the form A-B-O. They used samples containing Mg, Li and Ca as the alkaline earth supports with Ti, Mn, Zr, Fe and Ce as the transition elements. Of the thirteen combinations of catalysts they used, the ones which had Calcium in them showed the maximum conversion rates at 60 °C and 1:6 oil to methanol ratio. Yield ranged from 70 to 92%. This is supported by the report by Gryglewicz, (2007)

[39] that Calcium salts have a higher basicity and hence can be inferred a productive catalyst in biodiesel production.

Various other groups have worked on other catalysts that are based on oxides of Calcium due to its basicity and high conversion rates. Calcium methoxide was investigated as a prospective catalyst for biodiesel production by X Liu et al., in 2008 [40] and they found that at 60 °C and a 4% catalyst concentration (by weight of oil), calcium methoxide enabled a 98% conversion of soybean oil in 3 hours. Also since the calcium methoxide is sparingly soluble in methanol [39] reusability of catalyst should not reduce activity as metal leaching does not occur.

CaO as a catalyst has been extensively studied by L Liu et al., [41] for biodiesel in 2008. They used soybean oil as the triglyceride source and with 12:1 oil to methanol ratio and 8% catalyst at 65 °C to obtain a 95% conversion in 3 hours. The catalyst was reused for 20 cycles and at 1.5 h reaction time, there was no significant loss of catalytic activity. They also showed that this catalyst had some tolerance towards water content and 2.03% water content in methanol was found to enhance reaction rates. On comparison with KF loaded Aluminum catalysts, CaO stood out with longer lifetime and higher conversion. They even proposed a reaction mechanism for the transesterification of oil with CaO and the presence of a little water.

This work was furthered by Kawashima et al., [38] in 2008 to accelerate catalytic activity of CaO by activation of the catalyst in methanol for 1.5 h at room temperature. This activation resulted in a significant increase in initial reaction rate and with the use of 80% conversion was seen in 1 h of reaction at 60 °C at a 0.33% by weight (catalyst to oil). This is due to the increase in basicity of the catalyst on activation.

4. Economic analysis

Although biodiesel is definitely a positive breakthrough in tackling the fuel and environmental crisis, the economics of biodiesel production are not very encouraging. According to the National Biodiesel board, the biodiesel industry estimated the yearly cost of raw material, goods and services to be \$2.9 billion to produce 690 million gallons of biodiesel. Also, the investment on the infrastructure was \$90 million and an additional \$197 million on scientific research on feedstock and process development. This amounts to around \$4.63 per gallon of biodiesel.

Table 1: Economic analysis of industrial scale biodiesel production. These figures show that although the raw material cost is high for biodiesel production, with further research, if alternate feedstock could be used, biodiesel could provide a solution for the energy crisis.

Industry	Spending (Million \$)	GDP (Million \$)	Impact earnings (Million \$)
Infrastructure construction	90	160.0	95.7
Feedstock	2270.8	3319.6	1643.4
Industrial chemicals	195.1	273.9	140
Electric, natural gas and water	59.6	85.3	39.2
Maintenance and repair	10.6	18.5	10
Business services	8.6	14.6	7.8
Research and development	190.7	359.6	212.9
Earnings paid to households	33.1	31.3	15.6
Subtotals	2864.8	4263.4	2164.6
Plus value of biodiesel output		3194.7	23.5
Plus value of glycerine by product		87.3	
Total impact		7545.4	2188.1

Although the government has included certain benefits on use of biodiesel including a tax reduction and carbon credits for the production facility, the dollar amount of a gallon of biodiesel is nearly twice the cost of petroleum based biodiesel. An analysis of the above data shows that the maximum input cost is attributed to raw material and industrial chemicals. This is majorly the oil and the catalyst cost. These costs can be reduced drastically by using waste oil and by using waste materials that can be used as catalysts.

In the substitution of conventional base catalysts, since Ca and Mg salts have proved very useful in biodiesel production, research has moved towards using natural substances that have salts of Mg and Ca incorporated in their structure. In this direction, dolomite rock was investigated for use as catalyst as it contains Calcium rich phases of Magnesium calcite [42]. Calcined dolomite produced a conversion of nearly 90% at 60 °C reaction temperature. However, they reported that there may be mass transfer limitations for heavy oils.

In a similar direction, hen egg shells have been studied and reported to be composed of Calcium Carbonate (94% by weight). These shells are primarily disposed off in landfills due to their lack of use in any major industry [43]. Due to the inherent porous structure of egg shells and high Calcium Carbonate content, they prove as potential catalysts for transesterification of triglycerides [44]. They found that on calcination of the egg shells at 1000 °C and at a 65 °C reaction temperature, 9:1 methanol to oil ratio and 3% (by weight) catalyst, conversion of 99% was seen in 3 h. On reuse however, the shells completely lost activity after 17 runs.

A catalyst that could survive a larger number of experimental runs would be an ideal candidate for study as a base catalyst for biodiesel production. Since CaO has been reported to have survived an excess of 20 cycles, other sources of calcium are to be investigated that can ensure higher durability.

5. Catalysts in present study

Two catalysts have been explored in the present study; KI impregnated calcined oyster shells as base catalyst and acidified tobacco stalk char as acid catalyst. The inherent calcium in the oyster shells, added with the highly basic Potassium ion from the iodide is hypothesized to be a competitive base catalyst with high conversions of soybean oil to biodiesel. The tobacco stalk char is hypothesized to provide a carbonaceous porous matrix for the impregnation of sulfonic acid groups, making it a competitive acid catalyst for esterification of FFA.

5.1 Oyster shell catalyst

Studies have shown that marine organisms produce calcium carbonate in their sea-shell structure for protection against current and other harsh oceanic conditions [45]. These include shells or oysters, shrimp, eggs that are generally discarded and contribute to a lot of waste.

Aqua culture is a major contribution to the agricultural sector worldwide.

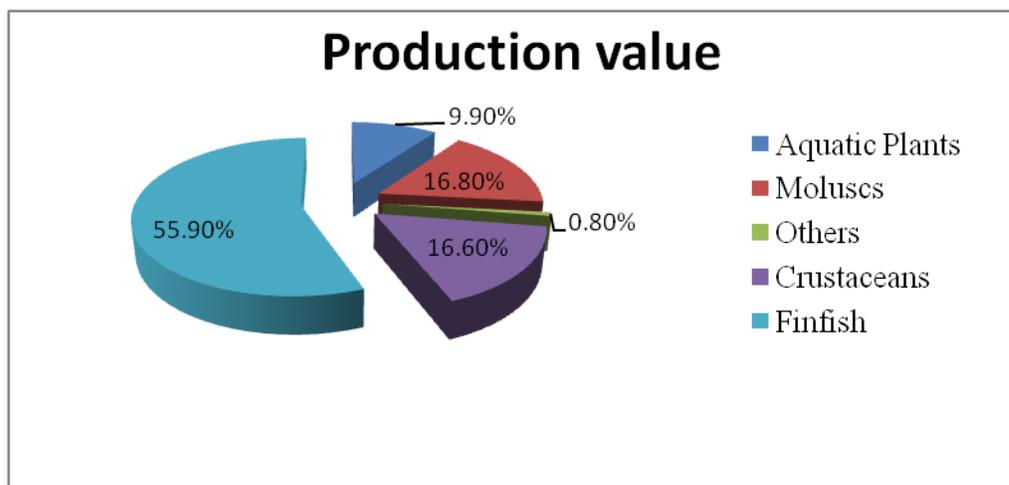


Figure 4: Production value of aquatic species grown by the Fisheries Department (FAO Fisheries department, USA)

The total revenue from aquaculture amounts about 56 billion dollars a year. Crustaceans account for about 16% of this total. This ends with a large amount of waste in the form of shells and exoskeleton that could be well managed as a source of calcium carbonate. The shells of these organisms are a biocomposites of which calcium carbonate accounts for about 95 to 99 % of the shell. This calcium carbonate may be used as the raw material for catalyst preparation.

The shells of oysters and shrimps are gaining importance in this regard for use as catalysts, these shells being waste material and can be obtained for a very small capital. This would eliminate the cost for catalyst procurement from the industry as pure metals. The shells may then be washed and dried and ground to produce nearly pure calcium carbonate. Calcination of calcium carbonate produces Calcium oxide, a potent catalyst for transesterification [46].

Shrimp shells were investigated as catalysts for biodiesel production. Yang et al., 2009 [47] used KF loaded on incompletely carbonized shrimp shells as catalyst for transesterification. The carbonization was found to increase surface area for KF to load. 89% conversion was reported at a 65 °C reaction temperature over 3 h with a 9:1 methanol to oil ratio and 2.5% catalyst (by weight).

Oyster shells are also being investigated. So far, work has been done by Nakatani et al., in 2008 [46] and has reported conversion rate of 73.8% with high purity (98.4%). There is a lot of scope for improvement in this catalyst so a higher conversion rate may be obtained. The kinetics study of the working of this catalyst and characterization is yet to be done and its application in treating waste oil is to be explored.

5.2 Acidified tobacco stalk char catalyst

In order to extend this work to the use of waste oil as feed-stock, pretreatment with acid catalysts need to be performed to reduce the FFA content to less than 1%. Since the overall goal of this research is to use feed with high FFA content to simulate waste oil characteristics, to produce value added FAMEs, tobacco stalks were chosen to provide the support for deposition of sulfonic groups to provide the necessary acidic active sites.

Although focus is being given to the use of discarded and waste cellulosic material for the production of ethanol, the possible contribution of this resource in the production of biodiesel may not be overlooked.

North Carolina State is presently the leading state in the production of tobacco and since the curing process is moving away from the stalk cure procedure, these stalks are now available for disposal, with the exception of tender stalk, that are capable of rising new buds. Although there is no significant amount of research in the area of using tobacco stalk as a support for catalyst production, wood fibers and other cellulosic substrates are being studied for the same purpose. With the presumption that these stalks will still be useful as a porous carbon support on carbonization, followed by addition of acid groups, tobacco stalk is being investigated in this project as a potential support for acid catalyst production.

6. Conclusion

Biodiesel as a clean fuel could be the solution to the world's growing fuel crisis. It has been proved to be efficient, biodegradable and eco-friendly. Despite these advantages the mass production of biodiesel is not yet economically feasible. With the cost of production greater than \$4 per gallon, it is necessary that the production process be improved so that a higher conversion is achieved with lower production cost. As 80% of the cost of production is attributed to raw material cost, research is being done to explore the usage of waste oil as raw material. Also, since conversion rates largely depend on the catalyst used, the focus of most research has been on improving catalysts used for biodiesel production. Homogeneous acid and base catalysts were first used. It was then proved that base catalysts were more efficient in biodiesel production than acids [36] with virgin oil feed stock. However, downstream processing and purification steps for the production of usable biodiesel were both energy

consuming and expensive and the waste produced was toxic [22]. Also, reusability of catalyst was not possible. Heterogeneous acid and base catalysts were then used to overcome these difficulties. For a base catalyzed reaction, research has shown that those bases that contained calcium groups showed higher conversion rates [38].

The use of transesterification as a waste management strategy in both industries that produce waste triglycerides and in agricultural waste disposal is a lucrative venture. But in order to commercialize such a scheme and precise kinetic studies is necessary. The present work includes exploring the use of calcined oyster shells and carbonized tobacco stalk as catalysts for biodiesel production. This includes characterization and testing of the conditions to generate highest yield of biodiesel and the study of kinetics to explain the rate of product formation from first refined vegetable oil and later, high FFA content oil to emulate waste oil.

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Objectives

Since biodiesel has been accepted globally as an alternate fuel, it is imperative to improve and increase global biodiesel production capacity, utilizing all plausible feedstock. This requires development of catalysts that can process waste oil sources. This research focuses on utilizing waste oyster shells, and activated carbon as catalysts to treat and transesterify waste oils to produce biodiesel. Specifically the proposed research focused on:

Phase 1: Base catalysis

- Synthesis of KI impregnated oyster shells via wet impregnation
- Determining the effects of reaction time, concentration, oil:methanol ratio, reaction temperature and reusability of catalysts for FAMES production from soybean oil .
- Characterization of catalyst surface using SEM, EDS, XRD and BET.

Phase 2: Acid catalysis

- Synthesis of solid acid catalyst using carbonized tobacco stalk as support material.
- Studying the effects of H₂SO₄ soaking time and reaction time on oleic acid esterification in batch reactors
- Characterization of catalyst surface characterization using SEM, BET and surface acidity.

Phase 3: Sequential acid-base catalysis

- Testing of a continuous packed bed reactor for sequential esterification and transesterification of simulated waste oil (15% FFA in soybean oil) .

**Solid base catalysts from agricultural wastes for production of fatty acid methyl esters
from soybean oil**

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Abstract:

Research on inexpensive and green catalysts is needed for economical production of biodiesel on a mass scale. The goal of this research is to synthesize inexpensive and green catalysts from agricultural wastes. The research objective was to test KI-impregnated oyster shell as a solid catalyst in biodiesel production. The catalyst was synthesized by wet impregnating KI on calcined oyster shells. X-ray diffraction analysis clearly indicated presence of portlandite and potassium iodide on the catalyst surface while the specific surface area increased by 31 times as a result of calcination and KI impregnation. The catalyst was tested in transesterification of soybean oil in 500 mL batch reactors equipped with methanol reflux. Analysis of reaction products indicated that the catalyst exhibited high activity towards transesterification. Biodiesel conversions up to 86% were obtained in batch reactor systems. The effects of temperature, catalyst loading, reaction time, methanol/oil ratio were investigated. Optimum reaction variables for this system were found to be 50 °C, 10:1 methanol/oil ratio, and 4 h reaction time. Considering the emerging aquaculture industry in south eastern United States, the results presented in this research could have significant positive economic implications.

Keywords: Biodiesel, solid catalysts, KI-impregnated oyster shells

1. Introduction

Due to the projected shortage of fossil fuels and the environmental effects resulting from consumption of fossil fuels, there is a strong worldwide interest in development of renewable fuels [1] [2] [3] [4] [5]. Biodiesel, a mixture of fatty acid methyl esters (FAMES), is a one such renewable fuel that can potentially replace petroleum diesel [6]. Biodiesel is a naturally oxygenated [7], non-toxic, sulfur-free [8] and biodegradable fuel [9] that can be directly used in the current configuration of the diesel engine [9], [10]. Further, biodiesel has a higher cetane number than petroleum diesel and has 95% energy content of petroleum diesel and has a positive net energy gain of 3-4:1 [11].

Biodiesel is usually produced via transesterification or esterification using basic or acidic catalysts [12] [13] [14]. The most common method is to facilitate a reaction between triglycerides and alcohol in the presence of a catalyst (NaOH or H₂SO₄) [10]. Methanol and ethanol are preferred due to low cost, polarity, smaller carbon chain, and their solubility in KOH and NaOH [10]. Although homogeneous biodiesel processes are fast and efficient, they have several disadvantages [15] [16]. The waste stream from the transesterification process is very toxic. Further, large amounts of water are required to separate the biodiesel and catalysts. Our experience suggests that for every unit of biodiesel produced, four units of water are required for cleaning and optimum separation of catalysts and glycerol. Hence current research on biodiesel is strongly focused on developing heterogeneous (solid) catalysts. Heterogeneous catalysts are less corrosive, offer easier separation, and reduce

water use and environmental pollution [17]. To this effect, researchers have tested a variety of catalysts successfully. For example, Boz et al., (2009) evaluated nano alumina impregnated with KF as a catalyst for soybean transesterification [18]. A similar test was conducted by Ebiura et al., 2005 [19] using potassium carbonate loaded alumina catalyst to study the selective transesterification of triolein to methyl oleate at 60 °C and reported 94% conversion in 1h. Similarly, Wilson et al., 2008 [20] tested dolomite rock as a catalyst in transesterification of glyceryl trioctanoate. Kawashima et al., 2008 [15] tested various calcium containing complexes, including CaTiO₃, CaMnO₃, CaFe₂O₅, CaZrO₃, and CaO-CeO₂ in the transesterification of rapeseed oil at 60 °C and reported conversions as high as 92% over 10 h of reaction. Another extensive study performed by Serio et al., 2008 [21] compared catalysts containing MgO, CaO and MgO-Al₂O₃ under varying reaction conditions. In supercritical methanol and microwave irradiation assisted method they reported yields as high as 99% as compared to 90% yield using just calcined MgO and CaO at 180 °C with 1:15 oil to methanol ratio. At methanol reflux conditions, a maximum conversion of 72% was reported. Also, in the work done by Singh et al., (2008) oxides of various metals were tested and conversions greater than 89% was reported [22]. However, at the present time, a few heterogeneous catalysts are being used in the industry due to the costs associated with the catalyst synthesis.

