AMPHIPHILIC PHASE-TRANSFORMING CATALYSTS FOR

TRANSESTERIFICATION OF TRIGLYCERIDES

A Dissertation

by

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ABSTRACT

Heterogeneous catalytic reactions that involve immiscible liquid-phase reactants are

challenging to conduct due to limitations associated with mass transport. Nevertheless,

there are numerous reactions such as esterification, transesterification, etherification, and

hydrolysis where two immiscible liquid reactants (such as polar and non-polar liquids)

need to be brought into contact with a catalyst. With the intention of alleviating mass

transport issues associated with such systems but affording the ability to separate the

catalyst once the reaction is complete, the overall goal of this study is geared toward

developing a catalyst that has emulsification properties as well as the ability to phase-

transfer (from liquid-phase to solid-phase) while the reaction is ongoing and evaluating

the effectiveness of such a catalytic process in a practical reaction.

To elucidate this concept, the transesterification reaction was selected. Metal-alkoxides

that possess acidic and basic properties (to catalyze the reaction), amphiphilic properties

(to stabilize the alcohol/oil emulsion) and that can undergo condensation polymerization

when heated (to separate as a solid subsequent to the completion of the reaction) were

used to test the concept.

Studies included elucidating the effect of metal sites and alkoxide sites and their

concentration effects on transesterification reaction, effect of various metal alkoxide

groups on the phase stability of the reactant system, and kinetic effects of the reaction

system.

The studies revealed that several transition-metal alkoxides, especially, titanium and yttrium based, responded positively to this reaction system. These alkoxides were able to be added to the reaction medium in liquid phase and were able to stabilize the alcohol/oil system. The alkoxides were selective to the transesterification reaction giving a range of ester yields (depending on the catalyst used). It was also observed that transition-metal alkoxides were able to be recovered in the form of their polymerized counterparts as a result of condensation polymerization subsequent to completion of the transesterification reaction.

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CHAPTER I

INTRODUCTION AND PROBLEM STATEMENT

Introduction

Problem Statement

Increasing the effectiveness of reactions that involve immiscible liquid/liquid (L/L)

reactants is challenging due to limitations associated with mass transport as a result of

unavailability of sufficient interfacial area. Although the L/L incompatibility could be

ameliorated by introducing a liquid surfactant, this causes downstream product

separation problems which reduces the effectiveness of such a system for practical

applications. [1] Nevertheless, there are numerous instances where two immiscible liquid

reactants (such as polar and non-polar liquid reactants) need to be brought into contact

with a catalyst such as in esterification[2,3], transesterification[4-7], etherification[8,9], and

hydrolysis.[10-12] So, there is a need for catalytic processes that can alleviate such phase

incompatibility.

For industrial purposes, it will be beneficial to have catalysts that are in a different phase

than the reactants, such as a heterogeneous solid in a liquid medium, which allows easy

separation of the catalyst subsequent to the completion of the reaction. However,

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introduction of a solid further aggravates the mass transport issues now due to the liquid/liquid/solid incompatibility.

The overall goal of this study was to develop a catalyst that 1) has emulsification properties which can make the two liquid-phase reactants compatible and 2) can be easily separated from the reaction medium once the reaction is complete.

This study was designed to identify chemical compounds that have catalytic and amphiphilic properties and understand the behavior of such catalysts under varying reaction conditions for the transesterification reaction. Transesterification was used as the reaction of choice since the substrates (oil and alcohol) are inherently immiscible in each other and would be a good benchmark to evaluate the effectiveness of the novel catalysts due to the abundant availability of catalysis data. The specific objectives and organization of the dissertation are discussed below.

Dissertation Organization

This dissertation consists of six chapters. Chapter I (this chapter) is a generalized introduction of the research problem and research objectives. Chapter II presents the response of a titanium isopropoxide-based phase-transforming catalyst on transesterification. This includes catalytic behavior of titanium isopropoxide at varying temperature and reaction times. Chapter III reports a study of effects of tail groups of

titanium alkoxides on the transesterification reaction. Chapter IV presents the effects of metal groups on the transesterification reaction. Chapter V discusses the amphiphilic ability of selected catalyst metal alkoxides. In this chapter, phase stability as well as the effect of some selected catalyst concentrations (that were able to form stable emulsions) on transesterification is presented. Chapter VI presents kinetic data for a selected system along with catalyst reusability data. Chapter VII reports overall conclusions and recommendations for future work.

The objectives and specific tasks for the research reported here are as follows:

Objective 1 - Evaluate the overall catalytic nature of partially polymerized metal alkoxides (preliminary study)

   Task 1- Analyze the effect of degree of polymerization of select metal isopropoxide on transesterification reaction

   Task 2- Analyze the effect of temperature on transesterification reaction

Objective 2- Elucidation of the effect of alkoxide group (tail group) on catalysis of the transesterification reaction

Objective 3- Elucidation of the effect of different metal groups on the catalysis of the transesterification reaction

Objective 4- Elucidation of effect of selected metal groups and alkoxide groups on the stability of the alcohol-oil-catalyst ternary system and its correlation to catalysis

Task 1- Elucidation of the stability of the ternary system as a function of different alkoxides

Task 2 - Elucidation of the emulsion stability as a function of degree of polymerization of the isopropoxide

Task 3- Elucidation of the effect of emulsification on transesterification catalysis

Objective 5- Determination of reaction kinetics and catalyst reusability

Task 1- Elucidation of reaction kinetics

Task 2- Yield optimization studies

Task 3 - Analysis of catalyst reusability after an initial run

CHAPTER II

RESPONSE OF TITANIUM ISOPROPROPOXIDE-BASED HETEROGENEOUS

AMPHIHPILIC-POLYMER-CATA LYSTS FOR TRANSESTERIFICATION [*]

Introduction

The goal of this study was to address aforementioned limitations of liquid/liquid

substrate incompatibility by developing a heterogeneous (solid) catalyst that acts as an

emulsifier (amphiphile) which essentially will be positioned at the interface between the

two immiscible liquids while catalyzing the reaction. It was conceptualized that the

amphiphilic catalyst first brings the two hydrophilic and hydrophobic liquid molecules

together and due to the emulsification properties of the catalyst, stabilizes the emulsion.

In the meantime, the catalyst will lend its active sites for the desired reaction to occur.

We selected the transesterification reaction to test our premise. This reaction has gained

much attention recently due to its use in the biodiesel industry. [13,14] Fatty acid methyl (or

ethyl) esters commonly known as biodiesel are a renewable alternative fuel for

compression ignition engines.[15-20] Typical raw materials used are triglycerides of either

plant or animal origin and used oils or fats. [7,13,19-25] Direct utilization of triglycerides as

diesel fuel is not feasible due to engine operational problems associated with poor fuel

injection properties and the formation of deposits as a result of the high viscosity and high molecular weight of triglycerides. Consequently, transesterification is employed to lower the fuel viscosity nearer to that of petroleum diesel.

Transesterification is an acid or alkaline catalytic reaction between triglycerides and alcohols (methanol, ethanol, etc.).[26] Due to superior activity and favorable economics, the most commonly used industrial catalysts are sodium and potassium hydroxides. However, alkaline hydroxides often produce saponifiable matter [27] which originates from the free fatty acid neutralization. This soap formation is undesirable as it partially consumes the catalyst, decreases biodiesel yield, and complicates the separation and purification steps. In addition, the removal of these homogeneous catalysts is technically difficult and adds extra cost to the final products.[28-30] Moreover, disposal of the catalyst-contaminated glycerin is increasingly becoming an environmental concern. Therefore, heterogeneous catalysis is desired to simplify separation and purification of the products.

 Nonetheless, heterogeneous catalysis in transesterification largely remains as an unsolved challenge. Present catalytic systems require extreme reaction conditions and are still plagued with problems associated with catalyst leaching and poisoning. The yield and reaction times are still unfavorable due to mass transfer limitations in liquid/liquid/solid (L/L/S) interface systems corresponding to triglyceride/alcohol/catalyst phases, respectively.[31] The concept of heterogeneous amphiphilic catalysis has the potential to reduce the mass transfer barrier associated with

the L/L/S phase-incompatibility. In general, improved L/L/S catalytic systems will be of

high significance where reactions involve hydrophilic and hydrophobic liquids in the

presence of solid catalysts. Such systems include esterification[3,32,33],

transesterification[6,7,34,35], etherification[8,9] and steam reforming[36-38] systems. Specifically,

amphiphilic catalysts could potentially be used in L/L catalytic environments such as

hydrolysis of propionic anhydrite catalyzed with sulfuric acid [39,40], oxidative

desulfurization of dibenzothiophene with molecular oxygen [41], oxidation of hydrophobic

alcohols using aqueous hydrogen peroxide [42], hydroamination reactions in a liquid-liquid

two-phase catalytic system [43], and reforming of hydrophobic substrates such as lignin to

produce biorenewable hydrogen using novel systems such as aqueous phase reforming

(APR).

Transport Aspects of Transesterification

Homogeneous catalysts, in addition to providing the acid and alkali sites for the

transesterification reaction to occur, provides the required amphiphilicity for emulsifying

the originally bi-phasic and immiscible reactant mixture. The amphiphilic nature of the

alkoxide intermediate (Figure 1) clearly depicts why the base catalyzed reaction occurs

much more favorably in comparison to the acid catalyzed process. The alkyl group of the

alkoxide is hydrophobic and would orient towards the continuous triglyceride phase

while the polar oxide would orient inward towards the discrete alcohol droplets making a

micelle. The reaction would occur at the oil/alcohol interface. On the other hand,

inorganic acid molecules are polar and would predominantly stay submerged in the

alcohol phase. The acid-catalyzed reaction would occur comparatively much slower

since there is no driving force (other than mechanical agitation) to drive catalyst

molecules towards the non-polar lipid phase for the reaction to occur.

Figure 1: Reaction mechanism of base catalyzed transesterification along with orientation of the catalyst amphiphile

Heterogeneous Catalysts in Transesterification

Heterogeneous catalysts that have been used in biodiesel production related transesterification include metal oxides such as ZrO_2-SiO_2, KOH/ZrO_2-SiO_2, Co_2O_3-SiO_2, Mo_2O_5-SiO_2, Na_2O-SiO_2 [16,44]; metals such as nickel powder, palladium powder, cast iron shavings, steel shavings [44,45]; zeolites [46-48]; ion exchange resins [16,49,50]; and salts such as sulfated zirconia.[2,25,51] Literature suggests that the heterogeneous catalysts that showed the best performance are zeolites - mainly the ETS-10 group.[52] ETS-10 with a catalyst loading of 11 wt% in a 1 ml vial reactor gave a conversion of 95.8% in 24 hours at 150 ^{o}C with a 6:1 molar ratio of methanol to soybean oil.[44] However, "Esterfip-H" offered by Axens is the only commercial process available that uses a heterogeneous catalysts.[14,53,54] This process uses a mixture of zinc oxide, aluminum oxide, and zinc aluminates as the catalysts and requires a temperature between 170-250 ^{o}C, a pressure of approximately 100 bar, and a two-stage reaction. By contrast, homogeneous basic catalysts give conversions near 100% at temperatures at or below 65 ^{o}C in less than 3 hrs.[31] The challenge in developing heterogeneous catalysts for transesterification is that the catalysts with strong catalytic activity require strong basicity and compounds with such strong basicity are inherently soluble in alcohol. Consequently, there is a tradeoff between solubility and basicity. Consequently, our approach looks at a highly basic catalyst that is insoluble in the hydrophilic alcohol environment.

The solid phase basic heterogeneous catalyst was titanium isopropoxide which was polymerized into dimeric, trimeric, tetrameric and polymeric/dendritic forms or mixtures of these by a sol-gel synthesis method. The focus of this study was to evaluate the catalytic aspect of the inorganic polymer for the transesterification reaction. In this case, soybean oil was used as the triglyceride and isopropanol as the alcohol. Isopropanol was used: 1) since the molecule has a larger hydrocarbon tail group (in comparison to methanol or ethanol) favoring miscibility in hydrophobic triglyceride phase and 2) to be compatible with the titanium isopropoxide which will exchange the alkoxide ligand with the alcohol during the transesterification (to ensure homogeneity of the alkoxide group).

Materials and Methods

The transesterification reaction was carried out in a high pressure thermal reactor (4570-Parr instrument, Moline, IL USA.). The reactor has a maximum operating temperature of 500 ^{o}C and pressure of 5000 Psi. The reactor was used in the batch mode. Pure soybean oil was purchased in bulk from STE Oil Company, San Marcos, TX USA. Titanium isopropoxide was purchased from Sigma-Aldrich chemical company. Isopropanol was purchased from EMD chemicals Inc., while pure biodiesel was purchased from SoyGold (Ag environmental products, LLC, Omaha, NE USA).

Catalyst Preparation

Titanium isopropoxide (99%, sigmaarldrich) was used as the catalyst precursor. Consequently, isopropanol was used as the alcohol for the transesterification reaction. Titanium isopropoxide was dispersed in isopropanol using ultrasonication. The dispersed catalyst-containing alcohol was a clear liquid prior to water condensation. Water condensation of the isopropoxide was also carried out under ultrasonication in isopropanol. Subsequent to water addition, the inorganic polymer molecules start to grow causing the solution to turn turbid (white). The reaction scheme associated with the water condensation process is given in Figure 2.
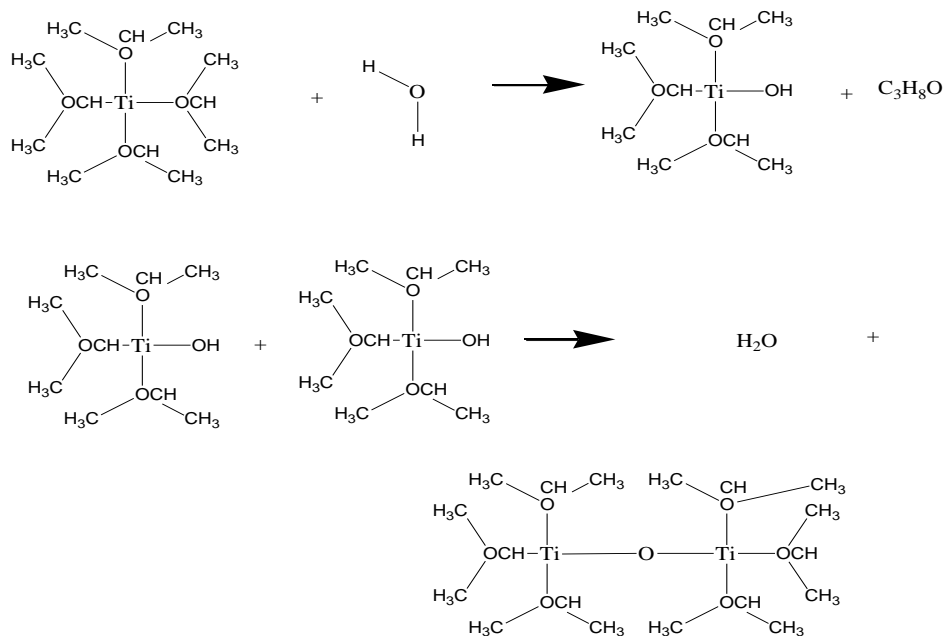
Figure 2: Hydrolysis and water condensation reactions of titanium isopropoxide

First, a water molecule hydrolyzes an alkoxide bond of the titanium isopropoxide

generating a hydroxyl group. Two such molecules having orthogonal hydroxyl groups

react to give -Ti-O-Ti- via water condensation. The degree of polymerization was

controlled by changing the isopropoxide:water ratio. Accordingly, five different catalysts

were prepared with water:titanium isopropoxide ratios of 0, 0.5:1, 1:1, 1.5:1, and 2:1 as

given in Table 1.

