

University of Nevada, Reno

**Biodiesel production from non food feedstocks  
using a bifunctional heterogeneous catalyst and  
glycerol byproduct utilization**

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE  
REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN

Materials Science and Engineering

by

Narasimharao Kondamudi

Dr. Mano Misra / Advisor

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## THE GRADUATE SCHOOL

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prepared under our supervision by

**NARASIMHARAO KONDAMUDI**

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Dr. Manoranjan Misra, Advisor

Dr. Maurice C. Fuerstenau, Committee Member

Dr. Carl C. Nesbitt, Committee Member

Dr. Qizhen Li, Committee Member

Dr. John C. Cushman, Graduate School Representative

Marsha H. Read, Ph. D., Associate Dean, Graduate School

December, 2010

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## **Abstract**

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Biodiesel is a fuel comprised of monoalkyl esters of long chain fatty acids derived from vegetable oils or animal fats. In the biodiesel industry, most biodiesel production is made from food sources, such as vegetable oils. The production of biodiesel from renewable and waste materials is an attractive alternative to the conventional agricultural feed stocks such a corn and soybean.

The conventional biodiesel production process poses several problems in processing feedstocks with high free fatty acids (FFAs) such as waste vegetable oils, in separation and purification of biodiesel. An efficient and clean process is required for large-scale production to make the biodiesel industry more sustainable. Heterogeneous solid catalysts have the potential to eliminate these problems, regardless of feedstock.

The glycerol is a byproduct of the biodiesel industry. Crude glycerol processing is expensive. Heterogeneous catalysis offers a solution to this problem by selective conversion of glycerol into value added chemicals.

In this study, two new feedstocks, for biodiesel production namely spent coffee grounds and feathermeal have been explored. A bifunctional heterogeneous catalyst has been developed for successful conversion of high FFA feedstocks into biodiesel and a cost effective, highly selective catalyst has been discovered for glycerol oxidation to glyceric acid.

Spent coffee grounds yield 10-15% oil depending on the coffee species (e.g., arabica, robusta). The biodiesel derived from the coffee grounds (100% conversion of oil to biodiesel) was found to be stable for more than one month under ambient conditions due to inherent antioxidants. Coffee grounds after oil extraction are ideal materials for garden fertilizer, feedstock for ethanol, biochar, bio-oil and as fuel pellets.

Chicken feather meal contains 11-15% fat content. This project describes an environmentally friendly approach to extract the fat content using water as a solvent for biodiesel production. Currently, feather meal has been used as an animal feed (high protein content) and as a fertilizer (high nitrogen content). The feather meal can be used to extract biodiesel feedstock (triglycerides) without altering, rather improving its existing uses as a better animal feed and a better fertilizer.

A method has been developed to produce biodiesel using Quintinite-3T (Q-3T) as a heterogeneous bifunctional catalyst. The reaction can be carried out using high FFAs containing feedstocks as well. The reaction times were shorter when compared to those for the existing heterogeneous catalysts. In this work, a complete characterization of Q-3T, catalytical activity, including acidic and basic site studies and catalyst recycling studies is presented.

Titanium disilicide ( $\text{TiSi}_2$ ) was identified as a cost effective and selective catalyst for conversion of glycerol into glyceric acid. An investigative study of *in situ* glycerol oxidation in aqueous media is reported.

## Table of Contents

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Section	Page Number
<i>Acknowledgments</i>	i
<i>Abstract</i>	iii
<i>Table of Contents</i>	v
<i>List of Tables</i>	ix
<i>List of Figures</i>	xi
<b>1. Introduction</b>	1
1.1. Non-Food and Inexpensive Feedstock	1
1.2. Biodiesel Production Methods	2
1.3. Feasible Solution for Excess Glycerol	4
1.4. Research Motivation and Objectives	4
1.5. Outline of the Thesis	5
<b>2. Literature Review on Biodiesel</b>	6
2.1. Introduction	6
2.1.1. Oils/Fats as Fuels	7
2.1.2. Problems in Direct Usage of Oils as Fuels	9
2.1.3. Modification of Vegetable Oils for Effective Usage	9
2.1.4. Biodiesel	10
2.2. Non-Food Sources for Biodiesel production	15
2.3. Conventional Homogeneous Catalytical Processes	17

2.3.1. Base Catalyzed Transesterification	17
2.3.2. Acid Catalyzed Esterification	20
2.3.3. Acid Catalyzed Transesterification	23
2.3.4. Drawbacks in Conventional Homogeneous Catalysis	24
2.4. Heterogeneous Catalysts for Biodiesel Production	26
2.4.1. Heterogeneous Acid Catalysts for Transesterification	26
2.4.2. Heterogeneous Base Catalysts for Esterification	27
2.4.3. Heterogeneous Acid Catalyst for Esterification	28
2.5. Oxidation Products of Glycerol	29
2.6. Approach to Method Development	31
<b>3. Materials, Methods and Characterization Techniques</b>	<b>33</b>
3.1. Materials	33
3.2. Experimental Procedures	34
3.3. Characterization Techniques	39
<b>4. Biodiesel from Spent Coffee Grounds and Feather Meal</b>	<b>44</b>
4.1. Biodiesel Production from Spent Coffee Grounds	44
4.1.1. Introduction	44
4.1.2. Results and Discussion	45
4.1.2.1 Extraction and Purification of Oil from Spent Coffee Grounds	45
4.1.2.2. Conversion of Oil to Biodiesel	47
4.1.2.3. Purification and Analysis of Biodiesel	50
4.1.2.4. Inherent Antioxidants in Coffee Biodiesel	57

4.1.3. Conclusion	59
4.2. Biodiesel Production from Feathermeal	59
4.2.1. Introduction	59
4.2.2. Results and Discussion	60
4.2.2.1 Extraction and Purification of Fat from Feathermeal	60
4.2.2.2. Conversion of Fat into Biodiesel	61
4.2.2.3. Purification and Analysis of Biodiesel	62
4.2.3. Conclusion	70
<b>5. Bifunctional heterogeneous catalyst for biodiesel production</b>	71
5.1. Introduction	71
5.2. Results and Discussion	73
5.2.1. Catalyst Characterization	73
5.2.2. Catalytical Activity and Optimization	77
5.2.2.1. Effect of Reaction time	77
5.2.2.2. Effect of Molar Ratio of Methanol/Oil	78
5.2.2.3. Effect of Reaction Temperature	79
5.2.2.4. Effect of Catalyst Loading	80
5.2.3. Acid Catalyzed Esterification	81
5.2.4. Base Catalyzed Transesterification	82
5.2.5. Simultaneous Esterification and Transesterification	83
5.2.6. Recycling Studies	86
5.3. Conclusion	88

<b>6. Selective Photocatalytic Oxidation of Glycerol to Potassium Glycerate Using Titanium Disilicide</b>	90
6.1. Introduction	90
6.2. Results and Discussion	92
6.2.1. Alkaline Oxidation of Glycerol to Glycerolate	93
6.2.2. Influence of $\text{TiSi}_2$ on Selective Oxidation of Glycerol	94
6.2.3. Catalyst Stability	96
6.2.4. Crude Glycerol and Purified Glycerol	99
6.3. Conclusion	99
<b>7. General Conclusions</b>	100
<b>References</b>	106
<b>Appendices</b>	126
<b>Biography</b>	131

## List of Tables

---

<b>Table Name</b>	<b>Page Number</b>
<b>Table 2.1.</b> Chemical structures of some fatty acids	8
<b>Table 2.2.</b> Comparison of the standards for diesel and biodiesel based on American Society for Testing and Materials	12
<b>Table 2.3.</b> ASTM standards for biodiesel	13
<b>Table 2.4.</b> Fatty acid compositions of some vegetable oils	14
<b>Table 2.5.</b> Present day major non-food feedstocks	17
<b>Table 2.6.</b> Typical solid acid and base catalysts employed for transesterification	26
<b>Table 4.1.</b> pH change of coffee oil with extracting solvents	47
<b>Table 4.2.</b> The retention factor calculations of some important FAMES present in the coffee biodiesel	53
<b>Table 4.3.</b> Quantitative analysis of coffee biodiesel	53
<b>Table 4.4.</b> ASTM results for coffee biodiesel	55
<b>Table 4.5.</b> Comparison of coffee oil with other waste feedstocks for biodiesel production	56
<b>Table 4.6.</b> Quantitative analysis of feather meal biodiesel	67
<b>Table 4.7.</b> ASTM analysis of feathermeal biodiesel	68
<b>Table 4.8.</b> Total poultry industry annual production of meal, waste products and tentative amounts of biodiesel produced in the year 2008	69
<b>Table 5.1.</b> ICP results for Q-3T synthesized using two different methods namely NaOH (Na-Q3T) and NH <sub>4</sub> OH (NH <sub>4</sub> -Q3T)	75

<b>Table 5.2.</b> ASTM analysis of non-conventional feedstocks namely, oil from spent coffee grounds and waste vegetable oil	86
<b>Table5.3.</b> Conversions obtained in recycling Q-3T in transesterification of coffee oil. The reaction conditions: Na-Q3T (10 wt%), coffee oil (20 mL), oil to methanol (1:12) stirred at 348 K for 2h. Conversion in cycle 1 is with fresh catalyst and those in cycle 2-5 were with recycled catalyst. Presence of MG, DG, and TG were tested using ASTM D6584 method	86
<b>Table 5.4.</b> Comparison of Q-3T catalyst with reported catalysts	87
<b>Table 7.1.</b> C/N ratio of the used coffee grounds before and after oil extraction process	101
<b>Table 7.2.</b> The stoichiometric equations of the CO <sub>2</sub> production per gram of each fatty acid	101
<b>Table 7.3.</b> Future market scenario of coffee biodiesel	102
<b>Table 7.4.</b> Total poultry industry annual production of meat, waste products and tentative amount of biodiesel produced from the waste products in 2008	103

## List of Figures

---

Figure Name	Page Number
<b>Figure 2.1.</b> Chemical structures of typical TG (2.1 a), FFA (2.1 b) and glycerol (2.1 c) molecules, where R, R <sup>I</sup> , and R <sup>III</sup> represent different free fatty acid chains	7
<b>Figure 2.2.</b> Mechanism of homogeneous base catalyzed transesterification	19
<b>Figure 2.3.</b> General biodiesel production steps	20
<b>Figure 2.4.</b> Schematic representation of two-stage biodiesel production	21
<b>Figure 2.5.</b> Mechanism of homogeneous acid catalyzed transesterification	22
<b>Figure 2.6.</b> Schematic of acid catalyzed transesterification	24
<b>Figure 2.7.</b> Mechanism of homogeneous base catalyzed transesterification	28
<b>Figure 2.8.</b> Oxidation products of glycerol	30
<b>Figure 3.1.</b> Experimental setup for oil extraction from spent coffee grounds	34
<b>Figure 3.2.</b> Centrifuge bottle showing fat separation from feathermeal	35
<b>Figure 3.3.</b> Experimental setup for photo catalytic glycerol oxidation in a batch reactor	39
<b>Figure 4.1.</b> Schematic representation of the biodiesel production process from spent coffee grounds	45
<b>Figure 4.2.</b> HPLC chromatogram of the oil extracted from spent coffee grounds	46

<b>Figure 4.3.</b> Scanning Electron Microscope (SEM) image of the dried spent coffee grounds	46
<b>Figure 4.4.</b> HPLC chromatogram of coffee biodiesel	48
<b>Figure 4.5.</b> <sup>1</sup> H-NMR of coffee oil	49
<b>Figure 4.6.</b> <sup>1</sup> H-NMR of coffee biodiesel	49
<b>Figure 4.7.</b> Gas chromatogram of coffee biodiesel	51
<b>Figure 4.8.</b> Gas chromatogram of fatty acid methyl esters standards from C <sub>8</sub> -C <sub>22</sub> shows a good separation for quantitative study	52
<b>Figure 4.9.</b> Coffee oil and biodiesel produced from spent coffee grounds	54
<b>Figure 4.10.</b> Spectroscopic monitoring of DPPH• reduction in presence of coffee biodiesel	58
<b>Figure 4.11.</b> DPPH activity reduction as a function of time	58
<b>Figure 4.12.</b> A schematic representation of biodiesel production from poultry waste	60
<b>Figure 4.13.</b> HPLC chromatogram of fat extracted from feathermeal	62
<b>Figure 4.14.</b> HPLC chromatogram of feathermeal biodiesel	64
<b>Figure 4.15.</b> Gas chromatogram of feathermeal biodiesel	65
<b>Figure 4.16.</b> TG (a) and biodiesel (b) obtained from feathermeal	65
<b>Figure 5.1.</b> A schematic representation of operating principle of Q-3T	73
<b>Figure 5.2.</b> XRD pattern of (a) as synthesized Na-Q3T, (b) Calcined Na-Q3T, (c) hydrated Na-Q3T and (d) as synthesized NH <sub>4</sub> -Q3T.	74
<b>Figure 5.3.</b> SEM image of as-synthesized NaQ3T. EDX spectrum (insert) shows the Al/Mg ratio to be 2.07	75

<b>Figure 5.4. A.</b> TEM image of as prepared Na-Q-3T which showed distorted spherical particles in the range of 40-60 nm.	76
<b>Figure 5.4. B.</b> HRTEM and FFT pattern of the particles	76
<b>Figure 5.5.</b> FTIR image of pyridine treated Na-Q3T showing the presence of both Brønsted acidic and Lewis acidic sites	77
<b>Figure 5.6.</b> Influence of reaction time on the conversion of canola oil feedstock	78
<b>Figure 5.7.</b> Influence of oil to methanol ratio on biodiesel production	79
<b>Figure 5.8.</b> Influence of temperature on biodiesel production	80
<b>Figure 5.9.</b> Influence of catalyst wt% on biodiesel production	81
<b>Figure 5.10.</b> GC chromatogram of (a) octanoic acid and (b) octanoic acid methyl ester.	82
<b>Figure 5.11.</b> Reaction kinetics of different feedstocks with variable FFA content using Na-Q3T as a catalyst	83
<b>Figure 5.12.</b> A comparison of coffee oil and coffee biodiesel HPLC chromatograms. The disappearance of oil peaks indicate the completion of the transesterification reaction	84
<b>Figure 5.13.</b> GC-MS chromatograms of coffee oil fatty acid methyl esters using (a) KOH and (b) coffee oil with >30 wt% FFA using Q-3T as a catalyst	85
<b>Figure 6.1.</b> HPLC chromatogram of pure glycerol and photocatalytic reaction products at 65oC, 1M KOH, 10 wt% glycerol (5g in 50 mL) and 1 wt% TiSi <sub>2</sub>	92
<b>Figure 6.2.</b> <sup>13</sup> C-NMR of the reaction end product (glyceric acid). A 100% conversion of glycerin to glyceric acid was confirmed	92
<b>Figure 6.3.</b> FTIR spectrum of reaction end product (glyceric acid)	93

<b>Figure 6.4.</b> Proposed mechanism of $\text{TiSi}_2$ assisted glycerol oxidation to glyceric acid. Surface stored oxygen of $\text{TiSi}_2$ acts as in situ oxidizing agent	95
<b>Figure 6.5.</b> Gas chromatograms of the gases evolved from the following reactions, (a). Water only, (b). 1M KOH solution and (c). 1M KOH and 5 wt% glycerin	96
<b>Figure 6.6.</b> HPLC chromatogram showing the conversion of glycerol at 6h of reaction time (64.3 wt %)	97
<b>Figure 6.7.</b> SEM images of catalyst ( $\text{TiSi}_2$ ) before (A) and after (B) the photo catalysis. EDX analysis (inset table) shows the excess oxygen present in the catalyst after 12h reaction.	97
<b>Figure 6.8.</b> XRD pattern of (a) $\text{SiO}_2$ , (b) $\text{TiO}_2$ , (c) $\text{TiSi}_2$ and (d) $\text{TiSi}_2$ after 10h photocatalytic reaction	98
<b>Figure 7.1.</b> KOH costs for the production biodiesel from feedstocks containing (a) 5% FFA (b) 10% FFA (c) 50% FFA and (d) 90% FFA. The Q-3T cost (e) is given for comparison	104

## **Chapter 1 † Introduction**

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Biodiesel is a mixture of mono alkyl esters of long chain fatty acids.<sup>1</sup> It has become an increasingly attractive fuel because it can be made from renewable resources and combines high performance with environmental benefits.<sup>2</sup> In industrial processes, highly refined vegetable oils, primarily consisting of triglycerides (TGs) are typically used as feedstocks. These feedstocks are reacted with low molecular weight alcohols, e.g., methanol and ethanol, using homogeneous alkali catalysts (such as NaOH and KOH). The resulted products are biodiesel and glycerol. The biodiesel industry is facing some problems, which make the fuel less sustainable, as discussed below.

### **1.1 Non food and inexpensive feedstocks**

More than 95% of the biodiesel production is made from edible oils. By converting edible oils into biodiesel, food resources are actually being converted into fuels. Moreover, the high cost of biodiesel production is largely attributed to the cost of virgin vegetable oils used as feedstock.<sup>3</sup> The other inexpensive feedstocks such as waste vegetable oils and animal fats contain high free fatty acids (FFAs).<sup>4</sup> However, synthesis of biodiesel from these low quality oils is challenging due to undesirable side reactions as a result of the presence of FFAs and water. Investigation of high quality, non-food, cheap feedstocks for biodiesel production is necessary for the biodiesel industry to thrive into the future.

## 1.2 Biodiesel production methods

The reaction between TGs and low molecular weight alcohols, such as methanol and ethanol, is called transesterification. Transesterification is catalyzed by the presence of a base or an acid or an enzyme in the reaction mixture.<sup>1,5,6</sup> In current day industrial practice, base catalyzed homogeneous catalysis using KOH or NaOH for the transesterification is well-known because it is cheap, easily available and easy to handle. However, base catalyzed transesterification needs a higher purity feedstock. The FFAs present in the feedstock react with the alkaline catalyst and forms soap. The soap formation consumes the catalyst and decreases the biodiesel yields. Moreover, the soap formed during the reaction prevents glycerol separation from biodiesel. Homogeneous base catalyzed transesterification of TGs is not an economical process if the feedstock's FFA exceeds 0.5 wt% of total TG content.<sup>7</sup> In general, feedstock with more FFA has been treated in two ways.

- (i) *Removal of FFA:* The FFA content in the feedstock can easily be removed using basic solution (KOH + water) to form soap. A simple centrifugation process will separate the pure feedstock from the soap. This technique is best for feedstocks containing less than 2% FFA. For feedstocks such as waste vegetable oil (10-15%), poultry fat (30-40%) and grease (75-100%), however, removal of FFA yields far less biodiesel.
- (ii) *(ii) Conversion of FFA to biodiesel:* With lower quality feedstocks, conversion of FFA to biodiesel yields higher product amounts. Generally, this process is done in a two-step process where acid catalyzed esterification is first used to convert

FFA into biodiesel and then a base catalyzed transesterification is used to convert the remaining oil to biodiesel.<sup>8</sup> However, the two-step process is tedious because of handling homogeneous acid catalysts such as sulfuric, phosphoric, hydrochloric and organic sulphonic acids due to their corrosion problems and environmental hazards. This process is also not feasible for biodiesel synthesis from multi-feedstocks because they have variable amounts of FFAs content.<sup>9</sup>

A heterogeneous catalyst is easier to remove from the reaction mixture, making the purification step easier. Biodiesel production costs could certainly be reduced by using a heterogeneous catalyst for transesterification reaction instead of a homogeneous catalyst. This heterogeneous process will provide higher quality esters and glycerol, which are more easily separable and eliminate expensive refining operations. A number of potential heterogeneous catalysts for biodiesel synthesis have been reported ranging from strong acid catalysts to strong base catalysts.<sup>10</sup> Solid acid catalysts can replace strong liquid acids and can eliminate corrosion problems and environmental hazards. Zeolites, heteropoly acids and sulphated zirconia are examples.<sup>11,12,13</sup> Solid base catalysts selectively react with glycerides and increase the yields of transesterification. The presence of FFA does not affect solid base catalyzed transesterification reactions. Basic zeolites, alkaline earth oxide based catalysts and alkali metal loaded alumina are examples.<sup>14,15,16</sup> However, they do not work for the esterification reaction. Most of the secondary feedstocks (such as waste vegetable oil, poultry fat and most other non-food feedstocks such as rubber oil) contain higher amounts of FFAs, thus limiting the application of heterogeneous base catalysts. So, the need for a cheap and recyclable heterogeneous catalyst for the biodiesel synthesis from both TG and FFA is essential.

### **1.3 Feasible solution for excess glycerol**

When biodiesel is produced the primary output other than biodiesel is glycerol. For every 10 pounds of biodiesel, about 1 pound of glycerol is also produced. Currently, 70 million gallons of glycerol is produced annually in the US and 392 million gallons are produced worldwide.<sup>17</sup> Although glycerol is used in pharmaceuticals, cosmetics, food and beverages, paints and many other products, the market for glycerol has been volatile in the past and the fear amongst the scientific and business communities is that extensive biodiesel production could flood the glycerol market and lower the glycerol price. Moreover, the biodiesel byproduct glycerol is in a crude form that needs to be refined in order to be used in industry, so biodiesel producers are paying to get rid of their glycerol or using it for dust suppression on country roads. The fear of glycerol market saturation has now become a reality called the “glycerol-glut” problem, thus green conversion of glycerol into more valuable chemicals is desired.

### **1.4 Research Motivation and Objectives**

The main aim of this research is to explore alternative sources for biodiesel feedstocks, to synthesize a successful solid heterogeneous catalyst for low-cost feedstocks, and to convert glycerol into value added chemicals. Being able to explore and identify solutions for the above stated problems is an important contribution to the biodiesel industry. The objectives of this research include:

- [1] Exploring different feedstocks for biodiesel production
- [2] Optimizing the process for individual feedstocks
- [3] Determining suitable solid catalyst for biodiesel production

[4] Synthesizing and characterizing developed catalyst

[5] Conducting kinetic and mechanistic studies of heterogeneous catalyst and

[6] Determining suitable solid catalyst for glycerol oxidation

### **1.5 Outline of the Thesis**

A basic overview of the current day biodiesel industry problems is discussed in Chapter 1. Chapter 2 presents a detailed literature review on current research directions on those problems while Chapter 3 presents the experimental methods and materials. Chapter 4 presents biodiesel production from spent coffee grounds and feather meal. Chapter 5 presents the heterogeneous catalyst for biodiesel production. Chapter 6 presents value added chemical production from glycerol and Chapter 7 presents the general conclusions of this work.

## **Chapter 2** † Literature Review on Biodiesel

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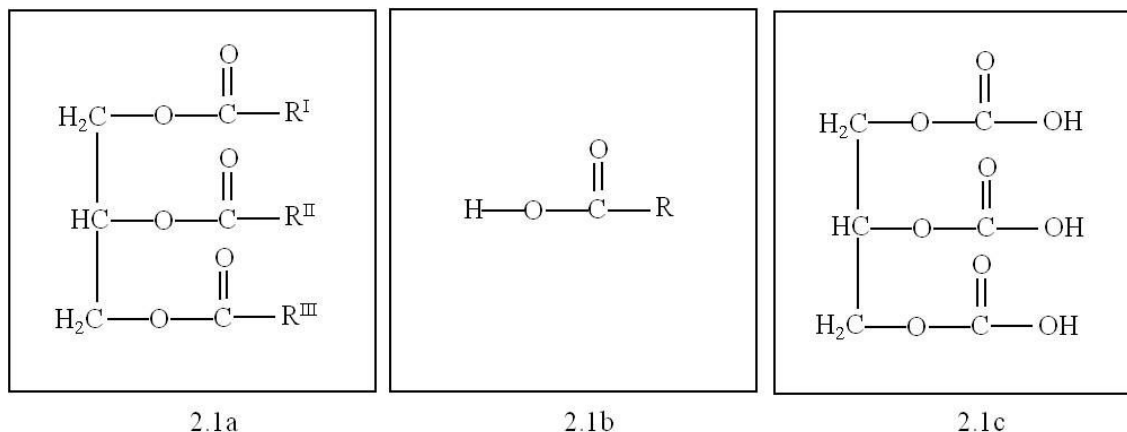
### **2.1 Introduction**

In the past few decades, fossil fuels such as petroleum, natural gas and coal have played an important role as major energy resources worldwide. However, energy resources are non-renewable and are projected to be exhausted in the near future. In the United States, oil is the primary fuel of transportation. The United States, with 5% of the world's population, consumes 25% of the world's petroleum, 43% of the gasoline, and 25% of the natural gas. According to the Oil and Gas Journal (O&GJ) estimates, worldwide reserves at the beginning of 2004 were 1.27 trillion barrels of oil and 6,100 trillion cubic feet of natural gas. These are proven recoverable reserves. At today's consumption rates, about 85 million barrels per day of oil and 260 billion cubic feet per day of natural gas, the reserves represent 40 years of oil and 64 years of natural gas.<sup>18</sup> The widespread use of fossil fuels makes it increasingly necessary to develop renewable energy sources of limitless duration and smaller environmental impact. Another major disadvantage of using petroleum-based fuels is the atmospheric pollution. Petroleum diesel combustion is a major source of greenhouse gas (GHG). Apart from these emissions, petroleum diesel is also a major source of other air contaminants including NO<sub>x</sub>, SO<sub>x</sub>, CO, particulate matter and volatile organic compounds (VOCs).<sup>19</sup> The problems of decreasing fossil fuel reserves and increasing atmospheric pollution have stimulated recent interest in alternative sources for petroleum based fuels. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable, and readily available.

One possible alternative to fossil fuel is the use of oils of plant origin such as vegetable oils and animal based fats. In this context, more specifically, biodiesel derived from vegetable oils and animal fats has been shown to be a potential alternative fuel replacing petroleum-derived diesel oil for diesel engines.

### 2.1.1 Oils/fats as fuels

The major components (90-98%) of vegetable oils is triglyceride (TG).<sup>20</sup> The minor constituents include small amounts of diglycerides (DG), monoglycerides (MG), free fatty acids (FFA) water, sterols, phospholipids, odorants, and other impurities. The chemical structures of a typical TG (2.1a), FFA (2.1b) and glycerin (2.1c) molecules are shown in Figure 2.1.

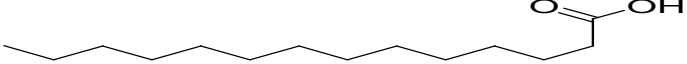
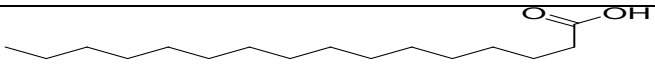
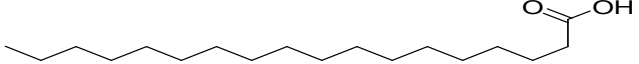
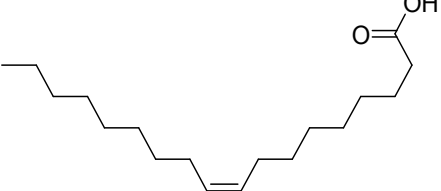
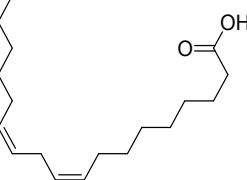
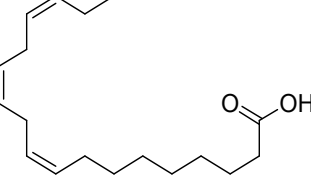
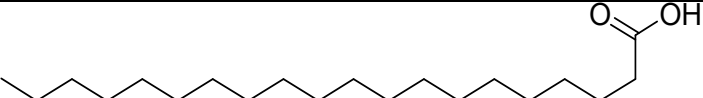


**Figure 2.1. Chemical structures of a typical TG (2.1a), FFA (2.1b) and glycerin (2.1c) molecules, where R, R<sup>I</sup>, R<sup>II</sup> and R<sup>III</sup> represent different fatty acid chains**

TGs are composed of three fatty acid molecules and one glycerin molecule. In a mole of TG molecules, the molecular weight of the glycerin is about 41 g, whereas the weights of fatty acid radicals are in the range from 650 g to 790 g. Thus, it is understood that fatty acid radicals comprise most of the reactive groups in the TG molecule and they greatly affect the characteristics of oils and fats. Fatty acids vary in their carbon chain length and in the number of double bonds (unsaturation level). Fatty acids are commonly

represented by these two characteristics. For example, C18:3 (linolenic acid) implies that this fatty acid has 18 carbon atoms and 3 double bonds. The common fatty acids, which exist in the TG molecule, are shown in Table 2.1.

**Table 2.1. Chemical structures of some common fatty acids**

Fatty acid	Notation	Chemical structure
Myristic acid	C14:0	
Palmitic acid	C16:0	
Stearic acid	C18:0	
Oleic acid	C18:1	
Linoleic acid	C18:2	
Linolenic acid	C18:3	
Arachidic acid	C20:0	

Vegetable oils having carbon chain length C16-C22 contain heat content of approximately of the same order as No.2 diesel (nearly 88%).<sup>21</sup> The use of vegetable oil

as alternative renewable fuel competing with petroleum was proposed in the beginning of the 1980s.<sup>22</sup>

### **2.1.2 Problems of direct usage of vegetable oils**

The major problems associated with the use of pure vegetable oils as fuels in diesel engines are caused by high fuel viscosity. The vegetable oils are all extremely viscous with viscosities ranging from 10 to 20 times greater than No.2 diesel fuel. Castor oil is in a class by itself with a viscosity more than 100 times that of No. 2 diesel fuel.<sup>23</sup> Although short-term tests using neat vegetable oil showed promising results, problems appeared only after the engine has been operating on vegetable oil for longer periods of time. Problems met in long-term engine tests, according to results obtained by early researchers may be classified as follows: Injector coking and trumpet formation on the injectors, more carbon deposits, oil ring sticking, and thickening and gelling of the engine lubricant oil.<sup>24,25,26,27</sup>

### **2.1.3 Modification of vegetable oils for effective usage**

There have been four primary methods to lower vegetable oil's viscosity and make them compatible with modern diesel engines.<sup>28,29</sup>

*i). Dilution:* This involves blending vegetable oil with diesel fuel in varying degrees. This is generally considered not satisfactory for use in diesel engines because of formation of double layers of diesel and vegetable oil.

