HETEROGENEOUS AND MONOLITHIC CATALYST DEVELOPMENT FOR
THE BIODIESEL PRODUCTION PROCESS AND EVALUATION OF STATIC
MIXERS FOR THE ESTERIFICATION PROCESS

A Thesis
Submitted to the Faculty of Graduate Studies and Research
In Partial Fulfillment of the Requirements
For the Degree of
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In
Industrial Systems Engineering
University of Regina

By
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Regina, Saskatchewan
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Nagarajan Annamalai, candidate for the degree of Master of Applied Science in Industrial Systems Engineering, has presented a thesis titled, *Heterogeneous and Monolithic Catalyst Development for the Biodiesel Production Process & Evaluation of Static Mixers for the Esterification Process*, in an oral examination held on June 26, 2012. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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Abstract

In the present biodiesel production process, sodium hydroxide and sulphuric acid are the conventional homogeneous catalysts used, in spite of their drawbacks, such as soap formation with high free fatty acid (FFA) feedstocks, substantial wastewater generation, issues with the downstream separation process, and corrosion of process equipment. Both of the catalysts mentioned above are difficult to regenerate and involve expensive treatments. Heterogeneous catalysts represent a very attractive alternative for overcoming technological and operational barriers associated with the use of homogeneous catalysts in the biodiesel production industry. Heterogeneous catalysts can be designed to provide high performance stability and durability, and they are economical to remove and reuse and offer an easy glycerol recovery. Also, heterogeneous catalysts are easy to handle and separate during post processing, and they can allow for single-step esterification and transesterification for high FFA feed stocks and can significantly reduce the corrosion and environmental challenges associated with the homogeneous catalysts. Based on a comprehensive literature survey, it was concluded that the heterogeneous solid acid WO$_3$/ZrO$_2$ catalyst is the best system for this process, as its inherent acidic, lattice structure and oxidizing properties enhance the catalytic activity of the catalyst. Furthermore, this catalyst was found to exhibit salient physical properties investigated by means of various characterization techniques such as x-ray diffraction, Fourier transform infrared spectroscopy, and temperature programmed desorption, etc. Therefore, this research focused on using the WO$_3$/ZrO$_2$ catalyst for biodiesel production from low quality feed stock. The obtained results were used as a benchmark for testing the performance of our in-house synthesised catalyst. Furthermore, to enhance the activity,
stability, and selectivity of the catalyst and to improve the economics of the production, the catalyst was supported on a stainless steel monolith substrate. This was studied by applying chemical coating techniques such as the sol-gel and wet impregnation methods to deposit MoO_3/Al_2O_3 on stainless steel supports. The metal monolithic catalyst prepared with this technique did not yield satisfactory results with respect to the coat adhesion stability.

Another important aspect of this work is to study and evaluate a static mixer designed reactor for biodiesel production process. In this study, a helical static mixer reactor was used to evaluate the performance of the esterification reaction under different operating temperatures and methanol-to-oil ratios. The reactor produced a high FFA conversion of 99% at a constant total flow rate of 1.6 mL/min, temperature of 65°C, and methanol-to-oil ratio of 15:1 using 1% w/w sulphuric acid catalyst.
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<th>Abbreviation</th>
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<tr>
<td>A</td>
<td>AMT</td>
<td>Ammonium Metatungstate</td>
</tr>
<tr>
<td>AHM</td>
<td></td>
<td>Ammonium Heptamolybdate</td>
</tr>
<tr>
<td>ASTN</td>
<td></td>
<td>American Society For Testing And Materials</td>
</tr>
<tr>
<td>FAME</td>
<td></td>
<td>Fatty Acid Methyl Ester</td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td>Carbon Monoxide</td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>CH₃OH</td>
<td></td>
<td>Methanol</td>
</tr>
<tr>
<td>CSTR</td>
<td></td>
<td>Continuous Stirred Tank Reactor</td>
</tr>
<tr>
<td>EPA</td>
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</tr>
<tr>
<td>Ea</td>
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<td>Activation Energy</td>
</tr>
<tr>
<td>FFA</td>
<td></td>
<td>Free Fatty Acid</td>
</tr>
<tr>
<td>HCs</td>
<td></td>
<td>Hydrocarbons</td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td>Water</td>
</tr>
<tr>
<td>HCl</td>
<td></td>
<td>Hydrochloric Acid</td>
</tr>
<tr>
<td>Chemical</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>HNO₃</td>
<td>Nitric Acid</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Sulphuric Acid</td>
<td></td>
</tr>
<tr>
<td>H⁺</td>
<td>Protons</td>
<td></td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann Constant</td>
<td></td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium Hydroxide</td>
<td></td>
</tr>
<tr>
<td>MoO₃/Al₂O₃</td>
<td>Molybdenum Oxide Supported Over Alumina</td>
<td></td>
</tr>
<tr>
<td>N/A</td>
<td>Not Applicable</td>
<td></td>
</tr>
<tr>
<td>NOₓ</td>
<td>Nitrogen Oxides</td>
<td></td>
</tr>
<tr>
<td>PM</td>
<td>Particulate Matter</td>
<td></td>
</tr>
<tr>
<td>psi</td>
<td>Pound Per Square Inch</td>
<td></td>
</tr>
<tr>
<td>Rpm</td>
<td>Revolution Per Minute</td>
<td></td>
</tr>
<tr>
<td>R-COOH</td>
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<tr>
<td>R-COOCH₃</td>
<td>Methyl Ester</td>
<td></td>
</tr>
<tr>
<td>SOₓ</td>
<td>Sulfur Oxides</td>
<td></td>
</tr>
<tr>
<td>THF</td>
<td>Tetra Hydrofuron</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>Temperature, °C</td>
<td></td>
</tr>
<tr>
<td>Vol%</td>
<td>Volume Percentage (%)</td>
<td></td>
</tr>
<tr>
<td>WO$_3$/ZrO$_2$</td>
<td>Tungstated Zirconia</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>---------------------</td>
<td></td>
</tr>
<tr>
<td>wt%</td>
<td>Weight Percentage (%)</td>
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CHAPTER 1

INTRODUCTION

1.1 TECHNOLOGY AND ENERGY

Mankind’s quest for knowledge over the centuries has made the human existence very simple. Through the channel of reasoning and guidance of experimentation, they have understood the intrinsic value of nature. The results are the development of new theories, which further lead to the pursuit of new technologies. Undoubtedly, these expansions have enhanced the living conditions of the human race in almost all possible ways. One of the major influences for this rapid expansion is due to the advancements in the field of energy and petroleum energy in particular. About 88% of the world’s fossil resources are used to produce primary energy production (Brennan and Owende, 2010). In other words, energy is the driving force of this era. But, the main threat to this dominance is the sustainability of the feedstock. It is important to control the effects of fossil-based energy before we are faced with a global energy crisis.

The primary constraint that influences the present energy challenges are: a) according to the present consumption rate, the world fossil reserves are estimated to reach a peak point by the year 2026 and “ on the basis of 2005 world crude oil production and current recovery techniques, the world oil resources are being depleted at an annual rate of 2.1%” (Nashawi et al., 2010); b) the effluents produced during oil production contain a lot of toxic components such as benzene, toluene, poly aromatic hydrocarbon, which is harmful to the environment; and c) the combustion of fossil fuels causes emission of carbon dioxide, carbon monoxide, nitrogen oxide, sulfur dioxide, and particulate matters,
thus becoming a major cause for air pollution and global warming, in the case of the greenhouse gas emissions. Considering the impacts created by fossil resources, humanity is now pushed towards the edge of finding an alternative source of fuel possessing a sustainable and eco-friendly nature.