Table 1 Corresponding structures with degree of polymerization
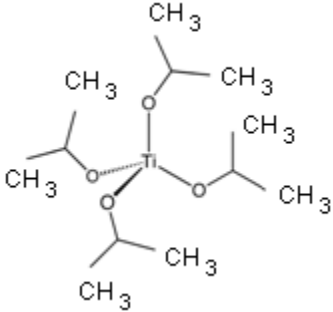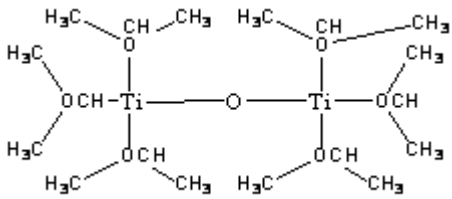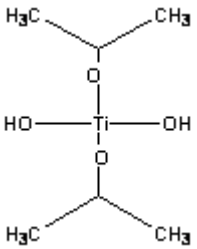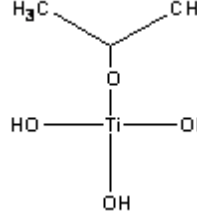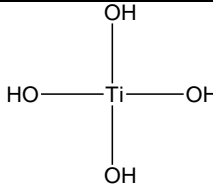
Water:Titanium isopropoxide ratio	Expected Resultant molecule
0	Monomer
1: 2 (0.5:1)	Dimer

Table 1 Continued

Water:Titanium isopropoxide ratio	Expected Resultant molecule
1:1	based polymer with two propoxide groups residing per monomer
3:2 (1.5:1)	base polymer with one propoxide group residing per monomer
2:1	condensing to TiO_2 polymer

In order to obtain the desired structures, water addition was done while the isopropoxide
– alcohol mixture was subjected to ultrasonication as indicated earlier. The sonication

system (UP400S, Hielscher ultrasound technology), was capable of producing 24,000

kHz waves with a power output of 400W. The reaction was carried out in a high pressure

reactor. A Schematic diagram of the high pressure reactor is shown in figure 3. The pressure reactor consisted of a magnetic drive stirrer with maximum speed of 2000 rpm and a tachometer module with accuracy ± 10 rpm. The stainless steel reactor vessel was capable of handling 500 ml of reactants. In order to initiate the transesterification reaction, 1% (w/w) of the catalyst was added to the triglyceride immediately after preparation and the reactor was sealed. Initial pressure of the reactor was kept constant at atmospheric pressure. The reaction was carried out at 6 different temperatures: 50, 100, 150, 200, 250, and 300 $^\circ$C. Samples were drawn from the reactor only after reaction temperature reached to the desired level for that experiment. However, ancillary data were collected in order to assess how much conversion had occurred from the onset of the reaction until the desired temperature was reached (it was observed that during temperature ramping there was only slight conversion). After temperature reached the set value, 6 samples were drawn from each experimental batch in 30 minute intervals up to 3 hours. The samples drawn were cooled immediately in order to cease the reaction from progressing further. Then, the samples were centrifuged at 10,000 RPM and 12 $^\circ$C to separate propyl esters and glycerol. Catalyst and product separation was done by a centrifuge system (Sorvall Legend 23 R- Thermo Scientific) that could reach up to 24,000 RPM and was capable of cooling to (-) 4 $^\circ$C.
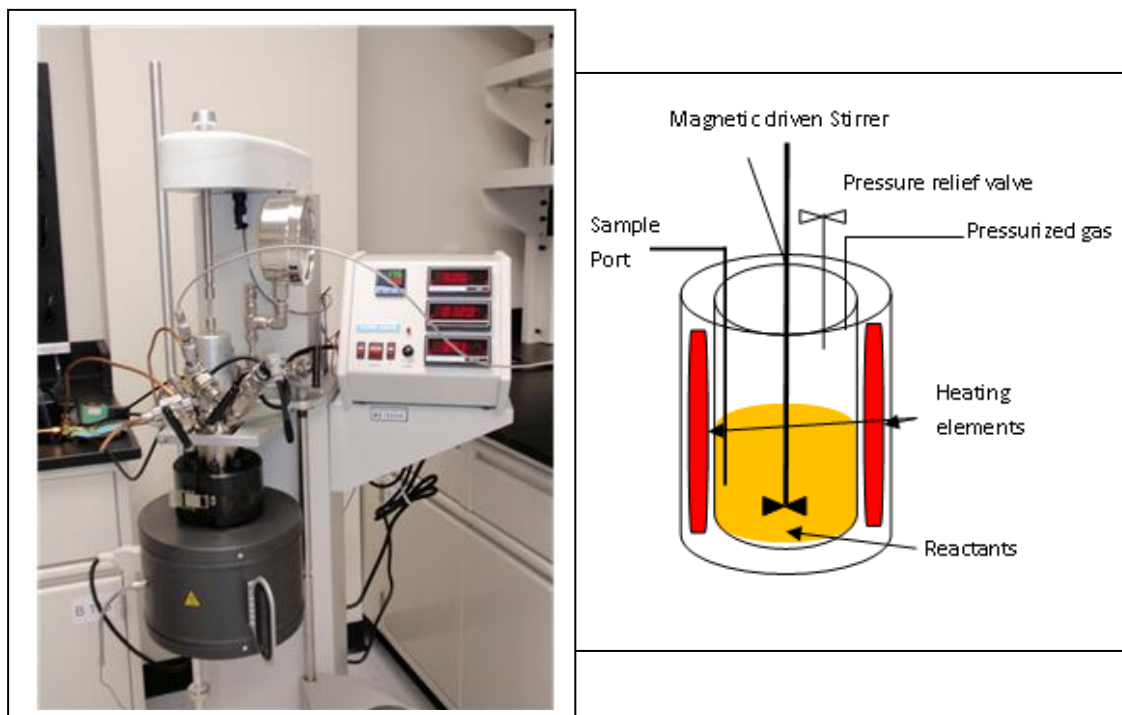
Figure 3: Actual setup of the reactor (a) and schematic of the reactor (b)

The top fraction of the products was analyzed for esters yield. Samples were analyzed by gas chromatography (GC-6850 Agilent Technologies, Santa Clara, CA USA). Auxiliary analysis was carried out by GC mass spectroscopy (GC-MS 7890 Agilent Technologies, Santa Clara, CA USA).

The fatty acid propyl esters yield with respect to the degree of polymerization, time of reaction and the temperature are discussed in following sections. The results were analyzed statistically using Design Expert software. A response surface reduced quadratic model was used to analyze the data. The GC method utilized for isopropyl esters detection is given below:

Table 2 GC method for isopropyl ester detection

Inlet Temperature	250 ^{o}C
Split ratio	50:1
Injection volume	1 µl
Column flow (Helium)	1.6 ml/min (constant flow)
FID temperature	280 ^{o}C
H$_2$ Flow	40 ml/min
Air flow	450 ml/min
Makeup gas (Nitrogen)	30 ml/min
Oven program	50 ^{o}C hold 1min, to 200 ^{o}C at 25 ^{o}C/min, hold 3 min, to 230 ^{o}C at 3 ^{o}C/min, hold 18 min
Column	30m x 0.25mm x 0.25µm (DB-Wax Column)

Results and Discussion

In the field of titanium alkoxides this is the first time such an extensive study of the behavior of the titanium isopropoxide system on transesterification at varying temperatures, degrees of polymerization and residence times has been performed. The primary objective of the study was to indentify the optimum combination of these parameters to maximize the transesterified product yield. In order to capture the correlation of all these parameters of the system as a whole, the following combinations were analyzed: Ester yield at varying temperatures and degrees of polymerization; yield

at varying degrees of polymerization and reaction time and; yield at varying temperatures and reaction time. Hypothesized surfactant formulation around the phase boundary is shown in figure 4.

The behavior of the titanium isopropoxide system with varying reaction times at increasing degrees of polymerization is depicted in figure 5. In these graphs, time begins after the reaction mixture reached the designated temperature. In certain instances, negative ester yields are reported. This means that the yields have fallen beyond the starting yield for that temperature.

At lower temperatures, i.e., 50 to 100$^\mathrm{o}$C, it is clearly noticeable that at lower residence times, the degree of polymerization does not have a significant effect on ester yields (Figure 5 A). However, as residence time increases, the polymers tend to produce lower ester yields than the monomeric and dimeric forms. It is also noteworthy that as the residence times increase, the yields increase regardless of the degree of polymerization.
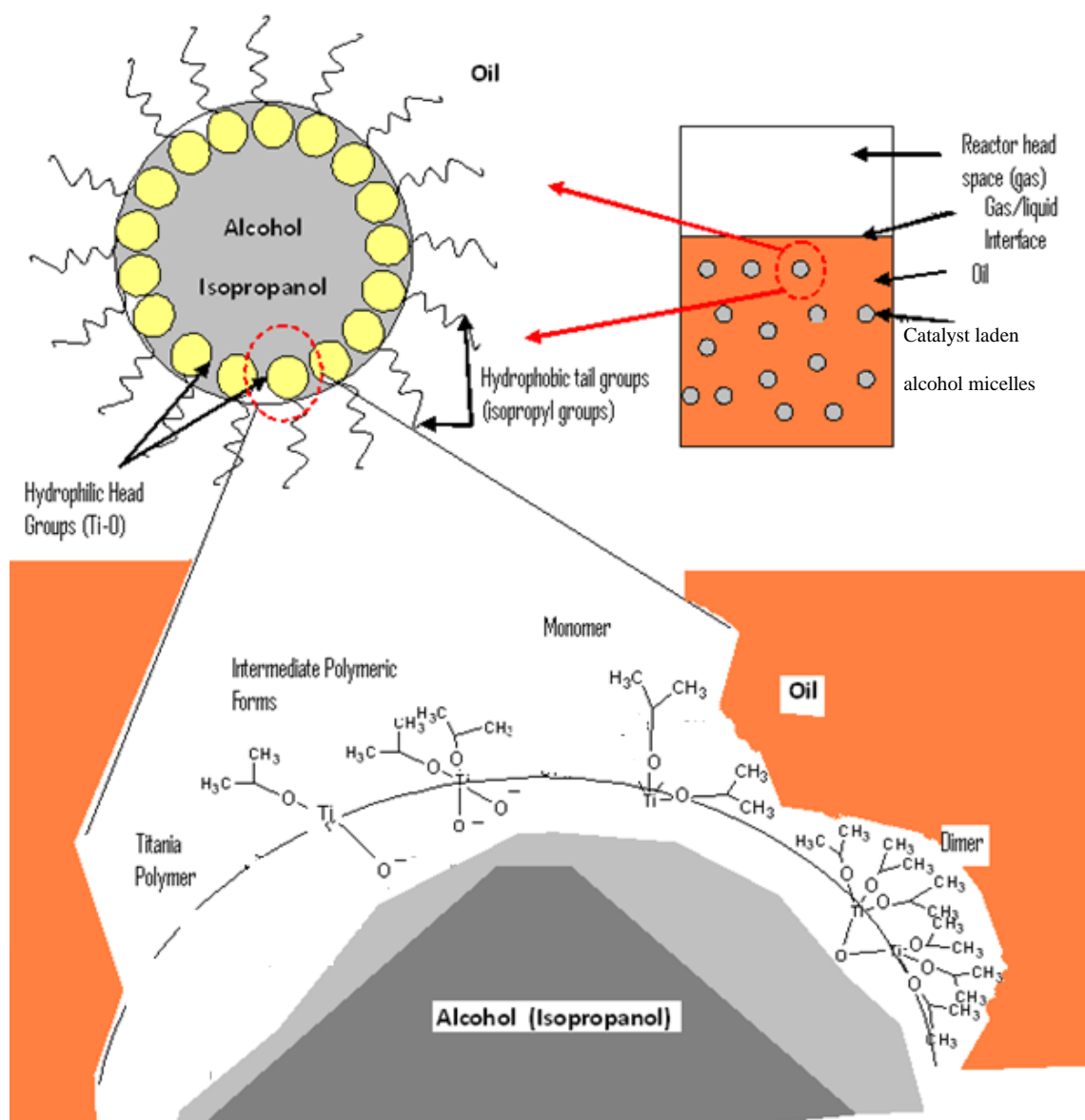
Figure 4: Orientation of titanium isopropoxide polymer in oil/alcohol interface

It was interesting to note that as the temperatures increased beyond 150°C, the trend reversed, i.e., lower residence times resulted in higher ester yields (Figure 5B). The turning point for this behavior was approximately 150°C (notice the two-way saddle point in Figure 5B). Interestingly, at higher temperatures, the polymeric forms tended to

result in higher ester yields as compared to monomeric and dimeric forms (although the overall yields were much less than those at lower temperatures). At longer residence times (and higher temperatures), the degree of polymerization seemed to be less significant for the transesterification reaction and produced very low ester yields.

The reason for low ester yields at lower temperatures may be due to less favorable kinetics (regardless of the number of active sites available in the reaction environment). At higher residence times, the monomeric form of the catalyst tended to produce more esters and this is expected due to the higher availability of OR^- groups per catalyst molecule. The monomeric isopropoxide has four active sites per molecule.