*ii) Microemulsification:* Micro emulsions are defined as transparent, thermodynamically stable colloidal dispersions in which the diameter of the dispersed phase particles is less than one-fourth the wavelength of visible light. Microemulsion based fuels are sometimes also termed hybrid fuels, although blends of conventional diesel fuel with vegetable oils

have also been called hybrid fuels. Microemulsions are classified as non-ionic or ionic, depending on the surfactant present. Microemulsions containing, for example, a basic nitrogen compound are termed ionic, whereas those consisting, only of a vegetable oil, aqueous ethanol, and another alcohol, such as 1-butanol, for example, are termed non-ionic. Short engine performances of both ionic and non-ionic microemulsions of ethanol in soybean oil were nearly as good as that of No.2 diesel.<sup>30,31</sup> All microemulsions with butanol, hexanol, and octanol met the maximum viscosity requirements for No. 2 diesel fuel. The 2-octanol was an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil.<sup>32,33</sup> Thus microemulsions address the high viscosity problem to some extent and have been reported to meet the requirements of No.2 diesel sometimes, but not always.

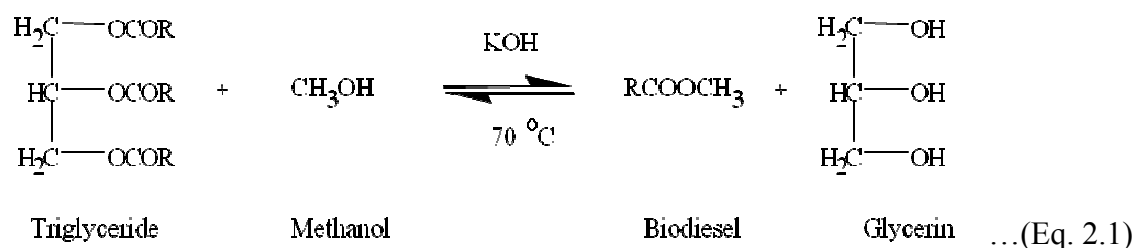
*iii) Pyrolysis:* Vegetable oils, fats and soap can be processed similarly to thermal cracking of petroleum oil. This is not considered to be efficient because of various reasons such as; lack of control over the side products, economics, and lack of an effective cracking catalyst. However, cracking produces fuels more similarity to gasoline than diesel.

*iv) Transesterification:* This is the preferred method to break down vegetable oils/fats efficiently to biodiesel for use in diesel engines. The transesterified products of vegetable oils/fats are called biodiesel.

#### **2.1.4 Biodiesel**

Transesterification is among the most effective solutions for reducing higher viscosities of vegetable oils. This process can also be applied successfully to animal fats. Although

several methods exist<sup>1</sup>, a simple and traditional base catalyzed transesterification method is shown in (Eq. 2.1).



Here 'R' represents an alkyl group of chain length C16-C22. The side product of this reaction is glycerol. Here, KOH is used as a catalyst. Theoretically, transesterification is an equilibrium reaction. In this reaction, however, more methanol is required to shift the reaction equilibrium to the right side and produce more methyl esters as the proposed products. The transesterification process separates glycerol from fatty acids and converts the fatty acids into methyl esters of fatty acids. Fatty acid methyl esters (FAMES) are less viscous when compared with the corresponding vegetable oils.

In many aspects, FAMES of vegetable oils are comparable with traditional diesel fuel, and hence, are called biodiesel. Table 2.2 shows some of the properties of both traditional No.2 diesel and biodiesel.

Because biodiesel is produced with different production scales from different vegetable oil sources and different animal fat sources with varying quality, it is necessary to install a standardization of fuel quality to guarantee customer satisfaction as well as engine performance without any difficulties. In the United States, ASTM standards were suggested for biodiesel.

**Table 2.2. Comparison of the standards for diesel and biodiesel based on American Society for Testing and Materials (ASTM).<sup>7</sup>**

Property	Diesel	Biodiesel
Standard number	ASTM D975	ASTM D6751
Composition	Hydrocarbon (C10-C21)	Fatty acid methyl esters (C12-C22)
Specific gravity (g/mL)	0.85	0.88
Flash point (K)	333-353	373-443
Cloud point (K)	258-278	270-285
Pour point (K)	243-258	258-289
Water (vol%)	0.05	0.05
Carbon (wt%)	87	77
Hydrogen (wt%)	13	12
Oxygen (wt%)	0	11
Sulfur	0.05	0.05
Cetane number	40-55	48-60

Table 2.3 shows the ASTM standards.<sup>7</sup> The standards contain specifications particular to biodiesel (for example, glycerol quantification) which are not given for conventional diesel fuel.

**Table 2.3. ASTM standards for biodiesel.<sup>34</sup>**

Property	Method	Limits	Units
Flash point, closed cup	D 93	130 min	oC
Water and sediment	D 2709	0.050 max	% vol
Kinematic viscosity	D 445	1.9 – 6.0	mm <sup>2</sup> /s
Sulfur ash	D 874	0.020 max	Wt.%
Total sulfur	D 5453	0.05 max	Wt.%
Copper strip corrosion	D 130	No. 3 max	--
Cetane number	D 613	47 min	--
Cloud point	D 2500	Report	oC
Carbon residue	D 4530	0.050 max	Wt.%
Acid number	D 664	0.80 max	mg KOH/g
Free glycerin	D 6584	0.020 max	Wt.%
Total glycerin	D 6584	0.240 max	Wt.%
Phosphorus	D 4951	0.0010	Wt.%
Vacuum distillation end point	D 1160	360 °C max, at T-90	% distilled

Biodiesel is a biodegradable, non-toxic, almost sulfur free and non-aromatic, environmentally friendly alternative diesel fuel. When a diesel engine is operated with biodiesel, exhaust emissions decrease; approximately 20% in CO, 30% in HC, 40% in particulate mater (PM), and 50% in soot emission, compared to the diesel fuel. In contrast to these decreases, NO<sub>x</sub> emission increases about 10-15%.<sup>35,36,37,38</sup> However, the high NO<sub>x</sub> problem can be overcome by retarding the injection timing.<sup>39</sup> Lubricity properties of biodiesel are much better than that of diesel fuel, especially low-sulfur diesel fuel. A little

biodiesel additive, even as little as 1%, is enough to significantly improve the conventional diesel fuel's lubricity.<sup>40,41</sup>

**Table 2.4. Fatty acid compositions of vegetable oil samples.<sup>42</sup>**

Feedstock	16:0	18:0	18:1	18:2	18:3	others
Cottonseed	28.7	0.9	13.0	57.4	0	0
Rapeseed	3.5	0.9	64.1	22.3	8.2	0
Safflower seed	7.3	1.9	13.6	77.2	0	0
Sunflower seed	6.4	2.9	17.7	72.9	0	0.1
Sesame seed	13.1	3.9	52.8	30.2	0	0
Linseed	5.1	2.5	18.9	18.1	55.1	0.3
Wheat grain	20.6	1.1	16.6	56.0	2.9	2.8
Palm	42.6	4.4	40.5	10.1	0.2	1.4
Corn marrow	11.8	2.0	24.8	61.3	0	0.3
Soybean	13.9	2.1	23.2	56.2	4.3	0.3
Bay laurel leaf	25.9	3.1	10.8	11.3	17.6	31.3
Peanut kernel	11.4	2.4	48.3	32.0	0.9	4.0
Hazelnut kernel	4.9	2.6	83.6	8.5	0.2	0.2
Walnut kernel	7.2	1.9	18.5	56.0	16.2	0.2
Almond kernel	6.5	1.4	70.7	20.0	0	1.4
Olive kernel	5.0	1.6	74.7	17.6	0	1.1
Coconut	9.7	3.0	6.9	2.2	0	65.8

For these reasons, several campaigns have been planned in many countries to introduce and promote the use of biodiesel.<sup>43</sup> The results of the campaigns helped discover a huge number of biodiesel feedstocks. The main plants whose oils have been considered as feedstock for biodiesel are: soybean oil, rapeseed oil, palm oil, sunflower oil, safflower oil & jatropha oil. Some other potential feedstocks are mustard and castor oils. Researchers developed genetically modified, non-edible, plant-based oils for biodiesel

production.<sup>44,45,46,47</sup> Table 2.4 shows some of the reported vegetable oils and their compositions, used for the biodiesel production.

## **2.2 Non food sources for biodiesel production**

Biodiesel has many environmentally beneficial properties. The main aspect of this claim is that it is a 'carbon neutral', because no net amount of carbon dioxide is released into the atmosphere.<sup>48</sup> However, this carbon neutrality is with respect to the amount of carbon dioxide produced by combustion of biodiesel and the amount of carbon dioxide absorbed by the plants for producing biomass. However, this carbon neutrality is not maintained in other concurrent operations such as fertilizer production, transesterification, solvent extraction, refining, drying and transportation. To be able to access the net balance in carbon neutrality, one has to carry out a detailed life cycle assessment (LCA). One such study on corn-soy bean agroecosystem for biodiesel production shows that the dominant air emissions resulted from crop farming, fertilizers, and on-farm nitrogen flows (e.g., N<sub>2</sub>O and NO). Seed production and irrigation provided no more than 0.002% to any of the inventory emissions or energy flows and may be neglected in future LCAs of corn or soybeans as feedstocks from the U.S. Corn Belt. Lime contributes significantly (17% of total emissions) to air emissions and should not be neglected in bioproduct LCAs.<sup>49</sup>

In addition, more than 95% of the biodiesel is made from edible oil resulting in a number of problems. By converting edible oils into biodiesel, food resources are actually being converted into fuels. Large-scale production of biodiesel from vegetable oils might bring global imbalance to the food supply and demand market. Recently, environmentalists have started to debate on the negative impacts of biodiesel production from edible oil on our planet. The biodiesel production has its effects on deforestation and destruction of the

ecosystem to certain extent.<sup>50</sup> Expansion of oil crop plantations for biodiesel production on a large scale has caused deforestation in countries such as Malaysia, Indonesia and Brazil to certain extent. Furthermore, the line between food and fuel economies is blurred as both of the fields are competing for the same oil resources. In other words, biodiesel is competing for limited land availability with the food industry. In fact, this trend is already being observed in certain parts of the world. There has been significant expansion in the plantation of oil crops for biodiesel in the past few years in order to fulfill the continuously increasing demand for biodiesel. Eventually, with the implementation of biodiesel as a substitute fuel for petroleum-derived diesel oil, competition might lead to the depletion of the edible oil supply worldwide.<sup>51</sup>

Because of these reasons, research is being conducted to discover non-food, non-main stream, and inexpensive feedstocks for biodiesel production. Waste cooking oil, which is much less expensive than pure vegetable oil, is a promising alternative to vegetable oil for biodiesel production.<sup>52</sup> Restaurant waste vegetable oils and rendered animal fats are less expensive than food-grade canola and soybean oil.<sup>53</sup> The production of algae to harvest oil for biodiesel is another commercially viable source. Also, biomass production need not compete with food production for either land or water. Both marine and freshwater algae may be used, so either sea water or fresh water can serve as the basis for the culture medium. And as land-based algal culture systems do not depend on soil fertility, barren land can be used. Some of the industrially viable non-food feedstocks are given in Table 2.5.

**Table 2.5. Present day major non-food feedstock sources.**<sup>42</sup>

Feedstock	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	others
Waste vegetable oil		12	-	53	33	1	
Tallow	3-6	24-32	20-25	37-43	2-3	-	
Lard	1-2	28-30	12-18	4-50	7-13	-	
Yellow grease	2.43	23.24	12.96	44.32	6.97	0.67	3.79
Brown grease	1.66	22.83	12.54	42.36	12.09	0.82	3.13
Jatropha oil	-	14.2	6.9	43.1	34.3	-	1.4
Rubber seed oil	-	10.2	8.7	24.6	39.6	16.3	-
Castor	-	1.0	1.0	3.0	4.2	0.3	90.5
Sea mango	-		6.9	54.2	16.3	20.2	2.4
Cottonseed		28.7	0.9	13.0	57.4	0	0

## 2.3 Conventional homogeneous catalytical process

### 2.3.1. Base catalyzed transesterification:

Though the basic reaction for transesterification is shown in Eq. 2.1, the overall transesterification reaction is given by three consecutive and reversible reactions, as shown in equations 2.2, 2.3, and 2.4.



where 'R' represents an alkyl group of chain length C16-C22.

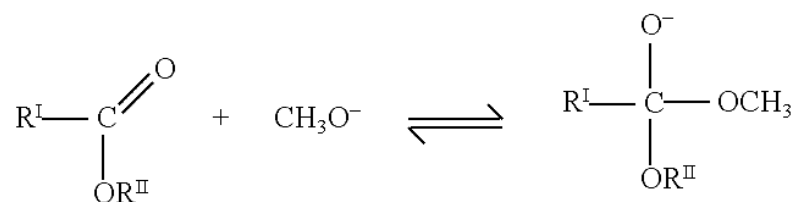
The key step in the transesterification reaction is formation of methoxide ion ( $\text{CH}_3\text{O}^-$ ).

The conventional process involves production of these methoxide ions using

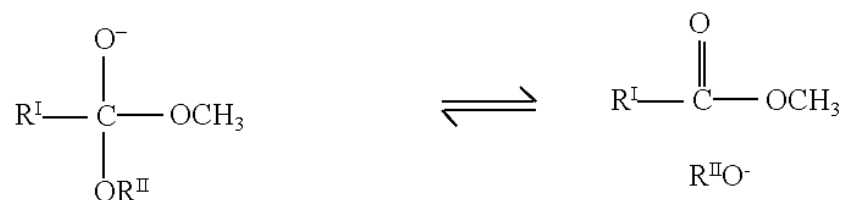
homogeneous base catalysts such as sodium hydroxide (NaOH) or potassium hydroxide (KOH). Such reactions catalyzed by a nucleophile (methoxide ions in this case) are known as nucleophilic substitution reactions. The mechanism of methoxide ion catalyzed reaction is illustrated below (Figure 2.2).

The mechanism of alkali-catalyzed transesterification is described in figure 2.2. The first step involves the attack of the alkoxide (here it is methoxide) ion to the carbonyl carbon of the triglyceride molecule, which results in the formation of a tetrahedral intermediate. This tetrahedral intermediate undergoes rearrangement to form a methyl ester of fatty acid and an alkoxide ion (glycerolyte). In the last step the glycerolyte ion reacts with methanol to regenerate the catalyst and a diglyceride molecule.<sup>33</sup> Again the diglyceride molecule undergoes the same set of reactions and forms another biodiesel molecule and a monoglyceride molecule. Finally, the monoglyceride molecule gives biodiesel and glycerol after reacting with another methoxide ion.

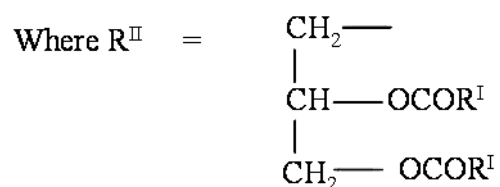
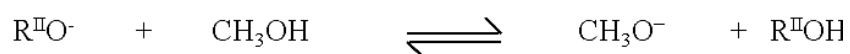
Step 1



Step 2



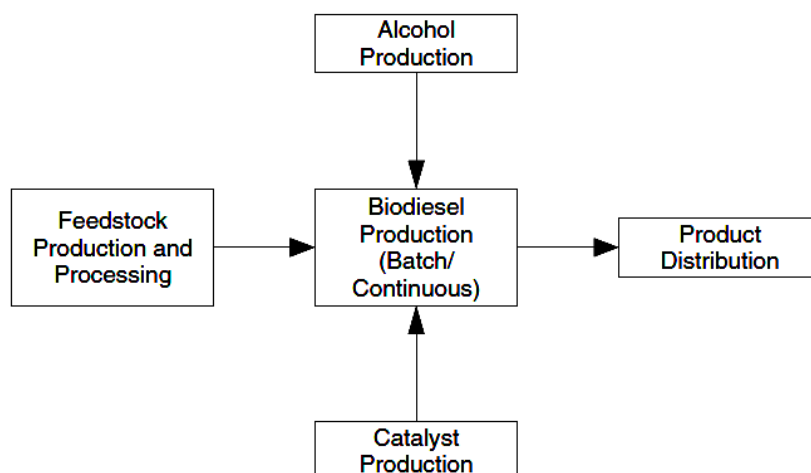
Step 3



$\text{R}^{\text{I}}$  = Carbon chain of fatty acid

**Figure 2.2. Mechanism of homogeneous base catalyzed transesterification.**

The general biodiesel production steps are shown in Figure 2.3. In the conventional homogeneous base catalyzed transesterification, the reaction temperature is  $\sim 70^\circ\text{C}$ , and it takes 30 to 60 minutes to finish the reaction depending upon the amount of methanol used in the reaction.<sup>33</sup>



**Figure 2.3. General biodiesel production steps (pure vegetable oil without free fatty acids).<sup>4</sup>**

The alcohol and the alkali metal hydroxide catalyst are first mixed before the reaction in a separate unit to form the metal alkoxide. The alcohol and alkoxide catalyst are then mixed with oil in the reactor. Oil and alcohol are immiscible and are constantly stirred. The transesterification reaction takes place at the interface of the two phases. The reaction is described by second order kinetics. The stoichiometric ratio of triglycerides and alcohol for the reaction is 3:1, but 6:1 molar ratio is the optimal molar ratio used to push the equilibrium to one side for maximum biodiesel conversion. 1 wt% catalyst is considered optimal for maximum activity.<sup>6</sup>

### **2.3.2. Acid catalyzed esterification:**

Low cost, non-food, and inexpensive feedstocks such as waste vegetable oil, restaurant grease, and animal fats such as beef tallow contain FFA up to 80% of the total triglyceride content. The conventional process needs a separate soluble acid catalyzed step prior to base-catalyzed reaction to process such feedstocks. Otherwise, the significant free fatty acid content would be wasted as soap and the soluble base catalyst would be wasted in

the formation of soap. In addition, it would be very difficult to separate biodiesel from the reaction products. A schematic representation of the two-stage process is shown in Figure 2.4.

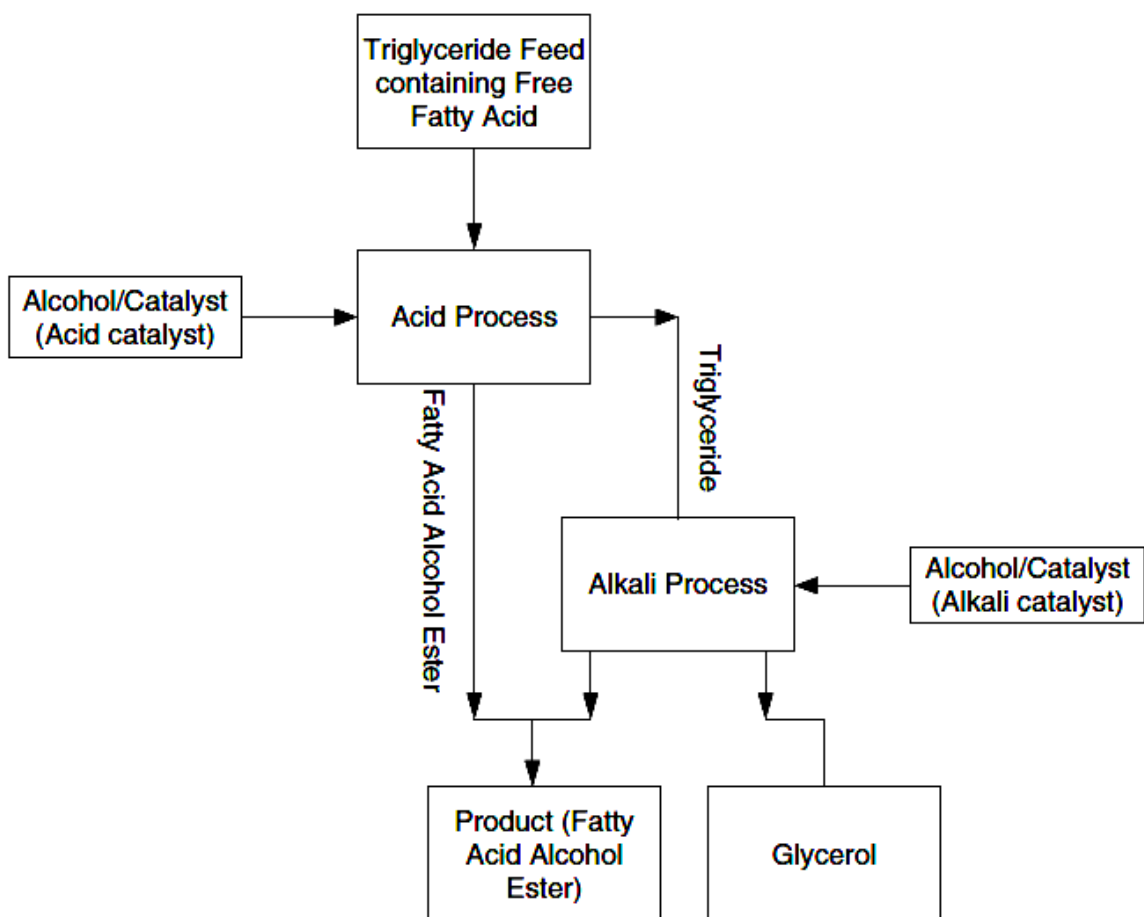
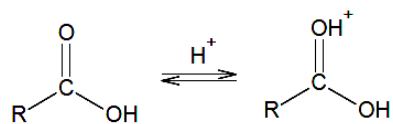


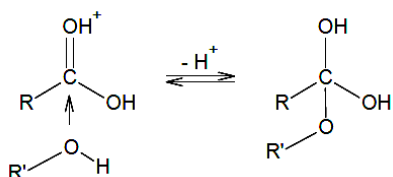
Figure 2.4. Schematic representation of two-stage biodiesel production.<sup>4</sup>

Sulfuric acid is the most commonly used acid catalyst. However, hydrochloric, formic, acetic, and nitric acids were also tested as homogeneous catalysts for both transesterification and esterification reactions.<sup>54</sup> This acid catalyzed process requires higher molar ratios.<sup>7</sup> The mechanism of acid catalyzed esterification is shown below.

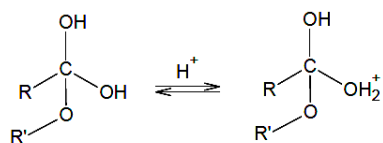
Step 1:



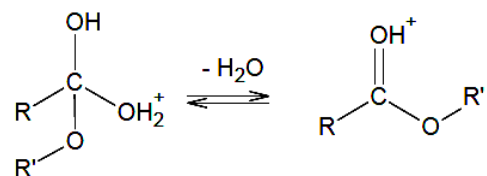
Step 2:



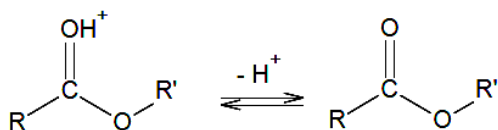
Step 3:



Step 4:



Step 5:



**Figure 2.5. Mechanism of homogeneous acid catalyzed transesterification.**

The esterification of free fatty acid to biodiesel follows a Fischer esterification mechanism. In Step 1, the carboxylic acid is protonated by the stronger inorganic acid

catalyst. In Step 2, the alcohol nucleophile (two lone pairs on the oxygen) adds at the  $sp^2$  carbon and the alcohol proton is lost. This is an important step in the mechanism because it is here that the new ester bond between the carboxyl group carbon and the alcohol oxygen forms. Then in Step 3, a series of fast equilibrium proton exchanges occur at either of the two acid  $-OH$  groups (which are equivalent). In Step 4 water elimination takes place. In Step 5, the excess proton leaves and regenerates the inorganic acid catalyst, and the cycle repeats.

### **2.3.3. Acid catalyzed transesterification:**

The liquid acid-catalyzed transesterification process does not enjoy the same popularity in commercial applications as its counterpart, the base-catalyzed process. The fact that the homogeneous acid-catalyzed reaction is about 4000 times slower than the homogeneous base-catalyzed reaction has been one of the main reasons.<sup>20</sup> However, acid-catalyzed transesterification holds an important advantage with respect to base catalyzed transesterification: the performance of the acid catalyst is not strongly affected by the presence of FFAs in the feedstock. In fact, acid catalysts can simultaneously catalyze both esterification and transesterification. Thus, a great-advantage with acid catalysts is that they can directly produce biodiesel from low-cost lipid feedstocks, generally associated with high FFA concentration. The reaction mechanism is different to that of the base catalyzed reaction, and this enables esterification of FFA as well as transesterification of triglycerides. The key step of the reaction is the protonation of the carbonyl oxygen, which makes the carbonyl more electrophilic. This more electrophilic carbon can attract the alcohol directly, instead of requiring a stronger nucleophile such as

methoxide ion as seen in the base catalyzed mechanism. The reaction mechanism is illustrated in Figure 2.5.

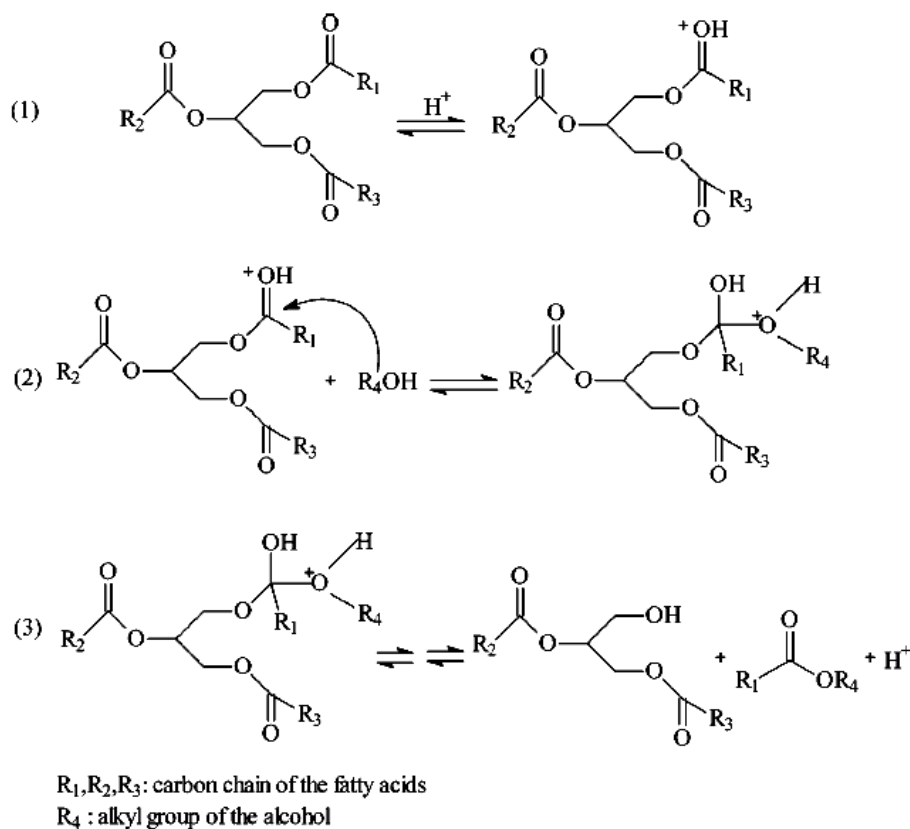


Figure 2.6. Schematic of acid catalyzed transesterification.<sup>7</sup>

In Step 1, the carbonyl oxygen is protonated by the acid catalyst. In Step 2, tetrahedral intermediate formation takes place due to the nucleophilic attack of the alcohol. In Step 3, proton migration and breakdown of the intermediate takes place. The same sequence will repeat twice to finish the reaction.<sup>7</sup>

### 2.3.4. Drawbacks of the conventional homogeneous catalysis

The drawback with the conventional homogeneous process is the use of soluble catalyst (NaOH, KOH and/or alkoxides) that end up contaminating the biodiesel and glycerol by product. In the case of sodium hydroxide, the sodium methoxide produced is dissolved in

the final product mixture, mostly in the glycerol and partly in the biodiesel phase. Also, a small fraction of the triglycerides are always wasted as soap due to the water produced by sodium methoxide reaction as shown in the following equation.



It is a tedious process to separate soap and sodium methoxide from the reaction mixture. They have to be washed out several times with water. The catalyst has to be wasted and a fresh catalyst has to be used for each batch. The alkali containing waste water must be neutralized before leaving the plant. For every gallon of biodiesel produced, about 8 gallons of waste water are generated. Biodiesel producers mention that water is one of the most expensive resources in their plants. Water remaining in the biodiesel is then usually removed by additional heat. The conventional process ends up having numerous extra processing steps before the produced biodiesel goes through the final polishing step.

Glycerol, the byproduct of the transesterification reaction, is only about 80% pure, as it is contaminated with catalyst, soap and water. It is either sold for a low value to glycerol refineries, or just disposed of. Contaminated glycerol requires vacuum distillation for purification. Pure glycerol carries good value for various applications.

The separation issues of the conventional process are illustrated by catalyst and soap contamination, numerous water washing steps, waste generated and water removal, disposal of the toxic alkali catalyst, the various additional processing units like catalyst-alcohol pre-mixing unit and FFA pretreatment, and contaminated glycerol purification. This makes the conventional process cumbersome and tedious. A simple, neat, efficient and robust process is needed for large-scale commercial production of biodiesel.

## 2.4. Heterogeneous catalysts for biodiesel production

A heterogeneous catalyst process eliminates the separation issues associated with the conventional homogeneous process because a solid catalyst would not dissolve in the reactant mixture. For the transesterification reaction, base catalysts are always preferred to acid catalysts wherever possible because of their higher activity. However, a variety of solid catalysts have been examined for the transesterification reaction and new materials/catalysts continue to be reported in the literature. Table 2.6 shows a few catalytical systems reported in the literature.