1.2 BIODIESEL AS AN ALTERNATIVE FUEL

Historically, fossils are formed on the earth’s crust from both biogenic and abiogenic source of alkanes. The sources for biogenic formation of hydrocarbons are usually due to the decomposition of organic matters (Sherwood et al., 2002), but at the same time, the sources for abiogenic formation of alkanes is thought to be due to the reduction of carbon dioxide, but this is still an hypothesis among geologists. The next possible sources of energy feedstock beyond fossil materials are the next higher level of living organisms (i.e. plants and animals). Plants and animals provide fuel in the form of fats, sugar, and starches. Such organic materials can be converted into useful energy products through thermal, chemical, and biochemical conversion methods.

Biodiesel is one such fuel that can be derived from a biomass source, which could prospectively replace conventional diesel fuel (Knothe and Van Gerpen, 2005). Biodiesel has many similar features as the diesel extracted from petro-based sources (e.g., similar cetane number) (Knothe and Van Gerpen, 2005). From the history of using fossil fuels, humankind has learned a lot about the nature of hydrocarbons, and from that outlook, biodiesel as an alternative fuel is quite promising. It offers most of the advantages of conventional diesel but with less environmental impact. Biodiesel has lower viscosity, higher lubricity and oxidative stability, and works well with slight modifications in
standard diesel engine models, in addition to being a more environmentally benign fuel (Dorado, 2003).

1.2.1 Sustainability

Sustainability, as applied to resources, means something that can survive economically, environmentally, and socially. From this standpoint, biodiesel can be sustainable if the cultivation of the plant feedstocks and other such factors are managed properly, which certainly lies in the hands of researchers, policy makers, industries, growers, and world leaders.

1.2.2 Emissions

A small vehicle operating on conventional diesel fuel emits a high percentage of pollutants such as carbon dioxide, carbon monoxide, nitrogen oxide, sulfur dioxide, hydrocarbons, and particulate matters (PM). According to Xue et al. (2011), there is a significant reduction of 53-69% PM emissions, 45-67% HC emissions, 4-16% CO emissions, 100% SO$_x$ emissions, 50-80% CO$_2$ emissions and an increase of 10%-23% NOx emissions when biodiesel is used in place of petro diesel.

1.2.3 Feed stocks

Vegetable oils and animal fats are the most commonly used feedstock for biodiesel production. Both of these are water insoluble, hydrophobic substances that are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides (Sonntag, 1979). Fatty acids are long chain carboxylic acid that is either saturated or unsaturated, and the most common fatty acids that are present
in vegetable oils and animal fats are palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid. Table 1.1 shows the list of various feed stocks and their fatty acid compositions.

**Table 1.1** Fatty acid compositions of various vegetable oils and animal fats (Lotero et al. 2005)

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Palmitic</th>
<th>Stearic</th>
<th>Oleic</th>
<th>Linoleic</th>
<th>Linolenic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rapeseed oil</td>
<td>3.5</td>
<td>0.9</td>
<td>64.4</td>
<td>22.3</td>
<td>8.2</td>
</tr>
<tr>
<td>Virgin olive oil</td>
<td>9.2</td>
<td>3.4</td>
<td>80.4</td>
<td>4.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Sunflower oil</td>
<td>6</td>
<td>4.2</td>
<td>18.7</td>
<td>69.3</td>
<td>N/A</td>
</tr>
<tr>
<td>Safflower oil</td>
<td>5.2</td>
<td>2.2</td>
<td>76.3</td>
<td>16.2</td>
<td>N/A</td>
</tr>
<tr>
<td>Soybean</td>
<td>10.6</td>
<td>4.8</td>
<td>22.5</td>
<td>52.3</td>
<td>8.2</td>
</tr>
<tr>
<td>Palm oil</td>
<td>47.9</td>
<td>4.2</td>
<td>37</td>
<td>9.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Choice white grease</td>
<td>23.3</td>
<td>11</td>
<td>47.1</td>
<td>11</td>
<td>1</td>
</tr>
<tr>
<td>Poultry fat</td>
<td>22.2</td>
<td>5.1</td>
<td>42.3</td>
<td>19.3</td>
<td>1</td>
</tr>
<tr>
<td>Lard</td>
<td>17.3</td>
<td>15.6</td>
<td>42.5</td>
<td>9.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Edible tallow</td>
<td>28.4</td>
<td>14.8</td>
<td>44.6</td>
<td>2.7</td>
<td>N/A</td>
</tr>
<tr>
<td>Yellow grease</td>
<td>23.2</td>
<td>13</td>
<td>44.3</td>
<td>7</td>
<td>0.7</td>
</tr>
<tr>
<td>Brown grease</td>
<td>22.8</td>
<td>12.5</td>
<td>42.4</td>
<td>12.1</td>
<td>8</td>
</tr>
</tbody>
</table>
1.2.4 Production Pathways

1.2.4.1 Transesterification

Transesterification is the most common method of producing biodiesel from fats (triglycerides). The triglyceride reacts with alcohols such as methanol in the presence of an acid/base catalyst to produce methyl esters (biodiesel) and glycerol as a byproduct. Base catalysts are used widely in the transesterification reaction, as they enhance the performance of the reaction and provide high biodiesel yield. A simple illustration of the transesterification reaction is as follows:

\[
\begin{align*}
\text{Triglyceride} & \quad + 3 \text{Methanol} \quad \xrightarrow{\text{Catalyst}} \quad \text{Methyl ester} \quad + \quad \text{Glycerol} \\
\end{align*}
\]

\[
\text{RCO}_2\text{R'} + \text{OH} \quad \xrightarrow{\text{Catalyst}} \quad \text{RCO}_2\text{R'} + \text{H}_2\text{O} \quad (1.1)
\]

1.2.4.2 Esterification

If the fatty acid content is high, then the triglyceride tends to form soap, which will significantly lower the quality of the product. In such cases, acid catalysts are employed to convert the fatty acids into another ester or biodiesel. This process is called acid esterification. A simple illustration of the esterification reaction is as follows:

\[
\text{RCO}_2\text{H} + \text{R'OH} \quad \xrightarrow{} \quad \text{RCO}_2\text{R'} + \text{H}_2\text{O} \quad (1.2)
\]
The challenges with the production of biodiesel via transesterification and esterification are discussed briefly in Chapter Two.

1.2.5 Production Process

1.2.5.1 Batch Process

The batch process method is the simplest method to produce biodiesel (Van Gerpen et al., 2004). One mole of oil reacts with three moles of methanol to produce biodiesel, since the transesterification reaction is a reversible reaction. Excess methanol is used to push the reaction forward for complete transesterification of the oil. The methanol-to-oil molar ratio of 6:1 has been reported to be very effective (Van Gerpen et al., 2004). The most commonly used catalyst is sodium hydroxide and potassium hydroxide. Feedstocks less than 0.5% of fatty acids are used to avoid soap formation during the process (Van Gerpen et al., 2004). Figure 1.1 shows a process flow diagram for a batch system:
“The oil is first charged to the batch reactor, followed by the catalyst and methanol. The system is agitated during the reaction time. In some processes, the reaction mixture is allowed to settle in the reactor to give an initial separation of the esters and glycerol. In other processes, the reaction mixture is pumped into a settling vessel or is separated using a centrifuge. Then the methanol is removed from both the glycerol and ester stream using an evaporator or a flash unit. The esters are neutralized, washed gently using warm, slightly acidic water to remove residual methanol and salts, and then they are dried. The finished biodiesel is then transferred to storage” (Van Gerpen et al., 2004).
1.2.5.2 Continuous Process Systems

“Another contacting process that can be used is to use continuous stirred tank reactors (CSTR) in series. The CSTR can be made in different sizes to allow for longer residence times to achieve a higher extent of reaction. After the initial glycerol byproduct is decanted, the reaction in CSTR 2 is quite rapid, with 98% conversion. The reaction mixture moves through this type of reactor in a continuous plug, with little mixing in the axial direction. This type of reactor, called a plug flow reactor, behaves as if it were a series of small CSTRs chained together. The result is a continuous system that requires short residence times, as low as 6 to 10 minutes, for near completion of the reaction” (Van Gerpen et al., 2004).