The reduction of overall ester yields at higher temperatures could be attributed to thermal cracking and associated reactions that include deoxygenation and polymerization of unsaturated chemical moieties. A GCMS study of the high temperature - high residence time products indicated the presence of aromatic compounds including benzene and cyclohexane suggesting deoxygenation (most likely via decarboxylation[55,56]).
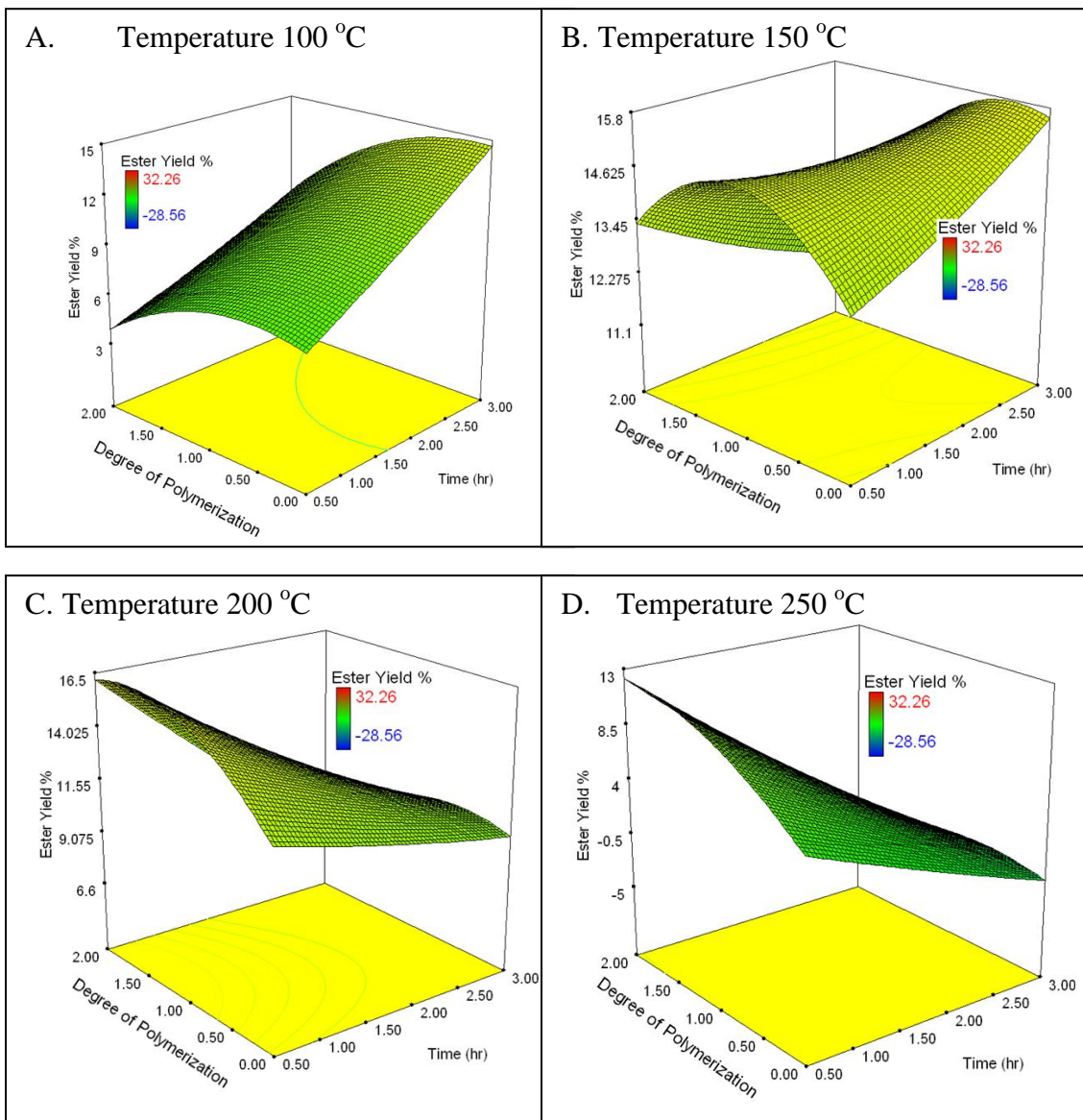
Figure 5: Time and degree of polymerization variation with ester yield at different temperature

One key objective of this study was to identify the operating point at which the

maximum esters yield occurs. The most straightforward to confirm was the response of

the system to temperature. The temperature response of the system to varying degrees of

polymerization and residence times is given in Figures 6 and 7. It was clear from our analysis that the optimum temperature for the reaction was between 150 and 200°C. Notice that regardless of degree of polymerization or the residence times, the maximum ester yields were obtained between these temperatures. The statistical analysis predicted the optimum temperature to be 181 $^{\circ}$C.
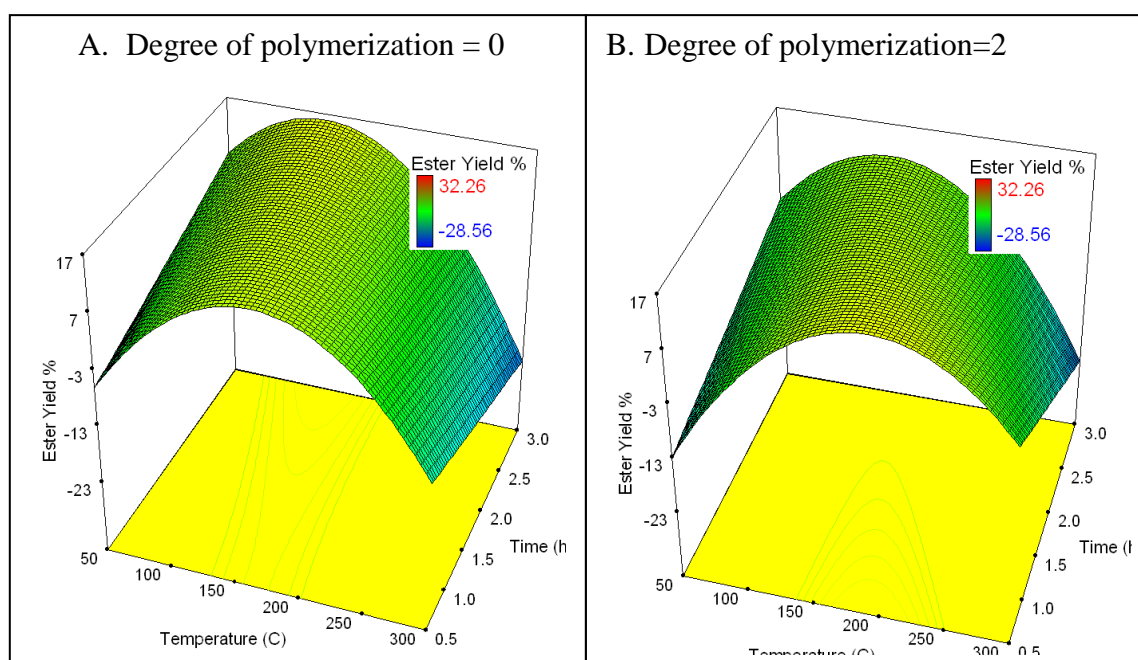
Figure 6: The effect of temperature and time on esters yield at (A) 0% and (B) 100%
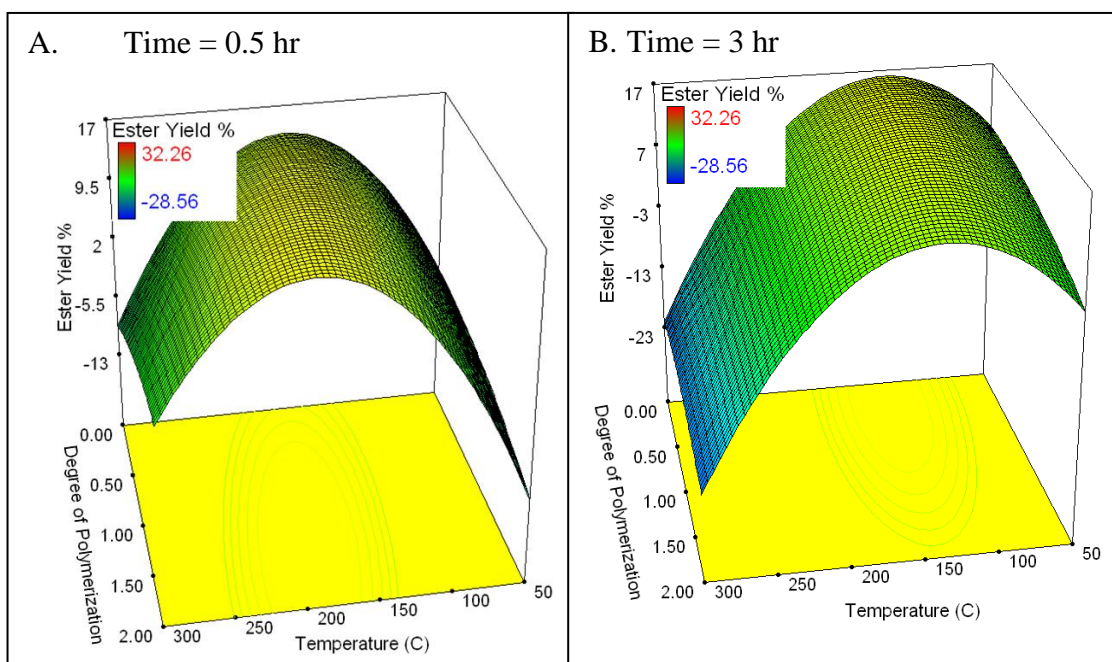
Figure 7: The effect of temperature and degree of polymerization on esters yield at (A) time =0 hr and (B) time = 3 hr

In order to determine the optimum residence time for the reaction, we did an analysis

similar to the one above, where the response of the system at 150 and 200°C was

evaluated at different degrees of polymerization and residence times. Again, referring

back to figure 5, it could be noticed that at 200°C, the highest ester yield was observed at

the shortest residence time of 0 hrs. This means that by the time the reactor reached

200°C, the maximum ester yield had already been reached. In order to further analyze

the yield behavior at these temperatures, the response of the system for varying

residence times were compared (Figure 8). In order to make the comparison easy, the

ester yields were adjusted to zero after the reaction medium reached the desired

temperature at 200 °C. The resultant maximum esters yield was 32.3 % at 150 °C after 2

hours of reaction with the monomeric catalyst. According to Figure 8, it could be noted

that most of the systems had reached equilibrium by 2 hours of reaction time.
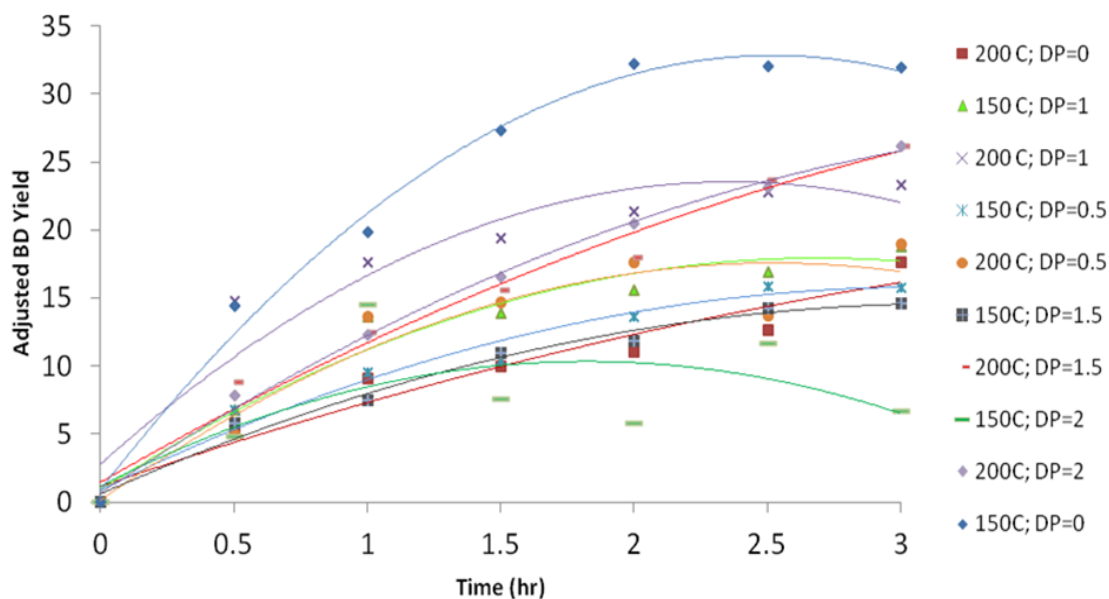
Figure 8: Time vs adjusted biodiesel yield at 150 and 200 ^{o}C, at various degree of polymerization

Subsequent to identifying the best operating temperature and residence time,

identification of the most active catalyst system was straightforward. According to

Figure 6, it could be noted that the most active catalyst was the titanium isopropoxide

monomer. The least active was TiO_2 inorganic polymer. Although statistically,

insignificant, the intermediate complexes had intermediate activity. For example, at 0.5

hr residence time, the best catalytic activity was displayed by the 1:1 dimer (Figure 8).

The only piece of literature that is available to compare these findings is on the efficacy

of titanium dioxide on transesterification.[35] They reported a yield of 79.6% with 0.3:1

moles catalyst: moles of oil even after an eight hour residence time span. Our observations suggest that although much weaker than the titanium isopropoxide counterparts, titania (TiO_2) has a respectable activity for transesterification at temperatures above 150^oC. Statistical analysis showed significant interaction between variables, temperature and degree of polymerization and also between temperature and residence time.

Specific Conclusions

This study confirms that monomeric, dimeric, trimeric, and polymeric forms of titanium propoxides and titania have significant catalytic activity toward transesterification with isopropanol. A maximum ester yield of 41.56% was observed at a reaction temperature of 200 ^{o}C after 3 hours of reaction with monomeric titanium isopropoxide. However, polymerization reached equilibrium yields after approximately two hours. It was observed that the reaction reached its optimum at temperatures between $150 - 200^o$C after 2-3 hours of reaction time. The statistical analysis concluded that only temperature and time had significant effects on ester yields. The temperature has the most profound effect. The interaction between temperature and degree of polymerization and the interaction between temperature and residence time were significant. The degree of polymerization had little effect on the reaction although it was noticed that the monomeric forms of the catalyst performed slightly better than the polymeric forms. Based on the observations, it is recommended that further experiments are needed to

elucidate the specific impacts of alkoxide groups and metals groups as well as the kinetic

effects of the reaction system.

CHAPTER III

EFFECT OF HYDROCARBON TAIL-GROUP OF TRANSITION METAL

ALKOXIDE BASED AMPHIPHILIC CATALYSTS ON TRANSESTERIFICATION[†]

Introduction

In the previous chapter, the effectiveness of titanium-isopropoxide-based monomers,

oligomers and polymers as transesterification catalysts was studied.[57] It was observed

that there was an optimal level of oligomerization that is most effective in

transesterification catalysis. The aforementioned study looked at the catalytic ability of

methoxide groups that are tethered to the Ti-O-Ti matrix of different polymeric

complexity. However, the study did not look at the behavior of such a system to alkoxide

groups with varying carbon composition. The importance of the carbon composition is

that in alcohol-in-oil systems where oil is the continuous phase, the longer the

hydrophobic tail, the better the ability of the amphiphile to stabilize an alcohol-in-oil

emulsion. The objective of this study is to fill this gap, i.e., understand the catalytic

behavior of titanium-based amphiphiles with alkoxide groups with varying carbon

numbers (in terms of length and enantiomers).

We selected transesterification reaction to test our premise due to a multitude of reasons. This reaction has gained much attention recently due to its use in the biodiesel industry.[13,14] Fatty acid methyl (or ethyl) esters, commonly known as biodiesel, are a renewable alternative fuel for compression ignition engines.[15-20] Typical raw materials used are triglycerides of either plant or animal origin and alcohols (methanol, ethanol, isopropanol).[19] The reaction is ideal since the reactants (triglyceride and alcohol) are immiscible in each other. Moreover, since the reaction has been widely studied, there is a large body of benchmark data with which to compare the effectiveness of heterogeneous amphiphilic catalysts that we are working on.

Transesterification is an acid or alkaline catalyzed reaction.[26] Due to superior activity and favorable economics, the most commonly used industrial catalysts are sodium and potassium hydroxides that are in a homogeneous phase with the reactants. However, alkaline hydroxides often produce saponifiable matter [27] which originates from the free fatty acid neutralization. The soap formation is undesirable as it partially consumes the catalyst, decreases biodiesel yield, and complicates the separation and purification steps. In addition, the removal of these homogeneous catalysts is technically difficult and adds extra cost to the final products.[28-30] Moreover, disposal of the catalyst-contaminated glycerin is increasingly becoming an environmental concern. Therefore, heterogeneous catalysis is desired to simplify separation and purification of the products. Development of a heterogeneous catalyst that also helps ameliorate transport limitations would be an added potential benefit of this study to the biodiesel industry.