**Table 2.6. Typical solid acid and base catalysts employed for transesterification.**

<b>Acid catalysts</b>	<b>Base catalysts</b>
Sulphonic ion exchange resin <sup>55</sup>	Sodium aluminates <sup>56</sup>
Amberlyst-15 <sup>57</sup>	Oxides such as MgO <sup>58</sup> , CaO <sup>59</sup> , La <sub>2</sub> O <sub>3</sub> , ZnO <sup>60</sup>
Nafion <sup>61</sup>	Hydrotalcites <sup>62</sup>
Unstated Zirconia-alumina <sup>63</sup>	CaCO <sub>3</sub> , Ba(OH) <sub>3</sub> <sup>64</sup>
Sulphated tin oxide <sup>65,66</sup>	Cs exchanged faujasites <sup>67</sup>
Sulphated zirconia/alumina <sup>68</sup>	Li promoted CaO <sup>15</sup>
Zeolite (H-Y) H-Beta, H-ZSM-5, ETS-4,10 <sup>11</sup>	K <sub>x</sub> X/Al <sub>2</sub> O <sub>3</sub> (X-halide ion or other mono/di-valent anion) <sup>69</sup>
MCM family <sup>70</sup>	Metal salts of ammonium <sup>73</sup>
Heteropoly acids <sup>71,72</sup>	
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> , H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub> <sup>74,75</sup>	
Organosulphonic acid on mesoporous silica <sup>76</sup>	
Mesoporous unstated zirconium phosphate <sup>77</sup>	

### 2.4.1. Heterogeneous acid catalysts for transesterification

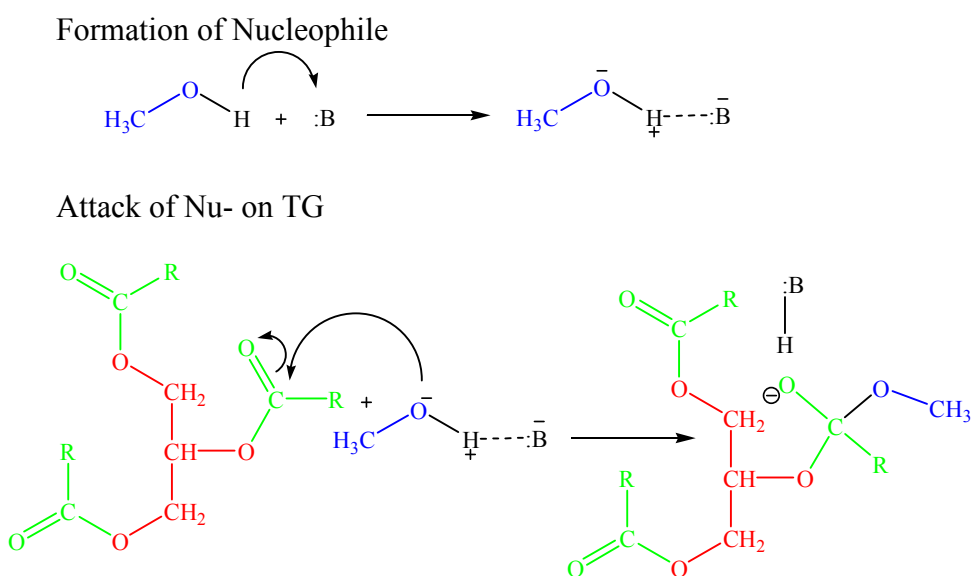
Solid acid catalysts can replace strong liquid acids thereby eliminating the corrosion problems associated with their use and consequent environmental hazards posed by them. Heterogeneous acid catalysts catalyze the transesterification reaction either by donating protons (Brønsted acids) or accepting electrons (Lewis acids). A proton donating acid

catalyst mechanism is similar to the homogeneous acid catalyzed mechanism (Figure 2.5).

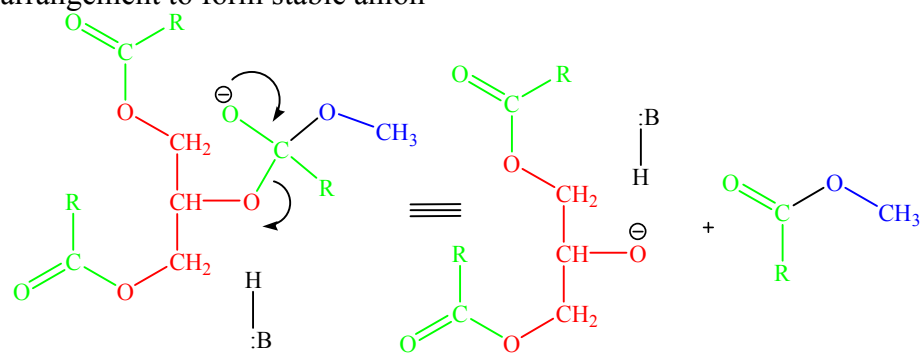
Solid acids have been widely used in the petroleum industry for applications such as cracking and reforming, and have been studied extensively. Aromatization, isomerization, synthesis of ethers, Friedel-Crafts acylation of aromatics, hydrogenolysis for propane production and alkylation of benzene are various other reactions where solid acids are used.

#### 2.4.2. Heterogeneous base catalysts for transesterification

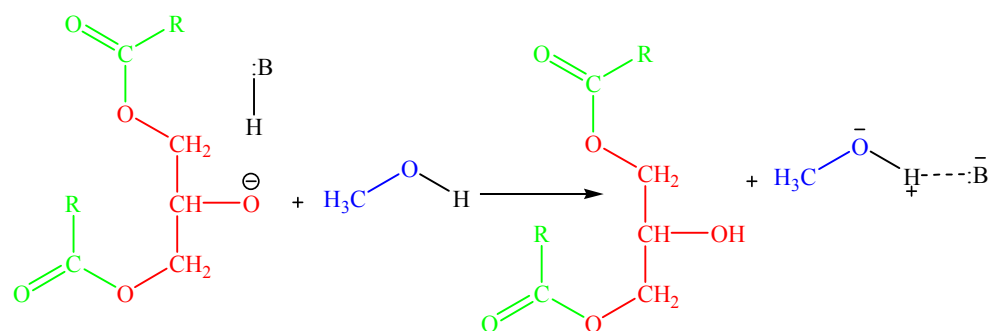
Heterogeneous bases catalyze transesterification reactions by donating electrons. Solid bases are tested for various organic reactions, including double bond isomerization, hydrogenation, amination, Aldol condensation, Michael addition, methylation and Knoevenagel condensations.<sup>78</sup> The mechanism of base catalyzed transesterification is described in Figure 2.7.



Rearrangement to form stable anion



Regeneration of the catalyst



Step 2 repeats until the formation of glycerol

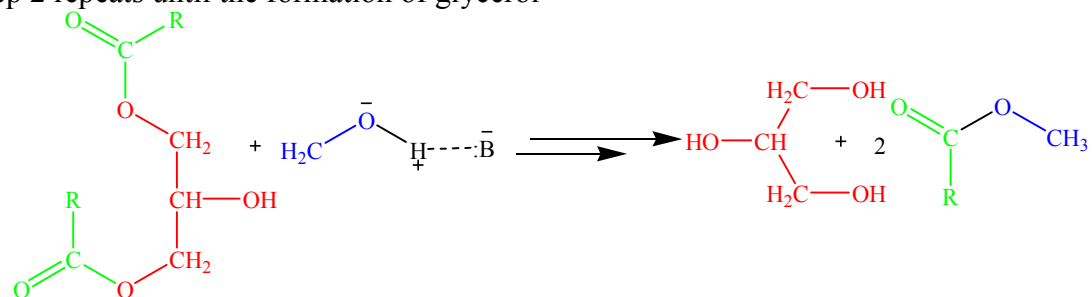


Figure 2.7. Mechanism of heterogeneous base catalyzed transesterification.

### 2.4.3. Heterogeneous acid catalysts for esterification

Several studies have contributed to the use of heterogeneous acid catalysts for esterification of carboxylic acid with alcohol. Esterification reactions can be catalyzed with catalysts having a medium acid strength; hence, ion-exchange resins such as Amberlyst-15 and Nafion<sup>®</sup> (high acid density and medium acid strength) are promising as

active catalysts for esterification.<sup>79,80,61</sup> Although, Amberlyst-15 and Nafion<sup>®</sup> contain highly acidic sites, in the reaction of carboxylic acids with long chains of hydrocarbon moieties, they show less activity due to diffusion limitations. The catalyst's activity strongly depends on the accessibility of the acid sites as determined by the degree of swelling of the material. In addition, the main drawback associated with using an organic resin catalyst is that the sulfonic acid cation exchange resins are not stable at temperatures over 140°C, inhibiting the implications of these catalysts in a reaction that requires high reaction temperatures. For this kind of application, inorganic catalysts are more desirable. The mechanism for esterification using a Brønsted acidic site is similar with homogeneous acid catalyzed esterification.

## **2.5. Oxidation products of glycerol**

Glycerol is a highly functionalized molecule and has a wider scope for production of valuable chemicals. A range of possible chemicals formed by oxidation of glycerol are shown in Figure 2.6. However, one of the key problems is the potential complexity of the products that can be formed, so control of the reaction selectivity by careful design of the catalyst is required. Numerous studies such as catalytic and biochemical methods were developed for glycerol oxidation.

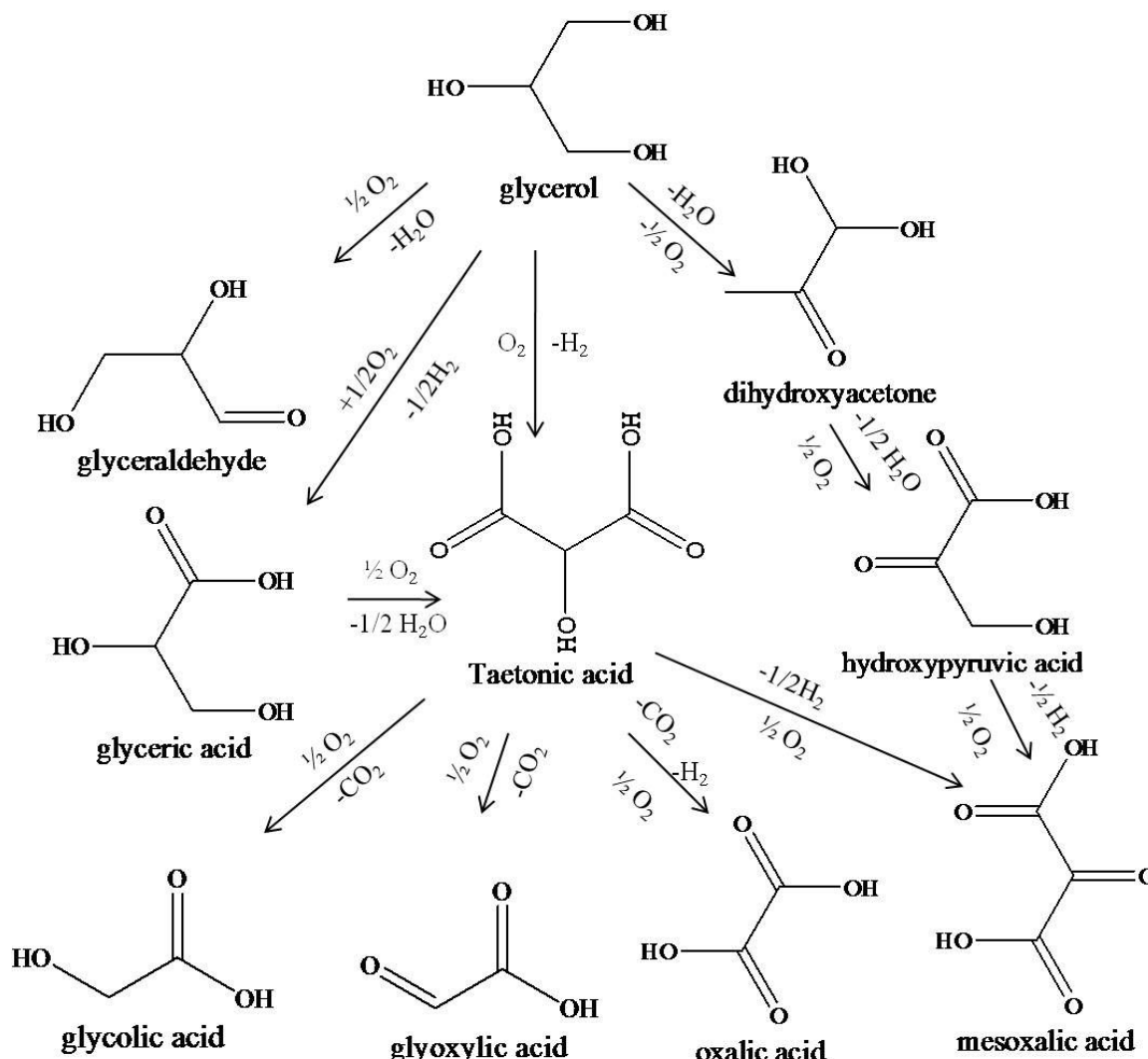


Figure 2.8. Oxidation products of glycerol (Figure adopted from ref.<sup>81</sup>)

Glycerol oxidation, in aqueous solution, has been extensively studied using supported palladium, platinum catalysts<sup>82,83,84,85,86</sup> Much more tunability on product selection obtained using gold catalysis as well.<sup>87,88</sup> Selective catalysis of glycerol has been achieved by noble metal catalysis. Hutchings and coworkers focus on gold nanoparticles for glycerol oxidation.<sup>89</sup> Prati and coworkers focused on liquid phase selective oxidation of glycerol using Au, Pt, Pd on carbon or graphite.<sup>90</sup> The Kimura research group did extensive research on glycerol oxidation using Ce, Bi and Pd/C catalysts.<sup>86,91,85,92</sup> The

Gallezot research group studied selective oxidation of glycerol using air and platinum or bismuth promoted platinum.<sup>93,83</sup>

However, glycerol obtained from the biodiesel industry is in crude form and is at a pH of ~11-14. The above reported selective oxidation of glycerol requires either expensive noble metal catalysts. Most of the reactions require the presence of oxygen or air for the effective promotion of catalytical oxidation.

## **2.6. Approach to method development**

One of the aims of this research is to investigate potential non-food, non-mainstream feedstocks for biodiesel production. Spent coffee grounds (coffee grounds after the brewing process), and chicken feather meal (hydrolyzed poultry feathers) have been shown to be potential biodiesel feedstocks. A complete extraction, purification processes, characterization study of produced biodiesel are discussed in Chapter 4.

Secondly, the separation problems with homogeneous catalysts were discussed. Literature review supports the fact that heterogeneous catalysts answer most of the problems faced by conventional processes. However, identification of a single catalyst with both acidic and basic sites in such a way that both esterification and transesterification can be done simultaneously is required. The scope of this work involves synthesis of Quintinite-3T (Q-3T), a suitable bifunctional (acid-base) heterogeneous catalyst for simultaneous esterification (of FFAs) and transesterification (TGs, DGs, and MGs).

Finally, glycerol oxidation reactions reported in the literature have the potential to solve problems associated with excess production of glycerol. However, instead of using noble metals and tedious operation conditions, a simple method which can use less expensive

chemicals and can use crude glycerol that is obtained from the biodiesel industry is much desired. The scope of this research covers identification of a suitable heterogeneous catalyst (Titanium disilicide) for selective oxidation of aqueous glycerol into glyceric acid.

## Chapter 3 † Materials, methods and characterization techniques

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### 3.1. Materials

Fatty acid methyl esters (99% assay), methanol ( $\text{CH}_3\text{OH}$ , HPLC grade, Sigma-Aldrich, USA), hexane ( $\text{C}_6\text{H}_6$ , HPLC grade, Sigma-Aldrich, USA), isopropanol ( $\text{C}_3\text{H}_8\text{O}_1$ , HPLC grade, Sigma-Aldrich, USA), 2, 2-diphenyl-1-picrylhydrazyl (DPPH, Sigma-Aldrich, USA), tannic acid (ACS grade, Sigma-Aldrich, USA), potassium hydroxide (KOH, 86%, Sigma-Aldrich, USA), hexane ( $\text{C}_6\text{H}_6$ , ACS grade, Sigma-Aldrich, USA), diethyl ether ( $\text{C}_4\text{H}_{10}\text{O}_1$ , ACS grade, Sigma-Aldrich, USA), dichloromethane ( $\text{CH}_2\text{Cl}_2$ , HPLC grade, Sigma-Aldrich, USA), Magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , ACS grade, Fluka), sodium carbonate ( $\text{Na}_2\text{CO}_3$ , ACS grade, Fluka), aluminum nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , analytical grade, JT Baker), sodium hydroxide (NaOH, Sigma-Aldrich, 97%), ammonium carbonate ( $(\text{NH}_4)_2\text{CO}_3$ , Sigma-Aldrich, 99%), ammonium hydroxide ( $\text{NH}_4\text{OH}$ , Fischer, ACS grade), heneicosane ( $\text{C}_{21}\text{H}_{44}$ , Sigma Aldrich, USA), octanoic acid ( $\text{C}_8\text{H}_{16}\text{O}_2$ , Sigma-Aldrich, ACS grade),  $\text{TiSi}_2$  (99.5 % metal basis, Alfa Aesar), phosphoric acid ( $\text{H}_3\text{PO}_4$ , ACS reagent grade, >86 wt% solution in water, Sigma-Aldrich, USA) and glycerol ( $\text{C}_3\text{H}_8\text{O}_3$ , ACS grade, Fluka) were used as received. Starbucks's (Reno, Nevada locations) "grounds for your garden" spent coffee grounds were used throughout and Foster Farms supplied the feather meal samples (chicken feather). Commercial soy and canola oils were purchased from a local store. A waste vegetable oil sample containing 15% FFA was provided by Bently biofuels, Nevada.

### 3.2. Experimental Procedures

*Oil Extraction from spent coffee grounds:* Spent coffee grounds were dried overnight in an oven (Isotemp 655G) at 50°C to remove excess moisture (mostly 50–60 wt%) and then refluxed for one hour with low boiling organic solvents such as n-hexane, ether and dichloromethane to extract the oil from the coffee particles (Figure 3.1). Three hundred mL of solvent was used for 100 g of dried spent coffee grounds (adjusted to 95% dry matter basic) for extraction of oil. All the experiments were carried out using a 1L round bottomed glass flask. The resultant solution containing 15 g oil was separated from the spent coffee grounds by filtration using a Buckner funnel under vacuum. The oil was separated from the solvents using a rotary evaporator. The solvents were reused in the next batch of extraction. The FFAs in the crude oil were separated by converting them into soap by mixing a basic solution with the extracted oil. Soap was removed from the pure oil by centrifuging the mixture for 30 min (4081×g; Beckman centrifuge Model J2-21).

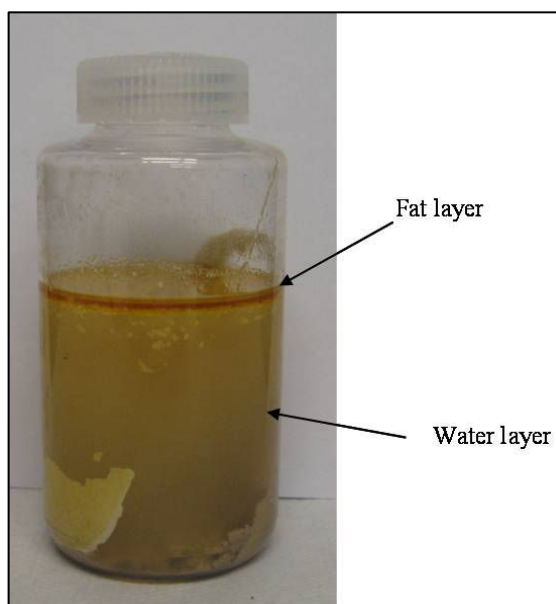


**Figure 3.1.** Experimental setup for oil extraction from spent coffee grounds (reflux with organic solvents).

*Procedure for antioxidant testing using DPPH redox indicator:* A  $6 \times 10^{-6}$  M solution of 2, 2-diphenyl-1-picrylhydrazyl (DPPH) in methanol was prepared in glove box at room temperature. Then 3 mL of the above solution was placed in a quartz cuvette, a 100  $\mu$ L sample of biodiesel was added, and the mixture was stirred vigorously for 1 min. The change in absorbance was measured using a UV-VIS apparatus at a fixed  $\lambda_{\text{max}} = 515$  nm over regular time intervals (1, 2, 3, 4, 5, 10, 15, 30, 60 min). A sample of pure DPPH/MeOH solution served as the 'blank' to measure the absorbance at  $t=0$  min. The DPPH scavenging activity in percentage was determined as follows:

$$\text{DPPH scavenging activity (\%)} = [(A_{\text{blank}} - A_{\text{sample}}) / A_{\text{blank}}] \times 100.$$

*Fat extraction from feathermeal:* 100 g of the feather meal sample was stirred with 300 mL of water at 70 °C for 20 min. The adsorbed fat on the protein content of the feather meal was melted and started floating on the surface of the water layer (Figure 3.2.). The top layer was decanted and centrifuged for 10 min (4081 $\times$ g; Beckman centrifuge Model



J2-21) to collect the fat content (7.5 g) of the feather meal. The collected fat was mixed with basic water to remove FFAs in the form of soap. The soap was separated from the fat content by centrifugation (4081 $\times$ g; Beckman centrifuge Model J2-21). The purified fat (6.9 g) was processed to the next step, transesterification.

**Figure 3.2.** Centrifuge bottle showing fat separated from feathermeal.

*Transesterification Process:* In a typical transesterification process, the TGs were heated to 100°C to remove the traces of water present, and the oil was mixed with 40% v/v methanol and 1.5 wt% catalyst (KOH). The reaction mixture was refluxed at ~70°C for the biodiesel production. Optimization of the reaction was carried out by varying the amounts of methanol, KOH and reaction time to get maximum yield as determined by HPLC analysis. The reaction time for a complete transesterification process was monitored through HPLC using methanol, hexane and isopropanol as solvents. The reaction was stopped when the oil (mostly triglycerides, TG) peaks in the HPLC analysis disappeared, and the peaks corresponding to biodiesel were saturated.

*Purification of biodiesel:* After the reaction was complete, the reaction mixture, was cooled to room temperature and allowed to stand overnight. The bottom layer of glycerin was separated from the biodiesel layer (top layer). The produced crude biodiesel was then washed twice with warm water (40–50 °C) and acidified water (0.5 wt% tannic acid) to remove the excess methanol and the traces of catalyst.<sup>28,94</sup>

#### *Quintinite-3T (Q-3T) Preparation*

Q-3T was prepared using a co-precipitation method. Two different catalysts were prepared using sodium and ammonium sources.

#### *Method 1: Preparation of Q-3T using sodium source (Na-Q3T):*

An aqueous solution (45 mL) of 0.1 mol Mg (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.05 mol Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O was added all at once to a second solution (70 mL) containing NaOH (0.35 mol) and Na<sub>2</sub>CO<sub>3</sub> (0.09 mol) at 333 K. The resulting mixture was kept at constant temperature for 24 h under vigorous stirring, after which the white precipitate was removed by filtration and washed several times to remove occluded NaOH. The mixed metal carbonate was

dried for 24 h at 393 K. The resulting white powder was calcined to 773 K for 6 h to obtain the mixed metal oxide which was again hydrated with de-carbonated water and dried at 373K to remove the water from the final catalyst Na-Q3T.

*Method 2: Preparation of Q-3T using ammonium source (NH<sub>4</sub>-Q3T):*

An aqueous solution (45 mL) of 0.1 mol Mg (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.05 mol Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O was added simultaneously to a solution (70 mL) containing NH<sub>4</sub>OH (0.35 mol) and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> (0.09 mol) at 333 K. The resulting mixture was heated at constant temperature for 24 h under vigorous stirring, after which the white precipitate was removed by filtration and washed several times to remove occluded NH<sub>4</sub>OH. The mixed metal carbonate was dried for 24 h at 393 K. The resulting white powder is calcined to 773 K for 6 h to obtain the mixed metal oxide, which was again hydrated with de-carbonated water and dried at 373 K to remove the water from the final catalyst NH<sub>4</sub>-Q3T.

*Q-3T catalytic activity:*

The prepared catalyst was tested for esterification and transesterification reactions separately. For esterification, octanoic acid was tested and for transesterification pure TGs were used (from soy and canola oil). After the catalyst was tested successfully for esterification and transesterification, simultaneous esterification and transesterification were performed using feedstocks with 15-30% FFA. The reaction was optimized using canola oil and then the best reaction conditions were extended to test other oils with variable amounts of FFA. All the reactions were carried using 10 wt% of the catalyst at 348 K until completion. Methanol to oil ratio was kept at 15:1 (mol:mol). The influence of the catalyst amount, methanol amount, time and temperature were also investigated.

The catalyst was filtered after the reaction, washed three times each with distilled water and hexane dried in an air oven, activated at 773 K for 6 h, and used for subsequent recycling studies. After the reaction, the catalyst was separated using centrifugation (4081×g; Beckman centrifuge Model J2-21), and the products were analyzed.

*Glycerol oxidation experiments:*

Glycerol oxidation was carried out in a 500 mL round bottom flask and the reactions were carried out at atmospheric pressure at 65°C. Magnetic stirring was used to mix the reactants well during the reaction process. The reaction flask was sealed except for a tube coming out of the flask with the other end inserted in a 50 mL Burette to monitor evolution of hydrogen. Prior to the experiment the flask was purged with nitrogen gas. The Burette was placed upside down into a 2 L beaker containing water. The volume of the gas evolved was measured from the displaced water from the Burette. After the reaction, the reaction mixture was neutralized using 1M HCl and the catalyst was separated by filtration. The water that remained in the filtrate was removed by vacuum distillation and the residual compound was analyzed using HPLC, FTIR and <sup>13</sup>C NMR.

All photocatalytic oxidative experiments were completed using a 300 W solar simulator (69911, Newport-Oriel Instruments) as a light source. An optical AM 1.5 filter (Newport) was used to illuminate to 1 Sun intensity (100 mW/cm<sup>2</sup>, measured by thermopile) on the catalyst at 25°C to 85°C. The oxidation of glycerol was carried out in a 100 mL round bottom (RB) flask containing 50 mL, 1M KOH, and 10 wt% solution of aqueous glycerol (5g) with 1 wt% TiSi<sub>2</sub> (500 mg). The RB flask was kept 15 cm from the light source. Catalytic testing was performed by dispersing TiSi<sub>2</sub> powders in the above solution under atmospheric pressure.

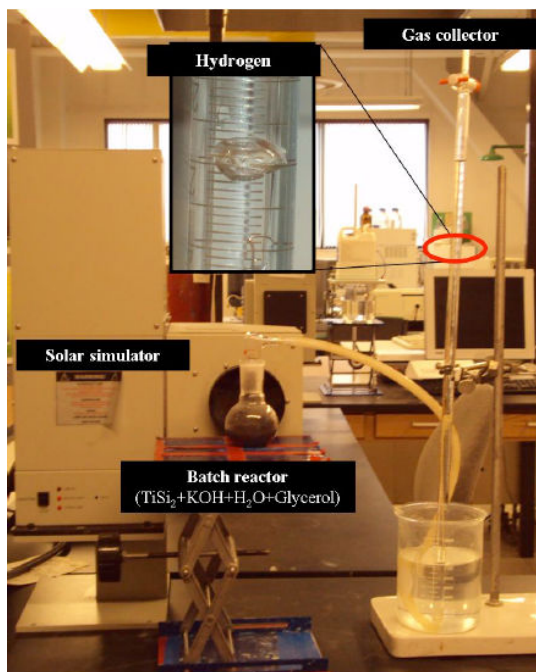


Figure 3.3. Experimental setup for photocatalytic glycerol oxidation in a batch reactor.

### 3.3. Characterization techniques

#### High Performance Liquid Chromatography (HPLC):

*HPLC column conditions for oil and biodiesel characterization:* The transesterification reactions were monitored using HPLC (Shimadzu LCsolution-20-AB). HPLC is the best tool for reaction monitoring as one can follow the formation of biodiesel peaks as well as depletion of TG, DG and MG peaks simultaneously. A *Restek Allure Reverse Phase* steel column was used with 150 X 3.2 mm packed with C18 particles with a diameter of 7  $\mu\text{m}$ . Gradient elution was set by mobile phases A (methanol) and B (Isopropanol : hexane = 4:5 by volume). The course of the gradient was: 0 to 20 min reached to 50% B, 20 to 21<sup>st</sup> min changes to 100% A, then it was continued at this condition for another 4 min. The dosing volume was 10  $\mu\text{L}$ , and the dilution of the sample was done 1: 20 in phase B.

Spectrophotometric detection in the UV region at 205 nm is used.<sup>95</sup> Percentage conversion of oil to biodiesel was calculated using area under the most intense peak (15-20 min region) in the oil chromatogram.