![Fig 1.2 Plug flow reaction system (Van Gerpen et al., 2004)](image)

1.2.5.3 Non–Catalyzed System – Biox Co-Solvent Process

“Co-solvent options are designed to overcome slow reaction time caused by the extremely low solubility in the triglyceride phase of the alcohol. This process uses a co-solvent, tetrahydrafuron (THF), to solubilise the methanol. The result is a fast reaction, in
the order of 5 to 10 minutes, and no catalyst residues appear in either the ester or the glycerol phase. The THF co-solvent is chosen, in part, because it has a boiling point very close to that of methanol. After the reaction is complete, the excess methanol and the tetrahydrofuran co-solvent are recovered in a single step. This system requires a low operating temperature, 30°C. The ester and glycerol phase separation is clean, and the final products are catalyst and water free. Co-solvents that are subject to the Environmental Protection Agency (EPA) list for air pollutants require leak-proof equipment for the entire system, including methanol/co-solvent recovery. Because of its toxicity, the maintenance of the system is expensive and difficult” (Van Gerpen et al., 2004).

![Diagram of Biox co-solvent process](Van Gerpen et al., 2004)
1.3 RESEARCH MOTIVATION AND OBJECTIVES

Most of the energy-based research at present is focused on technologies for waste management, energy conservation, and reducing impacts on the environment. The overview presented above is important to understand the present status of energy-based research as it relates to biodiesel production. The overall goal of the present work was aimed at exploring technologies to develop an efficient, economically sound, and environmentally friendly process for biodiesel production. This is to overcome challenges with the homogeneous catalyst-based system currently used for biodiesel production by using a more reliable and efficient, in-house developed heterogeneous-based system. Also, handling of process wastes and reducing undesirable byproducts by increasing the reaction selectivity to biodiesel was an important driving force for this project. Also, new process designs were sought to increase the efficiency of the process. Even though biodiesel has been found to be an attractive alternative to replace petro diesel, the process has not been commercialized at a large scale yet because of economic and environmental concerns.

The specific objectives of this thesis work were to (a) develop a heterogeneous catalyst with high activity and regeneration capacity to replace homogeneous sodium hydroxide catalyst and, hence, to have an improved property of tolerance to water and free fatty acids;(b) develop a metal monolithic catalyst with a suitable design to enhance the catalyst activity, and (c) study the performance of a static mixer reactor design for the biodiesel production process in order to make the process economic and, in turn, reduce the production cost of biodiesel.
CHAPTER 2

HETEROGENEOUS CATALYST DEVELOPMENT FOR

BIODIESEL PRODUCTION PROCESS

2.1 BACKGROUND

2.1.1 Catalysis

“A chemical reaction involves breaking of bonds between atoms and the formation of new ones. This process is associated with transformation of energy. The activation energy \((E_a)\) to be surmounted is usually provided by thermal energy \(kT\), with \(k\) being Boltzmann’s constant and \(T\) the temperature, and, accordingly, only a fraction of molecular encounters will be successful. An increase of the reaction probability can be achieved by either increasing the temperature or by lowering the activation energy \(E_a\). The latter is provided by the catalyst through the formation of intermediate compounds with the molecules involved in the reaction providing an alternate reaction path, as shown in Figure 2.1. This is associated with smaller activation barriers and, hence, a higher overall reaction rate. In the last step, the product molecules are released from the catalyst surface, which becomes available for the next reaction cycle. If the reacting molecules and the catalyst are in the same (gaseous or liquid) phase, the effect is called homogeneous catalysis” (Ertl, 2008).
2.1.2 Principle of Heterogeneous Catalysis

If the reacting molecule and catalyst are in different phases, the effect is called heterogeneous catalysis. “The atoms in the surface layer of a solid have fewer neighbours than those in the bulk and are, hence, chemically unsaturated and may form new bonds (chemisorption) with suitable molecules impinging from the adjacent gas or liquid phase. By this step, existing bonds will be modified or may even be broken (dissociative chemisorption). The surface species formed might jump from one site to neighbouring ones and then might react with others, and the formed molecules eventually leave the surface (desorption)” (Ertl, 2008).

2.1.3 Properties and Characteristics of an Industrial Catalyst

Heterogeneous catalysts play an important role in shaping the industrial process toward economic and environmental success. They are easier to prepare, and they can be easily separated from the reaction mixture. Also, they can be regenerated while maintaining a high level of the original activity and stability, which effectively helps reduce operating costs.
For industrial applications, it is not important to have an ideal catalyst, but it is important to have an optimum catalyst. Once a suitable catalyst is identified for a process based on its active species and supports, it is essential for the catalyst to possess certain properties and characteristics in order to be considered at an industrial scale. Some of the fundamental properties are the catalyst activity, selectivity, stability, mechanical strength, thermal characteristics, regenerability, and cost of manufacturing.

2.1.4 Homogenous Catalysis for Biodiesel Production Process

Presently, transesterification of refined oils via homogeneous catalysis is widely used and considered to be the most reliable process for biodiesel production (Knothe and Van Gerpen, 2005). Sodium hydroxide, potassium hydroxide, and sulfuric acid are the catalysts that are employed at the commercial scale. The main advantage of the base catalysts is that they immediately dissociate into methoxide anions and protonated catalyst when they react with methanol. They then follow the nucleophilic attack of the methoxide anion at the carbonyl group, thereby resulting in higher yield in shorter residence times. In the case of acid catalysts, they first dissociate into hydrogen ions and then attack the alcohol to form an intermediate molecule. Figures 2.2 & 2.3 shows the mechanism of acid esterification and base catalyst transesterification in vegetable oils.
Fig 2.2 Mechanism of the acid catalyzed transesterification of vegetable oils (Schuchardt, Sercheli & Matheus, 1998a)

\[
ROH + B \rightarrow RO^- + BH^+ \quad (1)
\]

\[
\text{R'COO} - \text{CH}_2 + \text{R''COO} - \text{CH} \rightarrow \text{R'COO} - \text{CH}_2 + \text{R''COO} - \text{CH}_2 \quad (2)
\]

\[
\text{R'COO} - \text{CH}_2 + \text{OR} \rightarrow \text{R'COO} - \text{CH}_2 + \text{R''COO} - \text{CH}_2 \quad (3)
\]

\[
\text{R'COO} - \text{CH}_2 + \text{BH}^+ \rightarrow \text{R'COO} - \text{CH}_2 + \text{B} \quad (4)
\]

Fig 2.3 Mechanism of the base catalyzed transesterification of vegetable oils (Schuchardt, Sercheli & Matheus, 1998b)
However, the catalysts require the absence of water, as they tend to form soap (hydrolysis), which reduces the yield of biodiesel production significantly. Some of the other drawbacks of using homogeneous catalyst are: (a) the free fatty acid neutralization can be avoided by using vegetable oil with a low free fatty acid content (>0.5%). “However, the most profitable raw materials (e.g., waste cooking oils and fats or low-value fats) usually have a high content of free fatty acid” (Vicente et al., 2004); (b) difficulties in downstream separation and purification process; (c) use of acid catalysts reduce the FFA problem but require high residence time and lead to corrosion of process equipment, and (d) regeneration of the catalyst poses challenges.