Selection of titanium as the base metal and its alkoxides as the active site with amphiphilic properties was based on several reasons. Titanium based alkoxides (especially titanium isopropoxide) is a widely used reagent in sol-gel chemistry [58] and chemical vapor deposition.[58,59] As a result, the chemistry of primary alkoxides is well characterized and understood. Also, titanium-based alkoxides have already been successfully used for transesterification in a previous study.[57]

Materials and Methods

The transesterification reaction was carried out in a high pressure thermal reactor (4570-Parr instrument, Moline, IL USA.) with maximum operating temperature rating of 500 ^{o}C and pressure of 5000 Psi. The reactor was used in the batch mode. Degummed soybean oil was purchased in bulk from STE Oil Company, San Marcos, TX USA. Catalysts titanium methoxide, titanium ethoxide, titanium propoxide, titanium isopropoxide, and titanium butoxide, were purchased from Sigma-Aldrich chemical company. Titanium isobutoxide was purchased from Alfa Aesar Company. Isopropanol was purchased from EMD chemicals Inc. Propanol and butanol were purchased from Sigma-Aldrich chemical company while ethanol and methanol were purchased from VWR International LLC. Isobutanol was purchased from Alfa Aesar Company. Pure biodiesel was purchased from SoyGold (Ag environmental products, LLC, Omaha, NE USA). Hammett indicators 2, 4-dinitroaniline, 4-chloro-2-nitroaniline, 4-chloroaniline,

crystal violet, dimethyl yellow, methyl red, neutral red, Nile blue, phenolphthalein and tropaeolin were purchased from Sigma-Aldrich chemical company.

Catalyst Preparation

All the catalysts were prepared by ultrasonic mixing with respective alcohols. Titanium methoxide based oligomer catalysts were prepared using ultrasonic mixing of titanium methoxide with methanol and then, prescribed amounts of water. The sonication system (UP400S, Hielscher ultrasound technology), was capable of producing 24,000 kHz waves with a power output of 400W for this purpose.

The catalyst polymerization was kept at 1:0.5 alkoxide: water mole ratio[57] to control the degree of polymerization via water condensation. Although adding stoichiometric ratio of water to alkoxide amount, this will not guarantee the hydrolysis of half of the alkoxides.[60-64] Adding limited water will limit the hydrolysis of alkoxides which will limit the particle size. It has been reported that alkoxides with larger tail groups are slower to hydrolyze and slower to diffuse.[65-68] Because of that large tail group alkoxides tend to make smaller polymeric particles.[64] Dilution of the water and alkoxide in a solvent affect the mean particle size of the product from hydrolysis and polymerization.[69] The water needed for condensation-polymerization was first diluted in the respective alcohol prior to addition to the titanium alkoxide monomer under ultrasonication. Dilution of water in alcohol makes the water well dispersed and in turn

helps in formation of a polymer with consistent molecular size. Although the probable

end product from the hydrolysis and condensation of alkoxide are oligomers, we have

given the dimerization reaction here for basic understanding of the reaction. An example

condensation dimerization reaction for titanium isopropoxide is given in Figure 9.
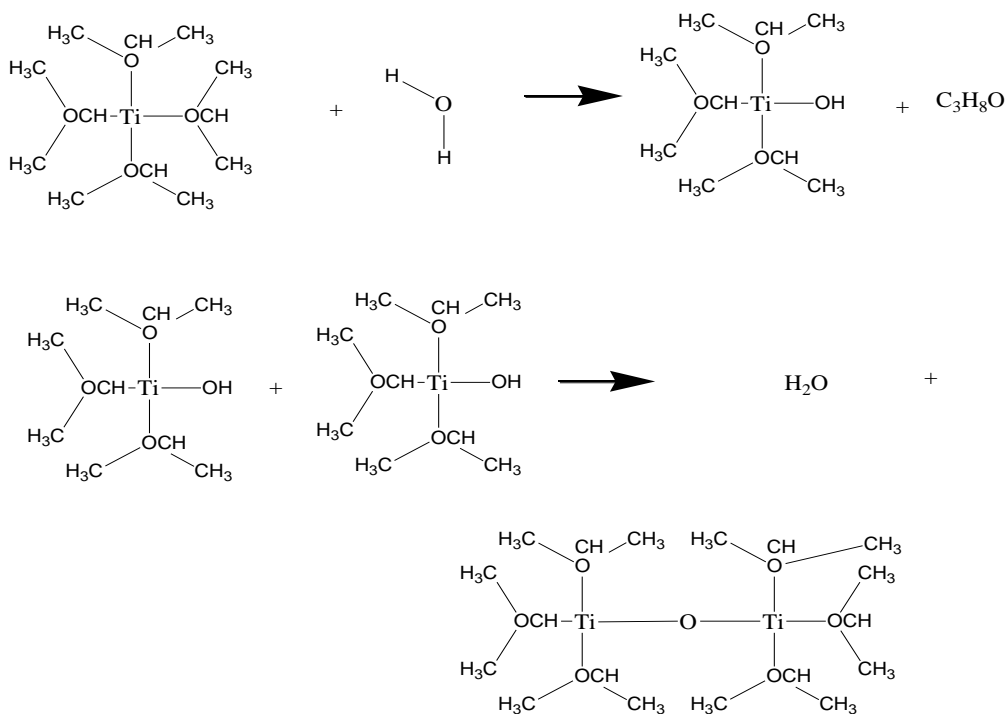
Figure 9: Hydrolysis and water condensation reactions of titanium isopropoxide

In this reaction, first, a water molecule hydrolyzes an alkoxide bond of the titanium

isopropoxide generating a hydroxyl group. Two such molecules having orthogonal

hydroxyl groups react to give -Ti-O-Ti- via water condensation. The degree of

polymerization of other metal alkoxides can be controlled by changing the

alkoxide:water ratios in a similar fashion. The starting monomers and resulting

oligomers are given in Table 3.

Table 3 Molecular configurations of the oligomers resulting from water condensation

Monomer	Resulting oligomer
Titanium methoxide	
Titanium ethoxide	
Titanium n-propoxide	
Titanium iso-propoxide	
Titanium n-butoxide	
Titanium iso-butoxide	

The transesterification reactions were carried out in a high pressure reactor with a vessel of 500 ml. The pressure reactor had a magnetic drive stirrer with maximum speed of 2000 rpm and a tachometer module with accuracy $\pm$ 10 rpm. In order to initiate the transesterification reaction, 1% (w/w) of the catalyst was infused into the reaction chamber containing triglyceride, immediately after the contents reached the designated temperature (200 ^{o}C) through a high pressure liquid pump (Eldex 5790, Eldex laboratories Inc. Napa, CA). It was noticed that when the reactor reached 200 ^{o}C, the pressure increased up to 10 psi. Samples were drawn from the reactor at 30-minute intervals up to 3 hours. The samples drawn were cooled immediately to cease the reaction from progressing further. Then, the samples were centrifuged at 10,000 RPM and 12 ^{o}C to separate products (alkyl esters and glycerol) and catalyst. The centrifuge system used (Sorvall Legend 23 R- Thermo Scientific) had a maximum rated speed of 24,000 rpm and minimum temperature of (-) 4 ^{o}C.

The top fraction of the products was analyzed for esters using gas chromatography (GC-6850 Agilent Technologies, Santa Clara, CA USA). Auxiliary analyses for confirmation of the products were carried out via GC Mass spectroscopy (GC-MS 7890 Agilent Technologies, Santa Clara, CA USA).

The gas chromatograph was calibrated with the respective alkyl ester standards each time prior to obtaining quantitative yields. Alkyl ester standards (pertinent to methyl,

ethyl, propyl, isopropyl, butyl, and isobutyl esters of C 16:0, 18:0, 18:1, 18:2, 18:3 fatty acid alkyl esters) were purchased from Nu-Chek Prep Inc.(Elysian MN 56028, USA). The GC method utilized (for isopropyl esters) detection is as described in chapter 2. The fatty acid alkyl esters yield was calculated by Chemstation software (Agilent technologies). An internal standard method was used to analyze the ester yields. The area under the peak from the FID chromatogram corresponded to the concentration of that component. These concentrations were determined using calibrations with pure ester standards along with an internal standard (C-12 ester). The results were statistically analyzed by Design Expert software.

Catalyst Characterization

The basic strength of the catalyst was determined by the Hammett indicator method.[70] The Hammett indicator method is used to determine qualitative information of the basic properties of solid catalysts. The Hammett indicator method is a fast and straightforward method to analyze the basicity and acidity of a catalyst. This method is only accurate for qualitative analysis because of potential issues associated with indicator molecules diffusing into the micropores.[70,71] Nevertheless, the basicities obtained using the Hammett indicator method are in good agreement with the catalytic findings.

About 10 ml of sample containing catalyst was shaken with 5 drops of Hammett indicator in methanol solution and left to equilibrate for 3 h. In the Hammett indicator

method, the base strength is quoted as being stronger than the weakest indicator which exhibits a color change, but weaker than the strongest indicator that produces no color change.[70,71] In these experiments, the following basic Hammett indicators were used: Neutral red (pKa value, 6.8), Methyl red (pKa value) 4.8), P-dimethylaminoazobenzene (pKa value) 3.3), and Crystal violet (pKa value) 0.8). The acidic Hammett indicators (for base site strength) used were Phenolphthalein (pKBH+ value) 8.2), Nile blue (pKBH+ value) 10.1), Tropaeolin (pKBH+ value) 11), 2,4-dinitroaniline (pKBH+ value) 15), 4-chloro-2-nitroaniline (pKBH+ value) 18.2), and 4-chloroaniline (pKBH+ value) 26.5). To measure the basicity of the catalysts, the method of Hammett indicator– benzene carboxylic acid (0.02 mol/L anhydrous methanol solution) titration was used [20–22].

Results and Discussion

The primary goal of this study was to understand the link behind the emulsifying ability of a molecule and its catalytic properties. Although this experiment did not measure the emulsification ability of the selected catalysts, it is an established fact that molecules having longer hydrophobic tails (with a hydrophilic head) will have better emulsifying ability in water-in-oil emulsions.[72] Analogously, it was conjectured that the catalysts with longer tail-groups will have better emulsifying abilities in alcohol-in-oil emulsions. The catalytic behavior of the selected amphiphiles is analyzed below with this premise in mind.

Figure 10 shows the respective ester yields with tail groups of increasing carbon numbers. The selected cubic model response surface indicates that, irrespective of time in reaction, ester yields tend to decrease with increasing carbon number on the tail. The maximum reported ester yield was 64.25 % and this was when titanium methoxide was used as the catalyst.
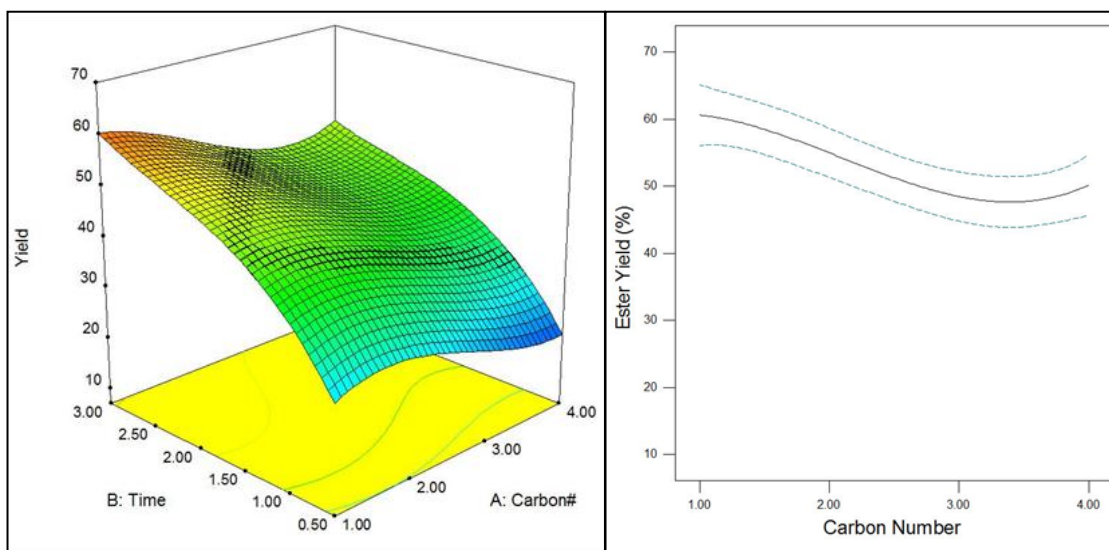
Figure 10: Ester yield variation with respect to amphiphiles with different carbon

The reason for smaller alcohols to display significantly higher catalytic ability may be due to favorable mass transport properties that smaller molecules have as compared to larger counterparts. Smaller methoxide molecules may be more mobile between phases assisting catalysis within the L/L/S system. The ester yields increased with increased

reaction time. The statistical analysis points out that although the two factors (time and carbon number) were significant, their interaction wasn't significant.

The right side graph of figure 10 depicts ester yield at 3 hrs along (with the (+/-) standard deviations lines) vs. the carbon number. It is interesting to note that a clear increase in esters yield is observable when butoxide is used instead of the shorter form, propoxide. The likely scenario in this instance would be the further reduction of transport limitations of the alcohol/oil system resulting from the increase of hydrophobicity of the alcohol. In such an instance, all three components (i.e., alcohol, oil and the catalyst) would be substantially hydrophobic. Alternatively, the alkyl groups in simple alcohols may not be large enough to generate such hydrophobicity.

Figure 11 depicts the yield differentiation between isomers with longer tail groups (propoxide and butoxide). In this case, the objective is to discern the catalytic variations of alkoxides due to linear and branched tail groups. Titanium isopropoxide and titanium isobutoxide were used against titanium propoxide and titanium butoxide to analyze the stereo-effects.
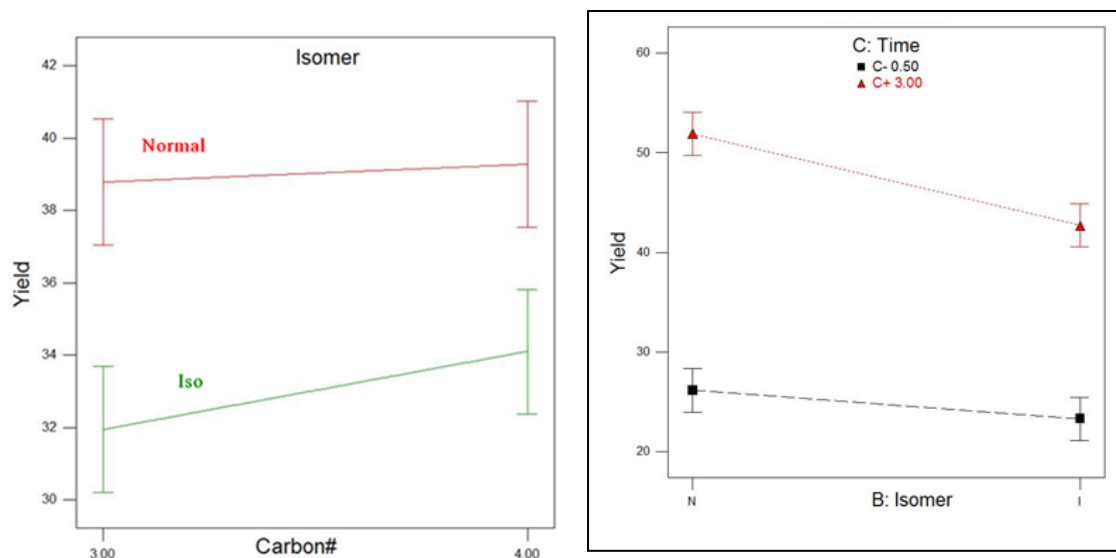
Figure 11: Ester yield with respect to different isomer type (for carbon numbers 3 and 4 only)

Figure 11 (left) shows how the carbon number affects the ester yields. The analysis depicts that the ester yields do not differ significantly between propoxide and butoxide From figure 11, clear yield increase is present when going from 3C to 4C alkoxides. However, the normal and iso forms significantly affect the ester yields.