*HPLC column conditions for glycerol and glyceric acid characterization:* The oxidation of glycerol was monitored using a High Performance Liquid Chromatography (HPLC, Shimadzu LCsolution-20-AB) with ultraviolet and refractive index detectors. Reactant and products were separated using an Aminex<sup>®</sup> HPX-87H ion exclusion column (300 mm X 7.8mm) heated to 40°C. The eluent used was a solution of H<sub>2</sub>SO<sub>4</sub> ( $5 \times 10^{-4}$  mol l<sup>-1</sup>) at a flow rate of 0.75 mL/min. Each time, the reaction mixture samples (10 µL) were diluted to 1 mL using the eluent solution and injected into the HPLC. The terms ‘glycerol conversion’ and ‘glyceric acid selectivity’ used herein are defined as follows:

$$\text{Glycerol conversion (wt \%)} = \frac{\text{Initial glycerol concentration} - \text{Final glycerol concentration}}{\text{Initial glycerol concentration}} \times 100$$

$$\text{Glyceric acid selectivity} = \frac{\text{Glyceric acid in products}}{\text{Total products formed}} \times 100$$

*Gas Chromatography-Mass Spectroscopy (GC-MS):* Most reports<sup>35,96,6</sup> on the use of GC for biodiesel analysis employed flame-ionization detectors (FID), although the use of mass spectroscopic detector (MSD) would eliminate any ambiguities about the nature of the eluting materials because mass spectra unique to individual compounds would be obtained.<sup>97</sup> A qualitative study and quantitative studies were obtained from GC-MS (Shimadzu GC-MS QP 2010). Rtx-5MS capillary column (29.5 m length, 0.25 µm thickness and 0.25 mm diameter) was used for the analysis. Ultra pure helium gas was used as a carrier gas. Temperature gradient was set from 373K to 523K in the course of

95 min (1.57 °C/ min), which showed good resolution between stearic (C18:0), Oleic (C18:1), linoleic (C18:2) and linolenic (C18:3) fatty acid methyl esters.

UV-Visible spectroscopy: A UV-VIS spectroscopy (Shimadzu UV-2401PC) was used for anti oxidant analysis.

Gas Chromatography (GC): A gas chromatography (GC, Agilant 6890) with thermal conductivity detector (TCD) was used in the glycerol oxidation experiments for the hydrogen evolution measurements. The molecular sieve 5A column was used for the separation of gases and nitrogen was used as the carrier gas. A flow rate of 30 mL/min was used. The oven and detector temperatures were set at 50°C and 200°C respectively.

Nuclear Magnetic Resonance (<sup>1</sup>H-NMR, <sup>13</sup>C-NMR): <sup>1</sup>H-NMR spectra were obtained at 400 MHz spectrometer (Varian-400). CDCl<sub>3</sub> was used as a solvent. The <sup>13</sup>C-NMR spectrum was obtained on a Varian unity plus machine with 11.75T magnetic strength and operating at 125 MHz (<sup>13</sup>C) in deuterated water (D<sub>2</sub>O). Samples of reaction mixture were neutralized with 12N hydrochloric acid and water was evaporated before adding D<sub>2</sub>O (for the identification of glyceric acid).

X-Ray Diffraction (XRD): Qualitative confirmations of Q-3T were measured using XRD. Measurements were carried out by using a powder diffraction apparatus (Philips automated XRD) with CuK $\alpha$  radiation ( $\lambda = 1.54018 \text{ \AA}$ ). Data were acquired on a PC using MDI Data scan software and processed using MDI Jade and ICDD PDF minerals data base.

Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS): ICP-MS was used to evaluate the elemental composition and leaching of the catalyst. Elemental analyses were performed using Micromass Platform ICP-MS. This instrument has a Hexapole collision

cell which eliminates many of the interferences present in conventional ICP-MS. The instrument was connected to a CETAC auto-sampler and a Merchantek UV laser ablation system which allowed analyses of solid materials using ICP-MS.

Field-Emission Scanning Electron Microscope (FESEM, Hitachi S-4700): FESEM was used to analyze the composition and distribution of the catalyst nanoparticles. The images were taken at an accelerating voltage of 20 kV. Energy dispersive X-ray (EDX) analysis was obtained using an Oxford detector.

Transmission Electron Microscopy (TEM): TEM measurements were carried out to find the particle size and crystalline nature of the prepared catalysts. A small amount of sample was placed on a carbon coated Cu-grid, and the data were obtained using High Resolution Transmission Electron Microscopy (HRTEM).

Fourier Transform Infra Red (FTIR) spectroscopy: Brønsted and Lewis acid sites in the Q-3T was recorded with a FTIR spectrometer (BioRad). The FTIR measurement is performed as follows. First, the fine powdered sample was outgassed under a high vacuum condition for 4 h at 473K. Second, the sample was cooled to ambient temperature to introduce into the vapor flow of saturated pyridine during 2 h. Third, the pyridine was removed by heating the sample at 473K for 1 h. And finally, the sample was compressed into self-supporting membrane with KBr to perform FTIR measurements.

Elemental analysis(C, H, N, S, and O analyzer): A Perkin Elmer Series II, CHNS/O analyzer Model 2400 was used to estimate the C/N ratio of the used coffee grounds before and after the oil extraction process.

ASTM analysis: All non conventional samples namely coffee biodiesel, feathermeal, and waste vegetable oils were tested using ASTM D6584 (for free glycerin, monoglycerides,

diglycerides, triglycerides and total glycerin content) to confirm the completeness of the reaction. All ASTM tests were performed at Bentley Tribology Services located in Minden, Nevada.

## **Chapter 4 † Biodiesel production from spent coffee grounds and feathermeal**

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The need for non-food, inexpensive and alternative feedstocks to vegetable oils was discussed in Chapter 2. This research work focuses on two new inexpensive and alternative feedstocks namely spent coffee grounds and feathermeal. This section is divided into two subsections (4.1 and 4.2) and explores the biodiesel production process from spent coffee grounds and feather meal, respectively.

### **4.1. Biodiesel production from spent coffee grounds:**

#### **4.1.1. Introduction:**

Coffee is one of the largest agricultural products that are mainly used for beverages. According to the United States Department of Agriculture, the world's coffee production is 16.34 billion pounds per year.<sup>98</sup> The amount of oil in the coffee source varies from 11 to 20 wt% depending on its types.<sup>99,100</sup> On average, the spent coffee grounds contain ~15% w/w oil, which can be converted to a similar amount of biodiesel using transesterification methods. This is quite significant compared to other major biodiesel feedstocks such as rapeseed oil (37-50%), palm oil (20%) and soybean oil (20%)<sup>51</sup>. This has the potential to add approximately 340 million gallons of biodiesel to the world's fuel supply. The biodiesel from coffee possesses better stability than biodiesel from other sources due to its high antioxidant content (which hinders the Rancimat Process).<sup>101,102</sup> The remaining solid waste can be utilized as compost as a feedstock to produce ethanol<sup>103</sup>

or as fuel pellets. The schematic diagram for the production of different alternative energy sources from spent coffee grounds is shown in Figure 4.1.

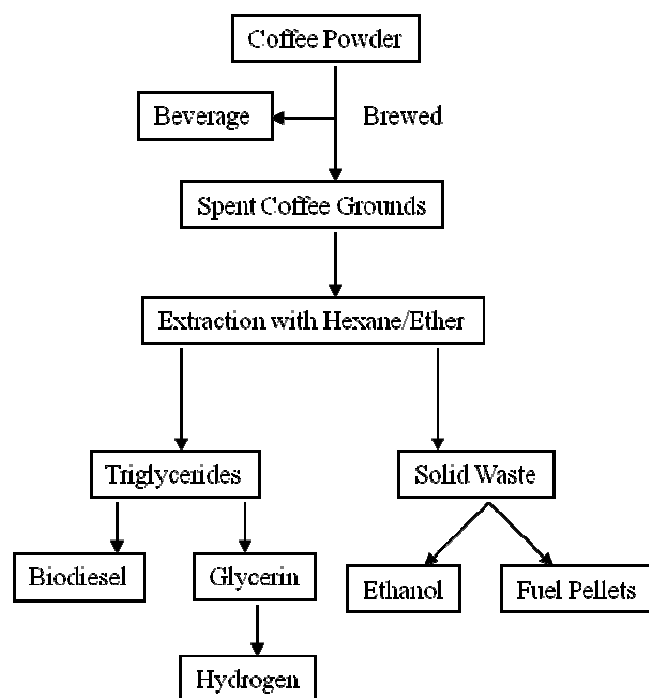
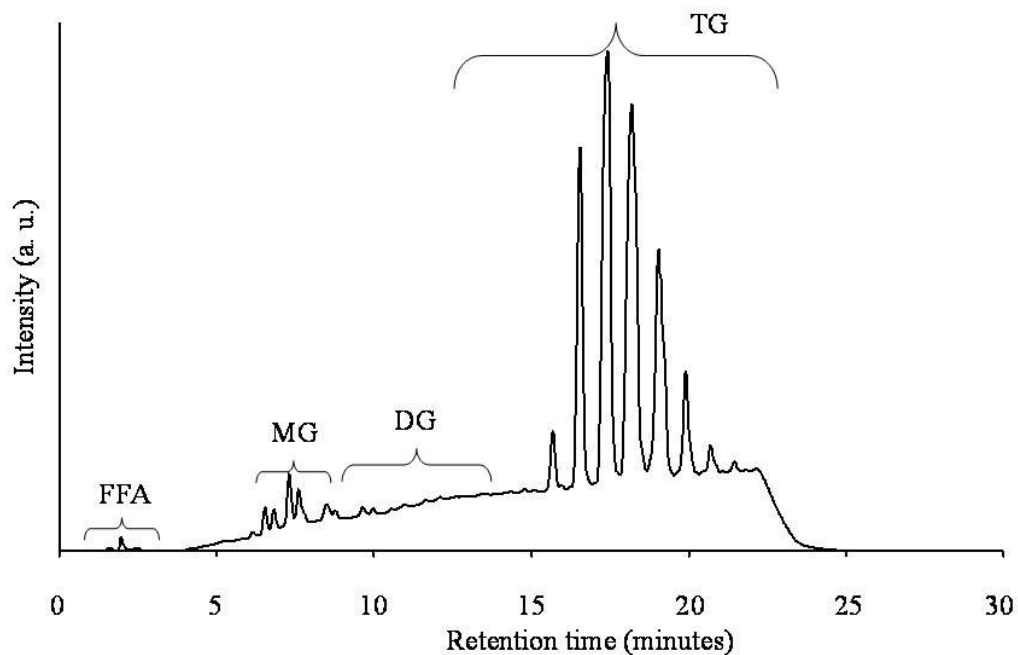


Figure 4.1. Schematic representation of the biodiesel production process from spent coffee grounds.

## 4.1.2. Results and Discussions

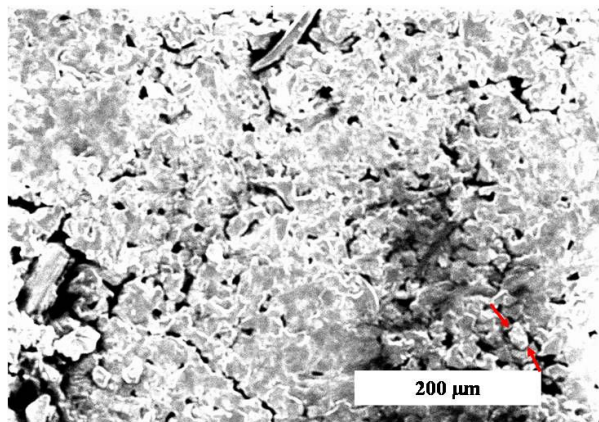
### 4.1.2.1. Extraction and purification of oil from spent coffee grounds:

Extraction of oil from spent coffee grounds was carried out using solvents such as hexane, ether and dichloromethane under reflux conditions. A 10  $\mu\text{L}$  sample of the solution was taken out in each 5 min of the reflux and was analyzed by HPLC. There was an increase in peak intensity for TG observed with an increase in reflux time. The saturation point was observed at 45 minutes for hexane extraction. A small amount of FFA, MG and DG was also observed in the oil (Figure 4.2).



**Figure 4.2.** HPLC chromatogram of the oil extracted from spent coffee grounds.

Because the particle size of the grains was around 20 mm (the grounds were pressed into pellets for the SEM and the micrograph was shown in Figure 4.3) a counter current-extraction<sup>104</sup> would be more economical for industrial purposes.



**Figure 4.3.** Scanning Electron Microscope (SEM) image of the dried spent coffee grounds.

The pH of the oil extracted from different solvents varied due to the difference in the FFA amounts. More polar solvents extracted more amounts of FFA which caused a decrease in pH and an increase in yields (Table 4.1).

**Table 4.1. pH change of coffee oil with extracting solvents.**

Solvents	% Yield	pH
Hexane	13.4	6.7
Diethyl ether	14.6	4.7
Dichloromethane	15.2	4.5

Hexane extraction resulted in a more neutral pH (6.8) as compared to the other solvents. No further washing was necessary. Hence, hexane was selected as a suitable solvent for the oil extraction process.

The FFAs present in the crude oil were separated by converting them into soap by mixing basic solution with the extracted oil (Eq. 4.1).

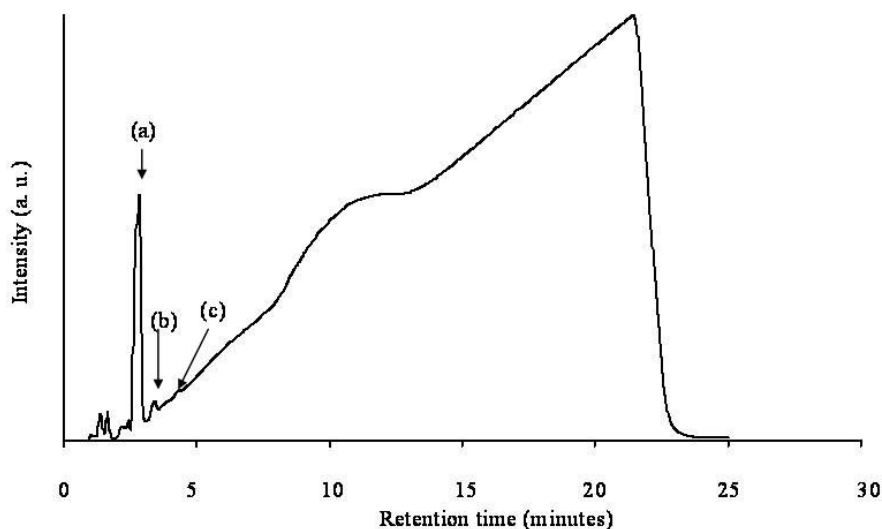


Soap was removed from the pure oil by centrifuging the mixture for 30 min (4081×g; Beckman centrifuge Model J2-21). Thus purified coffee oil (10 g) was collected for the next step: transesterification. FFA could be washed using organic solvents such as methanol, ethanol and propanol.

#### **4.1.2.2. Conversion of oil to biodiesel:**

The purified coffee oil was converted to biodiesel using the transesterification process (Eq. 2.1). The oil was mixed with a proper amount of solvent (methanol) and catalyst (KOH). The reaction mixture was refluxed at ~70°C for the biodiesel production. The

highly intense TG peak (retention time at 17.5 min) in the HPLC was monitored to estimate the progress of the reaction. The HPLC chromatogram is shown in Figure 4.4. Complete conversion of oil-to-biodiesel was observed when 1.5 wt% catalyst (KOH) and 40 vol% solvent (methanol) were used. The presence of Linoleic (a), Palmitic (b) and Oleic (c) acid methyl esters could be observed. The respective standards of the methyl esters were used to identify the peaks in the HPLC analysis.



**Figure 4.4. HPLC chromatogram of coffee biodiesel.**

Completion of the transesterification reaction was also confirmed using proton nuclear magnetic resonance spectroscopy ( $^1\text{H-NMR}$ ).  $^1\text{H-NMR}$  is an excellent confirmative technique for the monitoring of transesterification reaction. The first report on spectroscopic determination of the yield of transesterification reaction utilized  $^1\text{H-NMR}$  depicting its progressing spectrum.<sup>105</sup> The signal due to methylene protons adjacent to the ester group in TG appear at 2.3 ppm (Figure 4.5) and after the reaction the methoxy protons of the methyl esters appear at 3.7 ppm (Figure 4.6). The disappearance of the

glycerin protons from the biodiesel also confirmed the complete conversion of oil-to-biodiesel.

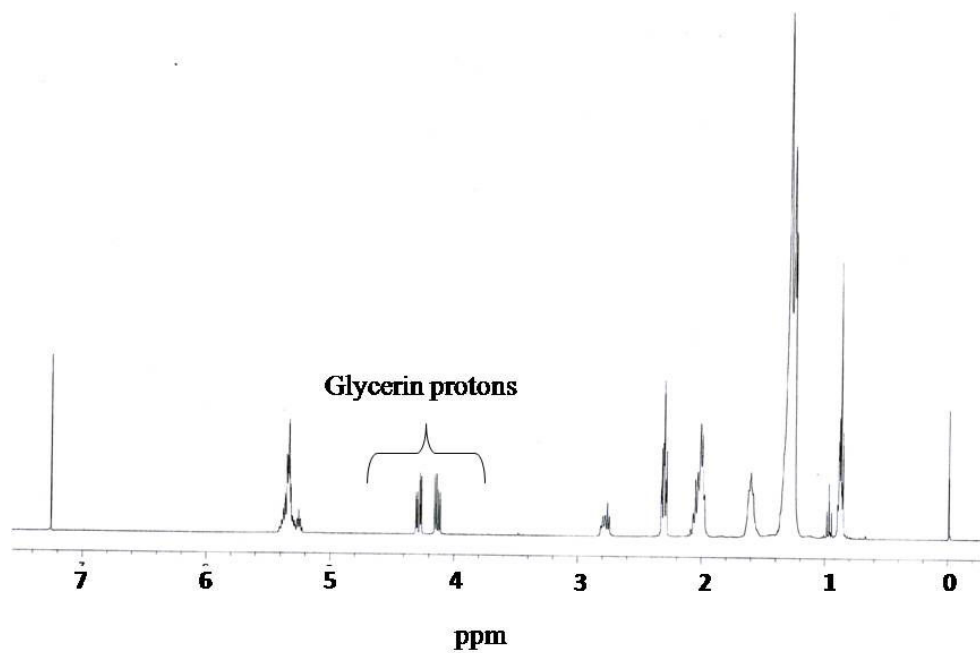


Figure 4.5.  $^1\text{H-NMR}$  of coffee oil.

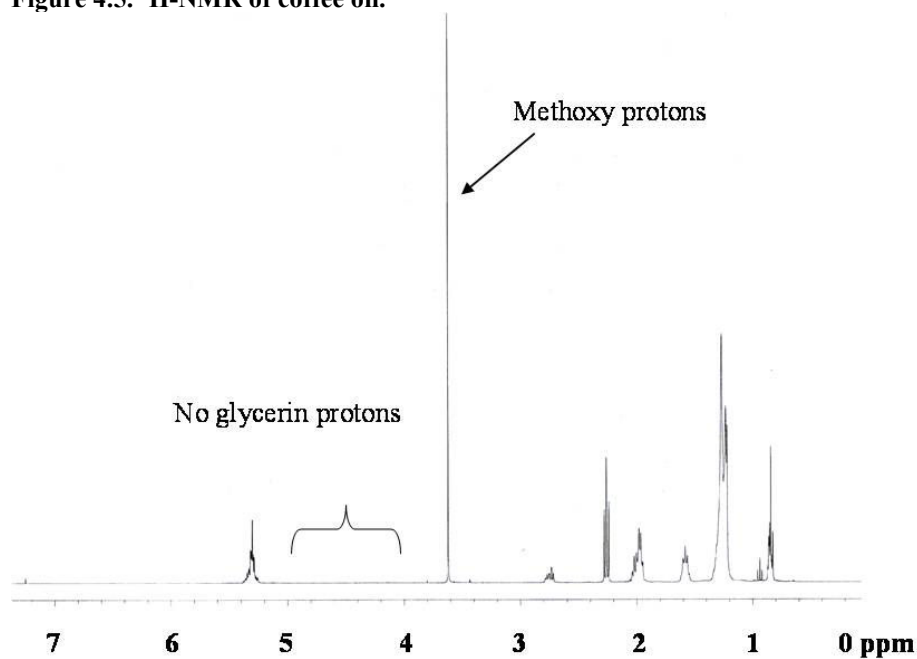


Figure 4.6.  $^1\text{H-NMR}$  of coffee biodiesel.

#### 4.1.2.3. Purification and analysis of biodiesel

The reaction mixture from the process contained biodiesel in combination with excess methanol, catalyst and glycerin. Several purification processes were carried out to separate the biodiesel from the reaction mixture. The reaction mixture was kept static overnight which resulted in two separate layers; biodiesel formed the top layer (light yellow) and glycerin and other impurities formed the bottom layer (light brown). The biodiesel was collected using a separatory funnel. The initial pH of the biodiesel was found to be basic (pH ~11.9). This indicated the presence of residual catalyst (KOH) in the biodiesel. The top layer was repeatedly washed with warm water to get rid of residual catalyst. After each wash with water, the pH of the biodiesel was reduced. The better solubility of the KOH in warm water helped to reduce the number of washings to achieve a neutral pH. The final pH of the biodiesel was 6.8, indicating a complete removal of the catalyst. Further the produced biodiesel was washed with an aqueous solution of 0.5% tannic acid (pH= 3.4) not only to remove the traces of the catalyst left over during warm water washing, but also to increase the antioxidant properties of the biodiesel. The presence of the phenolic groups in the tannic acid imparted antioxidant properties to biodiesel.<sup>52</sup> The solubility of trace amounts of tannic acid resulted in an acidic biodiesel (pH=6.8). These washing steps also diminished the intense color of the biodiesel, indicating the removal of any water soluble pigments. GC measurements of the biodiesel showed a combination of various types of methyl esters (Figure 4.7).

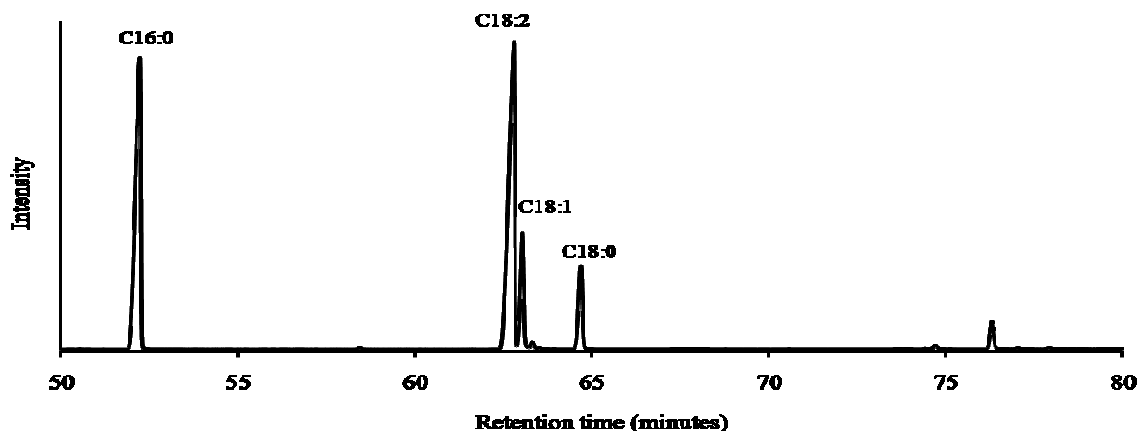
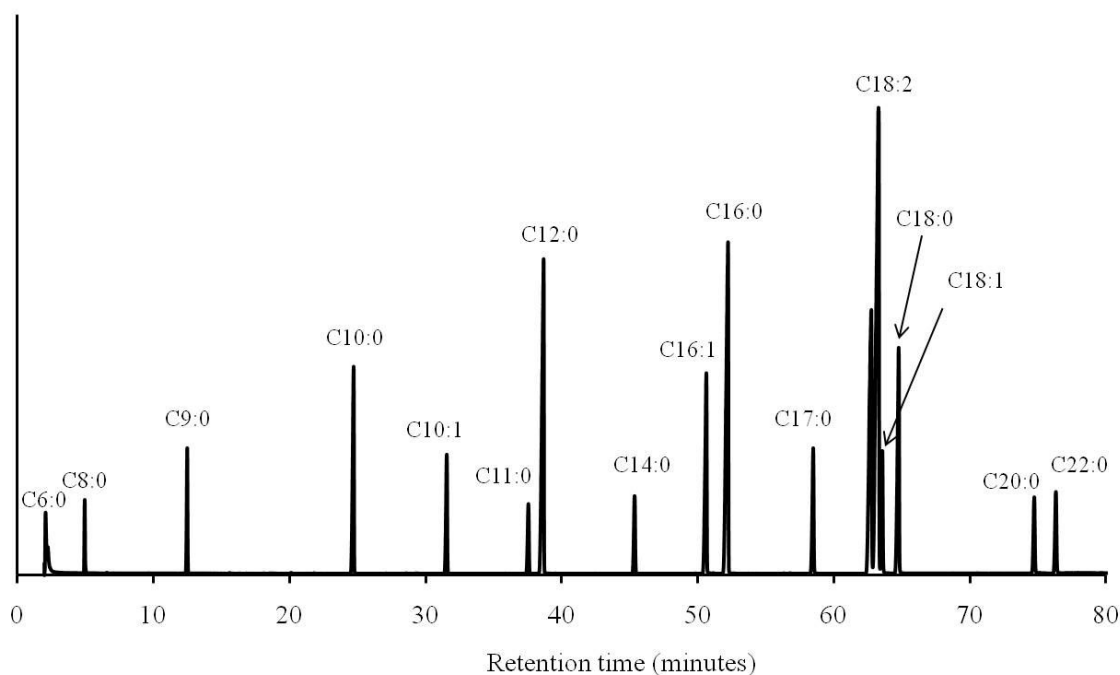


Figure 4.7. GC of coffee biodiesel.

Each component in the GC was separately analyzed using mass spectroscopy (MS) attached to the GC (GC-MS) and compared with the corresponding methyl esters. GC-MS analysis showed the presence of C18-C16 methyl esters of fatty acids (MS spectra were not shown). Coffee biodiesel consists of both saturated and unsaturated methyl esters.

A GC-MS method for the determination of methyl esters of fatty acids in coffee oil and feather meal has been developed for the Shimadzu GC QP 2010. SHR-5XLB capillary column (25 mm thickness X 30 m length) attached with a mass spectrometer operating in electron ionization (70 eV) using helium as a reagent gas, allowed the determination of all analytes in a single GC run. A temperature gradient was selected so that the temperature rose from 100°C to 240°C in 95.33 (1.5°C/min). Using this method, fatty acid methyl esters were identified in both coffee biodiesel and feather meal biodiesel. Quantitative analysis of coffee biodiesel was conducted using myristic acid methyl ester (C14:0) as an internal standard. A standard solution of pure fatty acid methyl esters

(FAMES) chain length varying from C12-C22 (Figure 4.8) was purchased from Sigma-Aldrich (USA).



**Figure 4.8.** GC of the fatty acid methyl esters standards from C6-C22 shows a good separation for quantitative study.

Retention factors for each FAME (Table 4.2) were calculated as follows.

$$R_{x/IS} = (A_x/A_{IS}) * (M_{IS}/M_x) \quad \text{Eq. 4.2}$$

Where,

$R_x$  = Retention factor of unknown compound x

$R_{IS}$  = Retention factor of internal standard

$A_x$  = Area of the unknown compound x

$A_{IS}$  = Area of internal standard

$M_{IS}$  = Mass of the internal standard and

$M_x$  = Mass of the unknown compound x

**Table 4.2. The retention factor calculations of some important FAMES present in the coffee biodiesel.**

FAME	Retention time (min)	Area under the curve	$A_x/A_{IS}$	$M_x$	$M_x/M_{IS}$	$R_x$
C14:0	38.64	326144187	1	1.06	1	1
C16:0	52.22	388567955	1.19	0.59	1.77	2.11
C18:2	62.78	336165580	1.03	0.59	1.77	1.82
C18:1	63.04	681042720	2.09	0.92	1.17	2.46
C18:0	64.78	205800173	0.63	0.26	4.08	2.58
C20:0	76.29	62828757	0.19	0.29	3.61	0.69

Known amounts of coffee biodiesel (2  $\mu$ L) with 1  $\mu$ L C14:0 as an internal standard were injected into GC-MS and the wt% of individual FAME (Table 4.3) was calculated using the following formula.

$$M_x = (A_x/A_{IS}) * M_{IS}/R_x \quad \text{Eq. 4.3}$$

**Table 4.3. Quantitative analysis of coffee biodiesel.**

FAME	Retention time (min)	Area under the curve	$A_x/A_{IS}$	$(M_{IS}/R_x)$	$M_x$	% Wt
C14:0	38.64	204513242	1	0.92	0.92	
C16:0	52.22	310115528	1.52	0.44	0.66	34.49
C18:2	62.78	361747942	1.77	0.50	0.89	46.50
C18:1	63.04	78749356	0.39	0.37	0.14	7.51
C18:0	64.78	56884713	0.28	0.36	0.09	5.18
C20:0	76.29	18727948	0.09	1.32	0.12	6.31
					1.91	99.99

The oil and biodiesel formed in this process were found to be stable over one month without any observable physical changes. The properties of coffee biodiesel were also analyzed by ASTM tests for biodiesel (Table 4.4). The analysis of the results showed that biodiesel obtained from spent coffee grounds is a potential candidate as an alternative to diesel<sup>106</sup>. The images of coffee oil and biodiesel produced from spent coffee grounds are provided in Figure 4.9.