One possible way to reduce the costs of the catalysts is to use agricultural wastes as catalytic materials. There are recent reports in the literature where several types of

agricultural wastes were explored as catalysts [23] [24] [25] [26]. In a recent study using oyster shells reported that 70% of soybean oil was converted into biodiesel after five hours of reaction using 25% (w/w) catalyst [27]. While this is encouraging, it may be possible to further enhance the activity of oyster shells by impregnating additional basic sites on the surface of the shells. To that effect there are several studies in the literature that tested the effects of depositing basic elements on neutral/basic supports. For example, Arzamendi et al., (2008) [28] conducted a comprehensive study of alkaline earth metal oxides with and without calcination for the transesterification of sunflower oil, and reported the significant yield improvement by addition of other basic groups on the catalyst. Alkali metal doped catalysts (Li, Na and K doped on CaO, MgO, Al₂O₃) were investigated by Macedo et al., (2006) [29]. The authors found that conversion was related to the basicity of the catalyst. They found that MgO doped with Li resulted in conversion rates of up to 95% in 40 min. Additionally, doping of the metal oxide increased basic strength and conversions greater than 90% were achieved in a 3 h reaction time. Wilson et al., (2008) [20] used catalysts synthesized from transition metal and alkaline earth metal of the form A-B-O. They used samples containing Mg, Li, and Ca as the alkaline earth supports with Ti, Mn, Zr, Fe and Ce as the transition elements. Of the thirteen combinations of catalysts tested, the catalysts containing calcium showed the maximum conversion rates (70-92%) at 60 °C and 1:6 oil to methanol ratio. This is supported by Gryglewicz, (2006) [30], who demonstrated that calcium-based catalysts have a higher basicity and hence could be used as a catalyst in biodiesel production. Additionally, Xie et al., (2006) [31] tested several potassium salts and concluded that KI has

highest basicity and activity in soybean oil transesterification. Based on their findings, we hypothesize that impregnating potassium iodide on oyster shell surface will enhance the catalytic activity of oyster shells towards transesterification. Hence the objective of this work was to evaluate KI-impregnated oyster shells as stable base catalysts for biodiesel production. Additionally, we investigated the effects of reaction time, methanol/oil, temperature, catalyst loading, and catalyst reusability on conversion of soybean oil into FAMES. This research is a part of our ongoing work on synthesizing catalysts from agricultural wastes. Oyster shells are of particular interest because the state of North Carolina has an emerging oyster culture industry.

2. Experimental

2.1 Catalyst synthesis

Discarded oyster (*Crassostrea virginica*) shells were obtained from a local restaurant. The shells were crushed in a grinder to a size of 1-1.7 mm and calcined at 1000 °C in a furnace (Paragon Industries) for 4 h similar to the procedure described by Nakatani et al., (2009) [27]. Subsequently the shells were impregnated with KI and dried in the oven at 106 °C and recalcined at 300 °C for 2 h [32].

2.2 Catalyst characterization

2.2.1 Surface area

The specific surface area of the catalysts was determined using a ChemBET PULSAR™ TPR / TPD (Quantachrome Instruments, USA) based on Brunauer-Emmett-Teller (BET) nitrogen adsorption method. Prior to the analysis, all samples were degassed at 300 °C for four hours to desorb the volatiles (if any) from the surface.

2.2.2 Scanning electron microscopy

A variable pressure scanning electron microscope (Hitachi S-3200) equipped with an energy dispersive X-ray analyzer (Oxford 10x10 mm SiLi detector, Advance Analysis Technologies amplifier, and a 4Pi pulse processor) was used for imaging and determining elemental composition of the catalysts. The samples were directly mounted on aluminum stubs and imaged using an accelerating voltage of 5 keV and an Everhart-Thornley secondary electron detector. Elemental analysis was performed with beam energy of 20 keV and an acquisition time of 120 s. The raw data was processed using Revolution software (4pi Analysis, Inc, Durham, NC) and subsequently exported into MS-Excel and Sigma Plot for graphing.

2.2.3 X-ray diffraction analysis

A Rigaku Smartlab XRD analyzer was used to examine the catalysts. Samples were ground at room temperature with an alumina mortar and pestle and placed on the XRD

holder. Samples were analyzed at 40 kV and 44 mA at an angle of diffraction (2θ) between 20 and 80° with a step-size of 0.2 and a scan rate of 0.5 ° min⁻¹.

2.3. Soybean oil transesterification

All experiments were performed (in triplicates) in 1-L batch reactor systems equipped with three-neck flat bottom flasks and reflux condensers (ACE Glass Inc., Vineland, NJ). Each experiment was carried out by mixing 30 mL of refined soybean oil (food grade) with 1 g catalyst and methanol at a given temperature. Based on our preliminary experiments with calcined oyster shells, 1 g of catalyst was used in all experiments. We tested the effects of methanol/oil ratios of 5, 10, 12, and 24, KI loading of 1, 3, 6, and 9 mmol/g, reaction time of 2, 4, and 6 h, and reaction temperatures of 30, 40, 50, and 60 °C on soybean oil conversion into FAMEs. The temperature of the reactor contents was regulated using a process-controlled hot plate (Isotemp, Fisher Scientific, Pittsburgh, PA). After the reaction, the catalyst was separated from the product mixture via vacuum filtration. Further, FAMEs and glycerol were separated from the product using 250 mL separator funnels. The FAMEs were washed with water to remove residual methanol and glycerol and heated to 106 °C for eight hours to remove any traces of water.

2.4 Viscosity measurements

To determine the conversion of soybean oil to FAMEs we relied on the mathematical relationship between the extent of transesterification and viscosity similar to the model

proposed by Defilippis et al., (1995) [33] . First, we synthesized FAMEs using conventional NaOH catalyst. Second, we diluted the neat FAMEs with soybean oil to obtain various levels of conversions (0-100%). Further, for each conversion, we measured density, kinematic and dynamic viscosities at room temperature using an SVM 3000 Stabinger Viscometer (Anton Paar USA Inc) as described previously [34]. The results were used to develop the following expression to relate viscosity to conversion which was used for all subsequent FAMEs synthesized in this work. A linear relationship was obtained between viscosity and conversion.

$$Conversion \% = \frac{1.6543 - \log(\text{dynamic viscosity})}{.0101}$$

2.5 FAMEs analysis

FAMEs samples were analyzed using a gas chromatograph equipped with a mass selective detector (Agilent 7890/5975C VLMSD). A HP-5 MS column was used to separate the FAMEs. FAMEs samples were diluted (1:1000) in hexane that contained an internal standard (GLC 90, SUPELCO). The chromatographic conditions include: injector: 240 °C, detector: 250 °C column: 100-200 @ 50 °C min⁻¹, 200-232 @ 2 °C min⁻¹, and 232-270 @ 30 °C min⁻¹. To minimize the sampling and instrumental error, three samples from each vial were analyzed. For each run, the ratio of FAMES peak area to the internal standard peak area (peak area ratio (PAR)) was calculated [35]. The purity of biodiesel was determined by modifying the equation proposed by [36, 37].

$$Purity = PAR \times \frac{Mass\ of\ Internal\ standard}{Mass\ of\ biodiesel} \times 100$$

Sampling and statistical analysis

All transesterification experiments were performed in triplicates. The viscosity and density of FAMEs were determined in duplicates. To determine the standard error (SE) associated with the purity, the following equation was used:

$$SE = \frac{Mass_{Internal\ Standard}}{Mean\ Mass} \times \sqrt{\left(\frac{\sigma_{Mass}^2}{6} \times \left(\frac{PAR\ Mean}{Mean\ Mass}\right)^2\right) + \frac{\sigma_{PAR}^2}{9}} \times 100$$

where σ_{Mass}^2 and σ_{PAR}^2 = sample variances of Mass and Peak Area Ratio.

Similarly for BET surface area experiments were performed twice. For AFM, SEM, XRD analysis, the 2-3 catalyst particles were selected randomly from a batch of 10 g.

3. Results and Discussion

3.1 Catalyst characterization

Figure 2.1 shows the surface morphology of the oyster shells. As expected, uncalcined shells exhibited a layered structure (Figure 2.1 A). Additionally, some shell particles appeared to be electrostatically attached to the surface. We also analyzed the surface using an atomic force microscope (AFM) in tapping mode and verified the presence of layered surface (Figure 2.2). The image (left) in Figure 2.2 depicts the absolute height

change as the cantilever tip (probe) moved across the surface. This is the phase image. Since the surface is flat, details of the surface are not perceivable. Slightly below the center, a clear change in the color contrast was observed suggesting that the probe encountered a large step in the surface topology. The image on the right shows relative phase change as a derivative of the image on the left. Surface details are perceivable and layered structure is clearly visible, suggesting the presence of differential layers on the surface.

The EDS analysis revealed the elemental chemical constituents as a mixture of calcium, carbon and oxygen, confirming that the shells were made of calcium carbonate. However, after calcination, the oyster shell surface clearly transformed from a non-porous to a porous structure probably as a result of volatilization of organic matter present in the shell matrix and removal of CO₂ (Figure 2.1, image B). This was also supported by the BET analysis, which indicated that the specific surface area of the shells increased by 9.5 times (from 0.19 to 1.8 m² g⁻¹) as a result of calcination (Figure 2.3). Additionally, the XRD analysis corroborated the formation of an active lime phase from the original calcite phase (Figure 2.4). The phase change from calcite to lime was in general agreement with Nakatani et al., (2009) [27].

After impregnation, a thick layer of potassium iodide appeared to have coated the surface of the calcined oyster shell (Figure 2.1, image 3). Subsequent XRD analysis confirmed the presence of portlandite and potassium iodide on the shell surface. We theorize that portlandite was formed as a result of reaction between calcined shells with water.

Impregnation also increased the surface area from 1.8 to 6 m² g⁻¹. As will be shown later, the increased surface area along with presence of portlandite and potassium iodide on the surface significantly enhanced the conversion of soybean oil into FAMES. It may be noted that we also tried to analyze the surface of the calcined and KI loaded shells using AFM. Due to enhanced porosity and undulating nature of the surfaces due to calcinations and KI deposition, the AFM tip was obstructed several times and analysis could not be successfully performed. In general, we found that calcination and impregnation enhanced the surface area and the catalytic activity of the shells.

3.2 Effect of reaction time

Because of the heterogeneous (3-phases) nature of our reaction, we expected longer reaction times. Figure 2.5 shows the comparison of both catalysts under identical conditions. It was clear that, KI-impregnated oyster shell provided substantially higher conversion than calcined oyster shell for 2 and 4 h. For example, after 4 h, KI- impregnated oyster shell enabled 80% conversion (purity 75.43 ± 0.22%) when compared to 45% (purity 49.41 ± 7.8%) obtained from calcined oyster shell. On a mass basis, our conversions are higher than the work done by Nakatani et al., (2009) [27] who reported 73.8% conversion after 5 h reaction time using 25% by mass loading of calcined oyster shells. Yang et al., (2009) [38] reported a lower reaction time of 3 h to achieve 89.1% conversion using calcined shrimp shells impregnated with KF. This was possibly due to the higher reactivity of the fluoride group and a higher reaction temperature of 65 °C. Similar results were obtained by He et al.,

(2008) [39] using CaO, who reported 95% conversion after 3 h of reaction perhaps due to higher mass loading of catalyst.

Additionally, we found that over a 6 h run, the KI-impregnated catalyst appears to have reached equilibrium while the activity of calcined shells appears to increase with time. Based on these results, 4 h appears to be an optimum reaction time for KI-impregnated oyster shell. Additionally, reaction times greater than four hours are impractical if biodiesel were to be produced on an industrial scale. A one way ANOVA was carried out for the three reaction times and the resulting P value ($P=0.0028$) showed a significant difference between the mean conversions obtained at each reaction time. Tukey's HSD analysis showed a significant difference between conversions after 2 h and 4 h, 6 h; but no difference between conversions after 4 h and 6 h. Work done by Peterson et al., (1984) [40] comparing CaO, MgO and Al₂O₃ reported that time required for reaction to reach equilibrium was between 6 to 12 h during the transesterification of rapeseed (canola) oil. Our results are also in tandem with those reported by Arzamendi et al., (2008) [28] who used sunflower oil as feedstock and reported 90% conversion by CaO after 10 h of reaction conducted at 50 °C and 1:12 oil to methanol ratio. In general, the activity of KI-impregnated calcined oyster shells were comparable with several of the catalysts tested for biodiesel production. Our results are encouraging considering the fact that the catalysts in our study were synthesized from agricultural wastes and are very inexpensive.

3.3 Effect of methanol to oil ratio

Increasing oil to methanol ratio from 1:6 to 1:10 resulted in a substantial increase in conversion as expected, from 67.4% to 79.5% (purity ranging from $72 \pm 1.46\%$ to $83 \pm 0.38\%$) (Figure 2.6). The enhanced conversion was likely due to increased availability of methanol at the oil-methanol interface [10]. Transesterification is a reversible reaction [10]. As per Le Chatelier's principle, increase in reactant concentration would shift the equilibrium to the right thereby promoting product formation. Our results were in line with Freedman et al. (1984) [41], Ebiura et al., (2005) [19], and Wei et al., (2008) [24] who found that increase in methanol yielded increased conversions. However, a further increase of methanol to 1:12 and 1:24 did not further increase conversion rates. On the contrary, conversion dropped by 7.8%, when 1:24 oil to methanol ratio was used. However, comparing mean conversions at each methanol to oil ratio showed no significant difference between conversions, at a 95% significance level ($P=0.3087$). It must be noted that during the performance of the experiment, the lower ratio of 1:6 though statistically is not significantly different from higher ratios, resulted in a slurry type mixture which proved difficult to handle. This result is in agreement with work done by Kawashima et al., (2008) [15] who reported maximum conversion (90%) at 1:10.8 oil to methanol molar ratio using methanol activated calcium oxide catalyst and rapeseed oil as feed. A similar trend was seen by [31, 32] with alumina loaded with KI as catalyst. They reported optimum conversion (96%) at 1:15 oil to methanol ratio with no further increase with further increase in methanol content.

3.4 Effect of catalyst loading:

KI was chosen as the active phase for this catalyst as studies have shown that the presence of an alkaline group increases the basicity and activity of the catalyst. Macleod et al., 2008 reported increase in catalytic activity of both CaO and MgO when doped with alkaline earth metals, with Na and K providing the highest conversion rates greater than 90% [42]. Additionally, they reported that the conversion rates of a catalyst increases with its basicity. Ebiura et al., (2005) [19] studied the selective transesterification of triolein to methyl oleate in the presence of alumina doped with alkali salts and reported a maximum conversion of 92% when potassium carbonate was used. The efficiency of potassium when added to the catalyst was also confirmed by Lukic et al., (2010) [43] when added to an aluminum silicate aerogel catalyst. In the present study, however, the amount of KI loaded on the calcined oyster shells did not have any marked effect on conversion (Figure 2.7). No significant differences between mean conversions at each loading were found ($P=0.8593$). Increasing the loading from 1 mmol/g to 3 mmol/g showed an increase in conversion from 74% to 79.5% (purity ranging from $77 \pm 1.88\%$ to $72 \pm 0.22\%$). A further increase of KI to 6 mmol/g and 9 mmol/g of calcined oyster shells resulted in a reduction in conversion to 77.1% and 71.1% respectively. The decrease in the conversion might partially be attributed to over impregnating KI on the calcined oyster shells that possessed a limited surface area ($1.8 \text{ m}^2 \text{ g}^{-1}$). As suggested by Smith (1981) [44], impregnating excess amounts of active phase on catalysts support might be detrimental. In the study performed by Xie et al., (2006)

[31] 2.1mmol/g loading of KI on alumina showed a maximum conversion of 87.4% conversion over 6 h reaction time.