According to Figure 11 (right), it is observed that the ester yields do not depend on the type of isomer at initial stage of the reaction. However, as time pass by, the normal alkoxides display greater activity than the iso-forms. The likely reason for this is the steric hindrance.

Catalyst basicity using Hammett Indicator method is depicted in Table 4. Based on the observations, the smaller forms, titanium methoxide and titanium ethoxide, had a pKa

value of 11.2 while the lager forms, titanium butoxide and titanium propoxide, had a

pKa value of 10.1. The basicity analysis indicates that the alkoxides with higher basicity

resulted in greater ester yields indicating that the shorter forms are more prone to

ionization in the medium as compared to the more bulky alkoxides. Since there was no

significant color change between iso and normal alkoxides, it was conjectured that these

forms had the same basicity.

Table 4 Acidity/basicity of oligomerized alkoxide catalysts

Catalyst	pKa value (Hammett Indicator Method)
Titanium methoxide oligomer	11.2
Titanium ethoxide oligomer	11.2
Titanium propoxide oligomer	10.1
Titanium isopropoxide oligomer	10.1
Titanium butoxide oligomer	10.1
Titanium isobutoxide oligomer	10.1

Based on above observations, the transesterification reaction mechanism given in

Scheme 1 is initially proposed.[73]

Scheme 1 Mechanism for metal alkoxide transesterification of soybean
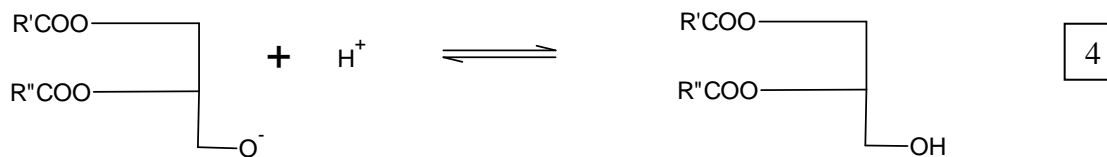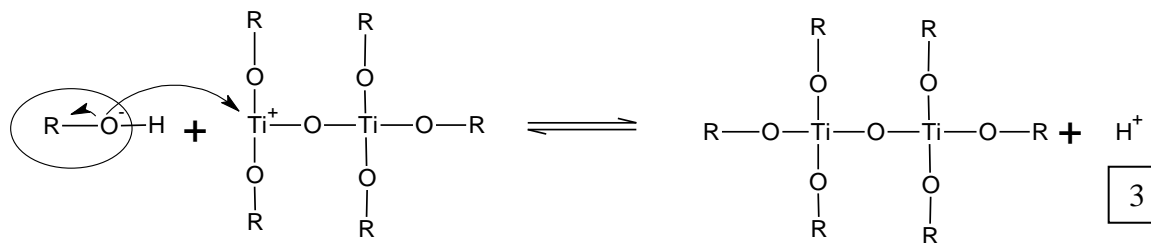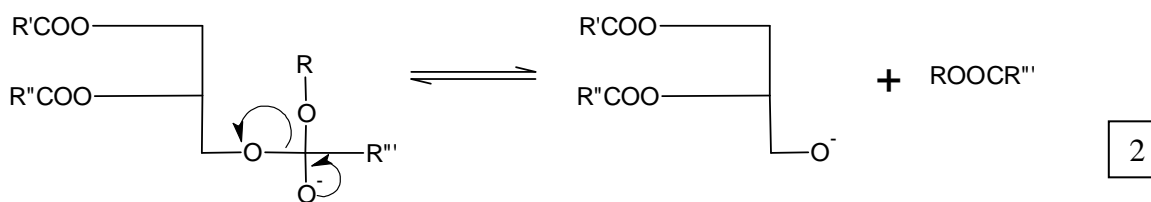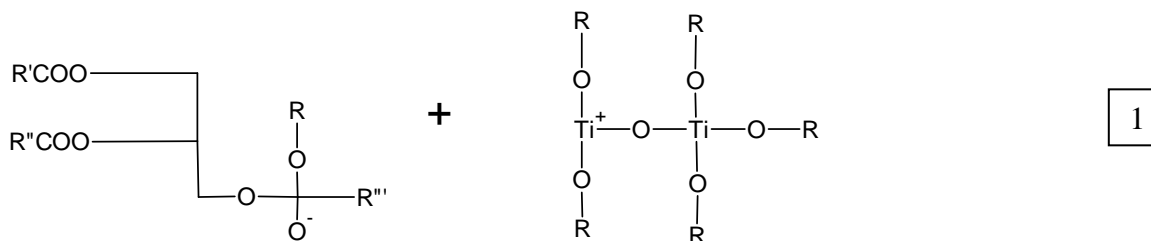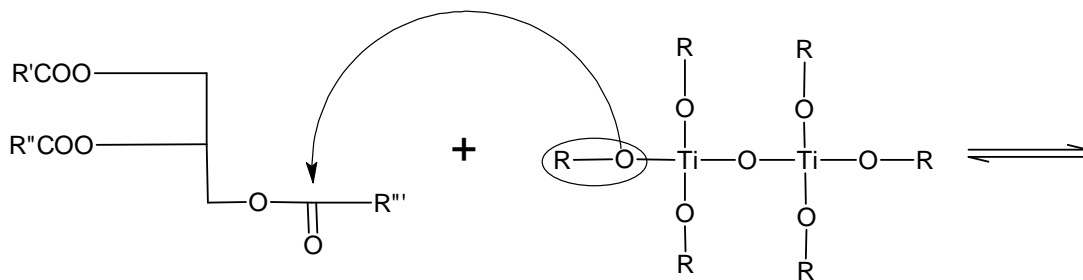
In the first step, titanium alkoxide will initiate the reaction by nucleophilic attack on a carbonyl group in the triglyceride (Eq. 1). This will create a positively charged catalyst and an intermediate (tetrahedral) which will produce a fatty acid alkyl ester and a diglyceride neucleophile (Eq. 2). The now electrophilic titanium catalyst will attack the respective alcohol with the alcohol getting deprotonated (Eq. 3). This will create an extra proton which will terminate the reaction by producing a molecule of diglyceride (Eq. 4). The reaction continues until glycerol and three molecules of fatty acid alkyl esters are produced. This scheme is proposed based on Bronsted basicity that the titanium alkoxides displayed (similar to main group metal alkoxides [73]) in which alkoxides of the outer-sphere migrate and attack the ester bond of the triglyceride.

However, another possibility is that the transesterification is a concerted process occurring at the Ti center. In this premise, there is no migration of the alkoxide group from the titanium to the ester resulting in a coordinately unsaturated titanium cation and an organic anion such as is shown in reaction 1 under scheme 1. It is likely that both of those species are thermodynamically unstable and would not form as discrete species in solution. Ti(IV) is a high valent metal and, as such, is a strong Lewis acid with vacant d orbitals to accommodate the lone pair from the ester (triglyceride). In this case, the triglyceride ester coordinates directly with the Ti and group migration occurs concertedly at the metal center, ultimately eliminating the new ester. This premise is proposed since there is never a time when any of the ionic species shown in the mechanistic scheme would exist in solution. Accordingly, the reaction mechanism in Scheme 2 is proposed.

Scheme 2 Mechanism for metal alkoxide transesterification of soybean
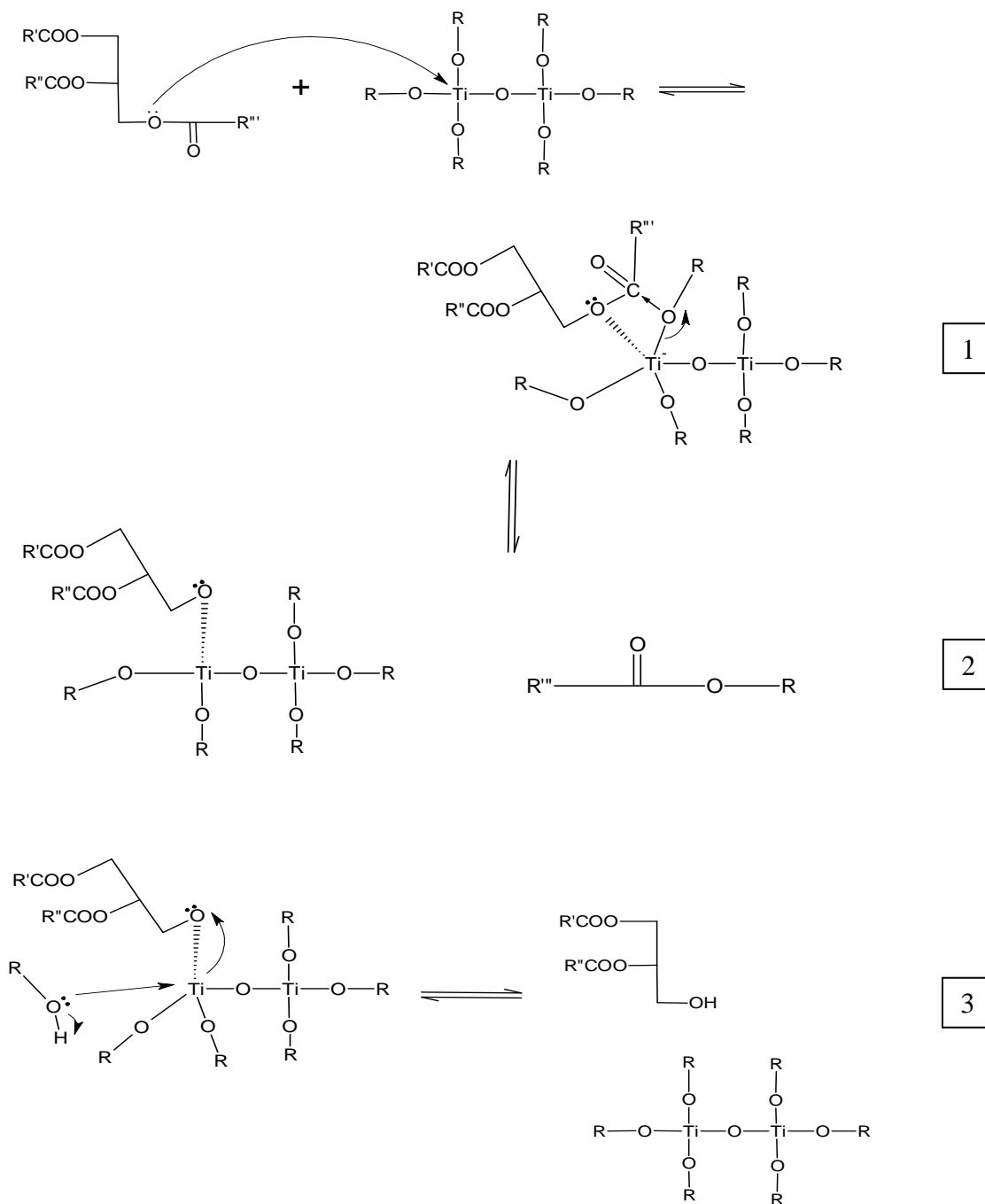
In the first step, titanium alkoxide will initiate the reaction by nucleophilic attack on carbonyl group in the triglyceride (Eq. 1). Here Titanium isopropoxide acts as a Lewis acid, and the non bonding electrons on the alkoxide oxygen forms coordinate bond with empty d orbitals on the metal[74]. This will create a coordinated intermediate (tetrahedral) which will produce alkyl ester and diglyceride neucleophile (Eq. 2). Then electrophilic titanium catalyst will get attacked by the respective alcohol while the alcohol getting deprotonated (Eq. 3). The reaction continues until glycerol and three molecules of fatty acid alkyl esters are produced.[74]

Mechanism proposed in Scheme 2 also gives a clue as to why the smaller Ti alkoxides are more reactive. It is likely that the sterically smaller alkoxides allow the ester to coordinate more easily to the metal. They also provide a much smaller barrier to group migration around the metal to achieve transesterification.

Specific Conclusions

This study looked at the catalytic behavior of oligomerized alkoxides with varying carbon numbers. The study confirmed that the number of carbons in alkoxides and their steric effects significantly affect the ester yields in transesterification. The maximum ester yield (64.25 %) obtained was with oligomerized titanium methoxide catalyst after 3 hours of reaction. Although the temperature and the number of carbon in the tail group significantly affected the ester yields, a statistically significant correlation was not

present (the two parameters affected ester yields independently). It was clear that the alkoxides with a smaller carbon numbers had a higher ester yields towards transesterification. It appears that the sterically smaller alkoxides allow the ester to coordinate more easily to the metal. They also provided a much smaller barrier to group migration around the metal to achieve transesterification. An interesting observation was the slight increase of esters yield when butoxides were used as the catalyst as opposed to propoxides. This behavior was attributed to overall increase of the hydrophobicity of the three-component system.

CHAPTER IV

EFFECT OF METAL GROUPS OF ALKOXIDE BASED CATALYSTS ON TRANSESTERIFICATION[‡]

Introduction

In a previous study, the effectiveness of titanium isopropoxide based monomers, oligomers and polymers as transesterification catalysts was studied.[57] It was observed that there was an optimal level of oligomerization that is most effective for transesterification catalysis. The aforementioned study looked at the catalytic ability of methoxide groups that are tethered to the Ti-O-Ti matrix of different polymeric complexity. In a follow-up study, we looked at how varying hydrocarbon tail groups affect the ester yields.[75] In that study it was evident that shorter carbon chains favored ester yields. A parallel need is to understand the effect of different metal ions on transesterification catalysis since the metal ion can alter the electronics and thus the acidity or basicity of the organometallic alkoxide. Accordingly, in this study we looked at the effect of eight different transition metals (Titanium, Iron, Chromium, zirconium, yttrium, nickel, lanthanum, lithium)alkoxides on their catalytic ability toward transesterification.