**Figure 4.9.** Coffee oil and biodiesel produced from spent coffee grounds.

**Table 4.4. ASTM results for the coffee biodiesel.**

Test name	Test method	Limit	Results
Free glycerin (mass %)	ASTM D 6584	MAX 0.020	0.006
MG (mass %)	ASTM D 6584	N/A	0.076
DG (mass %)	ASTM D 6584	N/A	0.027
TG (mass %)	ASTM D 6584	N/A	0.000
Total glycerin (mass %)	ASTM D 93	MAX 0.240	0.109
Phosphorous (ppm)	ASTM D 4951	MAX 10	2.0
Ca + Mg (ppm)	EN 14538	MAX 5	2.0
Na + K (ppm)	EN 15438	MAX 5	2.0
Viscosity @ 40°C	ASTM D 445	1.9-6.0	5.84
TAN (mg KOH/g)	ASTM D 664	MAX 0.50	0.35
Oxidation stability by rancimat (hours)	EN 14112	MIN 3.00	3.05
Cloud point (°C)	ASTM D 2500	N/A	11.0
Pour point (°C)	ASTM D 97	N/A	2.0
Sulfur, by UV (ppm)	ASTM D 5453	15	8.0

The quality of the coffee oil as feedstock for biodiesel production was also found to be a better quality and cost-effective compared to other waste sources available to date (Table 4.5).<sup>52,18</sup>

**Table 4.5. Comparison of coffee oil with other waste feedstock for biodiesel production.**

Source	Amount (million gallons/yr)	Advantage	Disadvantage
<b>Animal fat</b>	5.5 <sup>a</sup>	oxidative stability,	high sulfur content,
tallow, brown grease, pork fat (white grease), lard, fish oil, poultry fat		less expensive	high FFA (50-90%), bad odor, bad cold flow properties, high cloud point, high pour point, transportation costs, purification required
<b>Vegetable oil</b>			bad odor, high FFA
used vegetable oil	2.8 <sup>a</sup>	less expensive, readily available	
coffee oil	2.92	less expensive, higher stability, well established transportation, pleasant smell	extraction of oil from spent coffee grounds required

<sup>a</sup> Alleman, T. L.; McCormick, R. L. "Results of the 2007 B100 quality survey"

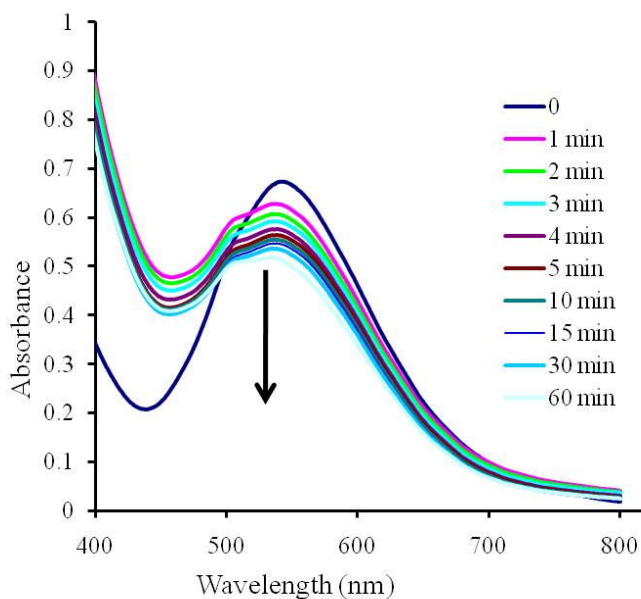
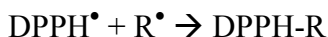
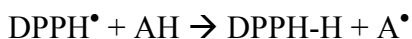
Currently, the use of spent coffee grounds is limited to gardens as compost for plants. Ideal coffee grounds for the soil need a C/N ratio (wt) of 20:1. The C/N ratio after the oil extraction process showed that there was no significant change in the C/N ratio before (19.8:1) and after (15.7:1) the extraction process. This indicated that the processed coffee grounds could still be used as compost for the garden and/or as fuel pellets (1 lb pellet  $\equiv$  8,691 BTUs of energy). Immediately after the oil is extracted from the grounds, the grounds could be pelletized into fuel pellets.

#### **4.1.2.4 Inherent antioxidants in coffee biodiesel**

Coffee is one of the most popular beverages in the world, and is the richest source of antioxidants. Coffee contains chlorogenic acids with the amounts varying between green and roasted beans.<sup>107</sup> Chlorogenic acids are a family of esters formed between certain hydroxycinnamates and quinic acid, and comprise a number of sub-groups among which the most widespread are caffeoylquinic acids, feruloylquinic acids and p-coumaroylquinic acids.<sup>108</sup> Some of the chlorogenic acid methyl esters get extracted into coffee oil during the hexane extraction process, which imparts oxidative stability to the coffee biodiesel.

Berset et al., reported a spectroscopic method to evaluate antioxidant activity using a free radical solution.<sup>109</sup> To evaluate antioxidant activity, the sample (here it is biodiesel) was allowed to react with a stable free radical, 2,2-Diphenyl-1-picrylhydrazyl (DPPH<sup>•</sup>) in a methanol solution. The reduction of DPPH<sup>•</sup> as indicated below was followed by monitoring the decrease in its absorbance at a characteristic wavelength during the reaction. In its radical form, DPPH<sup>•</sup> absorbs at 515 nm, but upon reduction by an

antioxidant (AH) or a radical species ( $R^\bullet$ ) the absorption disappears as shown in Figure 4.10.

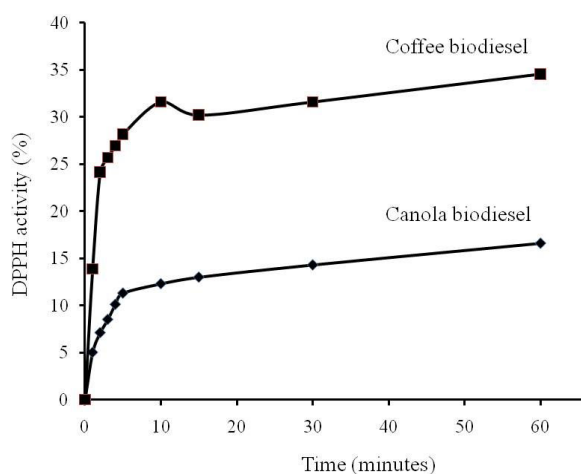


**Figure 4.10. Spectroscopic monitoring of  $\text{DPPH}^\bullet$  reduction in presence of coffee biodiesel**

activity because of the presence of phenolic compounds. The antioxidant activity of phenolic compounds might result from neutralization of free radicals initiating oxidation processes, or from the termination of radical chain reactions, due to their hydrogen donating ability<sup>110</sup>

For comparison purpose the same test was carried out using canola biodiesel prepared under similar conditions. Figure 4.11 showed the DPPH free radical scavenging activity of coffee biodiesel and canola biodiesel made under the similar conditions.

Coffee biodiesel showed more



**Figure 4.11. DPPH activity reduction as a function of time**

### **4.1.3. Conclusion**

We have demonstrated that spent coffee grounds can be used as a potential source to produce quality biodiesel. Around 15% w/w of the oil was obtained from spent coffee grounds and was successfully converted to biodiesel. GC-MS and HPLC analysis indicated that the coffee-biodiesel consisted of both saturated and unsaturated esters. ASTM analysis confirmed that this biodiesel can be used industrially as an alternative to diesel. This can add approximately 340 million gallons of biodiesel to the World's fuel supply. This work has given new insight into producing biofuels without growing plants and/or converting food-to-fuel.

## **4.2. Biodiesel production from feathermeal:**

### **4.2.1. Introduction:**

According to the U.S. Census Bureau, feather meal (hydrolyzed poultry feathers) is defined as “the product resulting from the treatment under pressure of clean, undecomposed feathers from slaughtered poultry”. Feather meal is also prepared by rendering the feathers with other waste materials such as blood and offal from the poultry industry using high pressure. The rendering process involves the hydrolysis of polypeptide chains of feather proteins using supercritical water.<sup>111</sup> The hydrolysis process converts high molecular weight, non-digestible proteins of the feather, such as keratins, into small and digestible proteins. The molecular weight and the nutritional values of the newly formed proteins or poly peptides depend upon the time, temperature and pressure of the supercritical hydrolysis process. Interestingly, these feather meal samples contain certain amounts of fat. The fat content of the feather meal varies from 2–12% depending upon the type of feathers and other waste products added. For example, chicken feathers

contain approximately 11% fat content, while turkey and duck feathers contain approximately 6.7% fat content. A brief description of the eco-friendly extraction of fat (biodiesel feedstock) from chicken feather meal and its successful conversion to biodiesel (Figure 4.12) is presented here.

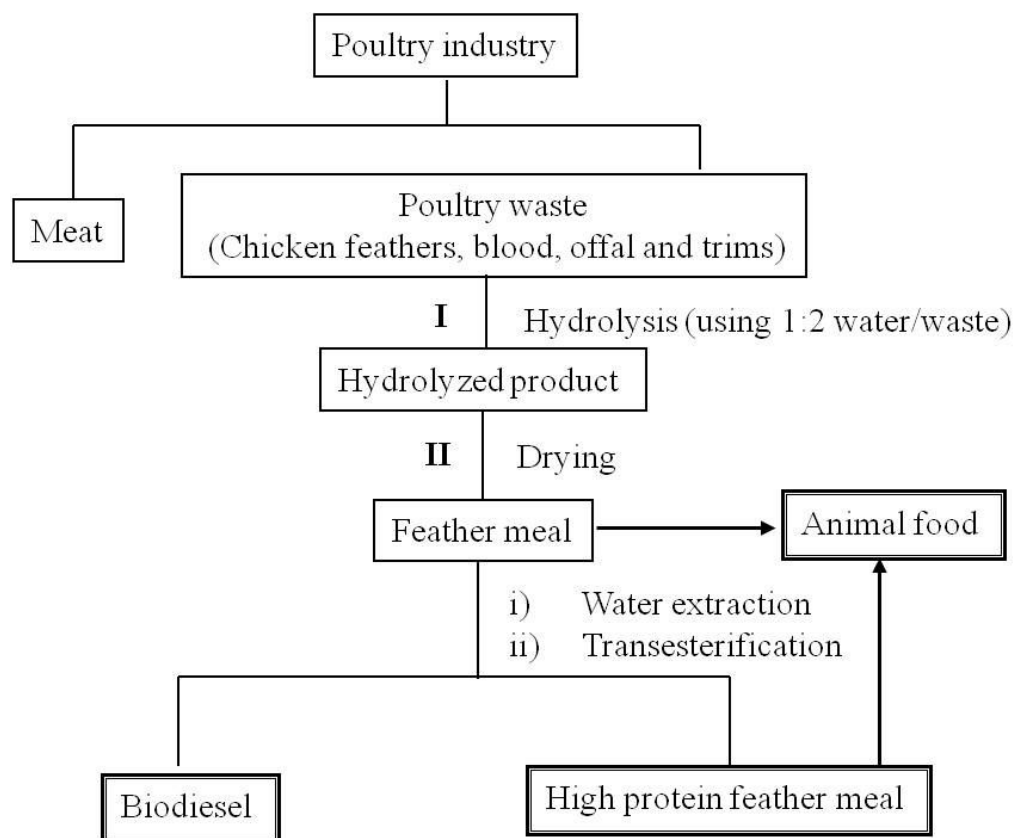


Figure 4.12. A schematic representation of biodiesel production from poultry waste.

## 4.2.2. Results and discussion

### 4.2.2.1. Extraction and purification of fat from feather meal

Fat extraction process from feathermeal using water as a solvent was discussed in chapter 3.2. In the process of hydrolyzing the proteins, the rendering process also releases the fat content of the feathers (which is approximately 2–4%). The fat from the feathers and the rest of the waste materials such as blood and offal are adsorbed on the low molecular

weight protein content of the feather meal. When the feather meal was stirred with hot water, the fat melted and started floating on the surface of the water. A total of 6.9% of the fat was extracted using water as a solvent under stirring for 20 minutes. The total fat content of the feather meal was determined prior to water extraction using hexane extractions on samples from the same batch. Hexane was used, instead of ether, for the solvent extraction to minimize the extraction of unwanted polar compounds, such as free fatty acids found in the feather meal. The total fat content from the test batch was approximately 11% w/w. Increasing the time of extraction and/or usage of ultrasonication may increase the fat extraction capabilities. The advantage of this process was that it eliminated the costs of additional solvent use. Moreover, using water as a solvent helps in the removal of FFA, which ultimately provides high quality feedstock. After stirring the feather meal with water, the pH of the water varied from 5.5 to 4.5, which indicated the dissolution of FFA in the water. Preheating of the fat prior to the transesterification helped to remove the trace amounts of water present in the reaction mixture. The FFAs present in the crude fat were separated by converting them into soap by mixing basic solution with the extracted fat. Soap was removed from the pure oil by centrifuging the mixture for 30 minutes (4081×g; Beckman centrifuge Model J2-21). Purified fat (10 g) was processed to the next step: transesterification. FFA can be washed away using organic solvents such as methanol, ethanol and propanol.

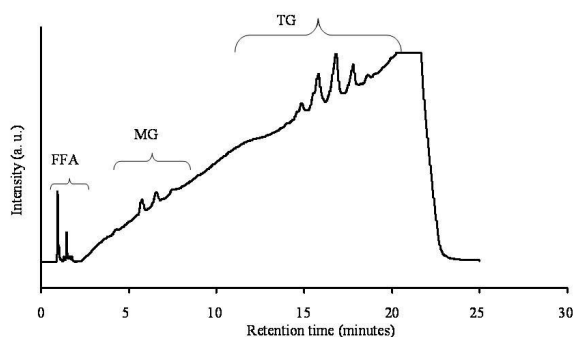
#### **4.2.2.2. Conversion of feathermeal fat into biodiesel**

Transesterification of the purified fat was converted to biodiesel. In this process, the fat was preheated to 100°C and cooled down to room temperature to remove the traces of water present, and a solution of methanol (1:9 molar ratio) and 1.5 wt% of potassium

hydroxide (catalyst) were added to the fat. The reaction mixture was refluxed at 70°C for 1h. Optimization of the transesterification reaction was carried out by varying the amounts of methanol and potassium hydroxide. Transesterification kinetics were measured by monitoring the TG peaks in the HPLC chromatogram. The same column conditions for spent coffee grounds were used for feather meal biodiesel. Complete transesterification was further confirmed by the American Society for Testing and Materials (ASTM) D 6584. Complete transesterification was observed within the first 15 minutes. Faster reaction times were attributed to the higher volume of methanol used in the reaction.

#### 4.2.2.3. Purification and analysis of feathermeal biodiesel

After the transesterification process, the reaction mixture was cooled to room temperature overnight. The bottom layer, glycerin was separated from the biodiesel. The top layer was then washed twice with warm water (40-45°C) and with acidified water (0.5 wt% tannic acid) to remove the excess methanol and the traces of catalyst.<sup>112,94</sup> The HPLC chromatogram of the fat content obtained from feather meal is shown in Figure 4.13. Small amounts of FFA and MG were also observed.



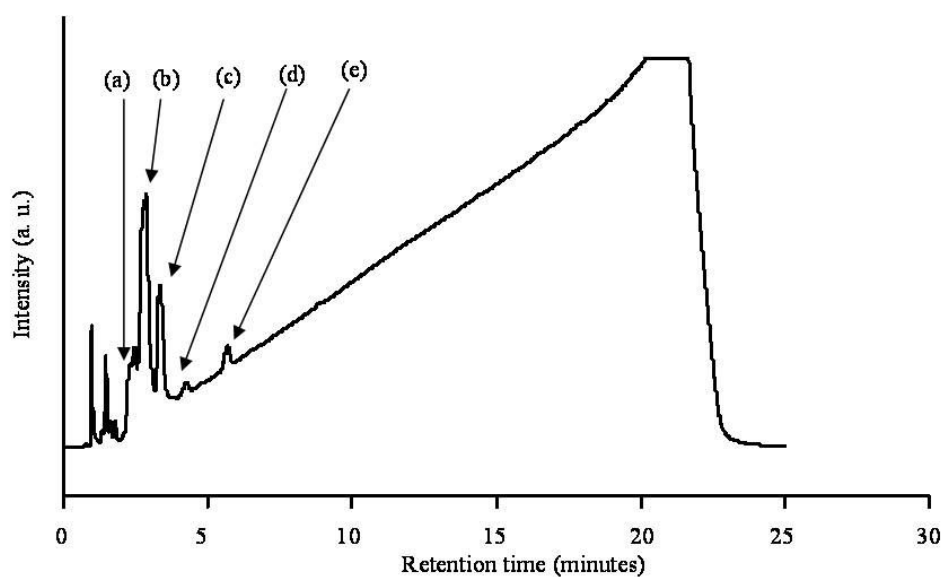
**Figure 4.13. HPLC chromatogram of fat extracted from the feathermeal.**

Extraction of fat content from the feather meal was carried out using two different solvents such as water and hexane. The hexane extraction process had a higher yield (11 wt %) as compared to the water extraction process (6.9 wt %). Even though the usage of water results in lower yields of the fat content, it eliminates the costs of hexane and makes the process more environmental friendly. Moreover, using water as a solvent helped in the removal of FFA. After the reflux process, the pH of the water was noted as 4.5 indicated the dissolution of FFA in the water. Preheating of the fat content prior to the transesterification helped in removing trace amounts of water present in the reaction mixture.

Different values of methanol and catalyst were tested and 1.5 wt% catalyst and 40 vol% methanol were selected as optimum conditions for the transesterification reaction.<sup>113</sup> Transesterification kinetics were measured by observing the TG peaks in the HPLC chromatogram. Complete transesterification was observed within 15 minutes. The reaction mixture from the process contained biodiesel in combination with excess methanol, catalyst and glycerin. Several purification processes were carried out to separate the biodiesel from the reaction mixture. The reaction was kept static overnight which formed two separate layers; biodiesel formed the top layer and glycerin and other polar impurities formed the bottom layer. The top layer (biodiesel) was collected using a separatory funnel. The initial pH of the biodiesel was found to be basic in nature (pH~12.0). This indicated the presence of residual catalyst, KOH, in the biodiesel. The top layer was repeatedly washed with warm water to get rid of residual catalyst. After each wash with water, the pH of the biodiesel reduced to a more neutral pH. The better solubility of the KOH in warm water helped to reduce the number of washings to achieve

the neutral pH. The final pH of the biodiesel was 6.8, indicating a complete removal of the catalyst. Furthermore, the washed biodiesel was washed with an aqueous solution of 0.5 wt% tannic acid (pH = 3.4). The presence of phenolic groups in the tannic acid imparted antioxidant properties to the biodiesel.

Standards of fatty acid methyl esters (FAME) were obtained from Sigma-Aldrich and were run through HPLC under the same experimental conditions. The HPLC chromatogram of feather meal biodiesel (Figure 4.14) showed the presence of various methyl esters of fatty acids such as oleic (a), linoleic (b), palmitic (c), stearic (d) and some small chain fatty acid (e).



**Figure 4.14. HPLC chromatogram of feathermeal biodiesel.**

GC measurements of the above prepared biodiesel showed a combination of various types of methyl esters (Figure 4.15), which are identical with the HPLC chromatogram.

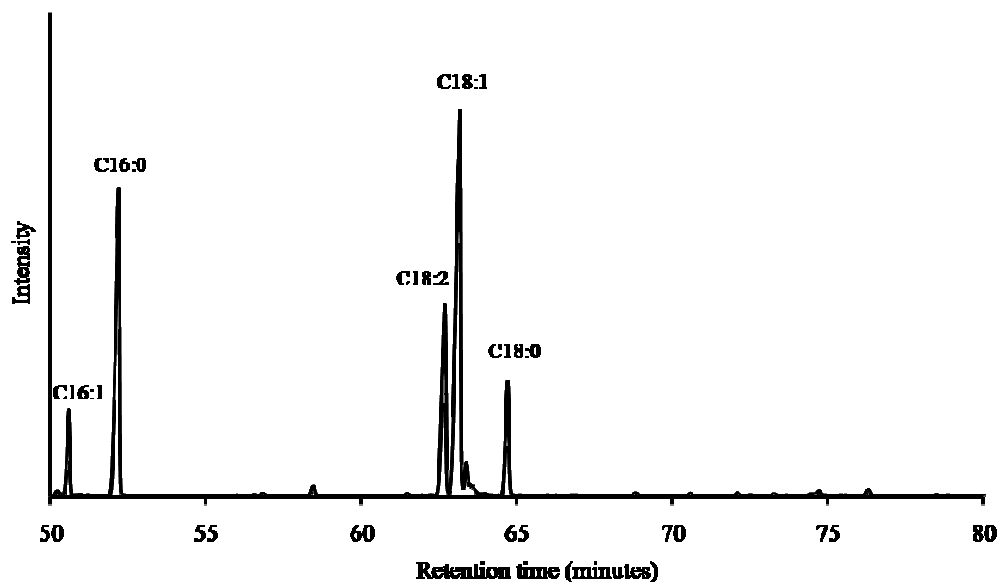


Figure 4.15. Gas chromatogram (GC) of feathermeal biodiesel.

Individual components were analyzed using mass spectroscopy (MS) and each peak in the GC was identified. At room temperature, feather meal fat was observed to be a solid because of the saturated TG. But interestingly, after the transesterification, the corresponding methyl esters were separated from the highly dense glycerin moiety and became liquid at room temperature. The difference is clearly visible in Figure 4.16. As the saturated fatty acid methyl esters dominated the biodiesel composition, feather meal biodiesel acquires higher oxidative stability when compared with other vegetable oil derived biodiesels (being dominated by unsaturated fatty acid chains).



Figure 4.16. TG (a) and biodiesel (b) obtained from feather meal.

Moreover, the degree of saturation of the fatty acid governed the quantity of energy contained within. Quantitative analysis (Table 4.6) of feather meal biodiesel was performed using GC-MS with the help of Equations 4.2 and 4.3. The fatty acid profile from feather meal did not differ significantly from the chicken fat fatty acid profile.<sup>114</sup> Feather meal biodiesel contained oleic acid (~46%) and palmitic acid (~29%). Biodiesel containing carbon chain length of 15 or higher produces superior quality fuel.<sup>115</sup> The presence of saturated fatty acids (~ 40 wt %) gave a good oxidative stability to the biodiesel.

ASTM (American Society for Testing and Materials) set the complete and comprehensive tests for biodiesel evaluation (ASTM D6751). While there are many different parts of the test, fuel must pass the entire battery of tests to be marketed as a fuel for use in diesel engines, and to comply with the Environmental Protecting Agency (EPA) standards. The complete ASTM analysis (Table 4.7) showed that it has a good cetane number, high oxidation stability, which are good qualities of a commercial biofuel.

**Table 4.6 Quantitative analysis of feather meal biodiesel.**

FAME	Retention time (min)	Area under the curve	$A_x/A_{IS}$	$(M_{IS}/R_x)$	$M_x$	% Wt
C14:0	38.64	337150347	1	0.92	0.92	
C16:0	52.22	229920645	0.68	1.95	1.33	28.86
C18:2	62.78	132988713	0.39	1.68	0.66	14.44
C18:1	63.04	316107080	0.94	2.26	2.12	46.10
C18:0	64.78	65766156	0.19	2.37	0.46	10.05
C20:0	76.29	3464494	0.01	0.64	0.01	0.14
					4.58	99.59

**Table 4.7. ASTM analysis of the feather meal biodiesel**

Test name	Test Method	Limit	Result
Free glycerin (mass %)	ASTM D 6584	MAX 0.020	0.004
Mono glycerides (mass %)	ASTM D 6584	N/A	0.061
Diglycerides (mass %)	ASTM D 6584	N/A	0.056
Triglycerides (mass %)	ASTM D 6584	N/A	0.003
Total glycerin (mass %)	ASTM D 6584	MAX 0.240	0.123
Flash point, closed cup (°C)	ASTM D 93	MIN 130	154
Sodium + Potassium (ppm)	EN 14538	MAX 5	5
KF Water (ppm)	ASTM D 6304	N/A	188
Viscosity @ 40°C (cSt)	ASTM D 445	1.9-6.0	5.48
Oxidative stability by rancimat (hours)	EN 14112	MIN 3.00	6.46
Sim. Dist., 90% recovery (°C)	ASTM D 2887	MAX 360	355
Cetane index	ASTM D 976	N/A	61
Cloud Point (°C)	ASTM D 2500	N/A	23
Pour Point (°C)	ASTM D 97	N/A	6

Currently, feather meal use is limited to animal food and a nitrogen fertilizer. Removal of the fat content from the feather meal increases the protein content and results in a higher grade animal feed. Additionally, because this process removes the fatty acid content in the feather meal, the nitrogen content is increased and this creates a better nitrogen source for fertilizer applications. Based on a 10% oil yield, the United State's poultry industry

could produce approximately 153 million gallons of biodiesel annually from feather meal (Table 4.8).

**Table 4.8. Total poultry industry annual production of meat, waste products and tentative amount of biodiesel that can be produced from the waste products in 2008.**

Poultry industry	Meat produced in U. S. (million pounds)	Poultry industry waste <sup>a</sup> (million pounds)	Total fat content (wt%)	Tentative biodiesel production (million gallons/yr)
Broilers	37,125 <sup>a</sup>	9,700	11 <sup>b</sup>	139
Turkeys	6,135 <sup>a</sup>	1,603	6.7 <sup>b</sup>	14
				Total =153 <sup>c</sup>

<sup>a</sup> Total mass loss from a living broiler to the meat is estimated 26.13%. It requires 50,257 million pounds of live chicken to produce 37,125 million pounds of meat (Haley, M. M. Livestock, Dairy, and Poultry Outlook; United States Department of Agriculture. LDP-M-165, March 19, 2008.)

<sup>b</sup> Total amount of fat in chicken feather meal (11%) and turkey feather meal (6.7%) (Dale, N. True metabolizable energy of feather meal. J. Appl. Poultry Res. 1992, 1, 331–334.)

<sup>c</sup> On an average of \$3/gallon, this process is estimated to have \$459 million dollars market. This is projected that a medium size plant should produce biodiesel at the cost of \$1 dollar/gallon using this process.

### **4.2.3. Conclusion**

A green process to produce biodiesel from feather meal was demonstrated. The removal of the fat content from feather meal produced a better food source for animals and fertilizer for agriculture. If this technology expands worldwide, it could potentially produce ~600 million gallons of biodiesel, according to the United Nations Food and Agriculture Organization Report for 2005. This technology can be expanded to other poultry industries (duck and turkey), and can potentially contribute to reducing demand on foreign oil and help solve further petroleum demands.

## **Chapter 5 † Bifunctional heterogeneous catalyst for biodiesel production**

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### **5.1. Introduction**

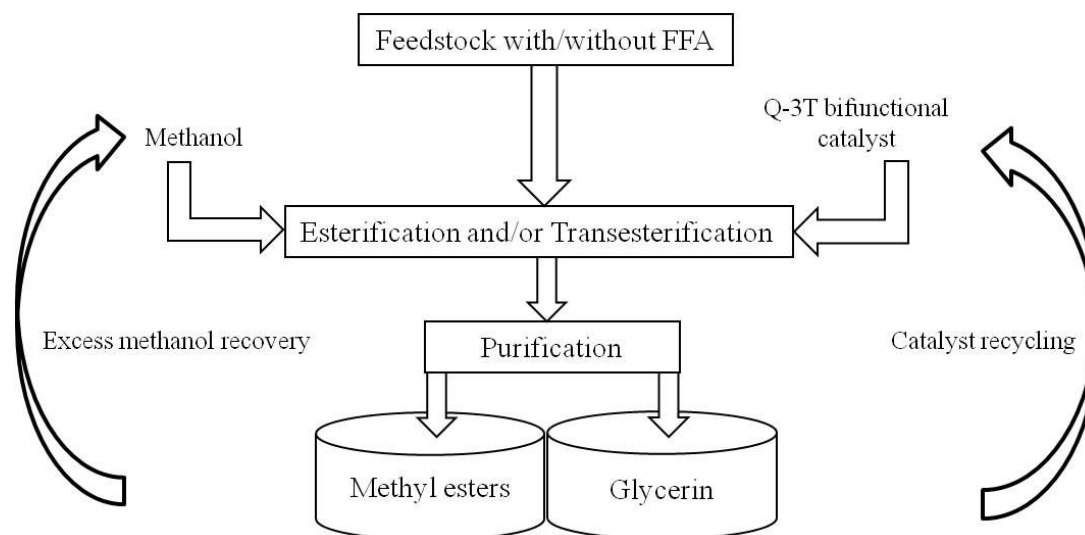
Layered double hydroxides (LDHs) are anion clays, composed of positively charged layers of general formula  $[M^{3+}_x M^{2+}_y Om(OH)_n]^{(3x+2y-2m-n)+}$ , and interlayer inorganic or organic anions compensating the positive charge, as well as hydrate water molecules.<sup>116</sup>

The large variety of compositions can be developed by altering the nature of the divalent ( $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ) and trivalent ( $Al^{3+}$ ,  $Ga^{3+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$ ) cations and the interlayer anions.<sup>117,118</sup> Proper selection of divalent and trivalent ions determines the acidity and basicity of mixed metal oxides.<sup>119</sup> LDHs attracted increased attention in recent years because of anionic exchange capacity, and the ability to capture organic and inorganic anions. LDHs find a vast variety of applications including catalysis, ion exchange, adsorption, pharmaceuticals, photochemistry and electrochemistry. The flexibility in composition of LDHs has led to an increase in interest in these materials. As a result of their relative ease of synthesis, LDHs represent an inexpensive, versatile and potentially recyclable source of a variety of catalyst supports, catalyst precursors or actual catalysts.

In this research work, we test the effectiveness of Quintinite-3T (Q-3T), a family member of LDHs, as heterogeneous bi-functional catalyst, to convert both FFA and TG into pure biodiesel. Layered nanomaterials, due to their unique structure consisting of stacked nano-sheets, represent an interesting opportunity to develop new hybrid materials with

intentional and controllable functionalities; therefore, these materials have found many industrial applications. Hydrotalcite is the most studied LDH in catalysis (hydrogenation, Ziegler-Natta, and bromination reactions) and adsorption (toxic elements such as lead, mercury, etc.) applications.<sup>120</sup> Quintinite is chemically similar with hydrotalcites (HT) with a general chemical structure  $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$  (6:2 minerals)<sup>62</sup> Q-3T is a trigonal structured moiety with a space group  $P3_112$  or  $P3_212$ ,  $a=10.558(2)$ ,  $c=22.71(3)$  Å,  $V=2129(3)$  Å<sup>3</sup>,  $Z=6$ ; however, hydrotalcites have a space group  $R3m$  with  $a=3.054$ Å and  $C=22.8$  Å.<sup>121</sup>

From super lattice reflections in the single-crystal X-ray photographs, Chao et al. reported that ordering of cations of the 6:2 minerals such as hydrotalcites are disordered, whereas the ordering is more defined in case of 4:2 minerals such as Quintinite<sup>121</sup> The higher Al/Mg ratio in Quintinite (0.5) compared with hydrotalcite (0.33) makes it more suitable especially for acid catalyzed reactions in addition to the base catalyzed reactions. The catalyst and the unused methanol can be recycled. A schematic of the process is shown in the Figure 5.1. Characterization of the catalyst and the reaction parameters of the transesterification reactions are discussed.