3.5 Effect of temperature

As expected, temperature has a substantial influence on transesterification reaction. The conversion increased initially from 56 to 85.9% with an increase in temperature from 30 to 50 °C (Figure 2.8). Interestingly as the temperature increased beyond 50 °C, the conversion did not increase any further suggesting that the ideal temperature for our system was around 50 °C. Pairwise comparison of unadjusted means between 30 °C and 50 °C showed significant difference ($P=0.029$) and 40 °C and 50 °C ($P=0.0433$) but showed no significant difference 50 °C and 60 °C ($P=0.0746$). However, overall comparison of means showed no significant difference ($P=0.0998$) It may also be noted that while testing for the effect of various factors on conversion efficiency, the effect of temperature accounts for 52.32 %. Interestingly as the temperature increased beyond 50 °C, the conversion did not increase any further suggesting that the optimum temperature for our system was around 50 °C. Our results are generally in agreement with Jeong et al., (2004) [45] who tested rapeseed oil using homogenous KOH catalyst and obtained a conversion of 84.5% at 45 °C within a 10 min reaction time. Similar results were obtained by Xie et al., (2006) [31] with soybean oil transesterification with NaOH catalyst. The authors observed a conversion of about 87% within a 6 min reaction time. In a different study, rubber seed oil was used to synthesize

biodiesel by Ramadhas et al., (2005) [46] using a sequential esterification and transesterification via sulfuric acid and NaOH catalysts respectively. Their results indicated that 45 ± 5 °C regime provided optimum conversion for NaOH transesterification. Because of the heterogeneous nature of our reactions, our reaction times were longer than the aforementioned studies. Nonetheless, our optimum temperature is about 10-15 °C lower than similar heterogeneous biodiesel production systems. For example, the results presented by He et al., (2008) [39] using calcium oxide as catalyst, showed that the optimum temperature was around 70 °C (90% conversion) and the conversion of soybean oil dropped to 80% to 80 °C. In another study, Yan et al., (2008) [47] evaluated transesterification of rapeseed oil using mixed MgO-CaO catalysts and found a similar trend. The conversion increased from 5 to 84% when temperature was increased from 25 to 64.5 °C and dropped to 72% when a reaction was performed at 70 °C suggesting that the drop in conversion was due to evaporation of methanol beyond the optimum temperature of 60-65 °C as determined by He et al., (2008) [39] and Boz et al., (2009) [18].

3.6 Kinetics

Overall reaction kinetics was studied for the base catalyzed reaction by sampling at half hour intervals and analyzing for biodiesel conversion. Fractional conversion at each point of time was determined and using reaction stoichiometry, oil concentration was obtained at each half hour interval. If C_0 be initial oil concentration and C_t be oil concentration at time t , using first order integral model of the rate equation, upon plotting $\ln(C_0/C_t)$ vs. time, a straight line

was observed. The rate constant k was determined by the slope and was estimated at 0.9677 h^{-1} . This value is an indication of the velocity of the catalyst and is considered the basis for comparison. A similar approach was taken by Jain et al., (2010) for the sequential esterification and transesterification of *Jatropha curcas* oil using NaOH and H_2SO_4 [48]. According to their results, they obtained a first order transesterification reaction with respect to oil but surprisingly, their k values are much lower, 0.186 h^{-1} for the transesterification reaction using NaOH. This could also be due to the presence of acid from the pre-treatment step and the presence of byproducts but we believe, due to our catalyst being heterogeneous in nature, in use in succession to an esterification step, would not result in such a decrease in activity. On the transesterification of palm oil using dimethyl carbonate in the presence of KOH was also documented as a first order reaction with oil with a k value of 0.048 h^{-1} at $65 \text{ }^\circ\text{C}$ and 0.1092 h^{-1} at $75 \text{ }^\circ\text{C}$ [49]. Another study by Singh et al documented first order reactions with respect to oil using heterogeneous catalysts of PbO, MgO, MnO_2 and CaO. The reaction constants are in the order of 0.192 h^{-1} ; 0.066 h^{-1} ; 0.51 h^{-1} ; 0.276 h^{-1} respectively [50]. This result also indicates the improvement on calcined oyster shell catalyst properties due to the impregnation of KI.

3.7 Effect of catalyst reusability

In order to assess the durability of the KI-impregnated calcined oyster shells, we performed repeated experiments using the same catalyst. Our results indicated that the catalyst maintained constant activity (85% conversion) for three consecutive runs. However,

during the fourth run, the conversion dropped from to 51% (Figure 2.9). A similar trend was found by Boz et al., (2009) [18] using KF-loaded γ -Alumina as a catalyst in canola oil transesterification. The authors reported that the conversion dropped from 97.7% to 60.1% after using the catalysts three times and attributed the loss of activity to leaching of potassium and decrease of γ -alumina/K during the transesterification reaction. In our work the loss of activity was observed only after three runs suggesting that leaching may not be a cause for the lower conversion. Hence we did not measure the extent of leaching of potassium ions in the liquid phase. We theorize that with repeated use under agitating conditions (400 rpm), the active catalytic surface of the catalyst (portlandite and potassium iodide particles) may have eroded resulting in loss of activity. Another possibility is the deactivation of the surface sites due to adsorption of glycerol as proposed by Kawashima et al., (2008) [15]. In general, the repeatability of our catalyst was slightly below par with other solid base catalysts tested (Table 2). For example Macedo et al., (2006) [29] demonstrated that the activity of tin and zinc oxide deposited over aluminum oxide catalysts yielded a conversion of over 80% even after four consecutive runs. Similar observations were made by Kouzu et al., (2006) [51] who used calcium oxide catalysts in soybean oil transesterification. It might be possible to enhance the catalyst's reusability by washing the catalyst between the successive runs as suggested by Yan et al., (2008) [47] and Ramadhas et al., (2005) [46]. However, in this work the catalysts were reused without any treatment. Overall, despite exhibiting high activity, the KI-loaded calcined oyster shell catalyst appears to have a

moderate life (three runs) and hence further research is warranted to enhance the regeneration and reusability of the catalyst.

Conclusion

KI-impregnated calcined oyster shells were tested as solid base catalysts in transesterification of soybean oil in batch reactor systems. The characterization results indicated that the catalyst surface was composed of portlandite and potassium iodide and the surface area increased by 31 times as a result of calcinations and impregnation. The catalyst showed optimum activity for transesterification at 50 °C, 400 rpm, 10:1 methanol ratio. However the reusability of the catalyst was limited to three runs. Hence future studies focusing on regeneration and enhancing the reusability of the catalyst are recommended.

Acknowledgements

The authors thank Dr. Roger McFeeters and Mr. Seth Fornea of USDA-ARS for help with biodiesel analysis, Chuck Mooney and Roberto Garcia for catalyst surface characterization, Rachel Huie and Ryan Libert for laboratory help; and North Carolina Agricultural Research Service for providing funding for this research.

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Table 2. Comparison of catalysts' reusability in heterogeneous transesterification reactions.

Catalyst tested	Substrate	Repeatability^a	Reference
KI-loaded calcined oyster shell	Soybean oil	3	This work
Tin and zinc oxide/ alumina	Soybean oil	4	[29]
Calcium oxide	Soybean oil	4	[48]
Tin oxide/Tungsten oxide	Oleic acid	5	[49]
Calcined Egg shell	Soybean oil	13	[24]
Calcium/ Dolomite	Palm kernel oil	3	[50]
Mg-Al Hydrotalcite	Rapeseed oil	5	[51]

^aRepeatability indicated the # of times the catalysts was tested before losing significant activity

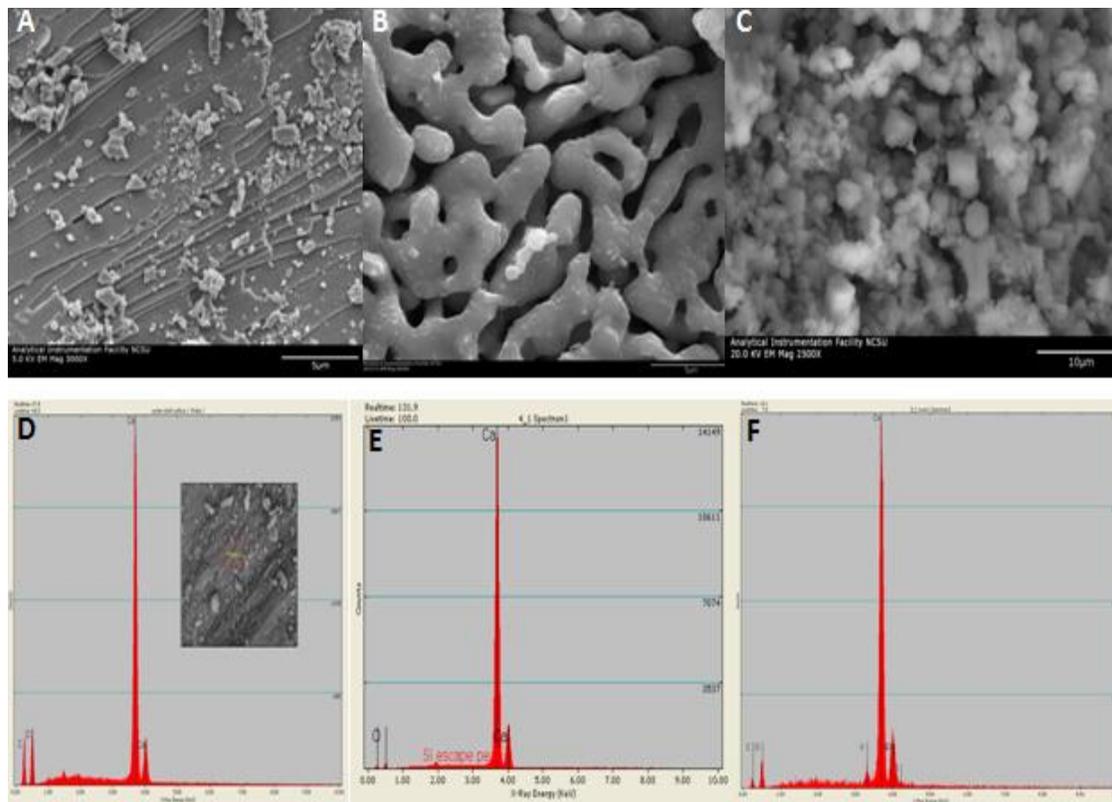


Figure 2.1. Images (top) of surfaces of untreated oyster shells (A) (5000X), calcined oyster shells (B) (5000X), and KI loaded calcined oyster shells (C)(2500X). Calcination resulted in a porous texture. The EDS analysis in the bottom shows the presence of carbonate (D) before calcination and oxide (E) after calcination. The EDS analysis (F) indicated the availability of K on the calcined surface after impregnation of KI on oyster shell surface.

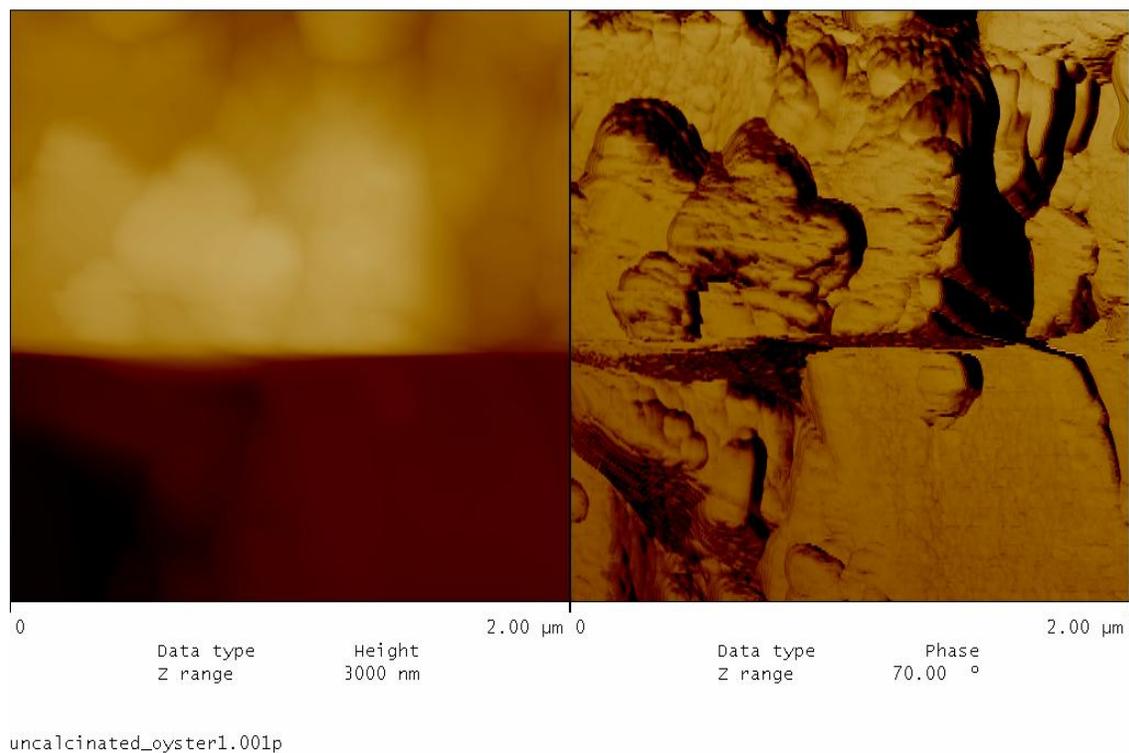
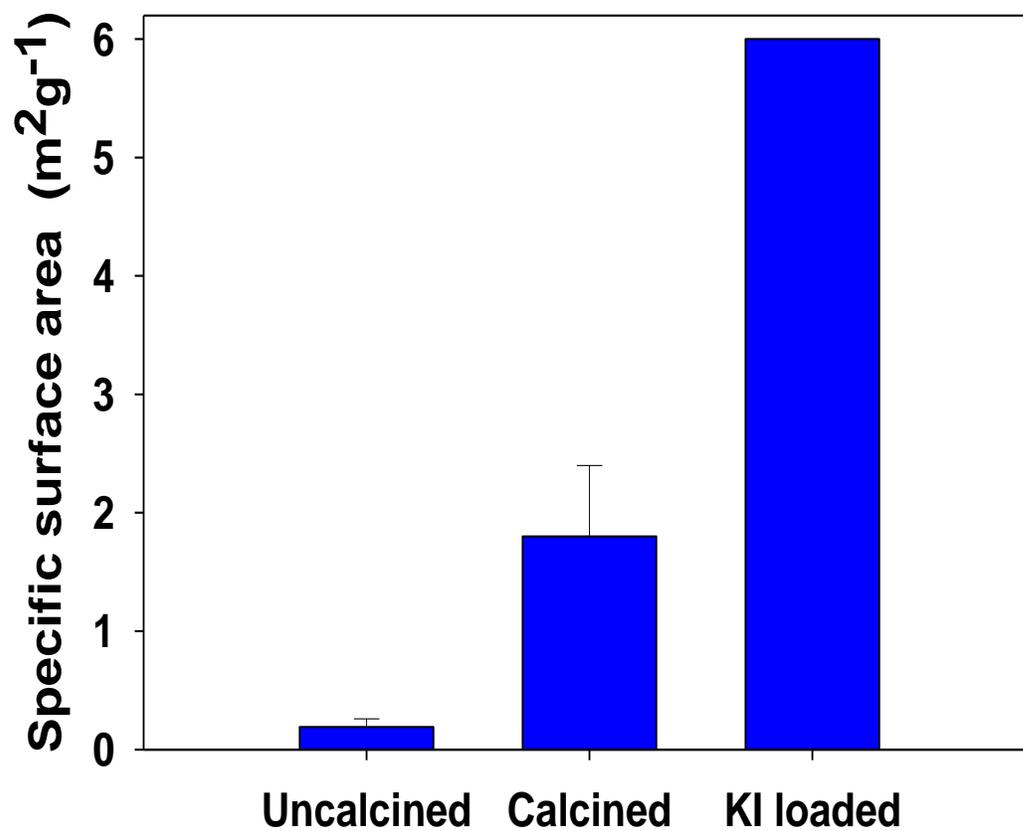


Figure 2.2. AFM image of untreated oyster shell. The image on the left is the absolute height. Relative phase change is shown in the right image suggesting differential layered structure.