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Materials and Methods

The transesterification reaction was carried out in a high pressure thermal reactor (4570-Parr instrument, Moline, IL USA.) a with maximum operating temperature rating of $500^{\circ}C$ and pressure of 5000 psi. The reactor consisted of a 500 ml vessel fitted with a magnetic drive stirrer having a maximum speed of 2000 rpm and a tachometer module with an accuracy $\pm$ 10 rpm. The reactor was used in the batch mode. Degummed soybean oil was purchased in bulk from STE Oil Company, San Marcos, TX USA. The typical fatty acid profile of soybean oil is: C16:0-11%, C18:0-4%, C18:1-23%, C18:2-54% and C18:3-8%.[76]

Isopropoxide was selected as the alkoxide group due to the wide availability of metal alkoxides in this form (as opposed to methoxides or ethoxides). Isopropoxides of nickel, iron, lanthanum, chromium, yttrium, and zirconium were purchased from Chemat Technology Inc. Titanium, sodium isopropoxide and sodium methoxide were purchased from Sigma-Aldrich Corp. Isopropanol and methanol were purchased from EMD chemicals Inc. Pure biodiesel was purchased from SoyGold (Ag environmental products, LLC, Omaha, NE USA).

Catalyst Preparation

All the catalysts were prepared by ultrasonic mixing with respective alcohols. Isopropoxides were diluted in isopropanol while methoxides were diluted in methanol. The sonication system (UP400S, Hielscher ultrasound technology) was capable of producing 24,000 kHz waves with a power output of 400W for this purpose. As different metal alkoxides have different numbers of alkoxide groups, monomers were chosen to ensure homogeneity. Catalysts were prepared according to previously developed methods[75]. Here it should be noted that not all the metal isopropoxides dissolved in isopropanol. In all cases, fine powder forms of metal alkoxides were used for the reaction and when not dissolved, a suspension of metal alkoxide in isopropanol was used. Titanium, iron, zirconium, yttrium, and sodium isopropoxides dissolved in isopropanol while nickel, chromium, and lanthanum isopropoxides didn't.

Transesterification

The transesterification reactions were carried out in the aforementioned high pressure reactor. In order to initiate the transesterification reaction, 1% (w/w) of the catalyst was infused into the reaction chamber containing triglyceride immediately after the contents reached the designated temperature (200 ^{o}C) through a high pressure liquid pump (Eldex 5790, Eldex laboratories Inc. Napa, CA). It was noticed that when the reactor reached 200°C, the pressure increased up to 10 psi. An alcohol to oil ratio of 3:1 (molar basis)

was used for the transesterification reaction. Isopropanol was used as the esterification reagent for all of the reactions with isopropoxide catalysts. Methanol was used as the esterification alcohol when sodium methoxide was used as the catalyst. Samples were drawn from the reactor at 30-minute intervals up to 3 hours. The samples drawn were cooled immediately in order to cease the reaction from progressing further. Then, the samples were centrifuged at 10,000 RPM and 12 ^{o}C to separate products (alkyl esters and glycerol) and the catalyst. The centrifuge system used (Sorvall Legend 23 R-Thermo Scientific) had maximum rated speed of 24,000 rpm and minimum temperature of - 4 ^{o}C.

The top fraction of the products was analyzed for esters using gas chromatography (GC-6850 Agilent Technologies, Santa Clara, CA USA). Auxiliary analyses for confirmation of the products were carried out via GC Mass spectroscopy (GC-MS 7890 Agilent Technologies, Santa Clara, CA USA). The gas chromatograph was calibrated with the respective alkyl ester standards each time prior to obtaining quantitative yields. Alkyl ester standards (pertinent to methyl and isopropyl, esters of C 16:0, 18:0, 18:1, 18:2, 18:3 fatty acid alkyl esters) were purchased from Nu-Chek Prep Inc.(Elysian MN 56028, USA).

The GC method utilized (for isopropyl esters) detection is as described in chapter 2. The amount of fatty acid alkyl esters yield was calculated via Chemstation software (Agilent technologies). The area under the peak from the FID chromatogram corresponded to the

concentration of that component. These concentrations were determined using calibrations with pure ester standards along with an internal standard (C-12 ester).

Catalyst Selectivity

There are many definitions for calculating selectivity in literature. IUPAC defines selectivity in two ways: 1) the discrimination shown by a given reactant A when it reacts with two alternative reactants B and C, or in two different ways (e.g. at two different sites) with a reactant B and 2) the ratio of products obtained from given reactants. In the context of this work, the following formula was used: [77]

$$Product\ Selectivity = \frac{Moles\ of\ a\ product\ component}{Total\ moles\ of\ product} \times 100\%$$

The results were statistically analyzed by Design Expert software.

Catalyst Characterization

The acidity and basicity of each catalyst was determined by the Hammett indicator method[70]. The Hammett indicator method is a fast and widely accepted method for determining the basicity and acidity of solid catalysts. However, it should be noted that this method is only accurate for qualitative analysis due to the potential issues associated with indicator molecules diffusing into the micropores when present.[70,71]

About 1-2 ml of sample containing the catalyst was shaken with 5 drops of Hammett indicator in isopropanol solution and left to equilibrate for 3 h. In the Hammett indicator method, the base strength is quoted as being stronger than the weakest indicator which exhibits a color change, but weaker than the strongest indicator that produces no color change.[70,71] In these experiments, the following Hammett indicators were used: Neutral red (pKa value 6.8), Methyl red (pKa value 4.8), P-dimethylaminoazobenzene (pKa value 3.3), Crystal violet (pKa value 0.8), Phenolphthalein (pKBH+ value 8.2), Nile blue (pKBH+ value 10.1), Tropaeolin (pKBH+ value 11) and 2,4-dinitroaniline (pKBH+ value 15). All the indicators were purchased from Sigma-Aldrich Co. LLC.

Results and Discussion

Experiments were carried out in two stages. During the first stage, the ester yields were evaluated using select transition metal alkoxides as catalysts. Then, the ester yields were normalized according to the number of alkoxide ligands bound to the metal. By doing this, it is possible to eliminate the yield differences due to variable numbers of alkoxide active sites. This also would help compare results of this work with other work that has been done in this area with other metal alkoxides.[74,78] It should be noted that the effect of thermal reactions (not-catalytic reaction due to high temperature) was studied previously and it was observed that no significant transesterification occurred during the time span of 3 hours without any catalyst at 200 $^{\circ}$C.[75]

Figure 13 depicts the ester yields of various metal isopropoxides with time. It was

observed that titanium and yttrium isopropoxide showed almost similar ester yields after

3 hours. However, titanium demonstrated a faster reaction rate at the beginning (while

the rate diminished toward to end of the reaction period). Yttrium, on the other hand, had

the same rate throughout the reaction period.
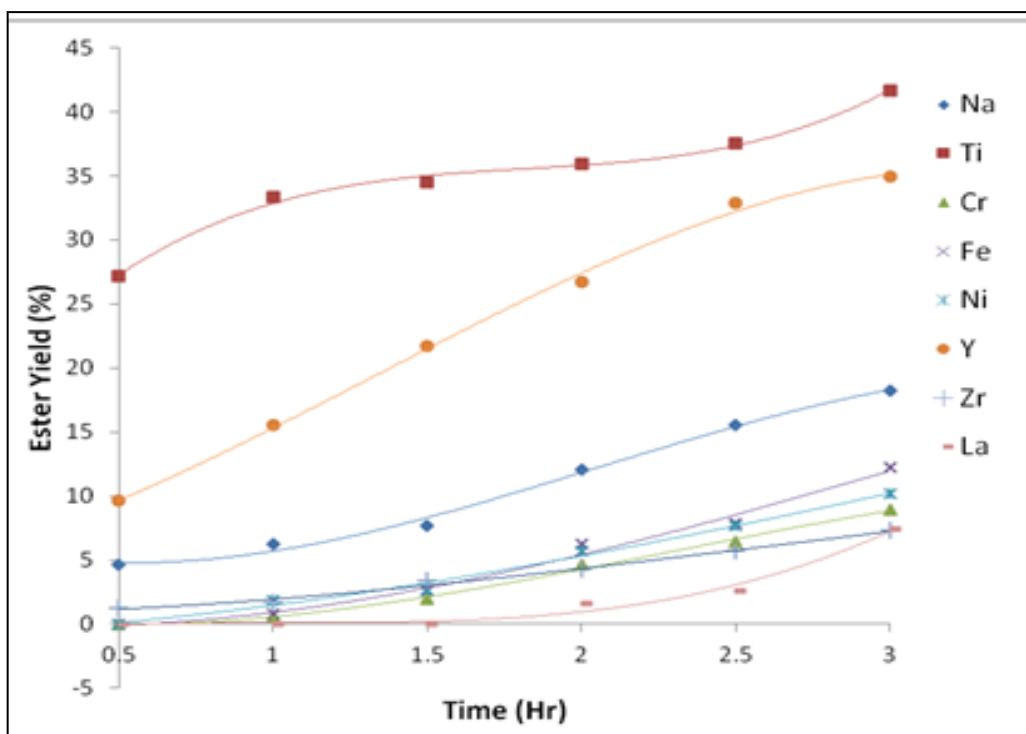
Figure 12: Ester yields with respect to time for alkoxide catalysts with different metal groups.

Na isopropoxide was used as the control to compare the performance of other

isopropoxides since alkaline metal alkoxides are the most widely used catalyst for

transesterification.[15,16] It is interesting to observe that Ti (42%) and Y isopropoxides

(35%) yielded higher amounts of esters as compared to Na (18%). The ANOVA table

for yield is shown in table 5. Statistical analysis indicates that the effect of time and

metal head group are significant. The analysis depicts that the ester yields for Cr, Fe, La,

Zr, Ni isopropoxides are not significantly different after three hrs. Also none of the

above isopropoxides displayed comparable ester yields to Ti or Y.

Table 5 ANOVA table for yield analysis with different metal alkoxides

ANOVA for Response Surface Reduced Cubic Model
Analysis of variance table [Classical sum of squares - Type II]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	13500.97	23	587.00	417.64	< 0.0001	significant
A-Head Group	11405.18	7	1629.31	1159.22	< 0.0001	
B-Time	1679.65	1	1679.65	1195.04	< 0.0001	
AB	376.90	7	53.84	38.31	< 0.0001	
B^2	6.40	1	6.40	4.55	0.0366	
AB^2	32.85	7	4.69	3.34	0.0042	
Residual	92.76	66	1.41			
Lack of Fit	32.35	24	1.35	0.94	0.5576	not significant
Pure Error	60.42	42	1.44			
Cor Total	13593.73	89				

The ester yields depicted in figure 12 are based on identical weights of catalyst. It should

be noted that the catalyzing reaction can take place at the Ti center (where Ti acts as a

Lewis acid) or at the alkoxide center (where the alkoxide acts as a Bronstead base,

depending on the metal used).[75] Presuming that the basic reaction is more dominant, the

yield variability may be as a result of the varying number of alkoxide ligands and not

due to the nuances of the metal center. To correct this situation we have normalized the

yields per moles of ligand group attached. For example titanium isopropoxide has 4

alkoxide ligands attached to the titanium center while nickel has only two. In order to

rectify this discrepancy, the ester yields per alkoxide branch were calculated (figure 13).

For this calculation we have based the yields of all alkoxides with respect to the one that

gave the highest ester yield (assigning it a 100% activity) per mole of active branches in

the reaction.
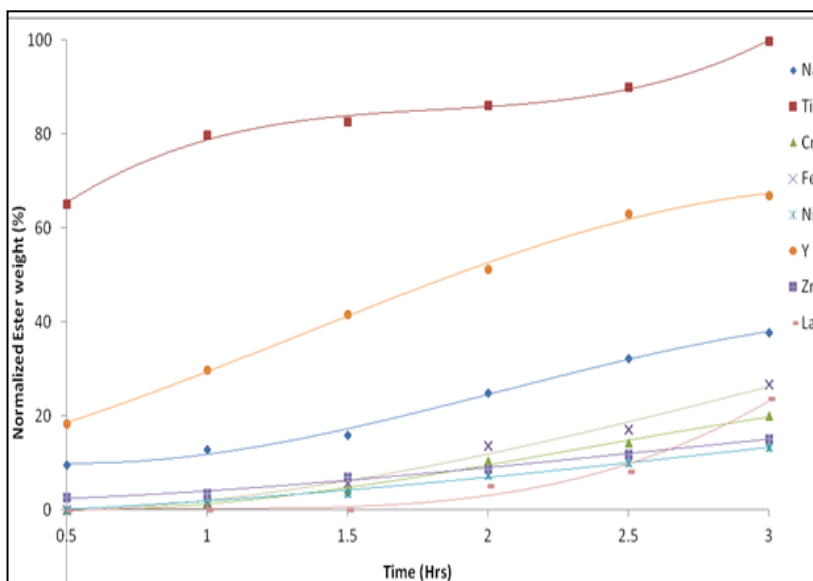
Figure 13: Normalized ester weight (%) with respect to the heights ester yield and number of active ligands.

It is evident that even after normalizing for the number of active sites, titanium based

catalyst renders the highest ester yield per mole of active branch. Nevertheless, only

titanium and yttrium resulted in significant ester yields. It is important to note that the

performance of sodium isopropoxide was still much inferior to that of titanium and

yttrium counterparts. The graph to the right compares the ester yields per ligand after during 3 h of reaction time. It is clear that in the early stages of reaction, titanium results in much higher ester yields as compared to yttrium and sodium.

It is important to compare the transition metal alkoxide catalytic activity to alkali metal catalytic activity since alkali metals are the most widely used in industry. Sodium and potassium alkoxides are the most prevalent catalysts for transesterification in the biodiesel industry.[15] Accordingly, the transesterification ability of sodium isopropoxide was compared to that of sodium methoxide (Figure 14). It is clear that the catalytic ability of sodium methoxide is far superior to that of the sodium isopropoxide. Sodium methoxide had a maximum ester yield of 83% after 30 min of reaction. This yield is several fold higher than the isopropoxide counterpart which yielded less than 20% esters even after 3 hours of reaction. In alkali metal alkoxide homologous series, molecular complexity increases with increasing carbon number in the alkoxide. Thus, there is higher covalence between metal and the oxygen atom for higher carbon alkoxide groups. This makes it harder for the higher carbon numbered alkoxide to participate in branch confirmation reactions. However it should be noted that alkali metal methoxides are metastable compounds compared to alkali metal isopropoxides. Therefore polymerizing to its oxide form is less favorable in methoxide than isopropoxide.[79] Accordingly, methoxides (to a large extent) would stay in solution as a homogenous catalyst while propoxides will oligomerize and eventually polymerize becoming a solid (heterogeneous catalyst). It is interesting to note that titanium methoxide, resulted in an ester yield of

64% after 3 hours of reaction. The titanium methoxide data were collected in a previous study.[75] The analysis suggests that the activity of titanium methoxide as a transesterification catalyst is not far from that of the sodium counterpart.
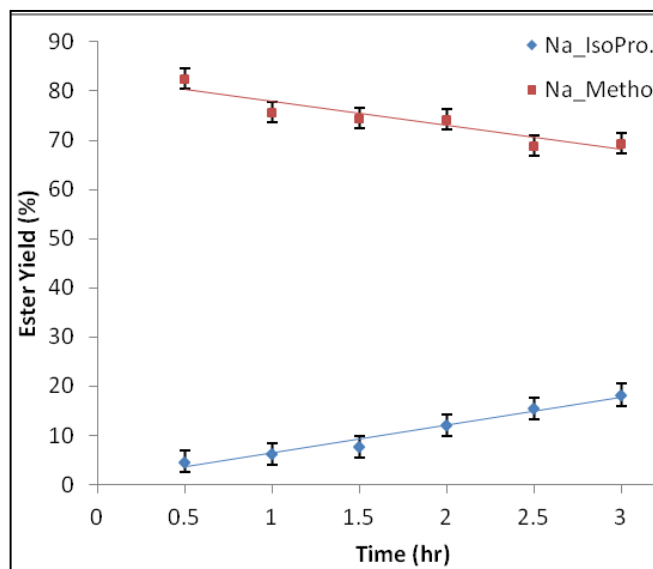
Figure 14: Ester yields sodium isopropoxide and sodium methoxide

Although sodium methoxide caused a reduction of ester yields with time, the yields are much higher compared to those of sodium isopropoxide. A possible explanation for low ester yields when using sodium methoxide in this experiment (although sodium methoxide is the most active catalyst for transesterification) is thermal degradation of produced esters. Results suggest that transesterification reaction occurs at a fast rate during the first 30 minutes of reaction time (our first sample was drawn after only 30 min). However, results from Figure 14 indicate that after three hours of reaction, the yields have decreased (when sodium methoxide was used as the catalyst). It is likely that

when sodium methoxide was used at $200^{o}C$, the yield of transesterification products peaked before 30 min.