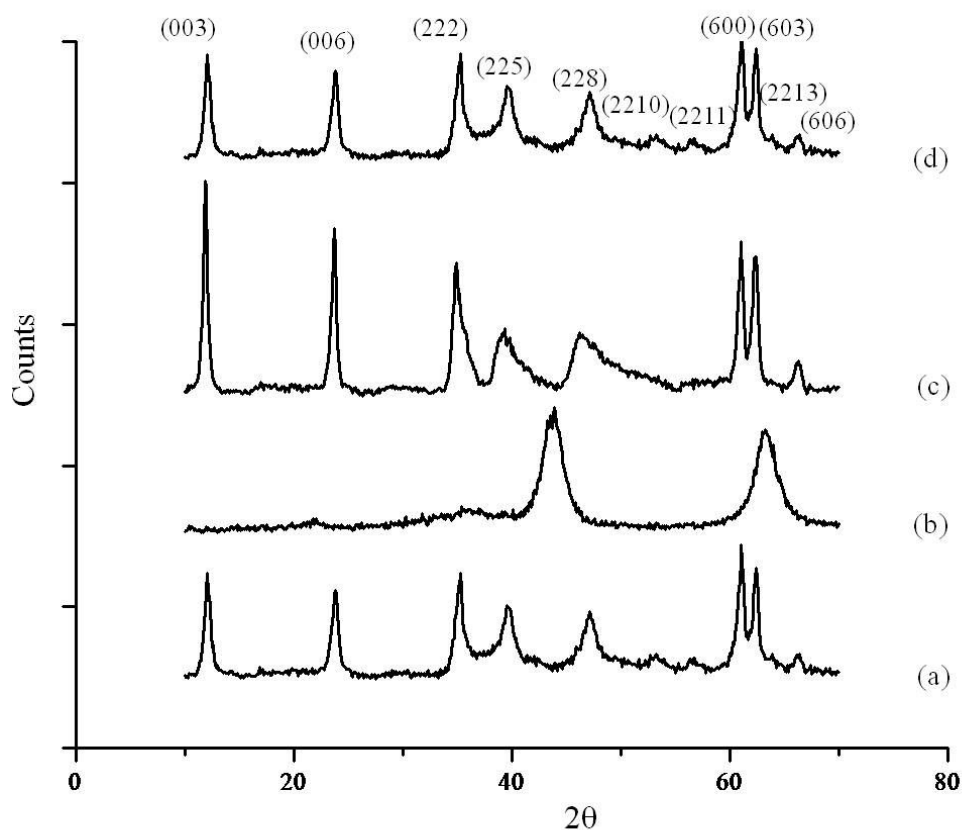


**Figure 5.1.** A schematic representation of operating principle of Q-3T

## 5.2. Results and discussion

### 5.2.1. Catalyst Characterization

XRD pattern of the synthesized samples showed well defined reflections corresponding to Q-3T structure (Figure 5.2a, 2d). The unit cell parameters were also matched with quintinite structure.<sup>121</sup>



**Figure 5.2.** XRD pattern of (a) as synthesized Na-Q3T, (b) Calcined Na-Q3T, (c) hydrated Na-Q3T and (d) as synthesized NH<sub>4</sub>-Q3T.

The chemical composition of the structure is  $\text{Mg}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3 \cdot 3\text{H}_2\text{O}$  and the XRD pattern confirmed the Q-3T structure. After calcining at 773K, peaks corresponding to MgO (periclase) and amorphous alumina were observed due to the destruction of the lamellar structure. The mixed oxide phase with reflections at  $2\theta = 43.27^\circ$ ,  $63.01^\circ$  corresponding to MgO and slight broad peak near  $35.05^\circ$  could be assigned to amorphous alumina. After hydration, the sample re-attained Q-3T structure (Figure 5. 2c). Hydration process using decarbonated water confirms that the peaks are due to hydration and not because of carbon dioxide absorption from the atmosphere. The hydrated calcined sample clearly resulted in the recovery of their original lamellar structure. The sample prepared

using  $\text{NH}_4^+$  source also showed similar XRD pattern (Figure 5.2d) with the samples prepared using sodium source (Na-Q3T). The SEM-EDX analysis of samples revealed an Mg/Al ratio of 2.1:1 (Figure 5.3), corresponding to Q-3T structure with formula  $\text{Mg}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3 \cdot 3\text{H}_2\text{O}$  (4:2 minerals).

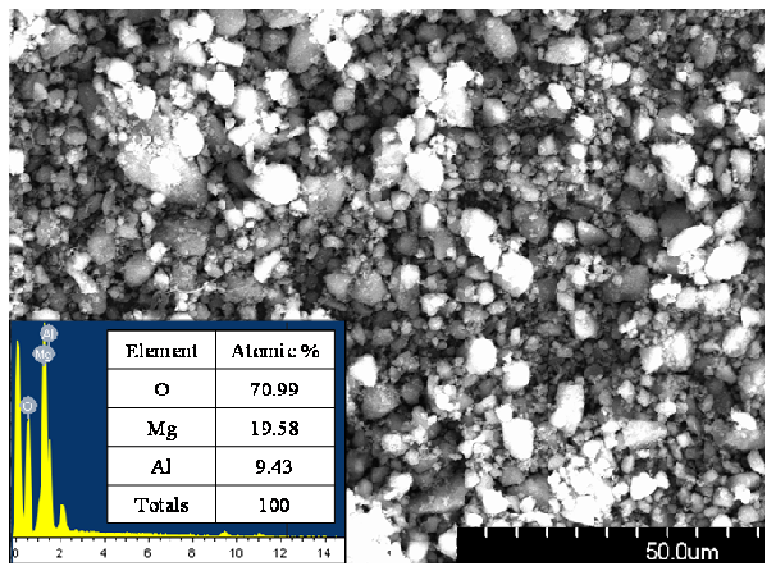
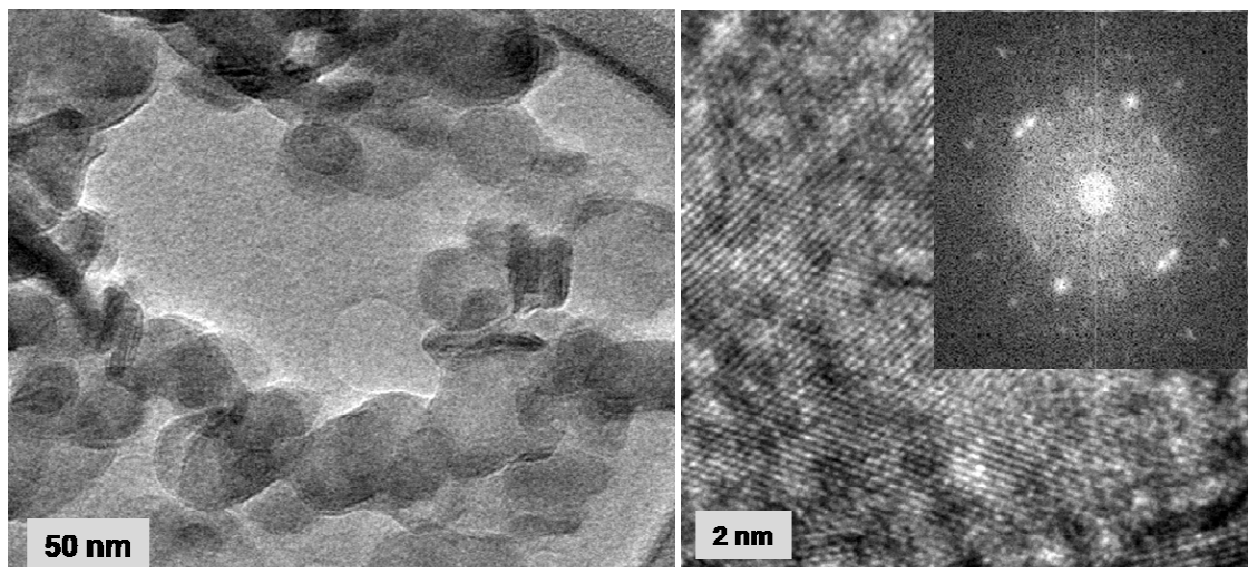


Figure 5.3. SEM image of as-synthesized Na-Q3T. EDX spectrum (insert) shows the Al/Mg ratio to be 2.07.

ICP-MS results were also indicated 4:2 mineral nature of the catalyst (Table 5.1).

Table 5.1. ICP results for the Q-3T synthesized using two different methods namely NaOH (Na-Q3T) and  $\text{NH}_4\text{OH}$  ( $\text{NH}_4$ -Q3T).

	Al	Mg	Na	Mg : Al
Na-Q3T	15.9	27.6	0.03	1.74 : 1
$\text{NH}_4$ -Q3T	16.5	28.8	N/A	1.75 : 1



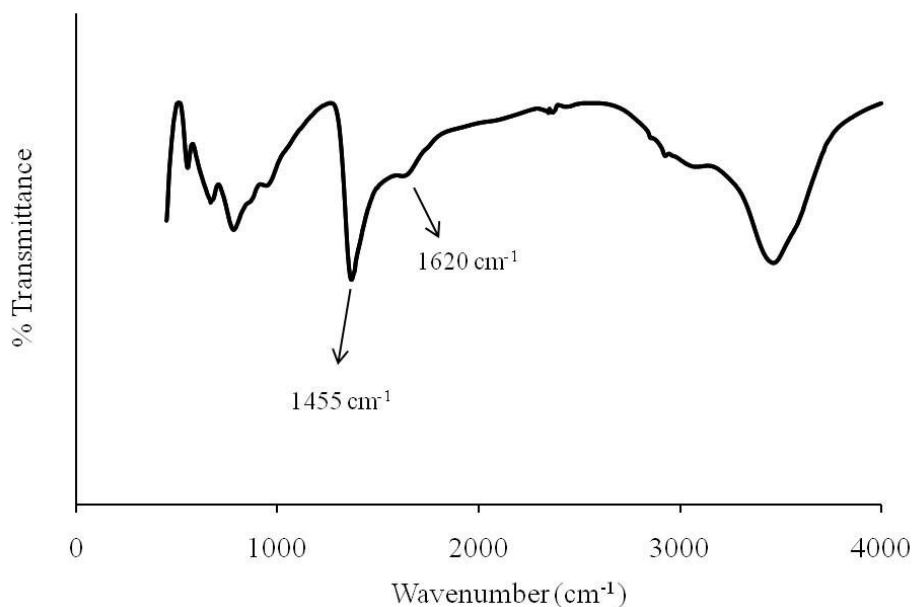
(A)

(B)

**Figure 5.4. (A) TEM image of as-prepared Na-Q-3T which showed distorted spherical particles in the range of 40-60 nm. (B) HRTEM and FFT pattern of the particles confirmed the crystalline nature of the particles.**

TEM image of the as-prepared sample showed a narrow particle size distribution in the range of 40 nm to 80 nm (Figure 5.4A). In the HRTEM image (Figure 5.4B), lattice fringes are clearly visible, which indicates the crystalline nature of the prepared catalyst. This is further confirmed by the Fast Fourier Transformation (FFT) pattern of the particles (Figure 5.4B, inset). The dotted pattern indicates that the sample has a crystalline form.

The relative concentrations of Brønsted and Lewis acid sites of Q-3T were assessed by the FTIR spectra of absorbed pyridine, and the results are presented in Figure 5.5.



**Figure 5.5.** FTIR image of pyridine treated Na-Q-3T showing the presence of both Brønsted acidic (1455  $\text{cm}^{-1}$ ) and Lewis acidic sites 1629  $\text{cm}^{-1}$ ).

The pyridinium ion signal (pyridine on Brønsted acid sites) appeared at wave numbers of 1620  $\text{cm}^{-1}$  and pyridine on Lewis acid sites appeared at 1455  $\text{cm}^{-1}$ .<sup>122</sup> From this spectroscopy, the presence of the Lewis acid sites as well as Brønsted acid sites are noted on the catalyst surface. The presence of Brønsted acid sites can be attributed to the presence of Mg—OH—Al bonds and Al—OH groups. Presence of  $\text{Al}^{3+}$  can account for the Lewis acidic sites. The catalyst was tested for soy, canola, coffee and waste vegetable oils. The selection of oils was based on their variable FFA content.

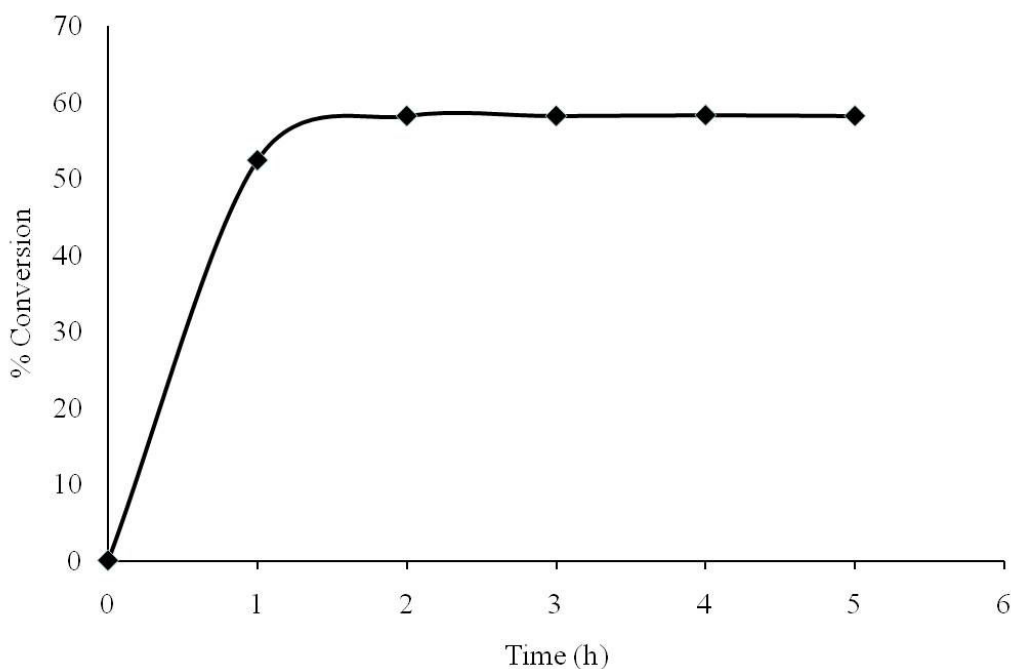
### 5.2.2. Catalytical activity and optimization

The optimization of the reaction conditions were carried out using canola oil and hydrated Na-Q-3T catalyst.

#### 5.2.2.1. Effect of reaction time:

In order to study the influence of reaction time on the biodiesel production, experiments were conducted using the same volume of canola oil (20 mL each time), and the same

amount of methanol (1:3 molar ratio) with different time periods of samples, such as 1, 2, 3, 4, 5 and 6 h respectively. The results are presented in Figure 5. 6. From the figure it is clear that after 2 h of reaction time there was no observable effect on conversion rates. Thus 2 h can be chosen as a suitable reaction time for the reaction.

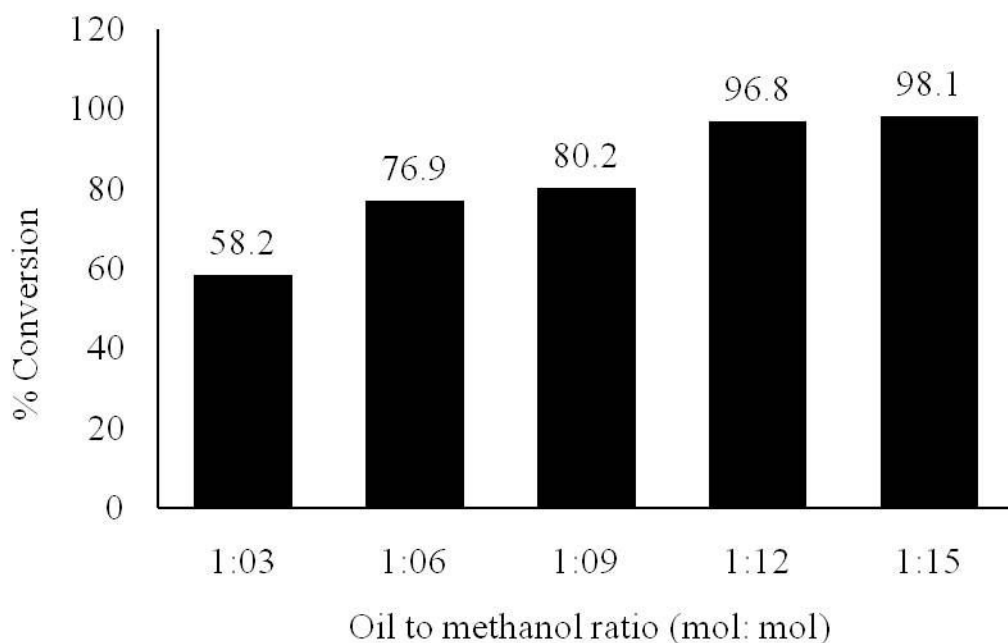


**Figure 5.6. Influence of the reaction time on the conversion of canola oil feedstock (20 mL of canola oil, 1: 3 molar ratio of oil to methanol at 348K and 10 wt% catalyst (Na-Q-3T) was used as reaction conditions).**

#### *5.2.2.2. Effect of molar ratio of methanol/canola oil:*

Ideally, 1: 3 molar ratio of oil to methanol was required for the completion of transesterification reaction because 1 mole of oil reacts with 3 moles of methanol. An excess amount of one of the reactants (methanol) favors the forward reaction. The effect of methanol quantity was observed by varying the molar ratio of methanol from 1:3 to 1:15. Results are shown in Figure 5.7. Highest conversions were observed at 1:15 molar ratio. So, oil-to-methanol ratio was set as 1:15. Further excess of methanol might cause

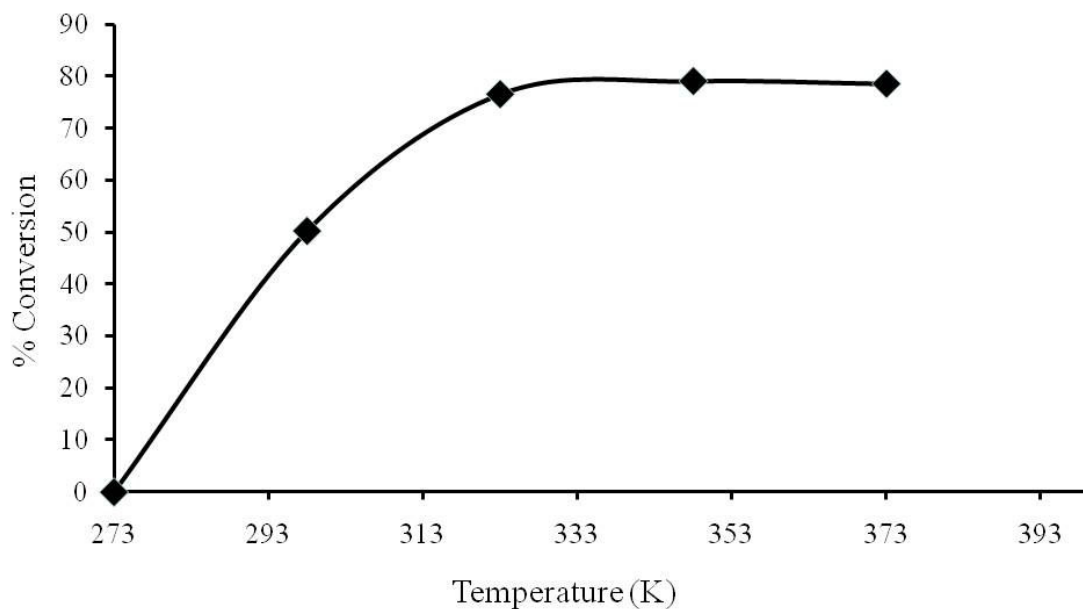
problems such as dissolving both biodiesel and glycerol, which poses separation problems for biodiesel.



**Figure 5.7. Influence of oil to methanol ratio on biodiesel production (10 wt% catalyst, 348 K, 2h reaction time were used as reaction conditions). Na-Q-3T was used as the catalyst.**

#### 5.2.2.3. Effect of reaction temperature:

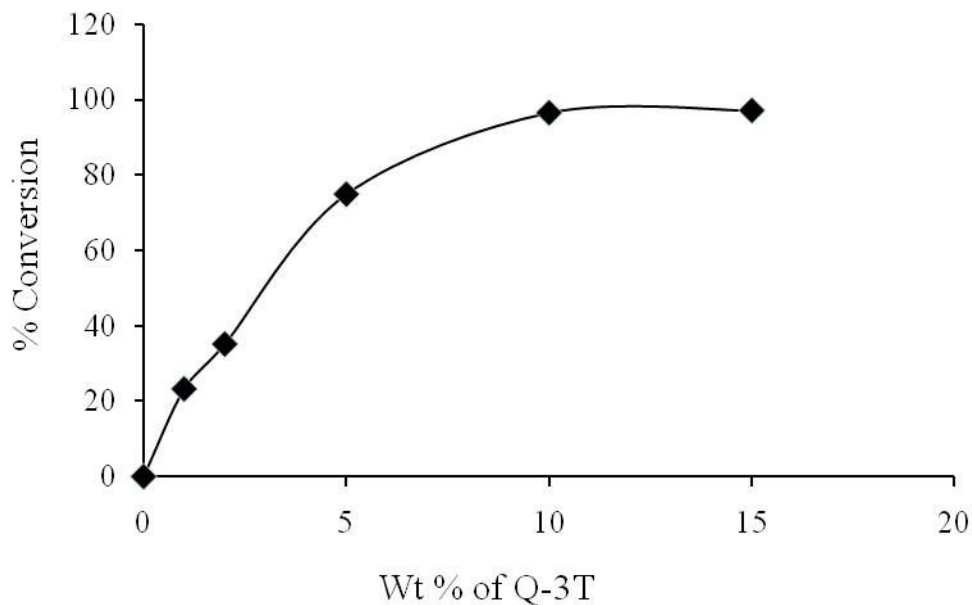
In order to study the influence of the reaction temperature on biodiesel production, experiments were conducted at 298, 323, 348 and 373K keeping the other parameters constant. The results are shown in Figure 5.8. 348K is found to be the optimum temperature for the biodiesel production.



**Figure 5.8.** Influence of temperature on biodiesel production (1: 6 molar ratio of oil to methanol, 10 wt% catalyst and 2 h reaction time). Na-Q-3T was used as the catalyst.

#### 5.2.2.4. Effect of catalyst loading:

The effect of catalyst loading was tested using different amounts of catalyst in the reaction keeping all the other parameters constant. The results for 1, 2, 5, 10 and 15 wt% catalyst are shown in Figure 5.9. From the figure there was a significant increase in percentage conversion from 5 wt% to 10 wt% (conversion increased from 74.8 % to 96.4%) observed, but further increase does not affect the conversion. So, the optimum catalyst amount for the reaction was set to 10 wt%.



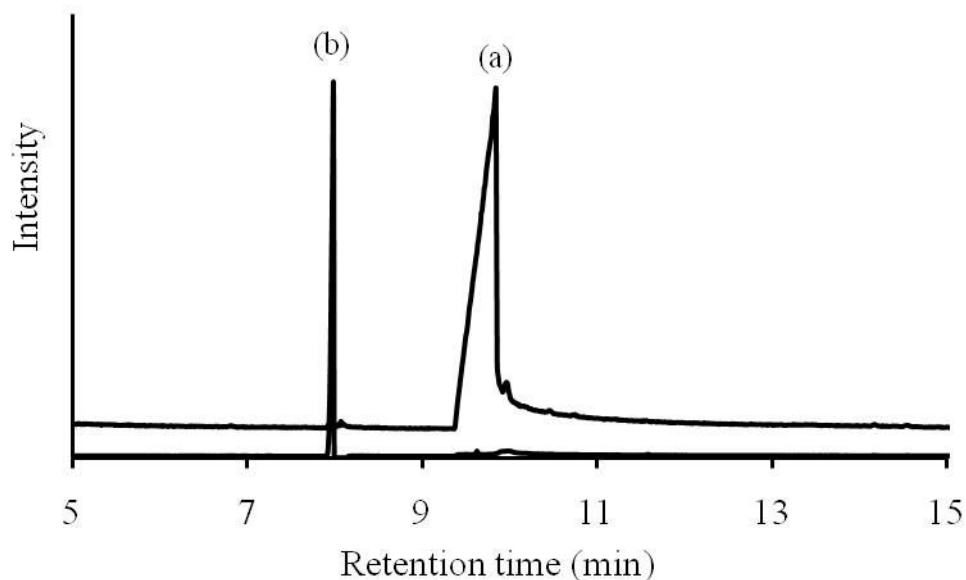
**Figure 5.9.** Influence of catalyst wt% on biodiesel synthesis from canola oil using Na-Q3T as a heterogeneous catalyst (reaction conditions: oil to methanol ratio 1:12, temperature 348 K and reaction time 2 h)

From the above optimization studies it was concluded that the best conditions for transesterification are: an oil to methanol ratio (mol:mol) of 1:12; temperature 348K; and 10 wt% catalyst.

### 5.2.3. Acid catalyzed esterification of FFA.

To confirm the acidic properties of this catalyst we have carried out esterification reaction of a standard FFA, octanoic acid. The catalyst successfully converted the octanoic acid into methyl ester of octanoic acid with 100% conversion and selectivity in 6 h (Figure 5.10). Q-3T exhibits acid and/or base properties depending on the chemical composition and preparation procedures.<sup>123</sup> The presence of alumina induced the Lewis acid properties to the catalyst. The Lewis acid character of mixed metal oxides is reported to increase with the increase of alumina content in the mixed metal composition<sup>124</sup>.  $Al^{3+}$

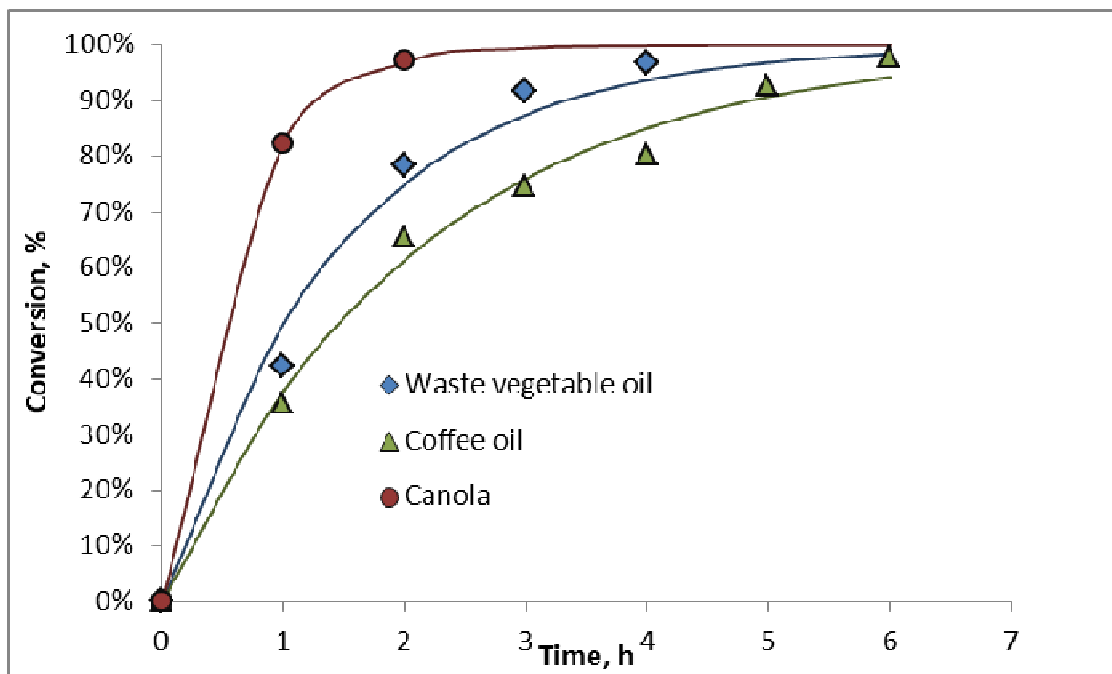
and  $O^{2-}$  which are of moderate Lewis acidity is expected to help progress the esterification process.