Oyster shell catalyst

Figure 2.3. Effect of calcination and KI impregnation on specific surface area. Overall, calcinations and impregnation resulted in an increase in surface area by 31 times.

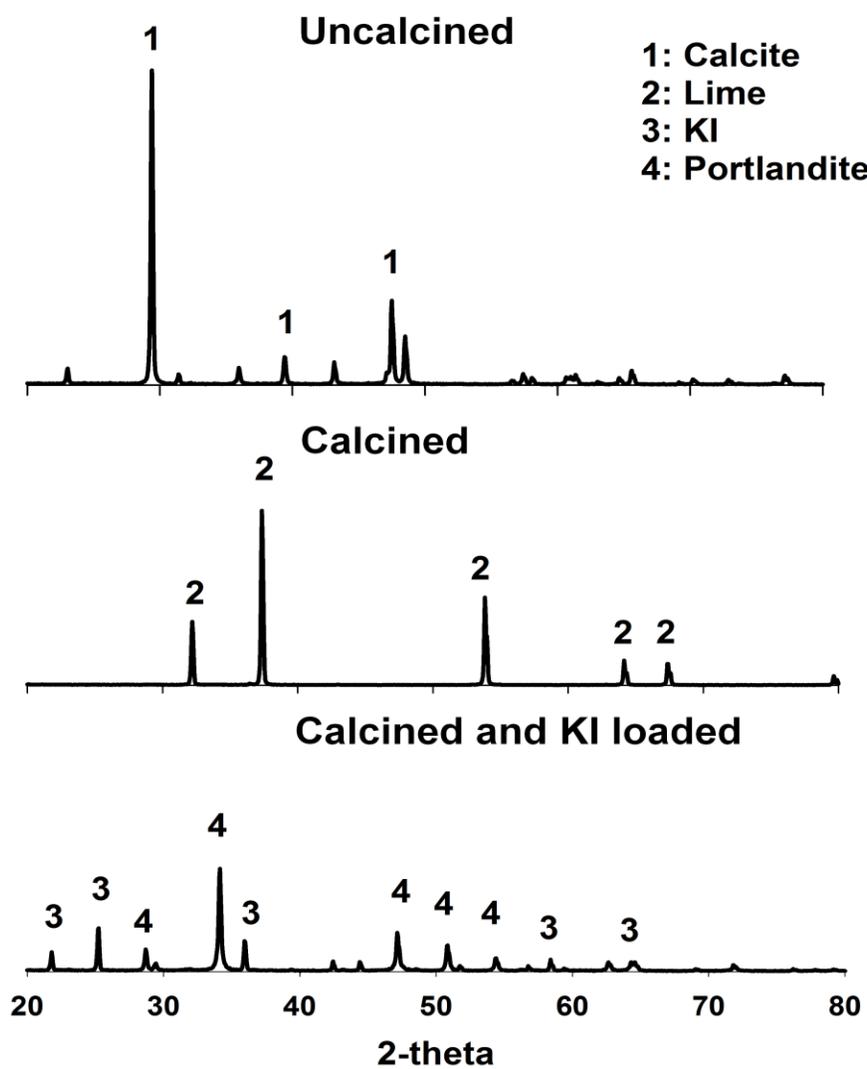


Figure 2.4. XRD spectra of the catalysts used in this study. Untreated shells (top) show predominantly consisted of calcite (CaCO_3) while calcined shells (middle) were made of lime (CaO). KI impregnation and calcination (bottom) resulted in formation of portlandite ($\text{Ca}(\text{OH})_2$) and KI.

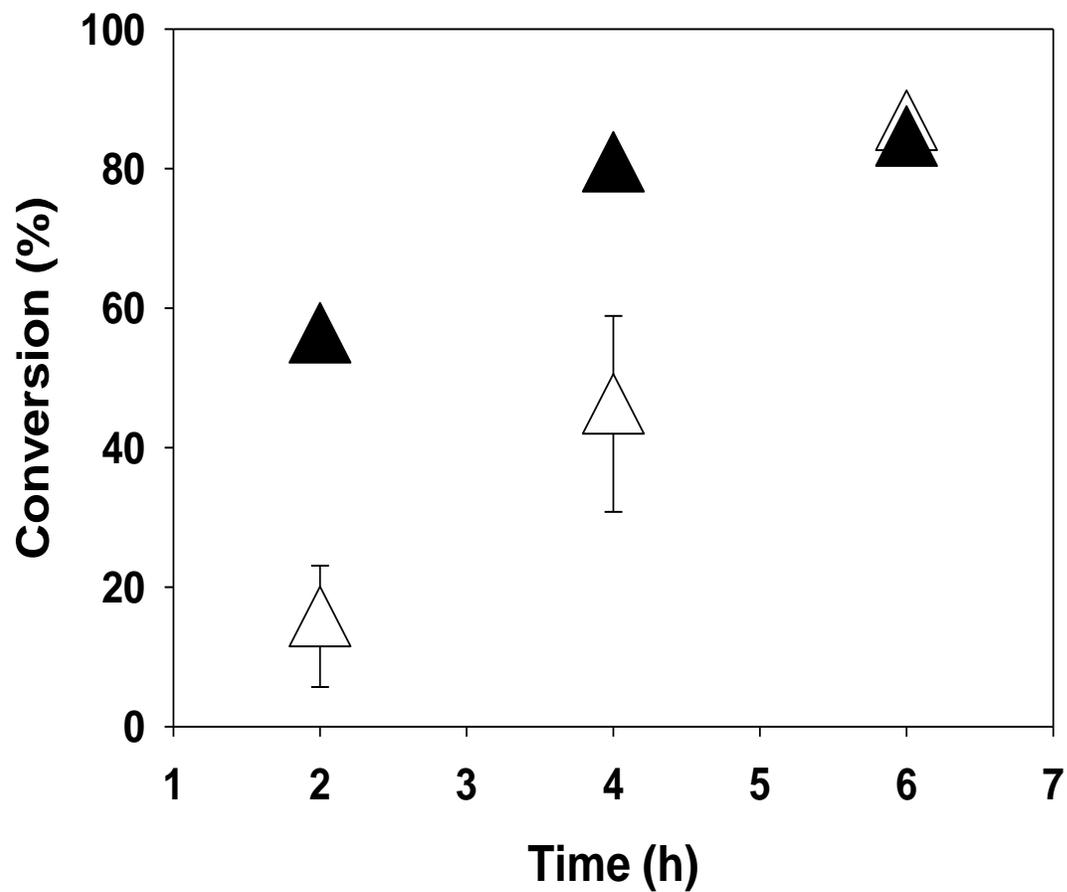


Figure 2.5. Effect of reaction time on conversion of soybean oil into biodiesel. After 6 h of reaction KI impregnated calcined oyster shells (▲) reached equilibrium while calcined oyster shells (Δ) have not.

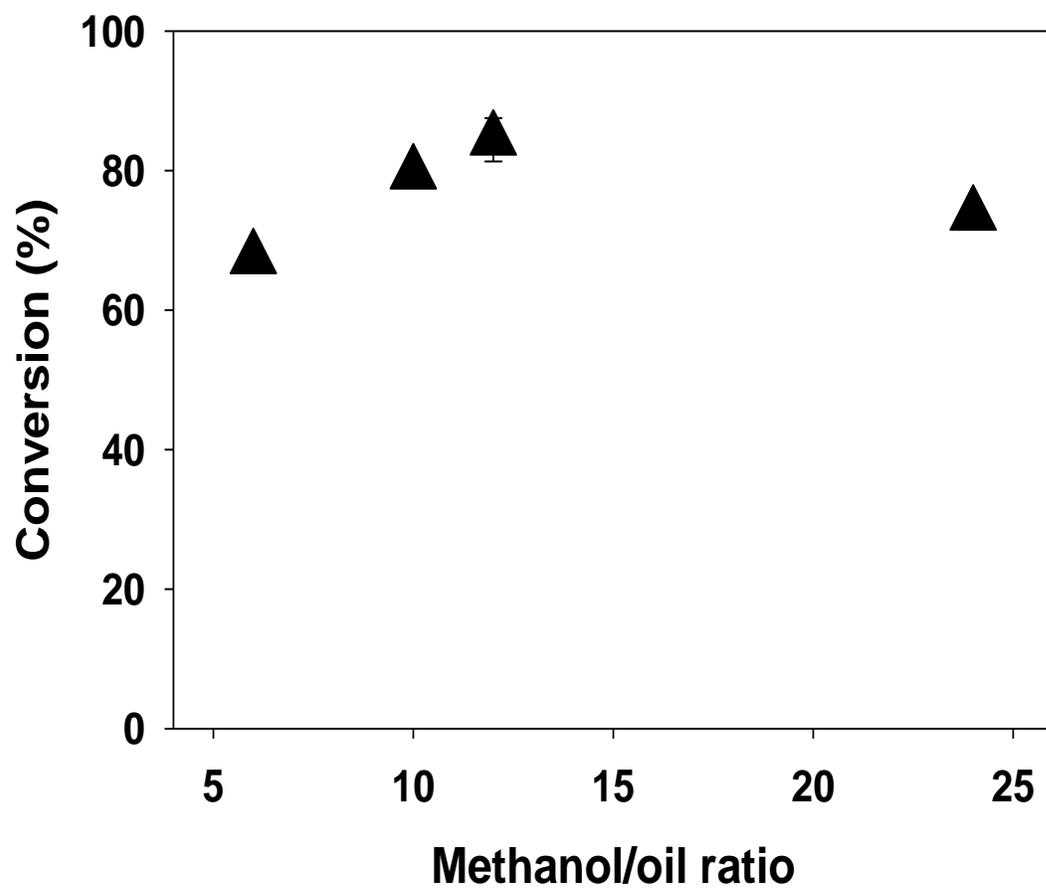


Figure 2.6. Effect of methanol/oil ratio on conversion soybean oil into biodiesel. 10:1 was determined to be optimum for this system.

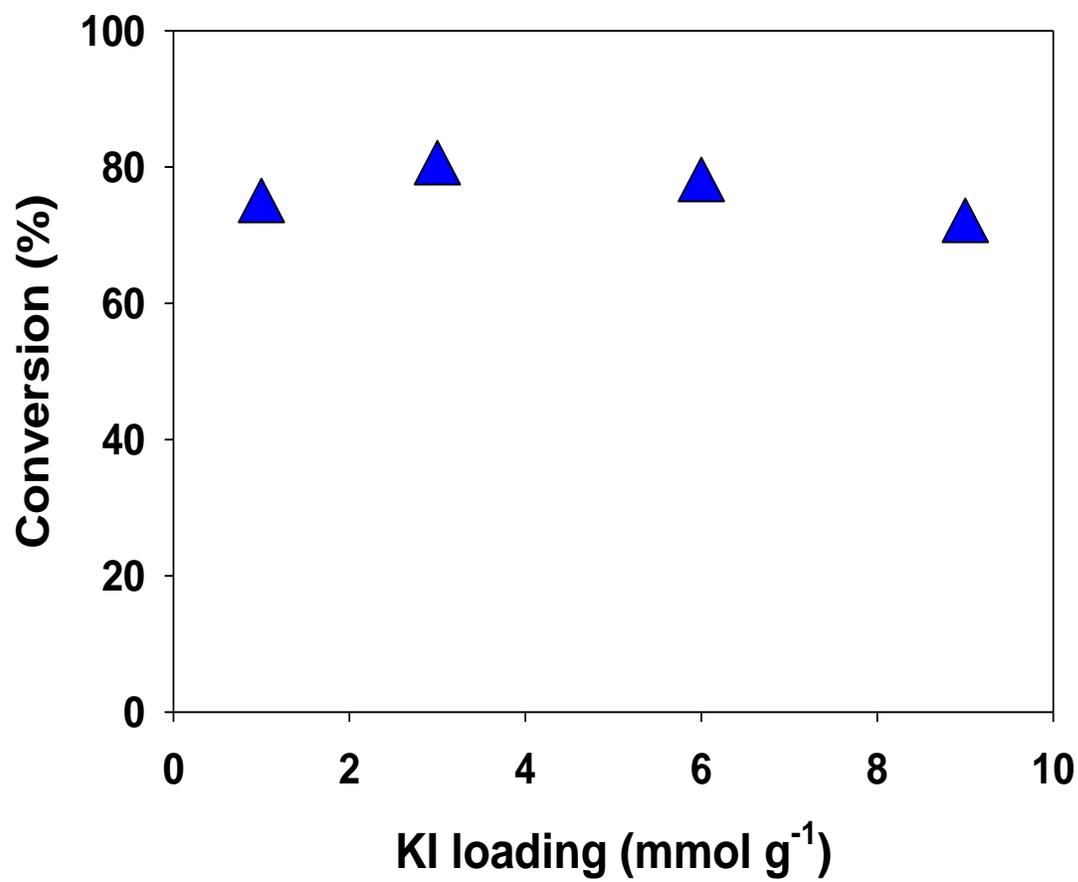


Figure 2.7. Effect of KI loading on conversion soybean oil into biodiesel. Beyond 3 mmol/g, no significant differences in conversions due to increased KI loading were found

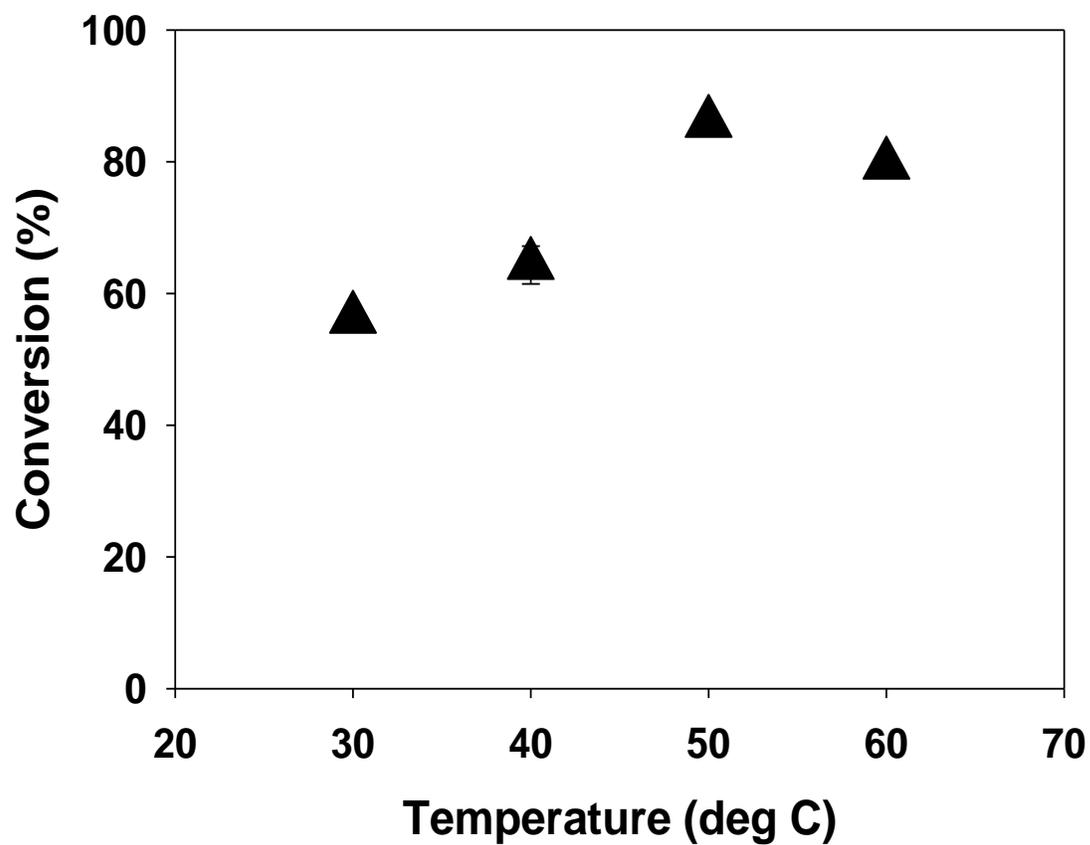


Figure 2.8. Effect of temperature on conversion soybean oil into biodiesel. 50 °C was found to be optimum temperature for KI-loaded calcined oyster shell catalyst.