Due to the above-mentioned limitations in the current practices for the biodiesel production process, the industry is faced with serious challenges to achieve widespread mass production level and to gain public acceptance. Currently, various blends of biodiesel with petro diesel are used in trucks and trains (Issues, 2010).

2.1.5 Heterogeneous Catalysts Versus Homogeneous Catalysts

To avoid undesirable soap formation and other challenges, a need for heterogeneous catalysts is inevitable, as they offer a number of advantages over the current technology. These advantages include the ability to use transesterification of low quality FFA feed stocks for biodiesel production, to better catalysts and glycerol recovery capabilities, to eliminate process equipment corrosion, to reduced environmental concerns, and to achieve overall process simplification.

In recent years, research has been extended to the search for a heterogeneous catalyst to solve some of the present challenges that face the biodiesel production
industry. A number of solid catalysts have been reported to be effective in the open literature and put forward as solving some of the difficulties associated with the homogeneous catalyst. However, none of the reported catalysts exhibited stability of acid sites and the control of surface properties to favour the diffusion of oily feedstock toward the acid sites (Melero et al., 2009).

2.2 EXPERIMENTAL SECTION

2.2.1 Screening of Potential Catalysts for Biodiesel Production

It was impossible to test all possible combinations of catalysts to find the optimum catalyst for the biodiesel production process within the allocated time frame of this research work. It was considered easier to formulate a screening procedure so that we could progress toward identifying a suitable catalyst from the bank of knowledge accumulated thus far in the field of catalytic science as it relates to the process at hand. About 200 publications have reported testing various heterogeneous catalysts for the biodiesel production process, and most of the studies have not expressed their work explicitly in terms of the active ingredients used or the reasons for their activities. The screening approach adopted for the current work is as follows:

a. analyze all the process catalysts that have shown high biodiesel yield for the transesterification process;

b. understand the physicochemical properties that have contributed toward the catalytic activity; and

c. develop a suitable catalyst for the biodiesel process.
Based on extensive literature review, certain properties seem to have a greater influence on the catalysts activity, resulting in higher yields of biodiesel. From various surface and bulk characterization techniques, it was found that the following properties have a significant impact on the catalytic activity: oxidation state; acid/base sites; pore structures; surface area; crystalline structure; calcination temperatures, and active species concentration.

### 2.2.2 Chemicals

The chemicals used in this study are listed in Table 2.1.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Catalyst Preparation</strong></td>
<td></td>
</tr>
<tr>
<td>Ammonium Metatungstate</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Zirconia Powder</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td><strong>Esterification</strong></td>
<td></td>
</tr>
<tr>
<td>Canola oil</td>
<td>Grocery Store</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Methanol</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td><strong>Sample analysis</strong></td>
<td></td>
</tr>
<tr>
<td>2-Propanol</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Toluene</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Potassium hydroxide</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Naphtholbenzein</td>
<td>Fisher Scientific</td>
</tr>
</tbody>
</table>

### 2.2.3 Catalyst Preparation

A standard solid acid catalyst, 20 wt% WO$_3$/ZrO$_2$ (Park et al., 2010), abbreviated hereafter as WZ, was reproduced and tested to act as the benchmark for the screening of catalysts. WZ catalysts have been reported to have high activity, lower residence time,
and good regeneration capabilities (Park et al., 2010; Zabeti et al., 2009; Vaidyanathan and Hercules, 2002; López et al., 2007; Suwannakarn et al., 2005; Jacobson et al., 2008).

A nominal 20 wt% WO$_3$ was loaded over the zirconia (Sigma Aldrich) by a standard wet impregnation procedure. Approximately 8 g of the catalyst support was immersed in 7.2 ml of a 0.1 M Ammonium Metatungstate solution. Then the solution mixture was allowed to age under constant stirring at 80°C maintained by a water bath for 4 hours. The resulting mixture was dried at room temperature and calcined at 400°C in an oven for 4 hrs. The final catalyst powder was not pelletized.

### 2.2.4 Catalyst Characterization: Physiosorption Analyses

The BET surface area, pore volume, and average pore size measurements for the catalyst were obtained by N$_2$ physisorption analyses at liquid N$_2$ temperature using a Micromeritics ASAP 2010 instrument. Prior to analysis, the samples were degassed at 180°C under vacuum for 4 hours. Average pore size and pore volume was analyzed using the desorption branch of the N$_2$-isotherm. Each sample was analyzed using N$_2$physisorption at least twice in order to establish repeatability.

### 2.2.5 Experimental Setup and Product Analysis

The performance of the heterogeneous solid acid catalyst for the esterification reaction was carried out in a bench-scale reaction system. The reaction system consisted of a 250 ml three-neck, flat bottom flask placed inside a 1000 ml water jacket for heating/cooling. The water jacket holding the three-neck, flat bottom reactor was placed on a plate-type heater equipped with a mechanical agitator. The reactor was designed for
operating pressures and temperatures of up to 35 psig and 100°C, respectively. The reactor head has three connecting ports: one for the condenser, one for sampling collection, and one for temperature measurement. The sampling port was equipped with a silicone rubber septum, making possible the collection of liquid samples without interrupting the reaction progress. Another thermocouple is placed inside the water jacket to measure and monitor the reaction temperature so that a uniform temperature distribution is maintained throughout the system.

Each liquid sample (3-ml) collected from the reactor was transferred to a test tube where 7 ml of de-ionized water was added. The test tube was shaken well and placed in a centrifuge operated at 4000 rpm for 8-10 minutes to separate the oil and methanol/catalyst phase. After the separation process, the oil phase was extracted separately using a syringe. The oil sample was subjected to acid number testing according to the ASTM D974-04 standard test. The collected sample was weighed for its mass and is then dissolved in a 100 ml titration solution (a mixture of toluene, water, and isopropyl alcohol with a volumetric mixing ratio of 100:1:99). Then, p-Naphtholbenzein (titration indicator) was added into the sample, which was finally titrated with 0.1N potassium hydroxide solution. The acid number was calculated based on the following equation:

\[
\text{Acid Number} = \frac{(A-B) \times M \times 56.1}{W} \quad (2.1)
\]

where,

(A-B) is the volume of KOH solution required for the titration of the sample,
M is the molarity of the KOH solution, and W is the weight of the sample in grams.

2.2.6 Experimental Procedure

The esterification reaction with solid acid WO$_3$/ZrO$_2$ (20 wt %) was carried out with an initial preparation of a mixture of canola oil and oleic acid to make a low quality feedstock. Oleic acid was used for this experiment because it is one of the most common fatty acids found in oils and fats. The mixture of canola oil and oleic acid was subjected to mixing at a constant speed, and, at the same time, methanol and catalyst were preheated to 60°C in a separate vessel. Then the methanol/catalyst mixture was charged into the reactor to start the esterification reaction. Since the reaction is reversible, excess methanol was added to move the reaction forward. A 9:1 ratio of methanol-to-oil was used in this process with a catalyst loading of 1% w/w. The reaction was conducted for 4 hours at a constant agitation speed of 650 rpm. During the reaction process, small quantities of samples were drawn from the reactor at specific intervals to determine the acid number. The purpose of the sample withdrawal is to determine the FFA depletion. Figure 2.4 shows the schematic diagram of the experimental setup.