The selectivities of selected catalysts towards different fatty acid components are shown in figure 15. It is evident that all three catalysts, sodium , titanium and yttrium isopropoxides had very comparable selectivities toward fatty acids (with only subtle nuances between the catalysts). At the onset of the reaction, the selectivity for stearate and linolinate was zero for all the catalysts (depicting that the product spectrum had only C16:0, C18:1 and C18:2 fatty acids). Ti was more selective for C18:1 fatty acids, compared to Na and Y. Sodium, on the other hand, had higher selectivity towards C18:2 linoleate ester (63%) at the beginning of the reaction.

At the end of three hours, stearate and linolinate esters also appeared in the product mix. At this point, titanium had higher selectivity for all the major fatty acids except C18:2 linoleate ester. It was noted that ester composition of triglycerides closely followed the selectivity numbers. Literature suggest that, fatty acids C16-12%, C18- 5%, C18:1- 25%, C18:2- 52%, C18:3- 6% by weight in soybean oil. The overall conclusion subsequent to the statistical analysis is that after three hours of reaction time, all the three catalysts are equally selective for component fatty acid hydrolysis.
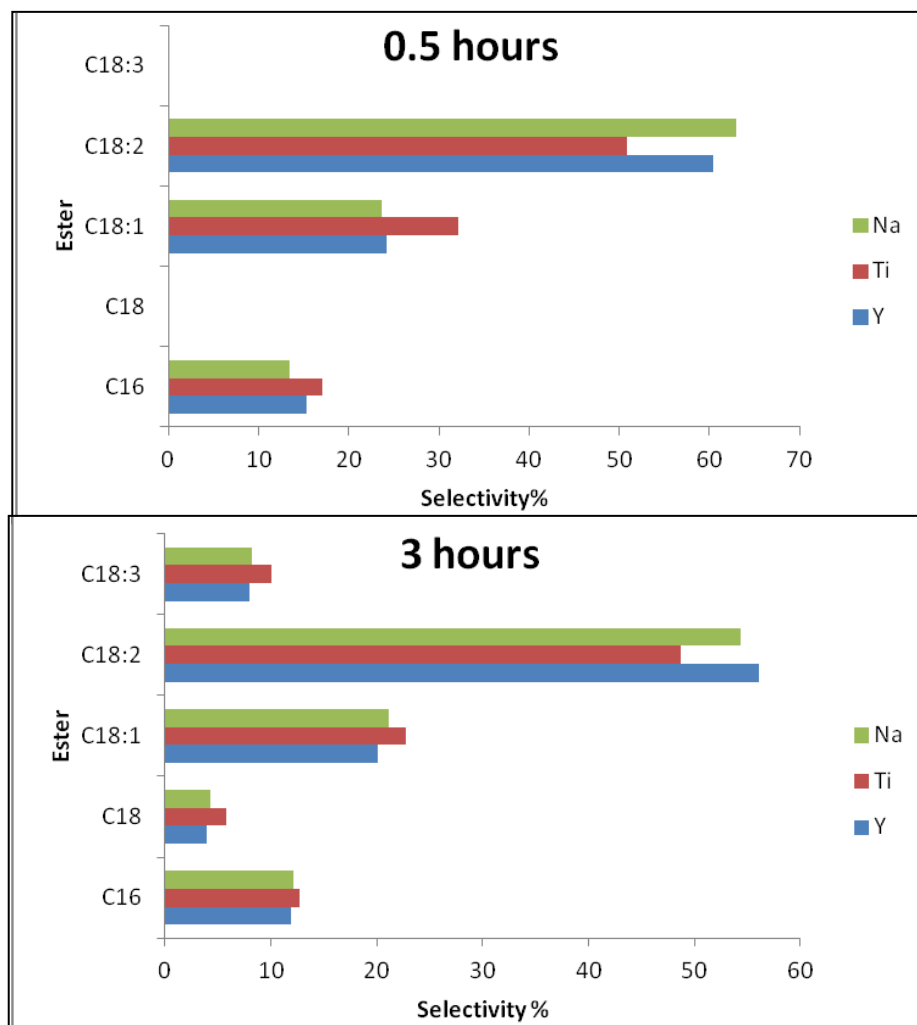
Figure 15: Product selectivity for different head group metals with respect to time

An interesting observation was that although all metal isopropoxides were homogeneous with the reaction medium at the onset of the reaction, most transition metal isopropoxides were separable as a heterogeneous product subsequent to the reaction. Figure 16 depicts that alkali metal catalyst cannot be separated (or visible) after vigorous centrifugation of the content. Nevertheless, most transition metal catalysts were able to

be separated from esters and glycerol. The transition metal alkoxides likely polymerized

via alcohol condensation at higher temperature.[11,58,59,72,80] This suggests that the

transition metal alkoxides also went through a concurrent polymerization reaction while

participating in the transesterification catalysis reaction. The fortuitous outcome is a

fully separable heterogeneous catalyst from the reaction medium subsequent to the

reaction. These observations are in line with findings from our previous studies that

partially polymerized transition metal alkoxides act as transesterification catalysts.[57,75]
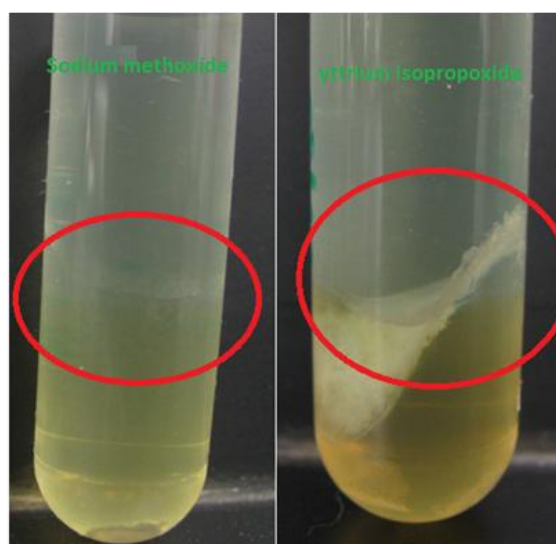
Figure 16: Transesterification products after centrifugation – homogeneous alkali metal alkoxide catalyst (left) and heterogeneous transition metal alkoxide catalyst (right)

The studies also suggest that the early transition metals are significantly more

catalytically active towards transesterification than the others tested. It is evident that

metal alkoxides in group III and IV in *d*-bock (transition periods) rendered the highest

transesterification yields. The reasons for this could be several-fold. At the beginning of the reaction, it is likely that all metal alkoxides would be in their monomeric (or the thermodynamically most stable forms). The group IVB metals possess the highest number of carbonyl ligands coordinated around the metal center. This translates to a higher number of catalytic active sites per mole participating the reaction and thus higher ester yields when compared to other metals in the same period.

However, as the transesterification reaction progresses, it is evident that the alkoxides oligomerize either via alcohol condensation or water condensation routes. It should be noted that all the metal alkoxides oligomerize even with traces of water present - and when they do oligomerize forming meta-loxo-alkoxides, the ligands arrange according to least complex formation. The main principle is that metal atoms attempt to achieve the highest coordination with the lowest possible molecular complexity.[81] Accordingly, when comparing the transition metal alkoxide homologs along the transition metal series, oligomerized Ti-oxoalkoxides would have the highest number of alkoxide ligands attached per metal center. This explains the significantly high activity of early transition metals (Ti and Y). Interestingly, zirconium, though an early transition metal did not perform as well as Ti. This could be due to the fact that all reactions with metal alkoxides depend on the electronegativity of the metal atom which decreases moving down a group.

It should be noted here that the heterogeneous forms of all the isopropoxides tested can be relatively easily transformed chemically to their original monomeric forms for reuse.[79] Regeneration can be achieved by chemically or thermally converting polymerized metal alkoxides in to monomers. More details about regeneration will be discussed in the last chapter.

Catalyst Characterization

The catalyst basicity matrix, using the Hammett Indicator method is depicted in Figure 17. It is important to notice that not all the metal alkoxides are basic. For example zirconium isopropoxide is strongly acidic. However, zirconium showed very low conversion throughout the experiment. Titanium and yttrium are highly basic metal alkoxides which gave high ester yields. Table 6 indicates the conjugate-base basicity of different metal alkoxides used in this experiment. It is clear from the analysis that Lithium isopropoxide which is an alkali metal alkoxide is strongly basic. It is evident that catalysts that showed strong basicity favored transesterification as opposed to the acidic counterparts.
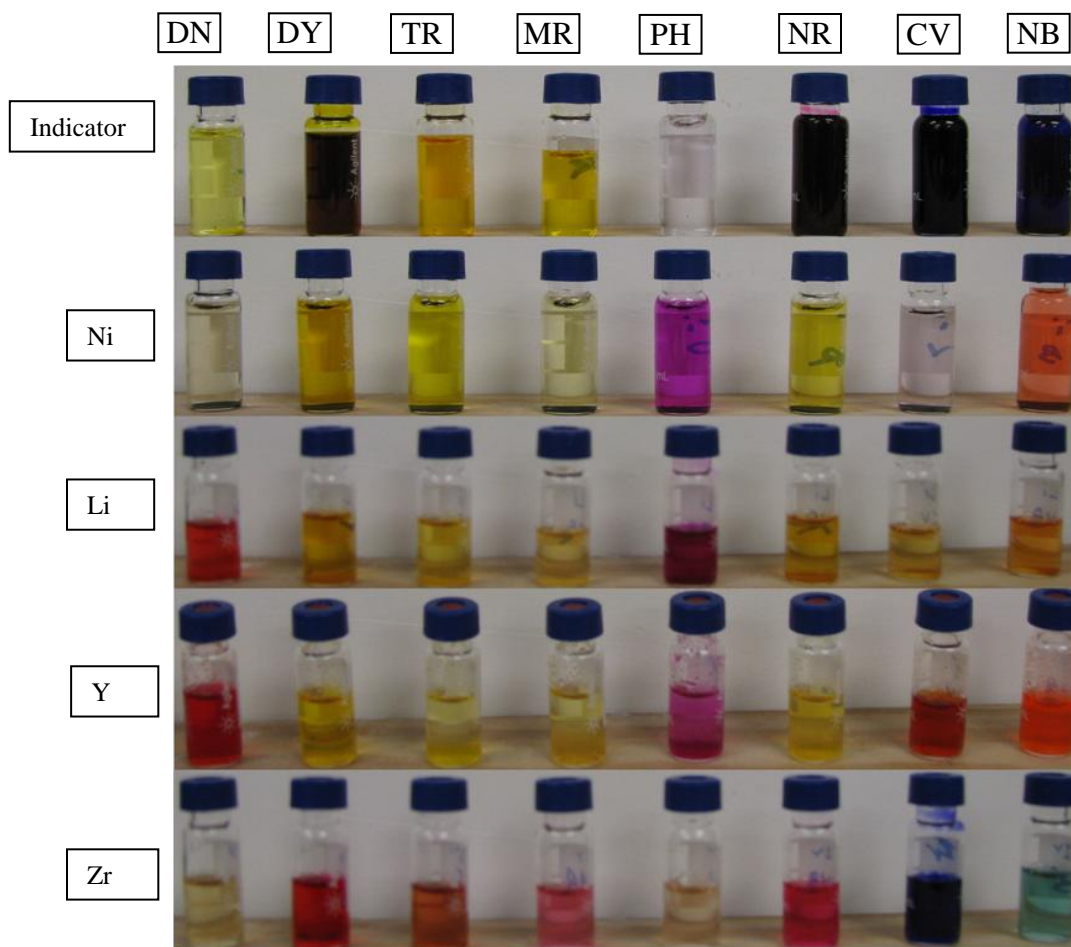
Figure 17: Hammett indicator method on different metal alkoxides

This analysis indicates that transition metal isopropoxides can catalyze transesterification using either alkoxide ligands located at the exterior of the metal complex via base catalyzed route or using the (acidic) metal center depending on the acidity/basicity of the complex. This has been explained in chapter 3.

Table 6 Acidity/basicity of selected metal alkoxide catalysts

Catalyst	pKa value (Hammett Indicator Method)
Lithium isopropoxide	11.2
Zirconium isopropoxide	3.25
Nickel isopropoxide	11.2
Titanium isopropoxide	10.1
Iron isopropoxide	6.8
Yttrium isopropoxide	11.2

Specific Conclusions

This study looked at the catalytic behavior of transition metal alkoxides toward transesterification. Maximum ester yields reported were 42 % for titanium isopropoxide, 35% for yttrium isopropoxide (both after 3 hours of reaction time) and 18% for sodium isopropoxide with 1% catalyst by weight. The ester yield was 83% with sodium methoxide after only 30 minute of reaction time. The study confirmed that of the transition metal isopropoxides tested, titanium and yttrium had the highest activity. The study also confirmed the superior catalytic ability of sodium alkoxides. It was established that the catalytic ability of the methoxide was far superior to that of the isopropoxides. After correcting for the number of active sites present per mole of catalyst, it was evident that the activity of titanium and yttrium isopropoxides was far superior to that of the sodium counterpart which was unexpected. The study also

revealed that the isopropoxide catalysts are equally selective toward component fatty acid hydrolysis.

An interesting finding is that transition metal alkoxides undergo a concurrent polymerization reaction while catalyzing the transesterification reaction. Although all the catalysts were homogeneous with the reaction medium at the onset of the reaction, as a result of this simultaneous polymerization, the transition metal alkoxide catalysts were easily separable from the reaction medium subsequent to completion of the reaction. The analysis also suggests that transition metal isopropoxides can catalyze transesterification using either alkoxide ligands located at the exterior of the metal complex via a base-catalyzed route or using the (acidic) metal center depending on the acidity/basicity of the complex. Ni, Ti and Yi isopropoxides displayed basic properties whereas Zr and Fe isopropoxides displayed acidic properties.