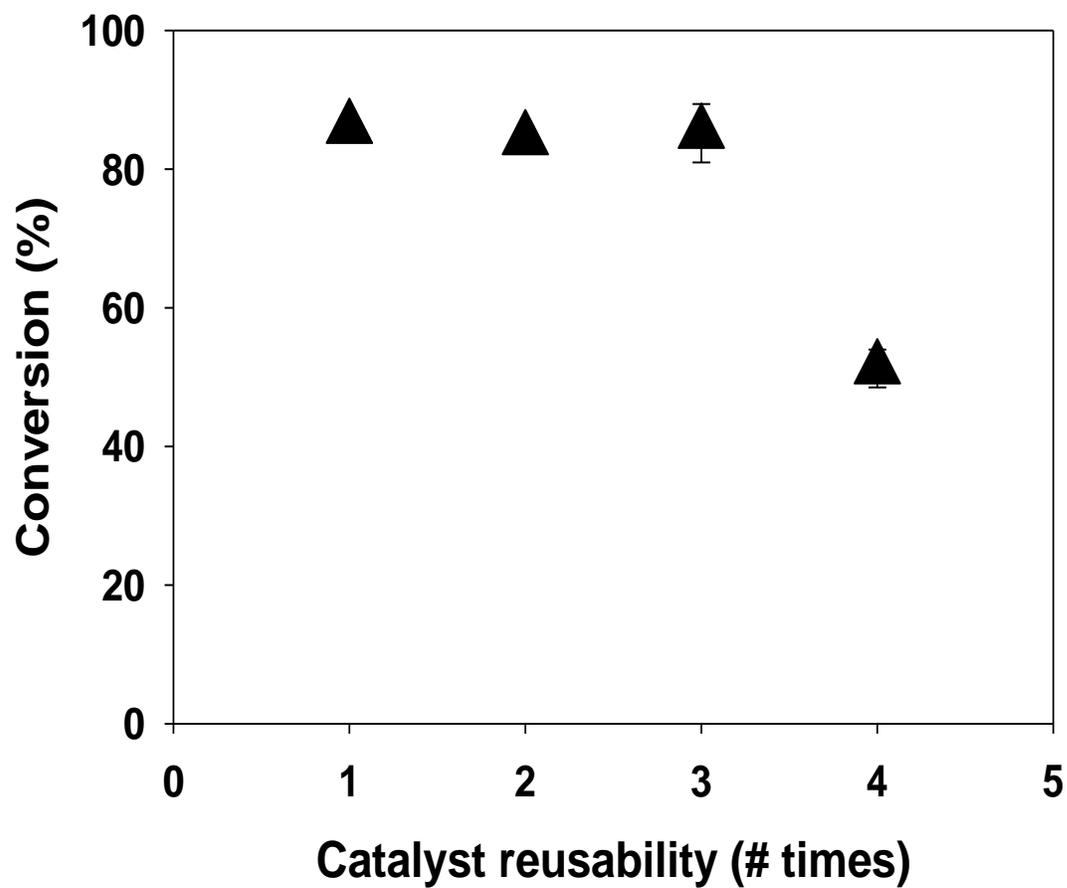


Figure 2.9. Effect of catalysts reusability on soybean oil transesterification. The catalyst activity appears to be reduced after three consecutive runs.

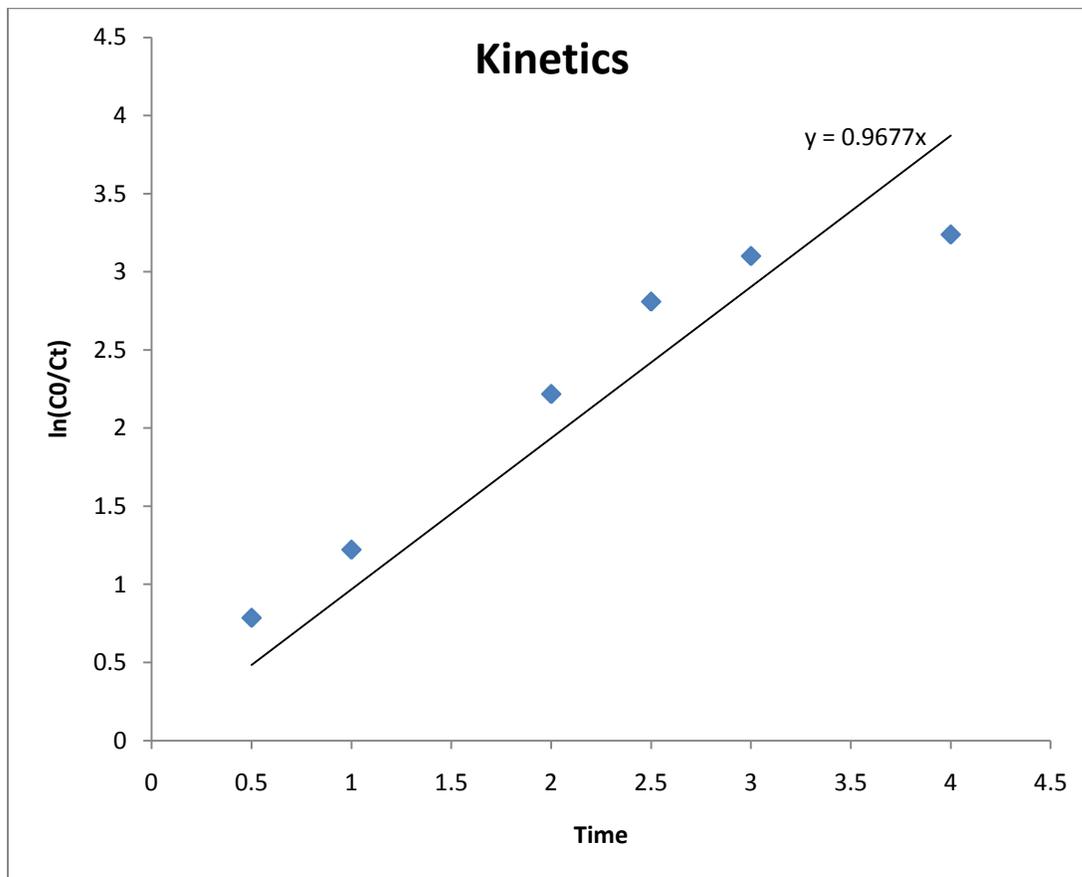


Figure 2.10: Batch reaction kinetics for 50 °C run. The plot shows a linear relationship between $\ln(C_0/C_t)$ vs time. This is characteristic of a first order reaction and has a reaction constant of $k=0.9667 \text{ h}^{-1}$.

Esterification of free fatty acids using sulfonated tobacco char as an acid catalyst

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Abstract

In progress towards the production of biodiesel from waste sources, acid catalysis is being studied to successfully pretreat free fatty acids (FFA) with high efficiency. Esterification of these FFAs is essential for subsequent transesterification of the waste oil for biodiesel production. The goal of this research was to synthesize sulfonated tobacco char as an acid catalyst for the esterification of oleic acid. The research objectives included the surface study of the sulfonated tobacco char catalyst; study the parameters of H_2SO_4 treatment time, reaction time and catalyst mass on the esterification of oleic acid. The batch kinetics of the esterification reaction was also studied. Imaging of the unused catalyst surface showed successful surface deposition of sulfonic groups. Further images of used and washed catalysts showed the presence of oil and continued presence of sulfonic groups, indicating continued activity of the catalyst. Through the course of this project it was found that 6 h treatment time with H_2SO_4 followed by 4 h reaction time and 1 g catalyst loading on the batch system enabled nearly 100% conversion of oleic acid to oleic acid methyl ester. Overall reaction kinetics was found to satisfy a second order reaction with respect to oleic acid with $k=4.3883 \text{ l/mole h}$. This catalyst was then used in a continuous packed bed reactor. On passing oleic acid and methanol as feed, complete conversion was achieved in 6 recycled passes. On using a high volume feed, equilibrium conversion was estimated at $10.57 \pm 0.4\%$ at a single pass. On addition of soybean oil with 15% oleic acid, equilibrium conversion dropped to $2.196 \pm 0.286\%$. Although these values are low, increasing residence time or

recycling could enable better pretreatment. Considering the importance of the tobacco industry in the state of North Carolina, the usage of these stalks as a support for catalysts provides a viable and promising market.

1. Introduction

Stemming from the mid 20th century, a steady increase on global temperature has been documented; causation being attributed to increases in human activity generated green house gas concentrations [1]. In reaction to this increase, renewable sources of energy are being evaluated for their net energy value, to provide the most energy-economic combination to combat the dependence on fossil fuels and to reduce the emission profiles of fuels [2]. Of the available alternatives, including sources of wind, hydro, solar and nuclear; bio-based fuels are most preferred owing to their energy densities being comparable with conventional fuels and that they can be used as replacements and blends of gasoline and petroleum diesel.

Biodiesel is a bio-based fuel, that has gained popularity due to its environment friendly usability with the attributes of biodegradability, non-toxicity, low emission profile and high energy content [1] [3] [4] [5]. It is produced on the transesterification of triglycerides (oils), in the presence of an organic alcohol, most often, methanol. The result of this reaction leads to the production of fatty acid methyl (alkyl) esters (FAME) or biodiesel; and glycerol as by-product. The major issue regarding its widespread acceptance is the cost, which relates back primarily to the cost of the raw material, virgin oil [6]. The use of a more economical feed stock could bring the cost of the fuel down, and in turn become competitive with diesel obtained from petroleum sources.

Since biodiesel is produced from triglyceride sources, a waste resource of similar nature would qualify as a potential feedstock. This opens avenues in the usage of used cooking oil,

animal fats and waste grease as potential feedstock substitutes for biodiesel production. It may be noted that the presence of many impurities in these sources would pose the additional pre-treatment of the feed stock. Also, the presence of free fatty acid is inherent to all the aforementioned sources of triglycerides. Direct alkaline mediated transesterification would no longer be an option for conversion, due to the production of soaps, upon reaction of the base and the free fatty acid.

As pretreatment of feedstock containing FFA becomes necessary, acid catalysts are being explored. It has been documented that acid catalyzed biodiesel requires more intense reaction conditions of higher temperature, methanol content and reaction time, in addition to the highly toxic nature of the waste stream including concentrated acid, increased risk to equipment corrosion and waste stream disposal issues. Heterogeneous catalysts could eliminate these issues, although introducing an additional reaction phase and hence increasing mass transfer limitations. This can be avoided if the porous structure of the catalyst is such that the reagents can orient and react to form the product [7].

To ensure these characteristics, various catalytic supports are being explored. Zeolites are microporous aluminosilicate supports which can be produced with controlled pore sizes and can be rendered acidic and hydrophobic by the incorporation of appropriate organic groups. Unless modified, zeolites produce a low conversion rate of less than 10%. This could be due to diffusion limitations due to its bulkiness [8]. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio can be altered to control the acidity of the structure and pore size. Other options in solid acidic catalysts are sulfonated

zirconia catalysts which are classified as super acidic compounds with reaction temperatures of about 140 to 160 °C but it has been reported that catalyst lost about 90% of its activity after the first round which ruled out its reuse [8]. Combinations of metal oxides of the type $(Al_2O_3)_X(SnO)_Y(ZnO)_Z$ have produced conversion percentages of about 80% in 4 hours or reaction time [9]. It has also been documented a 95% conversion rate in 2 h using acidic lanthanum and aluminium diphosphates [10]. Another category of complexes being investigated are heteropolyacids. There are very strong Bronstead acids and have high acidity, oxidizing ability and thermal stability. They can be used in both homogeneous and heterogeneous reaction, based on the nature of the compound. They can be made solid by their reaction with monovalent cations, to produce a salt [11]. Tungstophosphoric acids have been studied in this regard as homogeneous catalysts and heterogeneous catalysts. In one particular study conducted in Liverpool, UK, the esterification of hexanoic acid was observed in both states if the catalyst. At 60 °C and atmospheric pressure, nearly 100% conversion was achieved in the homogeneous scheme after 6 h of reaction and 1:20 acid to methanol ratio. In the heterogeneous scheme, approximately 45% conversion was achieved on a 15% loading of the HPA on support. A major issue through this experiment was the high leaching of the acid component. However, they did report that the intrinsic catalytic activity in both schemes was much greater than conventional acid catalysts [12]. To overcome solubility in aqueous phase, Cesium was added in varying concentrations, improving the complex's stability during the reaction and increasing reaction rates [13] [14]. Reactions were carried out at 60 °C at approximately 1:30 fatty acid to methanol ratio for 6 h. Maximum conversion was achieved

as 73% with high recyclability and very low leaching [15]. Another popular catalyst structure is the use of ion exchange resins. These are co-polymers of molecules like styrene, and sulfonic acid groups, grafted on benzene. The catalytic abilities of this polymer are dependent on its swelling capability, in order for the reactants to diffuse in, react and the product to diffuse out. For this to be achieved, the number of cross-links between the polymer chains should be low, but not too low so that the matrix loses its structural integrity. In the use of these catalysts, swelling is through soaking in typically ethanol and swelling time is also now a parameter, in catalyst reaction conditions [16]. These polymers, on supports like Nafion and Amberlyst have been used in both continuous and batch systems and have showed ranges of conversion efficiencies from 46% to 100% when used under moderate conditions of 60 °C to 65 °C at methanol to oil/FFA ratio ranging from 1:6 to 1:12 [17-20] . It may be also noted that through these studies, it has been a consistent observation that reusability of these catalysts are high and above 10 cycles. However, the only major drawback was the loss of catalyst after 10-12 cycles due to breakdown of the matrix. Also, the anion exchange resin is more effective in conversion of glycerides to FAME than the cation exchange resin for esterification of FFA [18].

Activated carbon has also been explored as supports for acid groups for catalysis in biodiesel production. However, due to its inherent inertness, the deposition of acid groups is not very effective and leads to leaching. This is overcome by using cellulosic substrates for production of the carbon [21]. The nature of this material being highly porous, enables the deposition of

active components on the surface and enables it high thermal and structural stability.