![Fig 2.4 Schematic Diagram](image-url)
2.3 RESULTS AND DISCUSSION

The prepared solid acid catalyst was evaluated for the esterification reaction of vegetable oils under a reaction temperature of 62°C, stirring speed of 650 rpm, 1% w/w catalyst, and 1:9 molar ratio of oil-to-methanol. Table 2.2 shows the list of methyl ester yield containing less FFA content during each sample withdrawal of the esterification process.

**Table 2.2 FFA content during each sample analysis**

<table>
<thead>
<tr>
<th>Time (Min)</th>
<th>% FFA</th>
<th>% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>2.28</td>
<td>42.79</td>
</tr>
<tr>
<td>60</td>
<td>1.56</td>
<td>60.91</td>
</tr>
<tr>
<td>90</td>
<td>1.44</td>
<td>63.99</td>
</tr>
<tr>
<td>120</td>
<td>1.17</td>
<td>70.66</td>
</tr>
<tr>
<td>150</td>
<td>1.08</td>
<td>72.76</td>
</tr>
<tr>
<td>180</td>
<td>0.86</td>
<td>78.32</td>
</tr>
<tr>
<td>210</td>
<td>0.61</td>
<td>84.62</td>
</tr>
<tr>
<td>240</td>
<td>0.53</td>
<td>86.64</td>
</tr>
</tbody>
</table>

% FFA = \( \frac{\text{Acid Number}}{2} \times 100 \)

2.3.1 Catalyst Characterization

The prepared solid acid catalyst \( \text{WO}_3/\text{ZrO}_2 \) (20 wt %) was characterized by \( \text{N}_2 \)-physisorption method to examine the textural properties of the catalyst. The characterization technique was performed at the laboratories of the International test centre for \( \text{CO}_2 \) capture (ITC), University of Regina. Table 2.3 shows the textural properties of the prepared catalyst.

**Table 2.3 Textural properties of the solid acid catalyst**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m(^2)/g)</th>
<th>Pore volume (cm(^3)/g)</th>
<th>Pore size (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 wt % ( \text{WO}_3/\text{ZrO}_2 )</td>
<td>5.866</td>
<td>0.010726</td>
<td>71.4646</td>
</tr>
</tbody>
</table>
According to (Park et al., 2010), 20 wt% WO$_3$ loading over ZrO$_2$, calcined at 800°C had a surface area of 56 m$^2$/g. The esterification of the dark oil was carried out in an autoclave batch reactor under various reaction conditions, and it was found to yield 96% conversion at a residence time of 2 hrs. The reaction temperature was 150°C and the methanol-to-oil ratio was 9:1.

The low surface area observed for the prepared catalysts compared to published data was attributed to errors in the catalyst preparation method. Also, the prepared catalyst was dried in an open dish at ambient conditions, and no special drying system was used. The very low surface area and pore volume of the catalyst would have caused diffusion limitations during the esterification reaction, resulting in a FFA conversion of 86% over a period of 4 hrs.

2.3.2 Catalyst Performance Evaluation for Biodiesel Production

Only one fixed value of the reaction parameter was used in this study. The esterification reaction was carried out at a 9:1 methanol-to-oil molar ratio with 1% w/w catalyst loading and at an operating temperature of 62°C. Figure 2.5 shows the FFA conversion profile with respect to time.

According to Park et al., (2010), Yeob et al., (2010) and Jacobson et al., (2008), the esterification reaction is reported to be highly successful (96% conversion) at operating temperatures of 150°C and 200°C, respectively, using high performance reactors. As shown in Figure 2.4, the conversion was comparatively good during the first
60 minutes of the reaction, but it only attained a 26% conversion for the remainder of the operation time.

**Fig 2.5** FFA conversion vs. Time (1% w/w catalyst loading, 9:1 methanol-to-oil ratio, 62°C and agitation speed of 650 rpm).

### 2.4 SUMMARY

The WO$_3$/ZrO$_2$ solid acid catalyst was evaluated for the esterification process under a reaction temperature of 62°C, stirring speed of 650 rpm, 1% w/w catalyst, and 1:9 molar ratio of oil-to-alcohol. The prepared catalyst exhibited a low surface area of 5.86 m$^2$/g and resulted in an 86.6% FFA conversion in 4 hrs.
CHAPTER 3
MONOLITHIC CATALYST DEVELOPMENT FOR THE
BIODIESEL PRODUCTION PROCESS

3.1 BACKGROUND

3.1.1 Monolithic Catalysts

Monolithic catalysts are single block, separated or interconnected channel catalytic walls that vary in length depending upon their application. Ceramic and metal monolithic types are the current monoliths employed in industry. Some of the most common materials supported on ceramic monoliths are silica, alumina, and cordierite (magnesia, silica, and alumina combined). Figure 3.1 shows a pictorial representation of a cordierite ceramic monolith. Cordierite is the most common material used to prepare monolithic catalyst structures, as it has high mechanical strength, can withstand high temperatures and temperature shocks, and has a low thermal expansion coefficient (Nijhuis et al., 2001). “Monolithic catalyst has been shown to be an effective catalyst in the gas–liquid–solid catalytic reaction with the advantages of low pressure drop, large geometrical surface area, high mass-transfer efficiency, ability to withstand high temperatures, and absence of catalyst attrition and catalyst separation step” (Zhao et al., 2009). Table 3.1 shows the characteristics and geometrical properties of materials like gamma alumina, silica, and cordierite supported on ceramic monoliths.
Fig 3.1 Cordierite Monoliths (Nijhuis et al., 2001)

Table 3.1 Characteristics and geometrical properties of available materials for ceramic monoliths (Nijhuis et al., 2001)

<table>
<thead>
<tr>
<th>Material</th>
<th>Cordierite (2MgO:5SiO2:2Al2O3)</th>
<th>Silica</th>
<th>g-Alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Characteristics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cell density (cpsi)</td>
<td>25–1600</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Pore volume (mL/g)</td>
<td>0.19</td>
<td>0.18</td>
<td>0.42</td>
</tr>
<tr>
<td>Pore volume (N2 BET, mL/g)</td>
<td>NA</td>
<td>0.08</td>
<td>0.47</td>
</tr>
<tr>
<td>Surface area (N2 BET, m2/g)</td>
<td>&lt;4</td>
<td>90-120</td>
<td>190</td>
</tr>
<tr>
<td><strong>Geometrical Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity (structure)</td>
<td>0.69</td>
<td>0.74</td>
<td>0.8</td>
</tr>
<tr>
<td>Channel diameter (mm)</td>
<td>1.5</td>
<td>1.09</td>
<td>0.93</td>
</tr>
<tr>
<td>Wall thickness (mm)</td>
<td>305</td>
<td>178</td>
<td>109</td>
</tr>
<tr>
<td>Geometrical area (m2/m3)</td>
<td>1850</td>
<td>2710</td>
<td>3450</td>
</tr>
</tbody>
</table>

The main engineering application of the monolithic supported catalysts started with the automobile industry as a step to control vehicle emissions, mainly the hydrocarbons, carbon monoxide, and nitrogen oxides formed during combustion, and carbonaceous particulate matter formed in diesel engines. After years of research, monoliths loaded with precious active metal components were found to be the most suitable automotive catalyst to control emissions, and they have been reported to withstand the harsh exhaust environment with an average lifetime of 8-10 yrs or 100,000
kilometers (Shelef & McCabe, 2000). Presently, the monolithic supported catalysts are mostly employed in the automotive and pharmaceutical industries, and only very limited open literature is available about the use of monolithic catalyst supports in other industries.