**Figure 5.10.** GC chromatogram of (a) octanoic acid and (b) octanoic acid methyl ester. Acid catalyzed esterification of FFA by Q-3T catalyst was tested using octanoic acid. A complete conversion of octanoic acid to octanoic acid methyl ester occurs, which confirms the acidic nature of the prepared catalyst

#### 5.2.4. Base catalyzed transesterification.

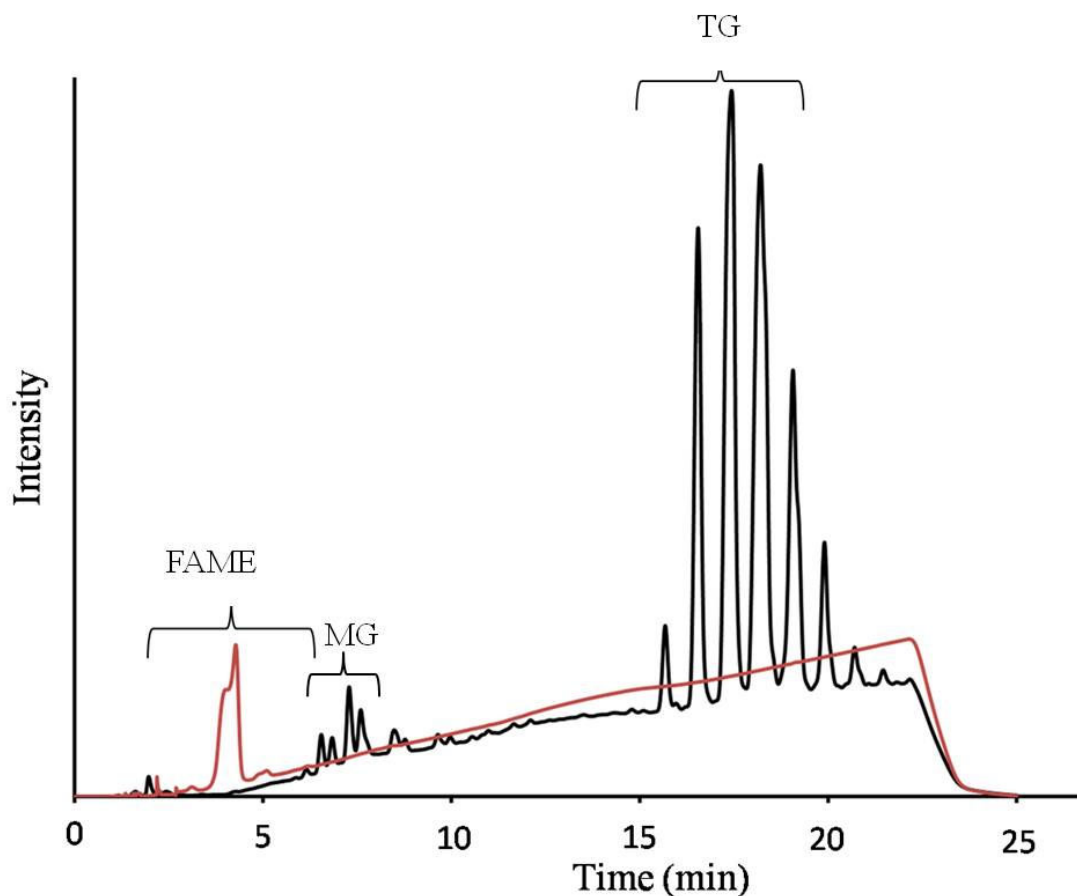
Alkaline earth metal oxides are reported as potential base catalysts. In particular, alkaline earth metal oxides are reported for transesterification of TG in vegetable oils as well as animal fats. The origin of basic sites might be because of the formation of  $Mg^{2+}$  and  $O^{2-}$  ion pairs.<sup>125</sup> The amount of surface oxygen content depends on chemical composition of the mixed metal oxide.<sup>126</sup> To confirm the basic properties of this catalyst we carried out transesterification of commercial canola oil with 100% TG. A complete transesterification was observed within the first 2 h of the reaction when the methanol to oil ratio was 12:1 (Figure 5.11). A similar result was also obtained using soy oil with 100% TG.



**Figure 5.11.** Reaction kinetics of different feedstocks with variable FFA content using Na-Q3T as a catalyst (The FFA contents in waste vegetable oil, coffee oil and canola oil are 15, 30 and 0% successively).

#### 5.2.5. Simultaneous esterification and transesterification reactions.

To evaluate the bifunctional nature of the catalyst we carried out both esterification and transesterification reactions simultaneously (Figure 5.11). Initially, waste vegetable oil with 15% FFA was tested with Q-3T catalyst. More than 97% conversion was observed. Unlike homogenous catalysts (e.g., KOH), Q-3T did not form any soap and a clear two layer separation (glycerin and biodiesel) was observed. Furthermore, the catalyst was tested for coffee oil with 30% FFA. More than 96% conversion was observed. The transesterification reaction of coffee oil was monitored using HPLC (Figure 5.12).



**Figure 5.12. A comparison of coffee oil (black) and coffee biodiesel (red) HPLC chromatograms**

Even though the acid can catalyze the transesterification process, the kinetics of acid catalyzed transesterification was very slow when compared to base catalyzed transesterification reaction. Although there are enough basic sites in the material, one cannot rule out the acid catalyzed transesterification reaction. The use of Q-3T catalyst did not affect the inherent antioxidants in the vegetable oil during the conversion of oil into biodiesel (Figure 5.13). The antioxidants in the coffee oil are mostly phenolic compounds that react with KOH forming water soluble salts and get lost in the purification (water washing) step. Whereas in the Q-3T catalytic process, because there was no

reaction between catalyst and phenolic antioxidants, most of the antioxidants remained intact within the biodiesel and enhanced the shelf life of the biodiesel.

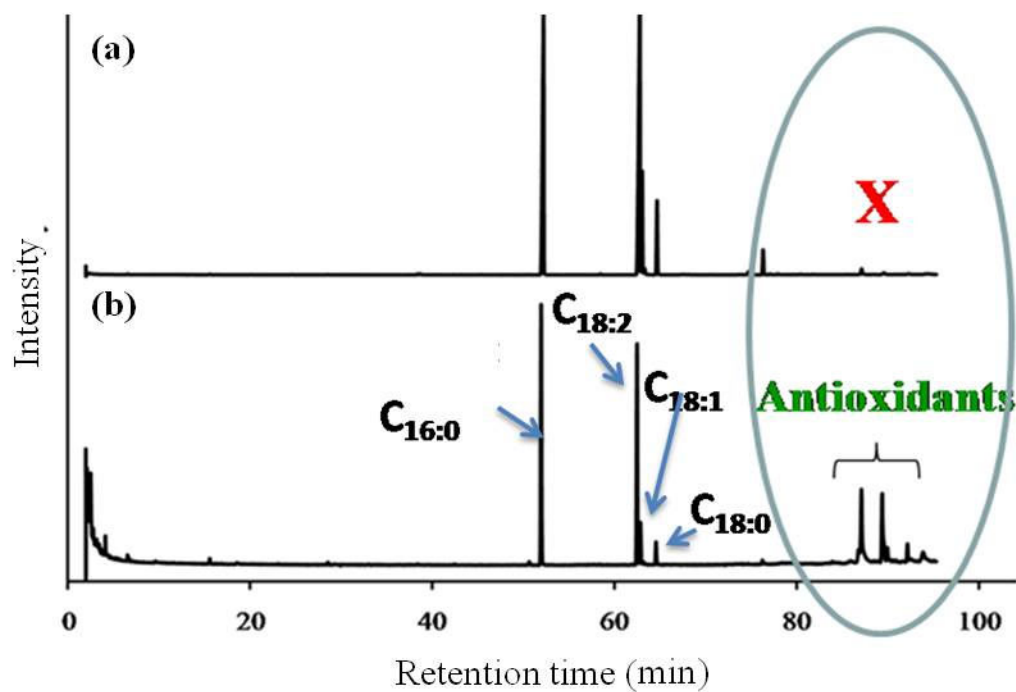


Figure 5.13. GC-MS chromatogram of coffee oil fatty acid methyl esters using KOH (a) and coffee oil with >30 wt% FFA using Q-3T as a heterogeneous catalyst (b). Q-3T as catalyst not only converts the oil into biodiesel but also preserves the intrinsic antioxidant properties of coffee oil.

Table 5.2 shows the confirmation of ASTM acceptable conversions of oils to biodiesel.

This indicated that this catalyst is a potential candidate to convert oils with high FFA content into biodiesel. Pure canola oil was transesterified within 2 h of the reaction.

**Table 5.2. ASTM analysis of non-conventional feedstocks namely oil from spent coffee grounds and waste vegetable oil**

Test name	Test method	Limit	Waste vegetable oil	Spent coffee oil
Free glycerin (mass %)	ASTM D 6584	MAX 0.020	0.000	0.003
MG (mass %)	ASTM D 6584	N/A	0.033	0.095
DG (mass %)	ASTM D 6584	N/A	0.022	0.042
TG (mass %)	ASTM D 6584	N/A	0.057	0.000
Total glycerin (mass %)	ASTM D 93	MAX 0.240	0.112	0.140
Oxidative stability by Rancimat	EN 14112	MIN 3.00	4.02	4.59
Cloud point (°C)	ASTM D2500	N/A	0	10
Pour point (°C)	ASTM D 97	N/A	0	9

Feedstocks with greater FFA content took longer to complete the reaction. This tendency might be attributed to acid catalyzed esterification, which takes an entirely different chemical pathway when compared to base catalyzed transesterification. Acid catalyzed esterification reactions are known to be relatively slower.<sup>7</sup>

*5.2.6. Recycling studies.* To check the reusability of the catalyst, five recycling experiments were carried out using coffee oil. After five recycling experiments the catalyst retained more than 95% of its activity (Table 5.3).

**Table 5.3. Conversion obtained in recycling Q-3T in the transesterification of coffee oil. Reaction conditions: Na-Q3T (10 wt%), coffee oil (20 mL), oil to methanol (1:12) stirred at 348 K for 2 h. Conversion in cycle 1 is with fresh catalyst and those in cycles 2-5 were with recycled catalyst. Presence of MG, DG, and TG were tested using ASTM D6584 method.**

Cycles	% Conversion (GC)	Mass % MG	Mass % DG	Mass % TG	Total glycerides
1	98.97	0.076	0.027	0.000	0.103
2	98.55	0.033	0.022	0.057	0.145
3	98.43	0.117	0.038	0.002	0.157
4	98.47	0.016	0.032	0.103	0.153
5	97.23	0.155	0.122	0.000	0.277

This observation was well supported by the SEM-EDX where Al:Mg ratio remained close to 2.1 even after 5 recycling studies. The XRD pattern of the used catalyst also showed no significant change compared to the fresh catalyst. These results demonstrated the true heterogeneous nature of the catalyst under the specified reaction conditions. A comparison of different metal oxide based heterogeneous catalysts listed in literature is shown in Table 5.4. The table shows that the activity of Q-3T is comparable with the existing basic heterogeneous catalysts.

**Table 5.4. Comparison of Q-3T catalyst with reported catalysts.**

Catalyst	Feedstock	Oil : Methanol ratio	Wt% catalyst	Reaction time (min)	% Yield	Temperature (°C)
Calcium ethoxide <sup>127</sup>	Soy	1:12	3	90	95	65
CaO <sup>128</sup> supercritical	Sunflower	1:41.1	3	6	50	192
Nanocrystalline CaO <sup>129</sup>	Soy	1:27	1.3	720	99	25
Lead oxide <sup>130</sup>	Soy	1:7	2	120	89	225
Zeolite Y756 <sup>131</sup>	Used palm	1:6	-	22	26.6	476
Propyl sulfonic acid SBA-15 <sup>13</sup>	Soy	1:10	6	120	95	180
MgO <sup>132</sup>	Palm	1:6	0.5	240	51.3	65
Hydrotalcite <sup>133</sup>	Sunflower	1:12	6	360	90	120
<b>Quintinite-3T (this work)</b>	<b>Coffee</b>	<b>1:12</b>	<b>10</b>	<b>120</b>	<b>98</b>	<b>70</b>

In addition, bi-functionality is an added advantage for Q-3T as it can convert the FFAs from the waste streams without any purification steps. However, Q-3T synthesis process uses NaOH as a raw material (Method 1), which itself is a catalyst for biodiesel production. Biodiesel feedstock (oils and fats) uses NaOH as a homogeneous catalyst in biodiesel synthesis. So, it is important to prove that there are no NaOH traces on the surface of the heterogeneous catalyst. Careful steps were followed to eliminate the above stated problem. Q-3T was washed several times so that the pH of washed water was neutral. EDX analysis (Figure 5.3) also supported the absence of  $\text{Na}^+$  ions on the surface of Na-Q3T. However, a different method was also used to synthesize Q-3T without using NaOH or  $\text{NaCO}_3$  (method 2) and the catalytic activity was compared with Na-Q3T developed by method 1. ICP data (Table 5.1) and XRD pattern (Figure 5.2) of samples prepared under different conditions showed similar compositions. Triolein (99.9% purity, Sigma Aldrich) was used as a feedstock for the comparison studies for Na-Q3T and  $\text{NH}_4$ -Q3T. Heneicosane ( $\text{C}_{21}\text{H}_{44}$ , Sigma Aldrich) was used as an internal standard for GC-MS analysis (Figure 15). Conversion efficiency of Na-Q3T (97.28%) is comparable with  $\text{NH}_4$ -3QT prepared from method 2 (95.84%). This confirmed that the activity of Q-3T catalyst was primarily due to structural acidity/basicity and not significantly affected by the soluble Na-species.

### 5.3. Conclusions

In conclusion, Q-3T successfully synthesized. It is a member of LDH with Al:Mg ratio of 2:1. XRD, SEM-EDX, TEM and FFT analyses proved that the material is crystalline. The catalyst showed excellent performance to convert FFA, TG and a mixture of both. This catalyst was recycled for 5 runs without significantly affecting the conversion

efficiency or selectivity of the catalyst. The structural integrity of the catalyst remained intact even after 5 successive runs. The experimental results showed the optimum conditions are a 12:1 volume ratio of methanol to oil, 10 wt% of the catalyst at 348K (75°C). Irrespective of FFA content (0-30% was tested successfully) in the feedstocks, more than 96% biodiesel yield was always obtained. This catalyst also can convert different types of oils and fats together, which makes it a strong candidate for large-scale multi-feedstock operations. If this catalyst develops as anticipated, it will significantly reduce the cost of biodiesel production.

## **Chapter 6 † Selective photocatalytical oxidation of aqueous glycerol to potassium glycerate using titanium disilicide**

### **6.1. Introduction**

When biodiesel is produced, the primary output other than biodiesel is glycerol (1,2,3-propanetriol). For every 10 pounds of biodiesel, approximately 1 pound of glycerol is also produced.<sup>134</sup> Currently, 70 million gallons of glycerol is produced annually in the US and 392 million gallons are produced worldwide.<sup>17</sup> With the advent of the biodiesel industry, conversion of glycerol into high value chemicals emerged as a new branch of research.<sup>135</sup>

Glyceric acid is one of the useful chemicals with medicinal and industrial value which can be obtained from glycerol oxidation. Glyceric acid (2,3-dihydroxypropionic acid) is naturally found as a phytochemical constituent in a variety of plants, such as peanuts, artichokes, tomatoes, apples, bananas, and grapes.<sup>136</sup> However, the use of glyceric acid is limited as it is not currently produced in bulk quantities.

Chemoselective catalytical oxidation of glycerol over metallic catalysts such as platinum, palladium and gold has been shown to be a good technique for obtaining selective oxidative products from glycerol.<sup>137,138,139</sup> The synthesis of glyceric acid from pure glycerol has been reported by several research groups<sup>140,141,137,90</sup> using external oxidants. Although glycerol's unique structure makes it possible to conduct the heterogeneous catalytic oxidative reactions using oxidizing agents such as air, oxygen and hydrogen peroxide, the extensive functionalization of the glycerol molecule with hydroxyl groups of similar reactivity renders its selective conversion particularly difficult. Higher glycerol

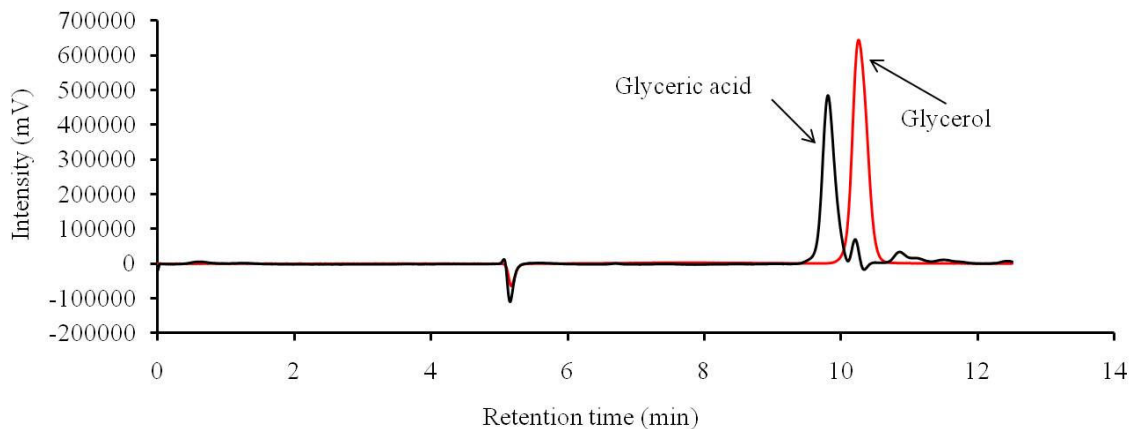
conversions with good selectivity are difficult due to over oxidation. Moreover, Garcia et al. reported that the oxidation of glycerin to glyceric acid is limited by the rate of diffusion of oxidants (oxygen) from the gas phase into the liquid phase.<sup>82</sup> However, increasing the partial pressures creates additional problems. Catalysts based on the platinum group metal suffer oxygen poisoning proportional to oxygen partial pressure.<sup>142,143</sup> These routes, while showing the high industrial potential for glyceric acid production, have important drawbacks for industrial development because of very low initial glycerol concentrations in the reactor, external oxidizing agents as well as need of a complex reactor design.

Demuth and his team explored the possibility of titanium disilicide ( $\text{TiSi}_2$ ) for photocatalytic hydrogen generation by a water splitting reaction.<sup>144</sup>  $\text{TiSi}_2$  has very unique optoelectronic properties that are ideal for use in solar applications: Broad-band reflectance measurements show a band-gap range from 3.4 eV to 1.5 eV for  $\text{TiSi}_2$ .<sup>144</sup> As a result, this material absorbs light over a wide range of the solar spectrum (360-800 nm), is easily available and inexpensive. In their work, they also proved  $\text{TiSi}_2$  has peculiar surface oxygen storage properties at lower temperatures up to 100°C.

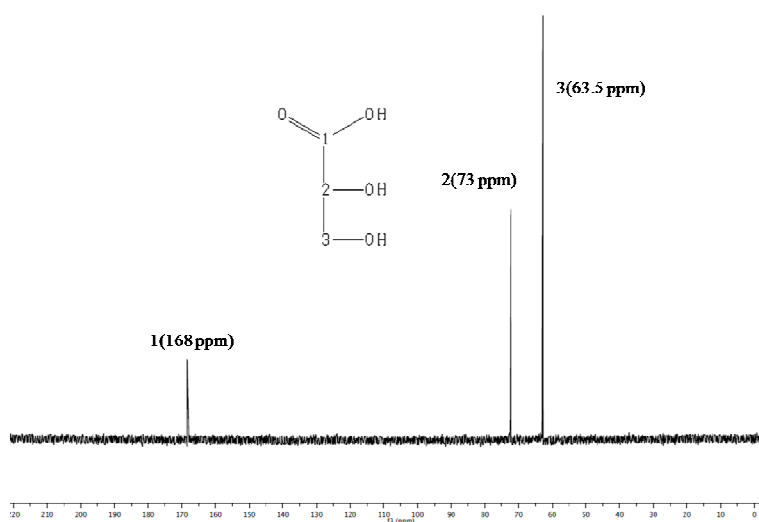
This work describes a simple photocatalytical oxidation of aqueous glycerol to glyceric acid by exploiting  $\text{TiSi}_2$  oxygen storing properties below 100°C when used as a photo catalyst. No external oxidants were used in glycerol oxidation except the *in situ* generated oxygen from the photocatalytic activity of  $\text{TiSi}_2$ . A mechanism for selective glycerate production is proposed considering the physisorbed oxygen on the  $\text{TiSi}_2$  surface.

## 6.2. Results & Discussion

A HPLC chromatogram of the reaction mixture for a reaction carried out at 65°C, 1M KOH, 10 wt% glycerol (5g in 50 mL) and 1 wt% TiSi<sub>2</sub> for 12h is shown in Figure 6.1.



**Figure 6.1.** HPLC chromatogram of pure glycerol and photocatalytic reaction products at 65°C, 1M KOH, 10 wt% glycerol (5g in 50 mL) and 1 wt% TiSi<sub>2</sub>



**Figure 6.2.** <sup>13</sup>C-NMR of the reaction end product (glyceric acid). A 100% conversion of glycerin to glyceric acid was confirmed.

As shown, glyceric acid was the only product observed with a glycerol conversion to glyceric acid to 97.6%. Glyceric acid formation was confirmed from <sup>13</sup>C-NMR. Position of each carbon (1, 2

& 3) and chemical shift corresponding chemical

shifts were given in Figure 6.2.

The formation of glyceric acid further confirmed from FTIR analysis (Figure 6.3).

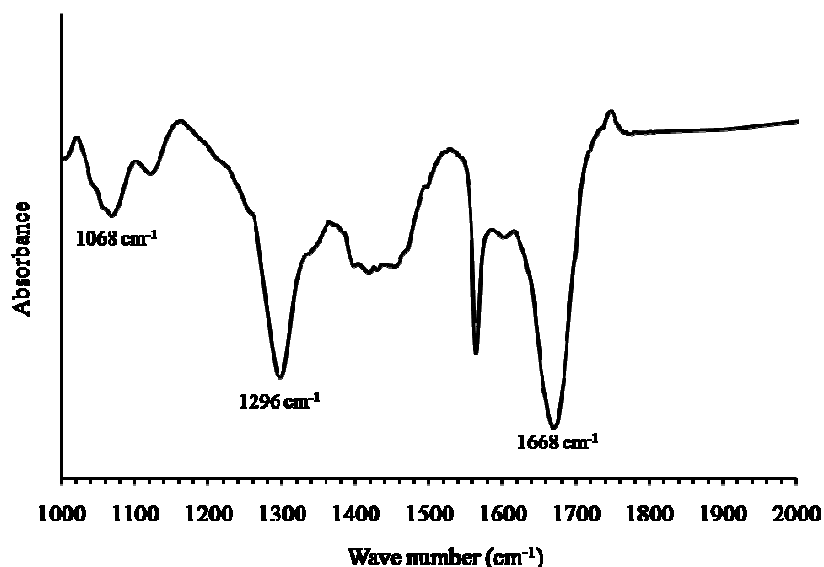
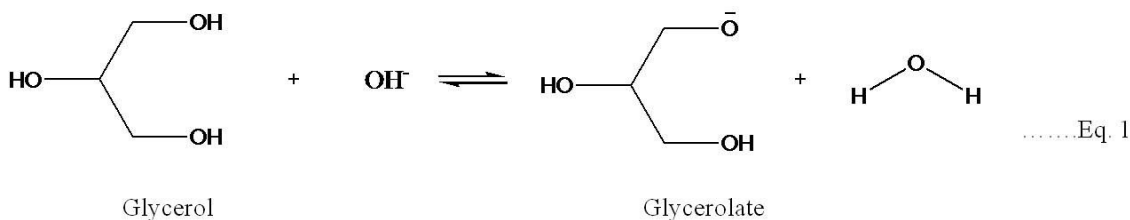


Figure 6.3. FTIR spectrum of reaction end product (glyceric acid)

The most intense and characteristic bands observed for glyceric acid were: 1068, 1296 and 1668 cm<sup>-1</sup>. The CO vibration was observed at 1068 cm<sup>-1</sup>. Glyceric acid also showed an intense band at 1296 cm<sup>-1</sup> which corresponds to the coupling of the CH<sub>2</sub> and CO groups. The glyceric acid also had a strong band at 1668 cm<sup>-1</sup>, which corresponds to the CO stretching. The effects of base and TiSi<sub>2</sub> are explained later.

### 6.2.1. Alkaline oxidation of glycerol to glycerolate

The crude glycerol obtained from biodiesel industry is at a pH of 11-14 due to dissolved KOH (catalyst for the transesterification reaction). Chemo-selective catalytic oxidation of glycerol experiments were reported as being favorable at a basic pH of 11.<sup>82</sup> Kishida et al. reported alkaline promoted deprotonation of glycerol to form glycerolate, which is a key factor in the initializing oxidation process (Eq.1).<sup>145</sup>



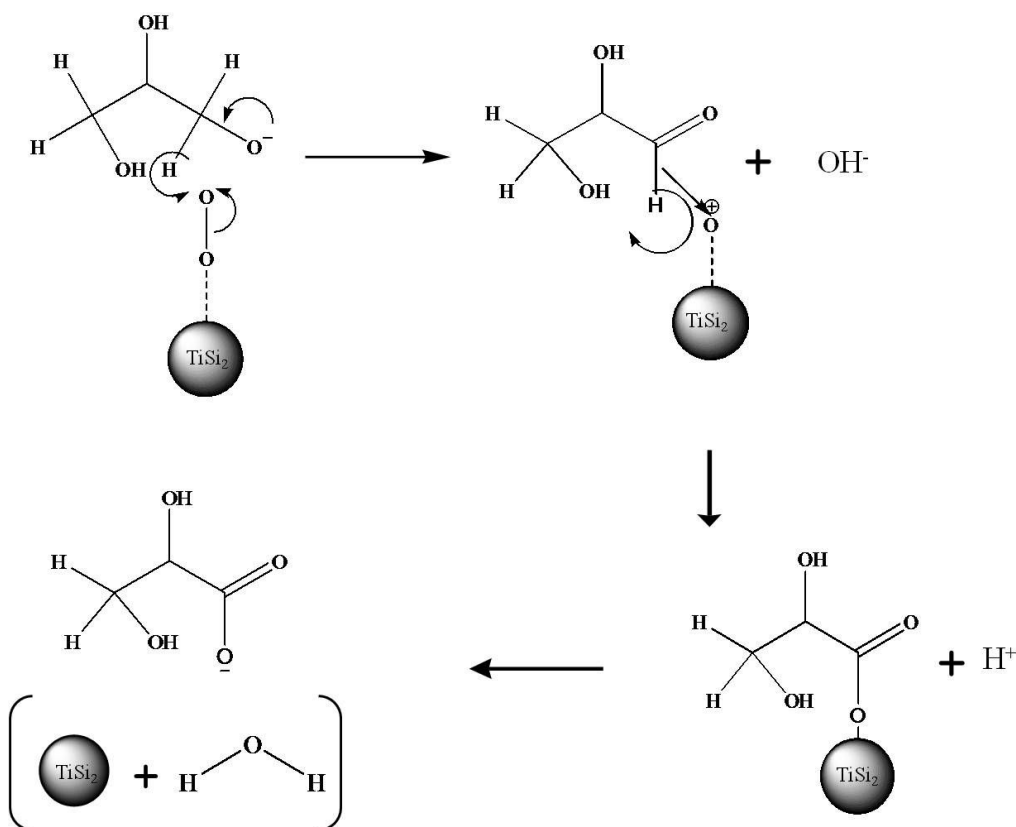
Hutchings et al. proposed that in the absence of base, initial dehydrogenation via H-abstraction is not possible. In presence of base, the H is readily abstracted from one of the primary hydroxyl groups of glycerol and overcomes the rate limiting step for the oxidation process.<sup>89</sup>

### ***6.2.2. Influence of $\text{TiSi}_2$ over selective oxidation of glycerol***

Water splitting reactions using  $\text{TiSi}_2$  as catalyst under sunlight, and its reversible oxygen and hydrogen storage properties were explored throughly by Demuth and his research group.<sup>144</sup> They reported that small amounts of hydrogen ( $5\text{-}7\text{ mL g}^{-1}$ ) physisorbed at  $50^\circ\text{C}$  when compared to  $20\text{ mL g}^{-1}$  at  $30^\circ\text{C}$ . However, the oxygen physisorbed on the  $\text{TiSi}_2$  surface remained intact well over  $100^\circ\text{C}$ . This result suggests that oxygen can still remain adsorbed by  $\text{TiSi}_2$  in presence of light at working temperature ( $65^\circ\text{C}$ ) of this proposed work. At this working temperature, influence of the hydrogen on the oxidation process is neglected as for all practical purposes physisorbed hydrogen amounts on  $\text{TiSi}_2$  surface remain low.

Thus, adsorbed oxygen (from water splitting) is proposed as an oxidative agent in the glycerol oxidation. The oxidation of hydrocarbons over metal oxides with reversible dioxygen storing capabilities was proven with  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ .<sup>146</sup> Surface adsorbed oxygen is sufficient to cause the oxidation, and more specifically, oxidation of glycerolate ion. First, a hydrogen on the deprotonated  $\text{CO}^-$  group is abstracted by surface oxygen, resulting in the transfer of electrons on the  $\text{O}^-$  to the C-O bond, forming a C=O group. The surface  $\text{O}_2$  undergoes O-O cleavage to form  $\text{OH}^-$ . In the second step, surface O or  $\text{O}_2$  attacks the carbony moiety, eliminating a  $\text{H}^+$ , and resulting in a surface bound

carboxylate species. A schematic of the proposed mechanism of glycerolate ion is shown in Figure 6.4.



**Figure 6.4. Proposed mechanism of  $\text{TiSi}_2$  assisted glycerol oxidation to glyceric acid.**

Surface stored oxygen of  $\text{TiSi}_2$  acts as *in situ* oxidizing agent

The selective oxidation of glycerol to glyceric acid was attributed to:

- The rate of oxidation of a primary alcohol function is higher than that of a secondary alcohol;
- Rapid oxidation of glyceraldehyde favors the formation of surface adsorbed glyceric acid;
- A basic pH increases desorption of the acid (as potassium salt) from  $\text{TiSi}_2$  surface (final step of the Figure 6.4).

### 6.2.3. Catalyst stability

TiSi<sub>2</sub> semiconductors are inexpensive and abundant. However, poor stability towards basic water is one disadvantage. Demuth and co-workers reported that the water splitting reaction is not stoichiometric when compared with TiSi<sub>2</sub>, indicating the catalytical nature of the material. However, formation of the passive layers of oxygen impedes the reaction rates. Removal of the adsorbed oxygen using glycerol showed enhancement in the water splitting reaction as shown in Figure 6.5.