Activated carbon has also been used as a support for other acidic groups like heteropolyacids, metal complexes etc and has grown in popularity because it is easily available, inexpensive and is reliable over repeated usage. We also agree with the previous researchers about the advantages of activated carbon derived from cellulosic materials as catalyst supports. Since the overall goal of this research is to synthesize inexpensive and green catalysts from agricultural wastes, tobacco stalks were chosen to provide the support for deposition of sulfonic acid as the necessary acidic active sites. Although focus is being given to the use of discarded and waste cellulosic material for the production of ethanol, the possible contribution of this resource in the production of biodiesel may not be overlooked.

North Carolina State is presently the leading state in the production of tobacco and since the curing process is moving away from the stalk cure procedure, these stalks are now available for disposal, with the exception of tender stalk, that are capable of rising new buds. Although there is no significant amount of research in the area of using tobacco stalk as a support for catalyst production, wood fibers and other cellulosic substrates are being studied for the same purpose. With the hypothesis that the stalk will still be useful as a porous carbon support on carbonization, followed by addition of acid groups, tobacco stalk is being investigated in this project as a potential support for catalyst synthesis.

In this study, the sulfonated tobacco char was tested for its ability to esterify oleic acid in methanol and oleic acid (15%) in oil in methanol (1:30 ratio). The objectives include

- Studying reaction parameters to obtain maximum conversion. The parameters tested were H₂SO₄ soak time and reaction time on conversion of oleic acid to oleic acid methyl ester.
- Testing the catalytic activity of the acid catalyst in esterification of oleic acid in a continuous flow packed bed reactor.

2. Experimental

2.1 Catalyst Synthesis

Discarded tobacco stalk were carbonized by heating at 300 °C in an inert, Nitrogen rich atmosphere (11 min⁻¹ flow) to drive off organic matter. This char was then soaked in conc. H₂SO₄ for varying time periods of 2, 4 and 6 h to determine the effect of soaking time on esterification. This soaked char was then washed repeatedly with DI water for 30 - 40 min under constant flow to remove any excess acid and dried at 106 °C overnight. To ensure binding of the sulfonic groups on the catalyst surface, the treated tobacco stalk was calcined in a Nitrogen rich atmosphere at 250 °C for 2 h. The resultant treated char was then ground in a mortar-pestle to a size of 1-2.86 mm and stored until used.

2.2 Catalyst characterization- Scanning electron microscopy

The SEM images were obtained using a variable pressure scanning electron microscope (Hitachi S-3200). This is equipped with an energy dispersive X-ray analyzer (Oxford 10x10 mm SiLi detector, Advance Analysis Technologies amplifier, and a 4Pi pulse processor)

which was used to image and elaborate the elemental composition of the sample on based on relative composition. Prior to analysis, the samples were plated with Gold- Palladium to enhance visualization. A few catalyst particles were plated and mounted on an aluminum stub and was exposed to a 5keV accelerating voltage for imaging with an Everhart-Thornley secondary electron detector. EDS was performed with a higher energy electron beam of 20keV and an acquisition time of 120 s. The data was processed using Revolution software (4pi Analysis, Inc, Durham, NC) and subsequently exported into MS-Excel and Sigma Plot for graphing.

2.3 Free Fatty acid esterification

Three-neck flat bottom flasks (1000 mL) and reflux condensers (ACE Glass Inc., Vineland, NJ) were used as batch reactors. Typically, 4.63 ml of oleic acid and 30 ml of methanol (methanol to oil at 1:24) was mixed (to simulate 15% FFA content) in presence of the catalyst at 60 °C. We examined the effect of catalyst mass (0.5- 2.0 g), reaction time (60- 300 min), and the effect of acid treatment time on conversion of oleic acid to oleic acid methyl ester. The temperature was maintained at 60 °C using an automated hot plate (Isotemp, Fisher Scientific, Pittsburgh, PA), (below boiling point of methanol) for safety and economic reasons. After the reaction, the mixture was centrifuged at 2400 rpm at room temperature for 10 min for phase and catalyst separation. All experiments were performed in triplicates unless noted otherwise.

2.4 Continuous reactor system

Most of the work on FAME synthesis was performed in batch systems. In this work, we tested the ability of a continuous packed bed reactor system in conversion of oleic acid into oleic acid methyl ester. Additionally, we also tested an acid-base continuous packed bed reactor system for sequential esterification and transesterification of simulated waste oil (15% FFA (oleic acid) in 85% soybean oil).

Typically, the reactor consisted of a glass tube (2.5 cm dia X 30 cm length) (ACE Glass, Inc) packed with 20 g sulfonated tobacco char bed (acid). For the sequential esterification and transesterification reaction we used a 20 g sulfonated tobacco char bed (acid) followed by a 5 g oyster shell bed (base) (Figure 1). Temperature in the acid bed was maintained using a heat ribbon to a steady state temperature of 60 ± 5 °C. Mixture of methanol and oleic acid were flown into the reactor using a peristaltic pump and a hypodermic needle.

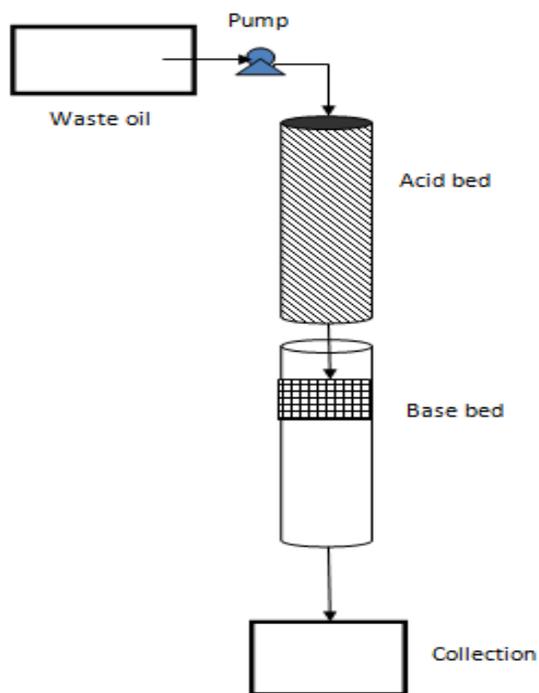


Figure 3.0: Schematic of the continuous flow system used for packed bed reactor.

The feed was introduced from a flask with a provision for constant discharge from the bottom. Constant mixing and heating was maintained using a stir plate (Isotemp, Fisher Scientific, Pittsburgh, PA). A reflux condenser was attached to the flask to prevent methanol evaporation. The flow rate was controlled with a peristaltic pump (medium flow) (Fisher Scientific, Pittsburgh, PA). In order to make quantify the conversions from the acid bed, a feed of methanol and oleic acid, with the same concentrations as used in the batch reactions, was tested. Samples from this reaction setup were collected at 5 min intervals and analyzed.

2.5 FAMES analysis

FAMES samples were analyzed using a gas chromatograph equipped with a mass spectrophotometer (Agilent 7890/5975C VLMSD). A HP-5 MS column was used to separate the FAMES. FAMES samples were diluted (1:1000) in hexane that contained an internal standard (GLC 90, SUPELCO). The chromatographic conditions include: injector: 240 °C, detector: 250 °C column: 100-200 @ 50 °C min⁻¹, 200-232 @ 2 °C min⁻¹, and 232-270 @ 30 °C min⁻¹. To minimize the sampling and instrumental error, three samples from each vial were analyzed. For each run, the ratio of FAMES peak area to the internal standard peak area (peak area ratio (PAR)) was calculated. Since the methyl ester obtained is soluble in methanol and there is no glycerol production for methanol quenching, a mixture of standard oleic acid methyl ester and methanol at equal molar concentration that would theoretically be achieved through the experimental setup was used to relatively measure the conversion and concentration of the methyl ester in each sample.

3. Results and Discussion

3.1 Catalyst Characterization

Figure 3.1A shows the surface of the carbonized tobacco. As was expected, the image clearly shows plant vessels in a repeated tubular fashion. EDS performed on the indicated area shows the presence of carbon, Potassium, Calcium and a small amount of other minerals, all of which we believe was taken up by the plant during the growth.

Figure 3.1B shows the surface of the catalyst, carbonized tobacco stalks impregnated with sulfonic groups. These added groups are seen on the surface as spheres attached to the surface. To confirm the presence of sulfonic groups, EDS was performed at the indicated area. The presence of a large Sulfur peak is indicative of successful deposition. The reduced size of the carbon peak can be attributed to the reduction in X-rays created by the carbon atom, having being covered by a layer of acid groups. As noted from the image, the distribution of these spheres is random and not uniform. Those areas of the catalyst with grooves have a higher density of sulfonic groups than the flat surfaces.

After reaction with oil in the packed bed reactor, the catalyst was re-examined in order to view any surface changes due to interaction with the feed and extent of leaching of sulfonic groups. From the image it is visible that there is a thick layer of oil on the surface of the catalyst. The EDS spectrum showed a very large carbon peak, covering the entire surface under inspection. This could be the reason that conversion was reduced after addition of oil. A similar result has been documented by Son et al., (2011) [19].

In order to reactivate the catalyst surface, we washed the bed with hexane by flowing 60ml through the bed. Images of the catalyst from the washed bed (Figure 3.1C) clearly shows that there is still oil on the surface of the catalyst but the EDS spectrum shows the presence of sulfur on the catalyst surface indicating that all activity is not lost and that past leaching of excess sulfur groups, some are still retained and may be able to facilitate further reaction cycles.

3.2 Effect of acid soaking time

In order to impregnate sulfonic acid groups on the surface of the carbonized tobacco stalk, concentrated H_2SO_4 soaking was carried out for 2 h, 4 h and 6 h to determine which would result in maximum deposition and hence highest conversion of FFA. Effect of soaking time was tested by running batch reactions of esterification of oleic acid in the presence of methanol at $60\text{ }^\circ\text{C}$ for 8 h, with samples being drawn at 2 h intervals. Figure 3.2 shows a comparative graph of conversions for each soaking time. After two hours, it appeared that the soaking time had no effect on the conversion. However, as the reaction time increased, 6 h soaked catalyst performed better than other catalysts. Nearly 100% conversion was achieved at 4 h, for the catalyst with a 6 h soak time. Equilibrium was reached and this was deemed the best and hence similar conditions were used for the following set of experiments. Our soak time is much lower than [22] other work where activated carbon was sulphonated for use as acid catalyst in esterification of FFA. We were successful in pushing the reaction to near completion with a 6 h soak time, while some groups have reported the requirement of an impregnation time of 15 h [21] [23] [24][22, 25] [26].

3.3 Effect of reaction time

Although there have been several reports to indicate that reaction times for acid catalyzed esterification are rather high, our results indicate that the reaction reached equilibrium and was at near completion after 4 h of reaction time (Figure 3.3). This can be attributed to the increased speed of esterification by acids when posed with competing reactions of

esterification and transesterification. It has been reported that acid catalysts catalyze in sequence the reaction with FFA and then the reaction with oils. Oezbay et al., (2008) reported a much lower reaction time of less than 2 h, although the stirring was at much higher rates and maximum conversion achieved was at 46% [18]. With the use of heteropolyacids on a carbon support, Alsalmeh et al., (2008) showed that in a heterogeneous batch system, they had no conversion of C-16 FFA until 4 h and at the end of 6h they reported a maximum conversion of 33% but with 10 times higher catalyst loading than the results present in the current study [12]. On using an ion exchange resin in a batch setup much similar to the experiment in question, equilibrium was reached by the most active combination of cross linking agents and active component at 5 h achieving a maximum of 80% conversion for a higher catalyst loading [17].

3.4 Effect of catalyst mass

Mass of catalyst used was varied from 0.5 g to 2 g. It was found that maximum conversion was achieved at 1 g loading. Figure 3.4 shows the trend in conversion for each loading rate for a 4 h reaction time. Since this catalyst has a high volume per unit mass, a higher loading rate was seen to clog the reaction mixture making mixing inefficient at the 400 rpm rotation speed. This could have caused the reduction in conversion at higher loading values. These values are competitive with those reported in the usage of similar catalyst supports with carbon as the support material. Hara in 2010 reported similar conversions after 4 h of reaction using 0.172 g catalyst per gram of oleic acid compared to our numbers being 0.241 g

catalyst per gram of oleic acid. It must be noted however that although our catalyst loading is higher, methanol used per unit of oleic acid is much lower (less by almost 4 times) [26]. It is also of interest to bear that the acid used by this group had carboxylic groups and phenolic OH groups to increase the acidity offered by the catalyst.

3.5 Kinetics

Overall order of the esterification reaction was determined over a reaction period of 4 h. Samples were drawn every 30 min and analyzed for conversion. Since conversion was well above 20%, integral model was used to determine reaction velocity k and order n . Using a second order integral model, we plotted $(1/C_0 - C_t)$ vs time (Figure 3.5), to obtain the slope and the intercept with slope being reaction constant k . The reaction constant is an indicative of the speed of the reaction at a given time. It has a real time application while comparing two catalysts. The scheme with the higher k value indicates a higher maximum velocity of reaction at same initial conditions, so a higher k points to a better catalyst, not holding other parameters in mind. This scheme was derived by integration of a second order rate equation. Hence, it may be concluded that the esterification of FFA in the presence of this tobacco stalk acid catalyst is a second order reaction with $k=4.3883$ l/mole h. The order of reaction is in tandem with work done by Shi et al., (2011) which reconfirms reaction order to be 2. Their reaction were run using different methanol ratios and they reported k values of 3.3 l/mole h for 13.5:1 and 6.768 l/mole h for 54:1 methanol to oil ratios [27] while the molar ratio for the current study was 1:50.3, placing the k values within the same ball park.

This also goes to show that the tobacco stalk based acid catalyst is in a competitive stature with the catalytic membrane used in their study with respect to reaction speed.

3.6 Esterification in a packed bed reactor

Initial tests were run on the acid bed to determine the amount of time that would be necessary for a feed to be completely esterified i.e. for complete pretreatment. When a feed of oleic acid in methanol was introduced through the bed, a retention time of 15 min was observed after which samples were drawn every 5 min and analyzed. Complete conversion was achieved in 6 passes on recycling feed after every pass (Figure 3.6). Upon introduction of a higher volume feed (300 ml feed of oleic acid and methanol) to test the longevity of the bed, conversion was high at first pass of 15 min at 66% while steady state conversion was achieved at $10.57 \pm 0.4\%$ after 45 min from introduction of feed into the reactor (Figure 3.7).

Oil was then added to the feed, such that oil to methanol ratio was maintained at 1:24 and the FFA content in oil was 15%. On this addition of oil to the FFA in feed, conversion at first pass reduced 7.86% while steady state conversion reduced to $2.196 \pm 0.286\%$ (Figure 3.8).

Results from the work published by Son et al., (2011) present a similar trend upon the addition of oil to the bed [19]. However, reaction temperature was maintained at 100 C leading to a misty gas phase introduction of methanol to the system which enhanced reaction rates. 97.5% conversion of oleic acid was achieved in a single pass. However, upon the addition of 25% FFA to oil, overall conversion of 30% was achieved. Although these

numbers are much higher than the ones reported in the present study, the reduction in conversion is noteworthy.

Upon introduction of the base bed, conversions dropped and no ester was detected in the outlet. However, on washing the bed with hexane, traces of ester was seen dissolved in the hexane. It is apparent that the product formed on first contact is accumulating on the catalyst and preventing it from further reaction. Work is being done currently to identify and bypass the root of this problem so that kinetic estimation for the fixed bed reactor may be studied.

Conclusion

Acidified tobacco stalk was tested as an acid catalyst in the esterification of oleic acid in the presence of excess methanol. Characterization results indicate catalyst protection by an oil envelope upon oil introduction into the system. However, on a single pass wash with hexane, traces of sulfur were still visible below the oil surface indicating possible reuse of the catalyst. Catalyst showed complete conversion of oleic acid at 60 °C, 400 rpm and 1:50 molar ratio of FFA to methanol. Upon usage in a fixed bed reactor, complete conversion was achieved after 6 passes on recycling. Addition of oil greatly reduced conversion numbers. The addition of the base bed resulted in no FAME concentration in effluent. This result is now being investigated for a possible explanation.