3.1.2 Monolithic Catalysts for Biodiesel Production

The application of monolith-based catalyst in chemical industries is very limited, and from a wide search of literature regarding the application of monoliths in the biodiesel production process, only one paper using ceramic monoliths was found. According to Kolaczkowski et al., (2009), zinc amino acid complexes were tested as catalysts for the transesterification process. Primarily, the zinc amino acid complexes were tested directly as powders and were found to have a conversion of 69%. Then, the catalyst loaded on a cordierite monolith via chemical coating methods was subjected to the transesterification process and the fatty acid methyl ester (FAME) conversion was found to be 57%. No literature was found on using metal monolithic supports as a catalyst for the biodiesel production process, and the studies that have employed metal monoliths have either used ferrous chromium alloy or aluminium as their substrate for the process and have reported partial deactivation (10%) due to the minimal loss of adherence during the process (Sánchez et al., 2009)
3.2 EXPERIMENTAL SECTION

3.2.1 Chemicals

Table 3.2 presents the chemicals used in this study.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst Preparation</td>
<td></td>
</tr>
<tr>
<td>Hydrochloric Acid</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Nitric Acid</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Aluminium Hydroxide</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Gamma Alumina</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Ammonium Heptamolybdate</td>
<td>Sigma Aldrich</td>
</tr>
</tbody>
</table>

3.2.2 Monolithic Catalyst Preparation

A solid catalyst, 10% MoO$_3$/Al$_2$O$_3$ – SS316 monolithic catalyst, was employed for this study. This catalyst was selected to (a) evaluate the performance of stainless steel as a substrate and (b) to test the performance of the active species MoO$_3$. One of the primary reasons for choosing MoO$_3$ is that it has been reported to be a good corrosion inhibitor (Etienne Maze, Carman Mocquery, Benoit Millet, Antonio Francisco n.d.).

3.2.2.1 Etching

The stainless steel (SS316) substrate is pretreated by immersing the rod into concentrated hydrochloric acid (98%) for 2 – 3 minutes at room temperature, and it is subsequently immersed into nitric acid solution at 80°C. The hydrochloric acid is used to remove the impurities and make the surface rough so that an efficient coating can be achieved while the nitric acid is used to promote the formation of superficial oxide (Valentini et al., 2001).
3.2.2.2 Bohemite Sol Preparation

Bohemite sol was mainly prepared to improve the adherence of the stainless steel substrate, so that an efficient layer of gamma alumina washcoat could be applied to the surface of the substrate. A Bohemite primer was prepared by dispersing 10% (w/w) aluminum hydroxide powder in a 0.4% (w/w) HNO₃ aqueous solution. After mixing for 30 min, a stable dispersion of Bohemite was obtained. The pH value of the dispersion was 4 - 4.5 after 48 hrs. The pretreated substrate was dipped into the Bohemite sol and was withdrawn at a speed of 1 cm/min and was dried at room temperature for 1 hr.

3.2.2.3 Deposition of gamma alumina

The deposition of gamma alumina on the stainless steel substrate was accomplished following the description provided by Valentini et al., (2001). Gamma alumina powder was dispersed in a HNO₃ aqueous solution with the following typical proportions:

\[
\text{HNO}_3/\text{Al}_2\text{O}_3 = 2.16 \text{ mmol/g} \\
\text{H}_2\text{O}/\text{Al}_2\text{O}_3 = 3.2 \text{ g/g}
\]

After vigorous stirring for about 13 h in a closed reactor at a constant temperature of 18°C, the dispersions were suitable for deposition. At this stage the supports that had already been pre-coated with the Bohemite sol were dipped in the alumina dispersion for 15 s and then withdrawn at a constant speed of 3 cm/min. The coated samples were dried for 2 hrs with a hand dryer and eventually calcined at 150°C for the first 30 min and then at 450°C for 2 hrs.
3.2.2.4 Wet Impregnation

A nominal 10 wt% MoO$_3$ was loaded over the gamma alumina (Sigma Aldrich) support using a standard wet impregnation procedure. About 8 g of the catalyst support was immersed in 19.8 ml of a 0.1 M Ammonium Heptamolybdate solution. Then, the solution mixture was allowed to age under constant stirring at 80°C in a water bath for 4 hours. The mixture was then dispersed in water and nitric acid in the exact proportions listed above for five hours to obtain a stable dispersion. At this stage, the support, already pre-coated with Bohemite sol and gamma alumina, were dipped in the prepared dispersion for 15 s and then withdrawn at a constant speed of 3 cm/min. The coated samples were dried for 2 hrs with a hand dryer and eventually calcined at 150°C for the first 30 min and then at 450°C for 2 hrs.

3.2.3 Experimental Setup

The experimental design was not constructed for testing the performance of the prepared metal monolith catalyst for the esterification process. Figure 3.2 shows the proposed design to carry out the performance evaluation of the monolithic catalyst.

![Fig 3.2 Proposed design to test the metal monolithic catalyst](image-url)
The coated catalyst substrate is placed inside the reactor as shown in Figure 3.2, and then hot water is to be passed through the coated stainless steel tubing in order to maintain a desired catalyst temperature. The feed (oil and methanol) is then to be introduced into the reactor from the top, as shown in Figure 3.2, at a constant reaction temperature of 60°C to prevent methanol vaporization.

3.3 RESULTS AND DISCUSSION

3.3.1 Weight Loss Analyses

To measure the total catalyst loading and adherence to the stainless steel substrate, a weight loss test was done during each preparation step of the monolithic catalyst. Figures 3.3 – 3.6 shows the appearance of the sample during each preparation step.

![Weight loss before and after pretreatment of the sample](image)

**Fig 3.3** Weight loss before and after pretreatment of the sample

a) Before pretreatment (28.3756 g) 

b) After pretreatment (28.1676 g)
c) Bohemite Sol (28.3682 g)    d) Deposition of gamma alumina (28.3902 g)

**Fig 3.4** Deposition of gamma alumina on the sample

e) After calcination (28.3918 g)

**Fig 3.5** After calcination of the sample
f) Impregnation of active species (28.4262 g) after calcination (28.4230 g)

Fig 3.6 Impregnation of active species on the sample

The weight of the sample was reduced by 20.8 mg after the etching process. The weight loss was attributed to the loss of impurities and roughening of the surface with hydrochloric and nitric acid. The weight subsequently increased by 13.4 and 22 mg after coating the surface with the Bohemite primer and gamma alumina, respectively.

After calcination, the weight increased by 1.6 mg. This was unexpected and most likely resulted from a measurement error or accidental powder carryover. The weight increased by 34.4 mg after the deposition of the active species, and then it decreased by 2.2 mg after calcination.

The final sample, 10% MoO$_3$/Al$_2$O$_3$ – SS316, was allowed to cool for 24 hours, and the adherence of the coating was found to be very weak. The poor adherence was
attributed to the lack of an effective drying procedure, as homogeneous distribution and adherence depend heavily on the drying method.