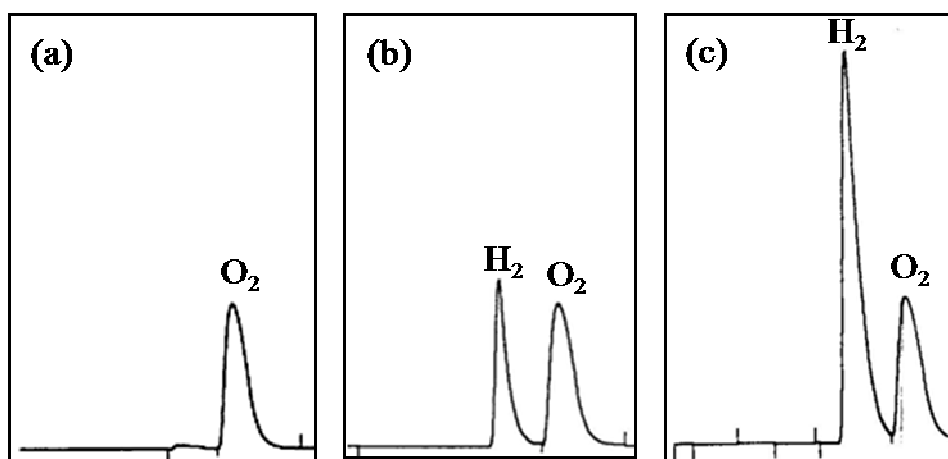
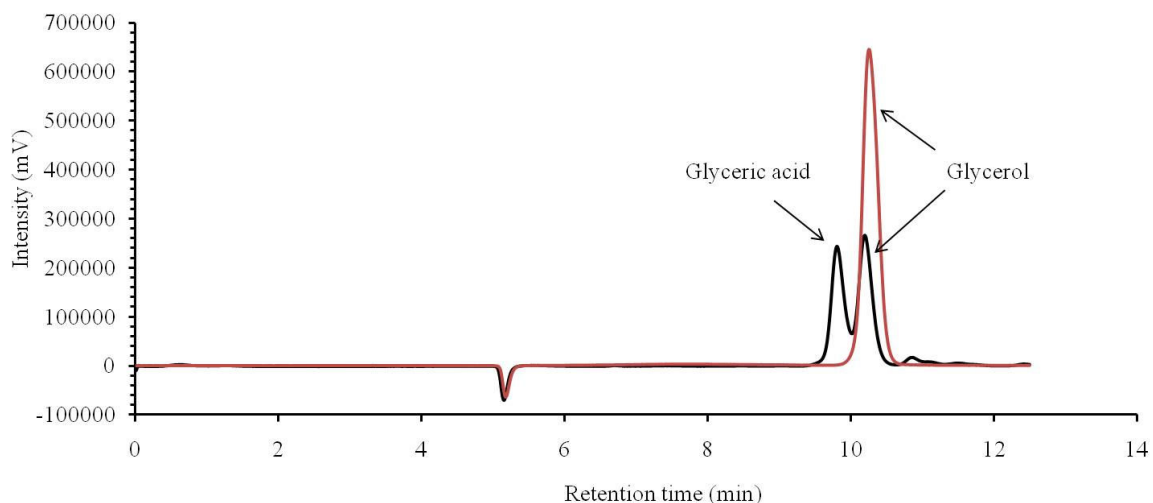


Figure 6.5. Gas chromatograms of the gases evolved from the following reactions, (a). Water only, (b). 1M KOH solution and (c). 1M KOH and 5 wt% glycerin (amount of TiSi<sub>2</sub>, temperature and light intensity were the same for all the above reactions).

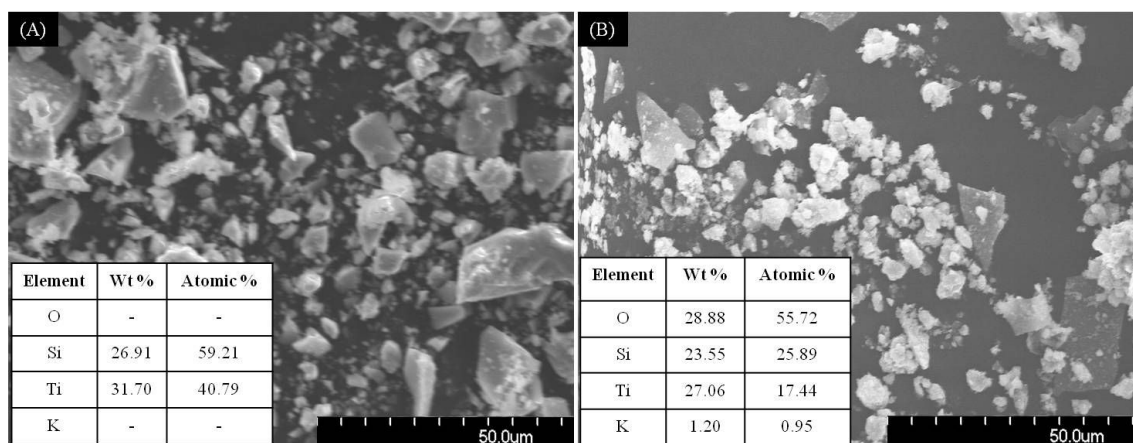
The production of hydrogen is enhanced in the presence of glycerol. All experiments were conducted in ambient conditions, thus the presence of an oxygen peak is predictable. However, no enhancement of the oxygen peak was observed indicating the oxygen capturing capability of TiSi<sub>2</sub> under working conditions. The presence of glycerol helps scavenge the surface oxygen molecules and promotes the water splitting reaction

without catalyst deterioration. The reaction after 6 h showed only 64.3% glycerol conversion but catalyst was still capable of generating hydrogen (Figure 6.7).



**Figure 6.7.** HPLC chromatogram showing the conversion of glycerol at 6h of reaction time (64.3 wt%)

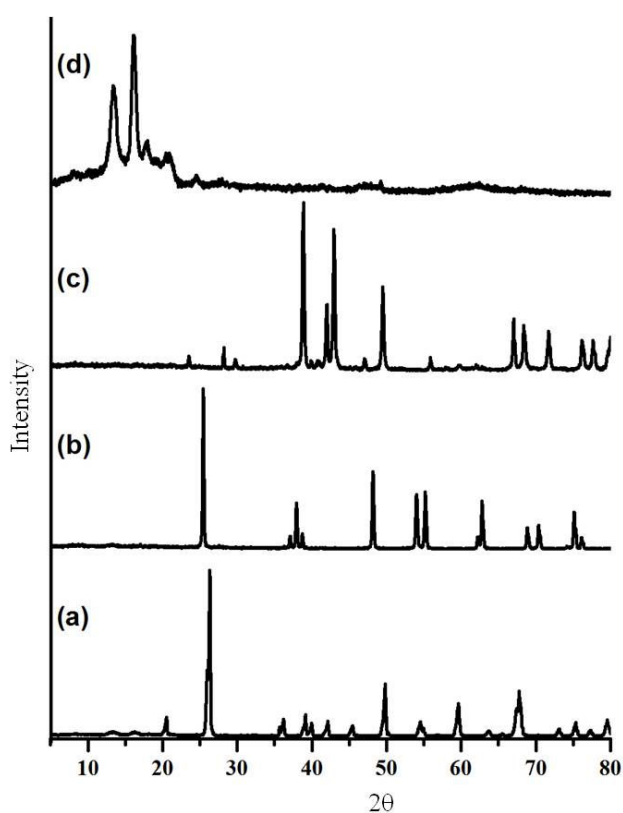
However, longer reaction times (12 h) completely destroy  $\text{TiSi}_2$ . Figure 6.8 shows the scanning electron microscope (SEM) images of (a)  $\text{TiSi}_2$  as obtained and (b) after the photo catalytical reaction over 12h.



**Figure 6.8.** SEM images of catalyst ( $\text{TiSi}_2$ ) before (A) and after (B) the photo catalysis. EDX analysis (inset table) shows the excess oxygen present in the catalyst after 12h reaction.

Though there is no considerable change in the particle size (Figure 6.8), Energy-dispersive X-ray (EDX) analysis (inset table, Figure 6.8) showed the formation of some

oxides. Excess oxygen due to the adsorption of KOH or glycerol or glyceric acid was ruled out as the samples were washed and centrifuged several times before the EDX analysis. Formation of  $\text{SiO}_2$  or  $\text{TiO}_2$  was also ruled out because the XRD pattern of the sample (Figure 6.9) does not resemble any of those materials. However, the appearance of  $\text{Sp}^2$  hybridized carbon peaks was attributed to the formation of glyceric acid (carboxyl carbon) over the surface of the catalyst. The disappearance of  $\text{TiSi}_2$  peaks was attributed to the poisoning of the catalyst material in basic medium.



**Figure 6.9.** XRD pattern of (a)  $\text{SiO}_2$ , (b)  $\text{TiO}_2$ , (c)  $\text{TiSi}_2$  and (d)  $\text{TiSi}_2$  after 10h photocatalytic reaction

Further heat treatment of the catalyst sample before XRD measurement was not carried out to retain the chemical structure of as-obtained catalyst after the reaction. Prolonged oxidation in water formed amorphous material from  $\text{TiSi}_2$ . However, the need to maintain an optimum concentration of glycerol in the reaction mixture to hinder the catalyst degradation should be explored further.

#### ***6.2.4. Crude glycerol and purified glycerol***

Crude glycerol was obtained from biodiesel production using spent coffee oil and feathermeal fat as biodiesel feedstocks as reported in Chapters 3 and 4.<sup>113,147</sup> The crude glycerol contained excess methanol, KOH (~2M) and other impurities. Centrifugation separates any solid soap like impurities. However, methanol interference with glyceric acid was ruled out because esterification of acid in the presence of base and water cannot proceed efficiently. A maximum glycerol conversion of 96.1% with 100% selectivity was obtained. The results revealed that the catalyst was active for even crude glycerol oxidation as well. Further optimization studies are in progress to investigate the correlation between the catalyst properties and selectivity over glyceric acid.

### **6.3. Conclusion**

This study showed that  $\text{TiSi}_2$  can be conveniently employed to selectively oxidize glycerol to glyceric acid using solar light, under mild conditions. Selectivity and conversion efficiencies were high. The presence of glycerol in aqueous solution helped  $\text{TiSi}_2$  in its water splitting reaction and in the formation of glyceric acid. However, replacing the batch reaction with the continuous (flow of glycerol) reaction and its effect on preventing the deterioration of the catalyst ( $\text{TiSi}_2$ ) is still needed to be explored. The effects of reaction parameters, particle size of  $\text{TiSi}_2$  on product selectivity will also be the subject of further study.

## **Chapter 7 † General Conclusions**

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The main aim of this research was to explore alternative sources for biodiesel feedstocks, to synthesize a successful solid heterogeneous catalyst for low-cost feedstocks, and to convert glycerol into value-added chemicals. Being able to explore and identify solutions for the stated problems represent an important set of contributions to the biodiesel industry. The objectives of this research include:

- [1] The exploration of different feedstocks for biodiesel production
- [2] Process optimization for individual feedstocks
- [3] Determination of suitable solid catalyst for biodiesel production
- [4] Synthesis and characterization studies of the developed catalyst
- [5] Kinetic and mechanistic studies of heterogeneous catalyst
- [6] Determination of suitable solid catalyst for glycerol oxidation

Spent coffee grounds were successfully used as feedstock source for biodiesel production. Currently, the use of spent coffee grounds is limited to gardens as compost. Ideal coffee grounds for the soil need a C/N ratio of 20:1. The C/N ratio after the oil extraction process showed that there was no significant change in the C/N ratio (Table 7.1).

**Table 7.1. C/N ratio of the used coffee grounds before and after oil extraction process.**

Spent coffee grounds	%C	%N	C/N
Before processing	48.76	2.45	19.86:1
After processing	41.16	2.62	15.7:1

This indicated that the processed coffee grounds can still be used as compost for the garden. Regardless of whether or not the coffee grounds are thrown in the garden or the garbage, there are adverse physical effects on the biotic life in the soil. The dumped oil from the ground coffee slowly decomposes to release CO<sub>2</sub> to the environment. The stoichiometric equations of the CO<sub>2</sub> production are shown in Table 7.2 (calculated based on the composition obtained from GC-MS and HPLC measurements). Each gram of the oil can produce 2.7 g of CO<sub>2</sub> into the environment. Because of the unprocessed coffee grounds, approximately 281,000 tons of CO<sub>2</sub> could be produced every year based on the total world coffee production.

**Table 7.2. The stoichiometric equations of the CO<sub>2</sub> production per gram of each fatty acid.**

Fatty acid	Chemical reaction with environmental oxygen	CO <sub>2</sub> produced (g/g)
Palmitic acid	$\text{C}_{16}\text{H}_{32}\text{O}_2 + 23 \text{O}_2 \rightarrow 16 \text{CO}_2 + 16 \text{H}_2\text{O}$ <p style="text-align: center;">256.4g                      704g</p>	2.7
Linolenic acid	$\text{C}_{18}\text{H}_{32}\text{O}_2 + 25 \text{O}_2 \rightarrow 18 \text{CO}_2 + 16 \text{H}_2\text{O}$ <p style="text-align: center;">280.4g                      792g</p>	2.8
Stearic acid	$\text{C}_{18}\text{H}_{36}\text{O}_2 + 26 \text{O}_2 \rightarrow 18 \text{CO}_2 + 18 \text{H}_2\text{O}$ <p style="text-align: center;">284.4g                      792g</p>	2.8

Even though it is not a significant impact on the environment, it is better to process waste coffee grounds and get biodiesel out of this untapped source. The potential market value of waste coffee grounds given in Table 7.3

**Table 7.3. Future market scenario of coffee biodiesel (based on waste generated from Starbucks's stores).**

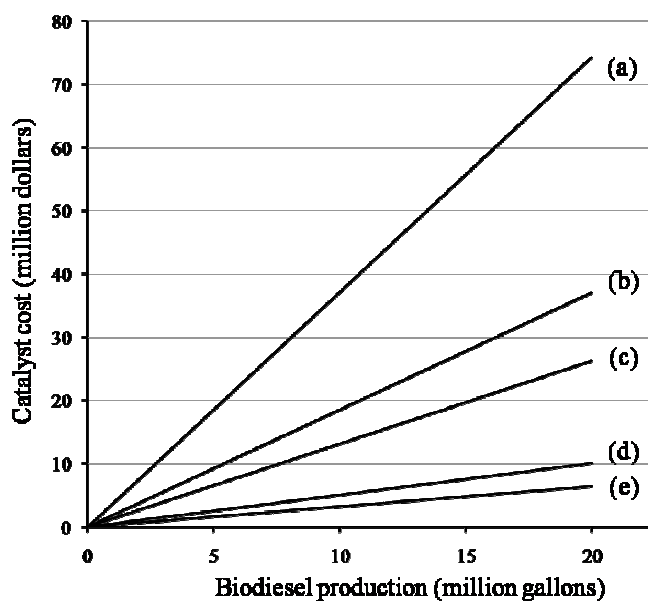
Starbucks's Market	USA	World	Overall World Market
Feedstock (lb/yr)	210,000,000	294,000,000	15,000,000,000
Bio-diesel (G/yr)	2,920,000	4,080,000	208,000,000
Pellets (tons/yr)	89,150	125,000	6,375,000
Revenue of bio-diesel	\$13,140,000	\$18,360,000	\$936,000,000
Revenue of pellets	\$20,080,000	\$28,114,000	\$1,434,375,000
Total revenue	\$33,220,000	\$46,474,000	\$2,370,375,000
Operating costs	\$25,200,000	\$35,280,000	\$1,800,000,000
Total profits	\$8,020,000	\$11,194,000	\$570,375,000

A successful business plan was produced from this study for the Lt. Governor's Cup Competition sponsored by the Nevada Center for Entrepreneurship & Technology (NCET) in 2008 (Biogrounds, LLC). An executive summary is attached in Appendix B. Chicken feathermeal was also shown as a feed source for biodiesel production. Currently, feather meal usage is limited to animal food and a nitrogen fertilizer. Removal of the fat content from the feather meal increases the protein content and results in a higher grade

animal feed. Additionally, because this process removes the fatty acid content in the feather meal, the nitrogen content increases and creates a better nitrogen source for fertilizer applications. Based on a 10% oil yield, the United State's poultry industry could produce approximately 153 million gallons of biodiesel annually from feather meal (Table 7.5). If this technology expands worldwide, it could potentially produce 593.2 million gallons of biodiesel, according to the United Nations Food and Agriculture Organization Report for 2005. This technology can be expanded to other poultry industries (duck and turkey), and can potentially contribute to reducing demand on foreign oil and help reduce further petroleum demands.

**Table 7.5. Total poultry industry annual production of meat, waste products and tentative amount of biodiesel that can be produced from the waste products in 2008 (On an average of \$3/gallon, this process is estimated to have \$459 million dollars market. This is projected that a medium size plant should produce biodiesel at the cost of \$1 dollar/gallon using this process).**

Poultry industry	Meat produced in U. S. (million pounds) <sup>148</sup>	Poultry industry waste (million pounds)	Total fat content (wt%) <sup>149</sup>	Tentative biodiesel production (million gallons/yr)
Broilers	37,125	9,700	11	139
Turkeys	6,135	1,603	6.7	14
				Total =153



**Figure 7.1. KOH costs for the production biodiesel from feedstocks containing (a) 5% FFA (b) 10% FFA (c) 50% FFA and (d) 90% FFA. The Q-3T cost (e) is given for comparison.**

In this work, a green process to produce biodiesel from feather meal was demonstrated. The removal of the fat content from feather meal produced a better food source for animals and fertilizer for agriculture. Considering the total

U.S. and World production of poultry waste, this process has the potential to create

approximately 139 million gallons and 593.2 billion gallons of biodiesel per year, respectively. This research will contribute significantly to the achievement of the goal: “food for hunger and waste for fuel”. In conclusion, these processes, if implemented, will help producing 933 million gallons of fuel from non-food waste sources.

Biodiesel can be produced from various feedstocks. The quality of the biodiesel depends upon the feedstock. Feedstocks containing more FFA are considered as lower quality feedstocks compared to refined vegetable oils. Yellow grease obtained from rendered animal fats and restaurant waste oils, has FFA levels up to 15 wt% and its price varies from \$0.09/lb to \$0.20/lb. Based on these low prices, use of waste vegetable oil, grease and poultry fat has been proposed as a way to lower biodiesel production costs. Conventional homogeneous base catalysis is not good for low quality feedstocks; However, heterogeneous bifunctional catalysts are the right choice for these types of

feedstocks. The advantages of Q-3T over homogeneous catalyst were shown in Figure 7.1. It is clear that Q-3T serves well as a economic catalyst when used with feedstocks containing higher FFA.

At the present time 70 million gallons of glycerin is produced annually in the US and 392 million gallons worldwide. Several investigators are working on the utilization of glycerol as chemical grade feedstock for the other applications<sup>150</sup>. However, high value-added co-production is yet to be developed. Selective oxidation of glycerol to glyceric acid on the bulk level is not yet reported. This research work, if implemented, can successfully convert crude glycerol to glyceric acid.

A successful business plan was made from the above research for the Governor's cup conducted by the Nevada Center for Entrepreneurship & Technology (NCET) in 2010 (Glyzen technologies, 1<sup>st</sup> place winner). An executive summary is attached in Appendix C.

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## **Appendix-A:** Abbreviations

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FFA – Free Fatty Acid

TG – Triglycerides

DG – Diglycerides

MG – Monoglycerides

ASTM – American Society for Testing and Materials

B100 – 100 % Biodiesel

B20 – 20 % biodiesel, 80 % petroleum diesel

GC – MS – Gas Chromatography – Mass Spectroscopy

HPLC – High Performance Liquid Chromatography

FTIR – Fourier Transform Infra Red Spectroscopy

USDA – United States Department of Agriculture

## **Appendix-B: Bio-grounds LLC**

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### **Executive Summary**

Bio-grounds' has assisted in the development of technology to create renewable energy sources from everyday waste products. Our company has developed a system to turn waste products, such as waste coffee grounds, into renewable bio-diesel feedstock oil (*to be made into bio-diesel*) and fuel pellets (*to be burned in pellet stoves*). Our technology utilizes a patent-pending process that allows us to turn waste streams into profit streams. The patent for this technology is still under review by the U.S. Patent and Trademark Office and was applied for by the University of Nevada, Reno. Bio-grounds has negotiated exclusive licensing rights with the University, giving Bio-grounds an enormous competitive advantage. This business plan will discuss the adaptation of this new technology to the marketplace and its ability to capitalize on clean and renewable energy.

Currently there is a high demand in the United States for bio-diesel fuel and the feedstock needed to produce it. Between 2005 and 2006, the demand for bio-diesel in the United States approximately tripled. This trend is expected to continue well into the future. As the bio-diesel market demand increases, so too does the demand for feedstock. This clean and effective technology will be used to meet the demand for bio-diesel feedstock and to provide an alternative source of fuel pellets.

Bio-grounds is proposing to utilize this new, clean, and renewable technology to build strategic plants around the country to supply the demand for bio-diesel feedstock oil and fuel pellets. Our process is sustainable due to the following advantages:

- the technology recycles waste products that would otherwise take up space in already crowded landfills
- the process utilizes its own waste streams to produce secondary products
- the production cost is low compare to other processes
- scalable process appropriate for a large array of markets
- continually growing coffee market
- flexibility in feedstock sources
- the patent-pending process will give Bio-grounds a competitive advantage

Bio-grounds will enter the market with a pilot plant located in Fremont, California. This pilot plant will serve to demonstrate the unit model's feasibility and fine tune process operations. Once established, this model will serve as the base for replicating our process on a larger scale. Initially, our plant will convert 3,125 tons of waste coffee from the surrounding Bay Area into 122,549 gallons of bio-diesel feedstock oil and 2,660 tons of fuel pellets.

Bio-grounds' financial analysis has revealed that it will be necessary to acquire an investment of \$250,000 in order to finance the first year of startup. As Bio-grounds' is leasing all of the equipment in the pilot plant, the initial capitol costs are extremely low. Financial backing and support will be sought from entrepreneurs and angel investors through debt, equity, or a combination of funding.

## **Appendix-C: Glyzen Technologies**

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### **Executive Summary**

Glyzen Technologies is an innovative organization with the ultimate goal of finding technological solutions to make environmentally friendly alternative fuel sources economically viable for our nation's future. We have developed a patent-pending glycerol conversion process (GCP) that will enable biodiesel producers to turn their waste glycerol into profits. The biodiesel industry is facing a problem with glycerol market saturation due to the large amounts of glycerol by-product that are produced during biodiesel processing. Biodiesel producers have to pay to get rid of the waste glycerol. Glyzen Technologies has developed a chemical process that will convert the waste glycerol directly from biodiesel plants into two value added chemicals: glyceric acid and hydrogen. Our process is relatively simple, easy to install and environmentally friendly. We project glyceric acid and hydrogen sales to be extremely profitable for the biodiesel industry.

Glyzen Technologies' plan is to sell license agreements to biodiesel producers and offer our engineering services in the construction phase and maintenance and support services thereafter. We have developed a license agreement schedule that outlines the price for a license agreement per plant capacity and what percentage of the sales of glyceric acid and hydrogen sales will be paid as royalties to our company (also based on plant capacity). Biodiesel production is projected to increase in the next 20 years as government

incentives and policies are making this fuel option an important part of our nation's transportation fuel portfolio.

We will be organized as a C-corporation with three founders. These three founders will be the only three employees for the first year we are in business. Glyzen Technologies is beginning talks with Bently Biofuels to build a pilot plant to verify our technology and process at a large scale before approaching biodiesel producers for license agreement sales. Our technology is patent-pending and we are also working on publishing our manuscript in the *Journal of Catalysis*. Our publishing efforts will continue in 2010 as will our exposure to the biodiesel industry through attendance of various biodiesel conferences and networking efforts.

We will progressively add employees to our company in order to have experienced people involved to help us in the pilot plant research and development phases and beyond. We understand that our success depends on the salability of glyceric acid and hydrogen so a significant portion of our marketing efforts will be geared towards these industries.

Costs associated with our GCP product including construction and hydrogen storage are high at \$30.75 million for a 10 million gallon per year biodiesel plant, but our calculated payback period for our customers is only 2.36 years. The projected profits after that are extremely good with over \$14 million of projected yearly profits.

Because Glyzen Technologies will be selling license agreements and services only, our cost of running the business is relatively low since we do not need to purchase real estate and equipment. We do not anticipate making our first sale until 2013. We will require \$200,000 to operate in 2011, \$200,000 in 2012 and \$100,000 for the first half of 2013

after which we do not require anymore external funds. 15% equity will be given to our investors. Equity positions will also be given to our employees that we hire early on.

Glyzen Technologies is proud to be on the leading edge of technology and intends to use profits to grow the company further and eventually branch out to research in renewable sources outside of the biodiesel industry and continue in our quest to offer green fuel solutions and free our nation of the dependence on foreign oil.

## **Appendix-D: Biography**

**Narasimharao Kondamudi**

Graduate Assistant

Materials Science and Engineering/388

University of Nevada, Reno, NV 89557

Contact: Ph # (775)813-0894; Fax: (775)327-5059

E-mail: raokondamudi@yahoo.com

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### **Education**

**2005-2010** Ph.D., Materials Science and Engineering, University of Nevada Reno

Advisor: Prof. Manoranjan Misra

**2003-2005** M. Sc., Chemistry, May 2005, Indian Institute of Technology Roorkee, India

### **Research Interests**

- Heterogeneous catalysis (Metal oxides)
- Biodiesel production from non-food sources (Spent coffee grounds, Feather meal)
- Glycerol oxidation (Metal silicides)
- Industrial azo-dye degradation (using functionalized 1D Titania nanotubes)

### **Patents**

1. “Biodiesel production methods” (United States Patent 20080184616)
2. “Methods, systems, and apparatus for obtaining biofuel from coffee and fuels produced there from” (CPT WO 2009015358)
3. “Hydrogen production system and method including catalyst and oxygen scavenger” (United States Provisional Patent Application 61/261,180)

### **Publications**

1. **Narasimharao Kondamudi**, Susanta Mohapatra and Mano Misra “Spent Coffee Grounds as a Versatile Source of Green Energy” *Journal of Agricultural and Food Chemistry* **2008**, *56*, 11757–11760.
2. Mano Misra, **Narasimharao Kondamudi**, Susanta Mohapatra “High Quality Biodiesel from Spent Coffee Grounds” *Proceedings of the Clean Technology* **2008** (Bio-Energy Fuels, Novel Sources & Policy) p.39-42.
3. Susanta Mohapatra, **Narasimharao Kondamudi**, Subarna Banerjee, Mano Misra “Functionalization of Self- Organized TiO<sub>2</sub> Nanotubes with Pd Nanoparticles for Photocatalytic Decomposition of Dyes under Solar Light Illumination” *Langmuir*, **2008**, *24* (19) 11276-11281.
4. **Narasimharao Kondamudi**, Jason Strull, Susanta Mohapatra and Mano Misra “A Green Process to Produce Biodiesel from Feather Meal” *Agricultural and Food Chemistry* **2009**, *57*, 6362–6368.
5. **Narasimharao Kondamudi**, Susanta K Mohapatra, Mano Misra, “Quintinite as a Bifunctional Heterogeneous Catalyst for Biodiesel Production” *Applied catalysis A: General*, doi:10.1016/j.apcata.2010.11.025.

6. **Narasimharao Kondamudi**, Susanta K Mohapatra, Mano Misra “Selective photocatalytical oxidation of aqueous glycerol to potassium glycerate using titanium disilicide” Manuscript submitted (*Catalysis Letters*)
7. Krishnan Raja, York Smith, **Kondamudi Narasimharao**, Manivannan A, Misra Mano, Vaidyanathan Subramanian “CO<sub>2</sub> photoreduction in the liquid phase over Pd-supported On TiO<sub>2</sub> nanotube and bismuth titanate photocatalysts” accepted for publication (*Electrochemical and Solid-State Letters*)

#### **Posters and Presentations**

1. Zhao, Ningfeng; **Kondamudi, Narasimharao**; Shearer, Jason. Nickel Superoxide Dismutase Modeling Complexes. Abstracts, 61st Northwest Regional Meeting of the American Chemical Society, Reno, NV, United States, June 25-28 (**2006**)
2. Misra, Mano; **Kondamudi, Narasimharao**; Mohapatra, Susanta K.; John, Shiny E. High quality biodiesel from spent coffee grounds. Clean Technology 2008: Bio Energy, Renewables, Green Building, Smart Grid, and Water, Technical Proceedings of the CTSI Clean Technology and Sustainable Industries Conference and Trade Show, Boston, MA, United States, June 1-5, 2008 (**2008**), 39-42.
3. Talk given on “Non-food Feedstocks for Biodiesel Production” at American Institute of Chemical Engineers (AIChE) annual conference in Philadelphia, PA in November **2008**

#### **Grants, Awards and Honors**

- Won AAA Green Light Initiative (GLI) Grant 2009 (\$ 15,000) for a successful proposal on development and awareness of green energy solutions
- Awarded **Nevada Board of Regents Scholar Award** for the year 2010
- Awarded **Outstanding International Graduate Student Award** for the year 2010 from GSA
- **Outstanding graduate student researcher** for the year 2009 from the University of Nevada Reno
- Nominated as vice president of R&D for “Bio-Grounds LLC”, A **Lt. Governor’s cup** winning (5000 USD) business Plan (**2008**) from the state of Nevada, USA
- Nominated as vice president of R&D for “Clean Bean LLC”, A **Commissioner’s cup** winning (2500 USD) business Plan (**2009**) from the state of Nevada, USA
- Nominated as Chief Technology Officer for “Glyzen Technologies”, A **Governor’s cup** winning (20,000 USD) business Plan (**2010**) from the state of Nevada, USA
- Graduate Student Association’s annual award for best presentation for the year 2009 from the University of Nevada Reno