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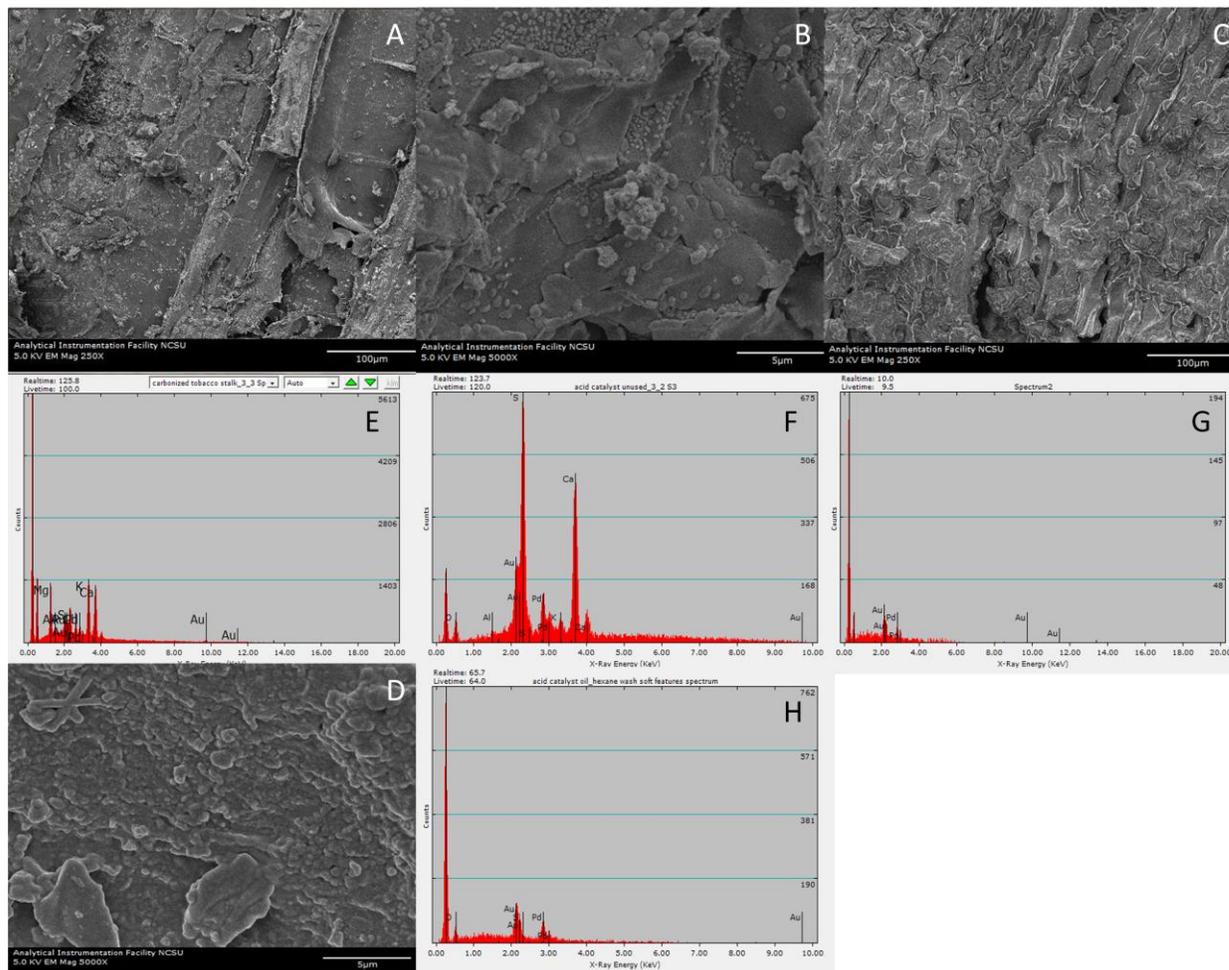


Figure 3.1: SEM images of acid catalyst, Tobacco char (A) at 250X magnification, acidified tobacco char (B) at 5000X magnification for visibility of sulfur groups, used acid catalyst (C) at 250X showing a thin blanket of oil on surface and catalyst washed with hexane (D) at 5000X. Corresponding EDS images (E), (F), (G), (H) show chemical composition of the analyzed section

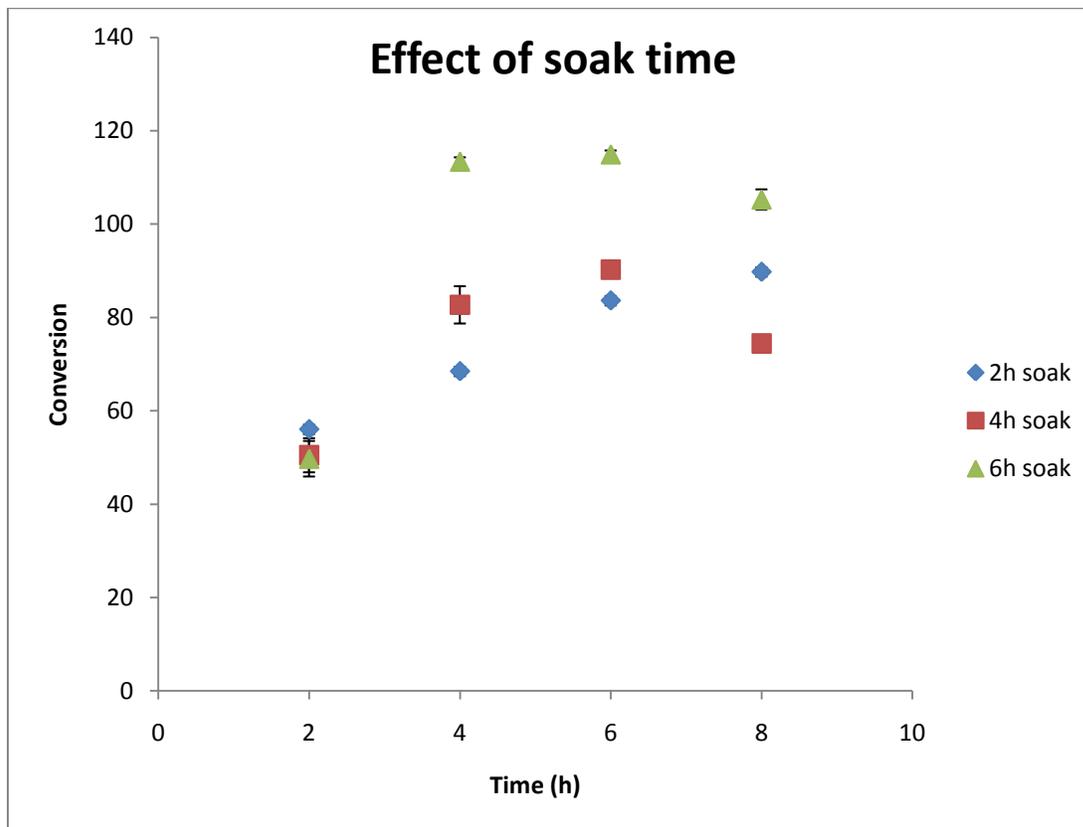


Figure 3.2: Effect of H_2SO_4 soak time on the activity of the catalyst. From the graph, the 6h acid soaked catalyst has maximum conversion and has reached equilibrium after 4h.

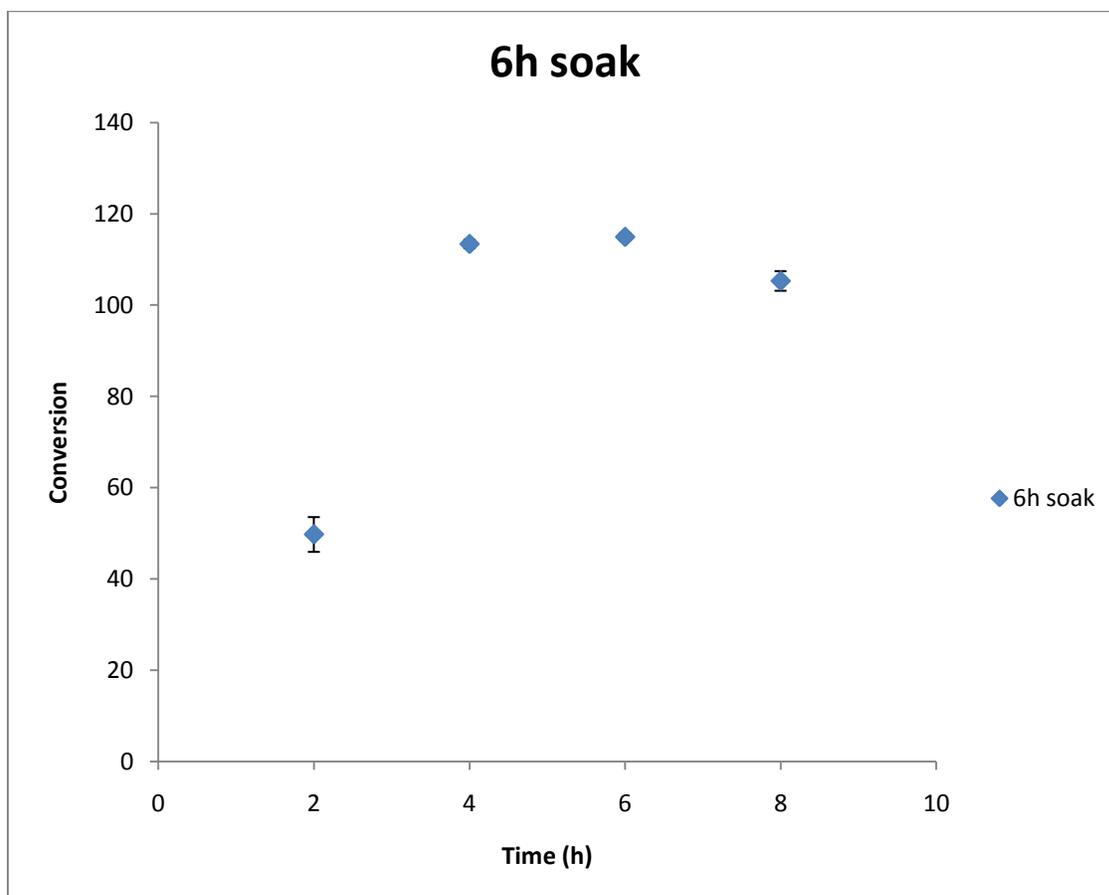


Figure 3.3: Effect of reaction time for achieving equilibrium. The 6h soaked catalyst achieved equilibrium and maximum conversion after 4h of reaction.

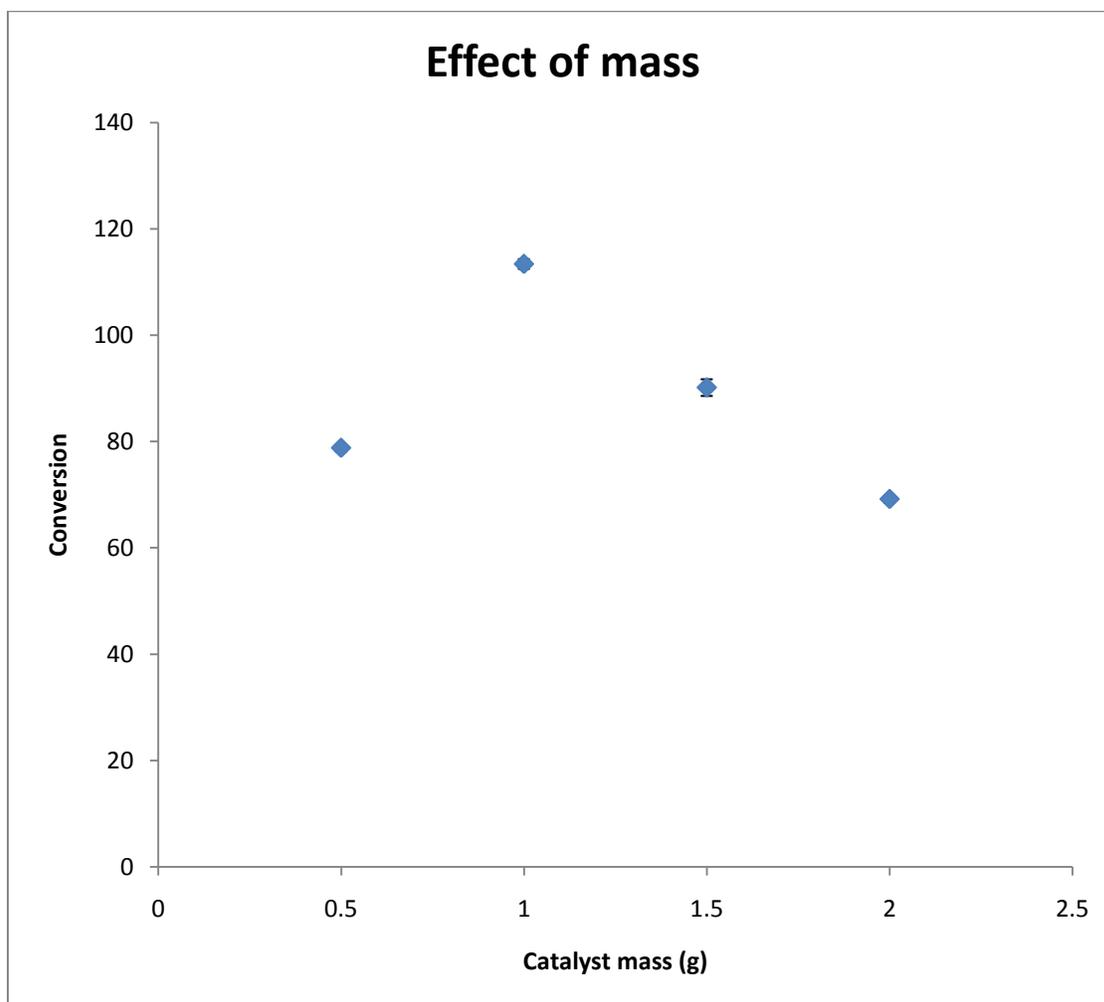


Figure 3.4: Effect of catalyst mass on conversion. 1g catalyst loading on the system showed maximum conversion after 4h of reaction.