3.4 SUMMARY

The 10% MoO$_3$/Al$_2$O$_3$ – SS316 monolithic catalyst was prepared for the evaluation of the esterification process. Due to the loose distribution of the catalyst material on the surface of the stainless steel substrate, the prepared monolithic catalyst showed poor catalyst adherence to the substrate. Hence, the esterification process could not be carried out with the prepared metal monolith. No characterization technique of the sample was done, so it was difficult to understand the properties and characteristics of the prepared sample.
CHAPTER 4

EVALUATION OF STATIC MIXERS IN A TRANSESTERIFICATION SYSTEM

4.1 BACKGROUND

4.1.1 Static Mixers

In most of the process industries, mixing plays a very important role in process conversion by mixing or blending different fluids and a lot of effort is applied to designing them to achieve effective mixing. Impellers and mechanical stirrers are the most common type of mixers employed at an industrial scale.

Static mixtures have no moving parts, and they are designed in such a way as to enhance mixing by placing a series of baffles inside a tube. “Most designs of static mixers are, geometrically, very different but, operationally, very similar” (Singh et al., 2009). They extract the energy required for mixing from the flow in the form of an increase in pressure drop. Ideally, this disturbs the flow in such a manner that desired flow conditions are obtained. The most commonly used static mixers are the SMX and Kenics static mixers (see Figure 4.1). Also, static mixers are less expensive and require less maintenance compared to conventional stirrers.

Fig 4.1 Example of Kenics mixer (Frederik and Wageningen, 2005)
4.1.1.1 Principle of Static Mixers

The basic principle of these mixers is to split, stretch, and recombine the fluid in order to achieve mixing. In a broader sense, the mixer relies on the principle of flow division, flow conversion, and flow inversion. The first step is the flow division; the first element divides the fluid into two flows and the next element into four and the next into eight and so on. After passing through the total number of elements, the liquid has been smoothly divided. The total number of layers formed can be calculated using the following equation:

\[ NL = 2^n \]  \hspace{1cm} (4.1)

where \( NL \) = number of layers

The next step is the flow conversion; when the direction of the flow changes along the streamlined surface of the twisted-shaped element, the flow is rotated in the direction of the axis. Under this force, the fluid flowing in the center section of the pipe is moved toward the peripheral section, and the fluid in the peripheral part of the pipe moves toward the center section as it is pushed. This causes the fluid to spread out along the element, gradually thinning the layer of the mixed fluid. The third step is the flow inversion; the fluid is induced into a clockwise turning flow while passing through the first element, and its flow direction is reversed to counter clockwise by the following element. The fluid is stirred by the turbulence of this rapid, reversing flow.
4.1.1.2 Static Mixers Versus Conventional Mixers

Static mixers are widely used in process industries as they consume very less energy and have short residence time compared to the conventional mixers. It is also very economic to produce. Table 4.1 summarizes the potential advantages of a static mixer over conventional mixers in the process industries.

Table 4.1 Advantages of static mixers over mechanically agitated vessels (Thakur et al., 2003)

<table>
<thead>
<tr>
<th>Static mixer</th>
<th>CSTR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small space requirement</td>
<td>Large space requirement</td>
</tr>
<tr>
<td>Low equipment cost</td>
<td>High equipment cost</td>
</tr>
<tr>
<td>No power required except pumping</td>
<td>High power consumption</td>
</tr>
<tr>
<td>No moving parts except pump</td>
<td>Agitator drive and seals</td>
</tr>
<tr>
<td>Small flanges to seal</td>
<td>Small flanges plus one large flange to seal</td>
</tr>
<tr>
<td>Short residence times</td>
<td>Long residence times</td>
</tr>
<tr>
<td>Approaches plug flow</td>
<td>Exponential distribution of residence times</td>
</tr>
<tr>
<td>Good mixing at low shear rates</td>
<td>Locally high shear rates can damage sensitive materials</td>
</tr>
<tr>
<td>Fast product grade changes</td>
<td>Product grade changes may generate waste</td>
</tr>
<tr>
<td>Self-cleaning, interchangeable Mixers, or disposable mixers</td>
<td>Large vessels to be cleaned</td>
</tr>
</tbody>
</table>
4.1.1.3 Static Mixers in Biodiesel Production Process

Only a very few open publications are available regarding the use of static mixers for the biodiesel production process. The authors of the paper have used different techniques to evaluate the performance of the static mixer. According to Alamsyah et al. (2010), transesterification reaction time to reach standard methyl ester content using a static mixer was faster than using a blade agitator, which indicates that the mixing mechanism by static mixer is more effective. This study was carried out in a static mixer reactor. Five static mixers were used, each with a 6 cm length and 5 cm width, and were inserted inside a single tube. The experimental results showed better activation energy values compared to the results with a blade agitator.

According to Avellaneda & Salvadó, (2011), the methyl ester conversion was found to be 96.5% using a micro mixer in a helicoidal reactor. The helicoidal reactor was submerged in a bath, and one end of the micro mixer was connected to the methanol input and the other end was used for the oil input.

4.2 EXPERIMENTAL SECTION

4.2.1 Experimental Setup

An helical type static mixer was used in this study to evaluate its performance for the esterification process. The reaction system consists of five, inbuilt, helical coil static mixers placed inside stainless steel tubing. The length of each reactor is 28 cm, and the volume of each reactor is 4.8 mL. Each helicoidal static mixer reactor was connected to each another consecutively. Three were assembled on the bottom level and the other two
were connected on the top. The configuration of the reactors is shown in Figure 4.2. The assembled reactor setup is submerged in a hot water bath.

**Fig 4.2** Configuration of static mixers

Feed is stored in two separate 400 mL cylindrical tanks each having a two-port valve. The valves are connected to a multi-tube flow meter, which in turn is connected to the reactor. An Ashcroft digital pressure gauge with 5 ports was connected to the reactor to monitor the pressure variations during the reaction. A nitrogen gas cylinder was connected to the feed tanks to pump the liquids to the reactor. The flow tube was calibrated for oil/oleic acid mixture and methanol/sulfuric acid mixture at 20 psi. Figure 4.3 shows the setup of the process.

**Fig 4.3** Process Setup
4.2.2 Experimental Procedure

The esterification reaction was carried out using a pre-mixed canola oil and oleic acid solution to make a low quality feedstock. Oleic acid was used for this experimental process because it is one of the most common fatty acids present in oils and fats. The mixture of canola oil and oleic acid was introduced from common feed tanks. The methanol/catalyst mixture was loaded into a separate feed tank. Excess methanol (methanol/oil ratio of 9) was used to ensure irreversible reaction in the presence of a catalyst loading of 1% w/w. Methanol/oil ratio were used in orders of three to evaluate its effects on the ester yield. The reactor was immersed in a water bath to maintain isothermal conditions of 65°C, and the nitrogen gas was introduced at 20 psi to pump the feed to the reactor. The port valve was opened, and the flow meter was adjusted to maintain a constant total flow rate of 1.6mL/min for oil and methanol.

The reaction was conducted by varying the number of static mixer reactors. In this study 1, 3, and 5 mixers were used alternatively to evaluate the effect of an individual versus multiple reactors for the esterification process. During the reaction process, small quantities of samples were drawn from the reactor at specific intervals to measure the acid number. The purpose of the sample withdrawal was to determine the FFA depletion.