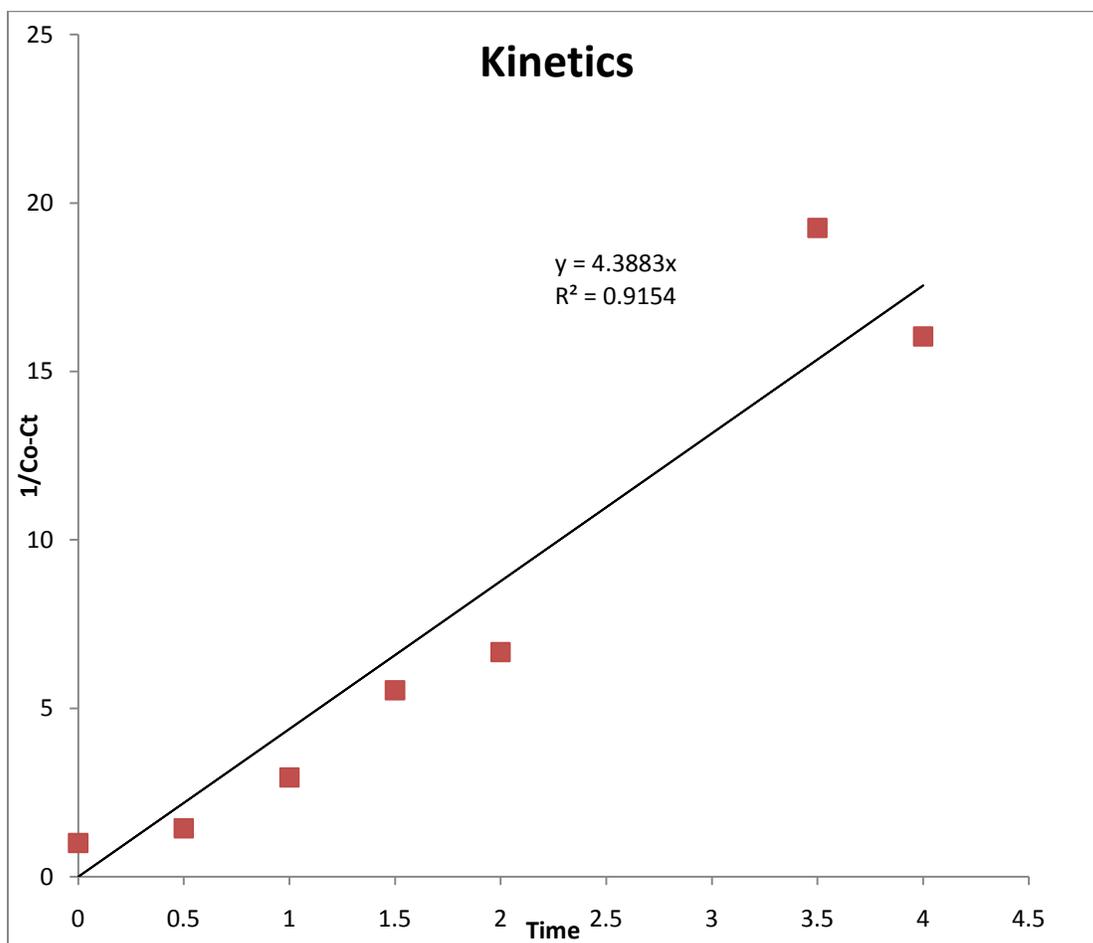


Figure 3.5: Kinetic data for batch esterification reaction. From the graph, the reaction was determined to be of second order and the rate constant $k=4.3883$ l/mol h.

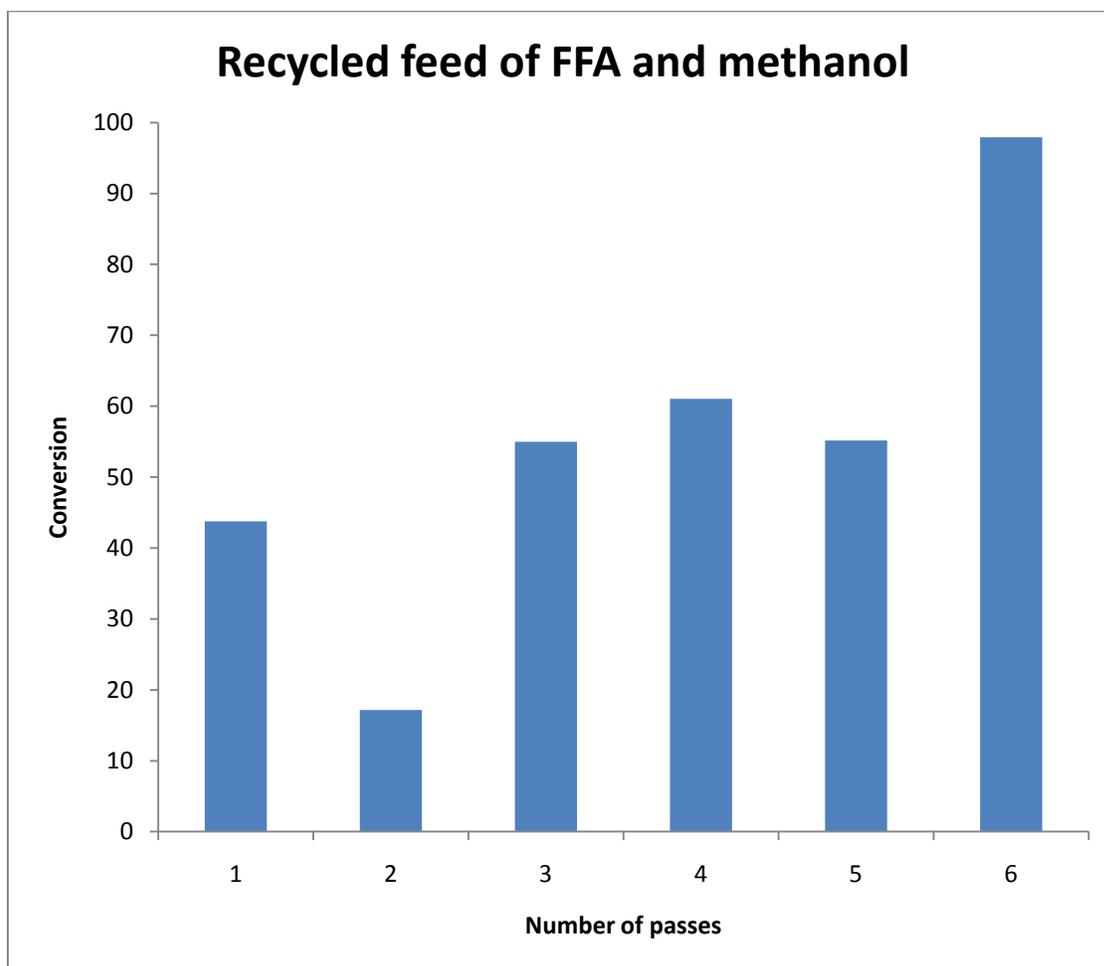


Figure 3.6: Conversions on recycling feed of oleic acid and methanol through packed bed to determine the number of passes required to achieve nearly complete conversion. From the figure it is evident that after 6 recycled passes of feed, 97.93% conversion is achieved.

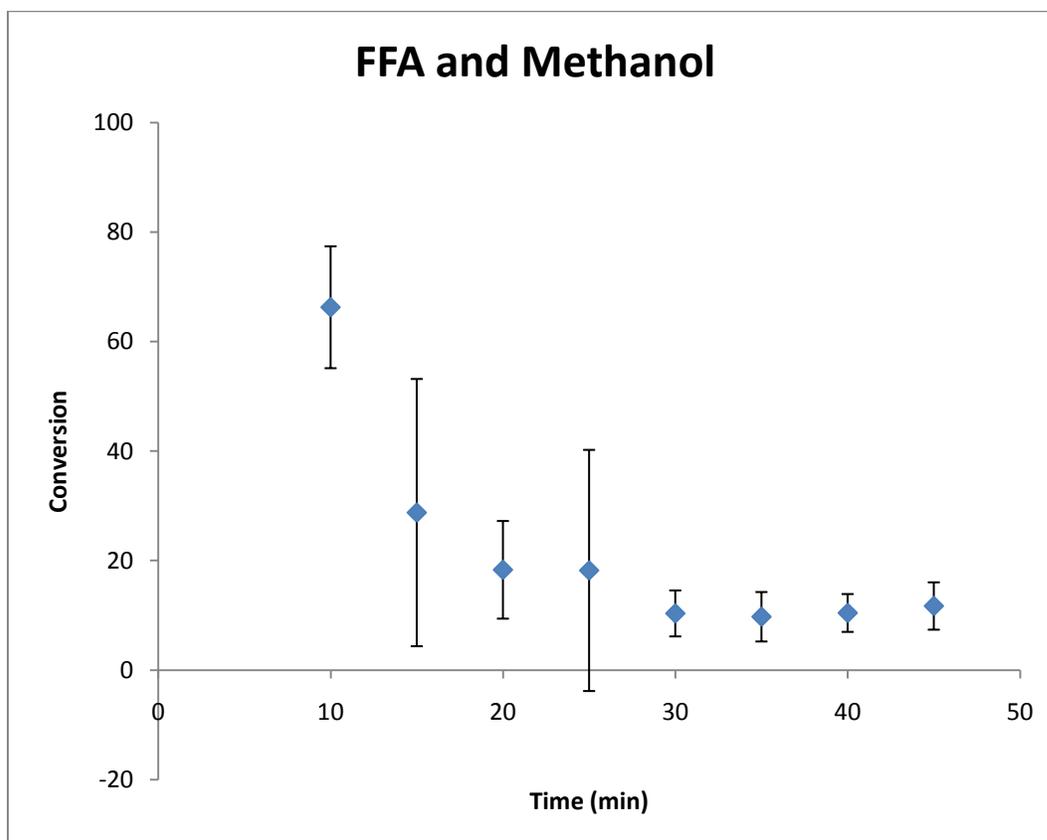


Figure 3.7: Continuous bed run using Oleic acid and methanol with samples taken every 5 min after immediate elution of product

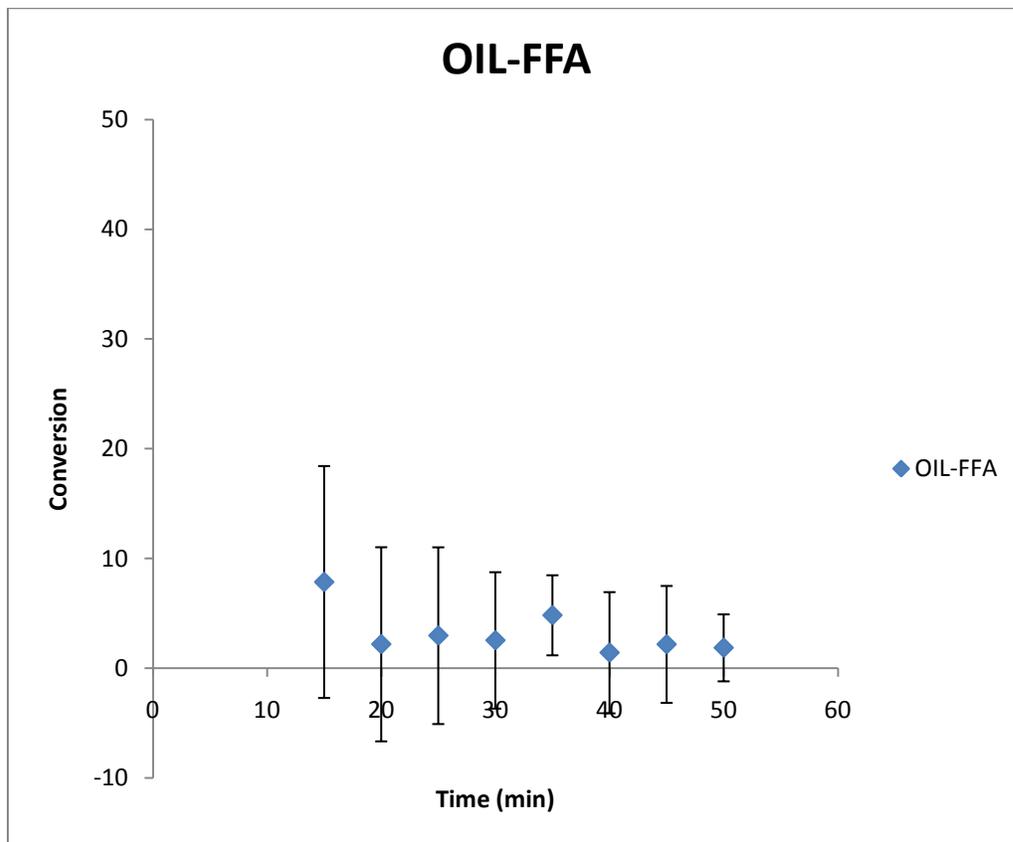


Figure 3.8: Continuous bed run using 15% FFA oil as 15% oleic acid in soybean oil. Equilibrium conversions are dropped to much lower upon the addition of oil to the oleic acid.

Summary and Conclusion

The goal of this thesis was to develop a solid base catalyst from agricultural waste material, for the production of biodiesel from waste oil. Biodiesel fuel is a mixture of fatty acid methyl esters, which is usually produced upon the transesterification of tri-glycerides or the esterification of free fatty acids. This is a broadly a catalyst mediated reaction. Since the goal of this research is extended to the use of waste oil, which contains both triglycerides and a percentage of free fatty acids, acid and base catalysts were synthesized, characterized and tested for conversion of feed to biodiesel. Specific focus was laid on the use of oyster shells. The supporting acid catalyst was developed using tobacco stalk, to facilitate pretreatment of oil before further treatment using the base catalyst. Work was completed in three phases.

In the first phase, oyster shells were used to synthesize a base catalyst. This production was based on the premise that the major component of oyster shells, Calcium carbonate, when calcined, is converted to calcium oxide, a material that has been documented to have strong base catalytic properties in the production of biodiesel. Upon testing, calcined oyster shells showed positive signs in the conversion of soybean oil to biodiesel. Supported by reports indicating increased catalytic activity upon impregnation with metal halides, KI was impregnated on the calcined oyster shells and tested for change in activity. Conversion increased from 45% to 80% upon impregnation with KI. BET analysis of the catalyst material indicated a 10 time increase in available surface area on calcination and a further increase by a factor of 3.33, upon addition of KI.

To facilitate high conversion of virgin soybean oil to biodiesel, conversion by varying the reaction parameters of catalyst mass, KI loading, oil to methanol ratio and temperature were studied. The results indicated that 1 g of 3 mmol/g KI loading gave high conversion of 86% for a reaction time of 4 h, with 1:10 oil to methanol ratio for a 50 °C run. The catalyst could be reused with no washing for five consecutive runs before losing activity.

In the second phase, tobacco stalk was carbonized and acidified using concentrated sulfuric acid and used as an acid catalyst. This was tested on a mixture of oleic acid and methanol to determine the working of the catalyst in the esterification process. The amount of oleic acid was selected based on the corresponding amount of 15% FFA in waste oil feed stock.

Keeping the temperature constant at 60 °C, just below the boiling point of methanol, and methanol content at the same amount that will result in a 1:24 ratio on oil addition, effect of acid soak time, reaction time and catalyst mass was tested. It was observed that after 4h of reaction, 1 g of 6 h acid soaked showed complete conversion in a batch reactor. Overall reaction kinetics was studied, keeping methanol concentration at a large excess. Reaction was determined as a second order reaction with reaction constant $k=4.3883$ l/mole h. The third phase was an integration of the two catalysts in a continuous, sequential fixed bed reactor with a 20 g acid bed and 4 g base bed. Inlet flow was controlled with a peristaltic pump and trickle flow was facilitated using a hypodermic needle. A 15% FFA oil was used as feed, to emulate waste oil. Although conversion was observed, the addition of waste oil greatly reduced conversion efficiency per pass and can be attributed to the additional mass transfer

limitations. This was confirmed by SEM images of the catalytic surface before and after usage. The entire surface was seen to be covered in oil, protecting catalytic sites from reacting with the FFA for esterification. It can then be inferred that the high FFA content in the oil prevented transesterification via the base bed, resulting in almost no conversion at the end of a single through-pass. Since conversion was observed in the two beds individually in preliminary studies, process improvement through recycle through acid bed separately, before passing through the base bed.

Future work in this area can be followed in the following directions

- Implementation of a continuous packed bed reactor system, ensuring complete FFA conversion before inlet into the base bed.
- Kinetic study of the combined bed overall reaction
- Study of effect of FFA concentration on overall conversion.

Biodiesel as a clean fuel could be the solution to the world's growing fuel crisis. It has been proved to be efficient, biodegradable and eco-friendly. Despite these advantages the mass production of biodiesel is not yet economically feasible. With the cost of production greater than \$4 per gallon, it is necessary that the production process be improved so that a higher conversion is achieved with lower production cost. Also, since conversion rates largely depend on the catalyst used, the focus of most research has been on improving catalysts used for biodiesel production. Considering the present research is based off the two most abundantly available waste resources in the state of North Carolina, there is a lot of scope for

continued research in this area. A breakthrough that can industrialize the usage of these materials will economize green fuel production in the state and accelerate the achievement of the 5% green house gas emission reduction and reduction of the state's carbon footprint.