4.2.3 Product Analysis

Each liquid sample (3-mL) collected from the reactor was transferred to a test tube where 7 mL of de-ionized water was added. The test tube was shaken well and placed in a centrifuge operated at 4000 rpm for 8-10 minutes to separate the oil and methanol/catalyst phase. After the separation process, the oil phase was extracted
separately using a syringe. The oil sample was subjected to acid number testing according to the ASTM D974-04 standard test. The collected sample was weighed for its mass and is then dissolved in a 100 mL titration solution (a mixture of toluene, water, and isopropyl alcohol with a volumetric mixing ratio of 100:1:99). Then, p-Naphtholbenzein (titration indicator) was added into the sample, which was finally titrated with 0.1N potassium hydroxide solution. The acid number was calculated based on the following equation:

\[
\text{Acid Number} = \frac{(A-B) \times M \times 56.1}{W} \quad (4.2)
\]

where,

(A-B) is the volume of KOH solution required for the titration of the sample,

M is the molarity of the KOH solution, and

4.3 RESULTS AND DISCUSSION

4.3.1 Effect of Temperature on Methyl Esters

The effect of reaction temperature on FAME was observed for four different temperatures and was evaluated for different methanol-to-oil ratios and total number of reactors. Other experimental conditions were fixed at 10% FFA and 1% w/w catalyst loading. The residence time for the entire operation was 15 minutes at a constant total flow rate of 1.6mL/min. Figure 4. 3 show the results of FFA conversion for different temperatures and oil-to-methanol ratios. The results show that the conversion was highest (99.26%) at a temperature of 65°C and 1:30 oil-to-methanol ratio. The conversion of FFA at an operating temperature of 65°C and 1:30 methanol ratio using a one-unit reactor
gives a conversion very close to the conversion of using 3 units at lower operating temperatures of 30°C and 45°C. The reason for this can be attributed to the change in density and viscosity of the reaction mixture at higher temperatures, which results in high conversion (McCabe, 1993).
Fig 4.4 Effect of temperature: (a) 1:9 oil-to-methanol ratio, (b) 1:12 oil-to-methanol ratio, (c) 1:15 oil-to-methanol ratio, (d) 1:30 oil-to-methanol ratio

4.3.2 Effect of Methanol-to-oil Ratio on Methyl Esters

The oil-to-methanol molar ratio is one of the most important parameters affecting FFA conversion. One mole of oil requires one mole of methanol for the esterification reaction. Since this reaction is reversible, an excess of methanol is used to move the equilibrium toward ester formation. Many papers have reported the use of high oil-to-alcohol molar ratios to obtain high conversion of the reactant (Furuta et al., 2004; Xie et al., 2006; Leclercq et al., 2001). In this study, the effect of oil-to-alcohol molar ratio was investigated, and an increase in oil-to-alcohol molar ratios from 1:9 to 1:30 had a significant effect on the level of FFA conversion. A 99% FFA conversion was achieved at 1:15 and 1:30 oil-to-methanol ratios. Therefore, the optimized oil-to-alcohol ratio was determined as 1:15 in this reaction system.

4.3.3 Effect of Residence Time on Methyl Esters

The effect of residence time was observed for three different times and was evaluated for different methanol-to-oil ratios and operating temperatures. Other
Experimental conditions were fixed at 10% FFA and 1% w/w catalyst loading. The residence times tested for this study were 15.4, 9.3, and 3.1 minutes. The reaction was carried out at a constant total flow rate of 1.6 mL/min. Figure 4.4 show the performance of the esterification reaction with different residence times using static mixers.
The esterification reaction using static mixer reactors was evaluated at three residence times, corresponding to the number of reactors used. In this study, the residence time using 5 units was 15.4 minutes and 9.3 and 3.1 minutes for 3 and 1 units, respectively. Figure 4.4 shows that at the higher residence time, the FFA conversion was very close to 97 – 99% for different methanol and oil ratios and for operating temperatures between 30°C and 65°C. With low residence times, the conversion of FFA for all different parameters ranged from 78 – 92%. The yields of the products are favoured by an increasing residence time. The reason for this is the influence of the higher residence time in achieving high selectivity for methyl ester formation.

4.4 SUMMARY

The results from the static mixer tests show that the esterification of canola oil can be carried out efficiently in static mixer reactors. Higher conversions of FAME were possible at a temperature of 65°C, a 1:30 oil-to-methanol ratio, and with a residence time of 15.4 minutes. Even though it had a higher conversion, 1:30 oil-to-methanol ratio was not an optimum concentration condition. However, 1:15 oil-to-methanol molar ratio
resulted in very comparable values for FFA conversion. Therefore, a suitable oil-to-methanol ratio for the esterification reaction using a static mixer reactor was found to be 1:15 moles.
CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

Heterogeneous catalysis plays an important role in the biodiesel production process to make it sustainable both economically and environmentally. This particular work has helped to understand the behaviour of the solid acid catalyst $\text{WO}_3/\text{ZrO}_2$ in terms of the esterification process. The catalyst was evaluated for the esterification process under reaction condition of temperature of $62^\circ\text{C}$, stirring speed of 650 rpm, 1% w/w catalyst, and 1:9 molar ratio of oil-to-methanol. This obtained an 86.6% FFA conversion in 4 hrs, even though the surface area of the catalysts was very low (5.86 m$^2$/g). A number of other characterization results such as thermogravimetric analyses, x-ray diffraction, FTIR spectroscopy, topography studies and Raman spectroscopy would further help to understand the physicochemical nature of the catalyst. Furthermore, developing a structure activity relationship for the esterification process would be possible with the existence of such data.

This study was also helpful in understanding the application of a metal monolithic catalyst to an esterification reaction. One of the objectives of this research was to gain insight about catalyst coating techniques on a stainless steel substrate and the adhesion stability of the substrate. A 10% MoO$_3$/Al$_2$O$_3$ – SS316 monolithic catalyst was prepared for the evaluation of the esterification process, and due to the non-uniform distribution of the catalyst material on the surface of the stainless steel substrate, the prepared monolithic catalyst resulted in poor adherence. Hence, the esterification process could not be carried out with the prepared metal monolith. Characterization techniques such as scanning electron microscopy, x-ray photon spectroscopy and chemisorption analysis of
the sample would have aided significantly in gaining and understanding of the physicochemical properties of the prepared catalyst. Other high-end coating techniques like chemical vapour deposition, electro-deposition, and thermally-treated coatings are some of the other alternatives that can be applied for the preparation of a metal monolith. Aluminum substrate could be a better alternative than stainless steel substrate, as aluminum substrates are rough and rich in surface oxides like Al₂O₃. They might even provide higher surface area compared to the stainless steel substrate.

Finally, the use of a static mixer in process industries has a number of advantages over the conventional mixers. In this thesis work, a helicoidal static mixer was used to evaluate the performance of the esterification reaction, and the results show that the esterification of canola oil using a static mixer reactor showed a very good performance. Higher conversions of FAME were achieved at temperature of 65°C, oil-to-methanol ratio of 1:30, and a residence time of 15.4 minutes. Even though it had a higher conversion, a 1:30 oil-to-methanol ratio is not in the optimal performance range, and the results were similar using 1:15 moles of oil-to-methanol ratio. Hence, the suitable oil-to-methanol ratio for the esterification reaction using a static mixer reactor is 1:15. As an extension, in future work, static mixer reactors with different lengths and volumes could be used to test the esterification performance. This could significantly reduce the interdependence of the reactor units and, in turn, result in an even shorter residence time. Energy optimization and byproduct reduction studies can be applied to the static mixer reactor to get a better overall outlook on its performance in the biodiesel production process.
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