CHAPTER V

PHASE STABILITY OF OIL/ALCOHOL/SURFACTANT SYSTEM

Introduction

The specific objective of this study was to elucidate the phase behavior of the

alcohol/triglyceride system in the presence of selected metal alkoxides. During previous

studies, the impact of metal groups and alkoxide groups of transition metal alkoxides on

the catalytic ability of the transesterification reaction was elucidated. This study is

geared toward understanding the concomitant impact of the alkoxide on the phase

stability, i.e., the stability of an emulsion and the catalysis of the reaction. Understanding

the effect of the amphiphilicity of the catalyst on the reaction system will help in

determining the best component compositions that will help catalyze as well as

ameliorate conditions for effective progression of the reaction.

It should be noted that in the absence of surfactants, reactants that involve immiscible

liquids have to be constantly and vigorously mixed to allow adequate reactant contact.

However the use of surfactants may help in reducing the energy penalty required for

mixing and heating.

Materials and Methods

Degummed soybean oil was purchased in bulk from STE Oil Company, San Marcos, TX USA. Surfactants titanium methoxide, titanium ethoxide, titanium propoxide, titanium isopropoxide, and titanium butoxide, were purchased from Sigma-Aldrich chemical company. Titanium isobutoxide was purchased from Alfa Aesar Company. Isopropanol was purchased from EMD chemicals Inc. Propanol and butanol were purchased from Sigma-Aldrich chemical company while ethanol and methanol were purchased from VWR International LLC. Isobutanol was purchased from Alfa Aesar.

Initially, alcohol and the surfactant were mixed before adding the triglyceride (oil). A vortex mixer (VWR Model# 58816-121) was used to rapidly mix the three components. The vortex mixer had a maximum power rating of 150W. All the samples were mixed for 1 minute at room temperature (25 $^{\circ}$C). The mixed samples were kept for 3 hours to allow phase separation. Ternary phase diagrams were plotted on CHEMIX (School Version 3.51) software.

The experiment was carried out in two stages. The first stage was adopted to analyze the effect of alkoxide tail group on phase stability of the ternary system while the second stage looked at the alkoxide polymerization effect on the stability of the system. We have discussed the effects of tail group and polymerization in earlier studies.[57,82] In the first stage, titanium ethoxide, titanium propoxide, and titanium butoxide were compared

for their effect on the phase stability of the system while in the second stage the effect of titanium isopropoxide was elucidated. All the experiments were carried out at room temperature.

In order to identify the spatial distribution of the alkoxide among different liquid phases, confocal images were obtained. The experiments were carried out with titanium isopropoxide as the surfactant-catalyst. Pyrene (sigma-aldrich Co. LLC, St. Louis, MO), which has excitation wave length of 335 nm and emission at 380 nm was used as the fluorescent agent. Pyrene was used as a florescent agent in titanium-based molecule identification [83], but this is the first instance where pyrene was attempted as a florescent-agent in a titanium-isopropoxide-based oil/alcohol emulsion system.

A Bio Tek synergy 4 microplate reader was used to initially evaluate the excitation and emission wave lengths of isopropanol, isopropanol with pyrene, titanium isopropoxide in isopropanol with pyrene, and titanium isopropoxide in isopropanol with pyrene mixed with oil. After analyzing the wavelengths, a Zeiss 510 META NLO multiphoton Microscope was used to image oil in alcohol and alcohol in oil emulsions. A 458nm laser was used for excitation and the emission wavelength of pyrene was detected at 420 nm.

Results and Discussion

The phase behaviors of partially polymerized titanium alkoxides are depicted in Figure 18. It is clearly evident that with addition of water, the phase stability of the system reduced significantly. The amount of water added did not seem to impact much, i.e., the addition of even a small quantity of water dramatically reduced the area of a single phase in the phase diagram. The reason for the shrinkage of the single-phase area in the phase diagram can be attributed to the polymerization effect via water condensation (producing oligomers and polymers of different complexity with the fully polymerized form being titanium dioxide). This is because of the insufficient surfactant in the system due to heavy polymerization of titanium isopropoxide via condensation reaction.

The subsequent study focused on elucidating the effect of the hydrocarbon tail group of titanium-based alkoxides (butoxide, propoxide, ethoxide and methoxide) or subsequent alcohol depending on need of surfactant on the phase stability of the alcohol-oil ternary system.
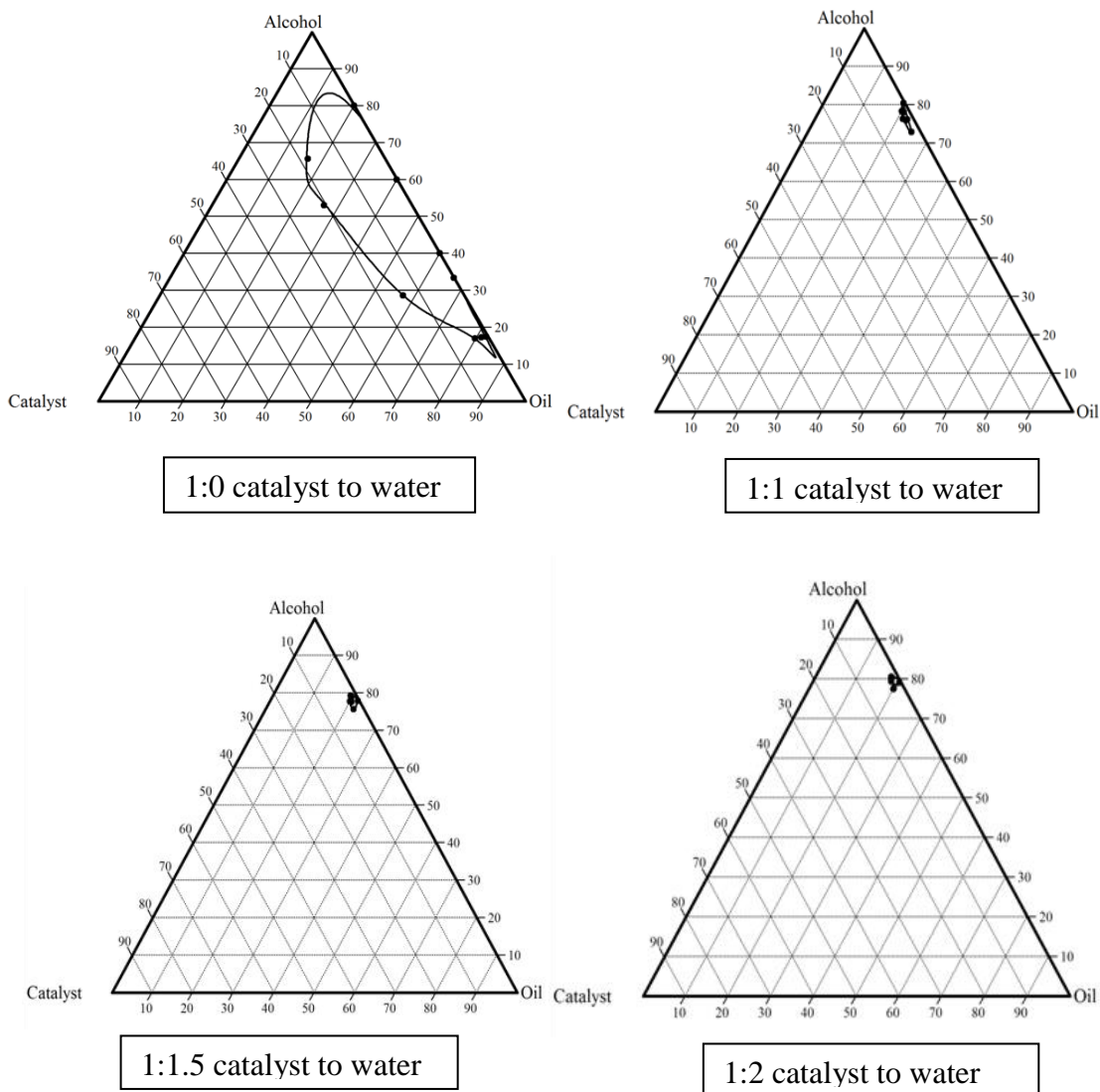
Figure 18: Ternary phase diagrams of alcohol (isopropanol), oil (soybean oil) and titanium alkoxide (catalyst prepared with different isopropoxide:water ratios) system. Note: areas enclosed by the phase boundaries are single-phase regions.

The resultant ternary phase diagrams are depicted in figure 19. It was noted that n-butanol and isobutanol mixed well with oil even in the absence of an emulsifier. Because of this, the effects of the surfactant-catalyst on the stability of these systems were not

established for n-butanol and isobutanol. N-propanol also resulted in a stable emulsion

with little addition of the emulsifier (catalyst). This could be attributed to increasing the

hydrocarbon tail of alcohols becoming more non-polar and being more miscible with

hydrophobic oil. Molecules with longer hydrocarbon tails would also be better alcohol-

in-oil surfactants having a larger affinity toward the continuous oil phase.
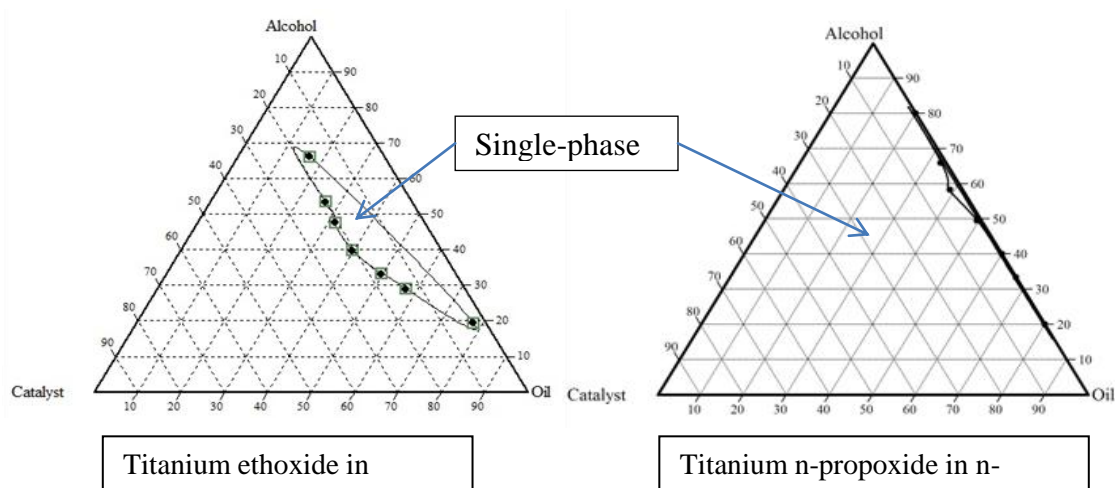
Figure 19: Tail group effect on phase stability-ternary phase diagrams.

From the observations, it is clear that alcohols with smaller tail groups have a lesser

propensity to create single phase systems with oil compared to those with longer tail

groups. Consequently, the amount of surfactant (titanium ethoxide) needed to create a

stable emulsion was comparatively higher than titanium n-propoxide in the n-

propanol/oil system. Since ethanol did not create a single phase, a higher amount of

surfactant was needed to create a stable emulsion. On the other hand, n-propanol:oil

resulted in a single-phase system at most composition ratios and only less than 1 % of

surfactant was needed to form a stable emulsion. Thus, larger carbon-numbered (tail-group) surfactants work well with alcohol-in-oil immiscible systems.

It was observed that titanium isopropoxide and titanium n-propoxide has significantly different responses in terms of phase stability. Isopropoxides rendered a lesser stability (smaller single phase area) to the system in comparison to n-propoxide. This is mainly due to the less nonpolar tail group of isopropoxide compared to the n-propoxide.

To enumerate the correlation of the surfactants ability to emulsify the alcohol and the oil system as well as to catalyze the transesterification reaction, selected samples that produced stable single phase emulsions were analyzed for ester composition. Accordingly, samples with oil: alcohol: surfactant ratios of 7:3:2.5 and 6: 4: 2.5 (volume base), were analyzed for ester composition after the samples were allowed to equilibrate at room temperature. Samples were drawn after 1 hour and 2 hours. The results are depicted in Figure 20. It was interesting that the samples contained high quantities of esters (c.a. 50% ester yields) despite the fact that the samples were only at room temperature (25 ^{o}C). It should be noted that previous studies presented in chapters 2 and 3 even after 3 hours of reaction time at 200 ^{o}C did not show this level of ester yields.[57,82] This significant observation exemplifies the importance and impact of catalysts that have amphiphilic properties on reactions that involve immiscible or poorly miscible reactants.
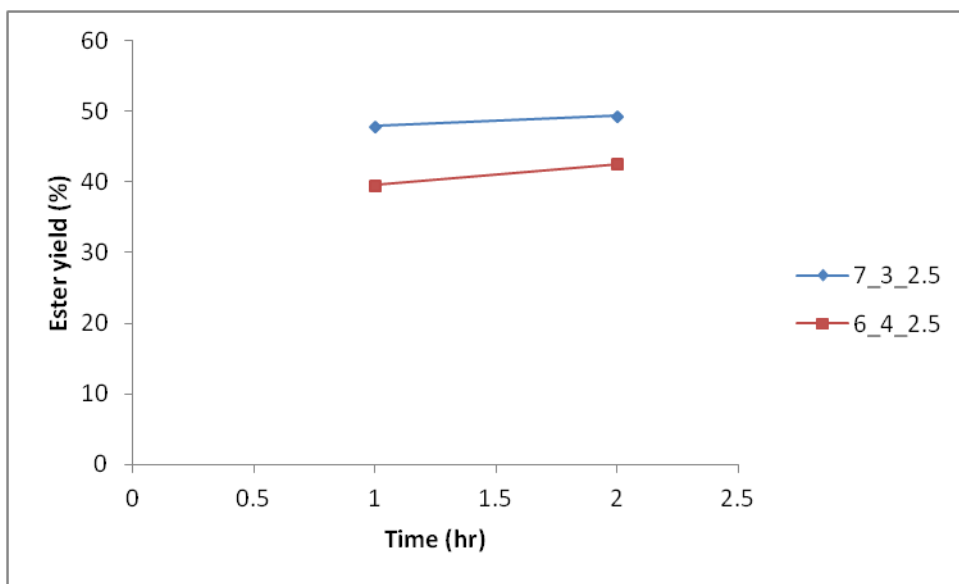
Figure 20: Ester yields for single phase system at room temperature. The legend depicts oil: alcohol: catalyst (titanium isopropoxide) volume ratios

Figure 20 shows significant ester yields on both samples. However, 7: 3: 2.5 (oil:alcohol:catalyst) mixture resulted in higher ester yields than 6: 4: 2.5 mixture. Note that in both samples, the catalyst concentration is the same. It is interesting to note that having different oil: alcohol concentrations results in different ester yields – with the system with better stability, rendering better yields.

To further understand the impact of catalyst phase on the reaction, another experiment was conducted with a series of partially polymerized titanium isopropoxide oligomers to fully polymerized titania (rutile). Figure 21 depicts the ester yields of the three catalysts. It is clear that using titanium isopropoxide increases the ester yield significantly over titanium dioxide. The intermediate oligomerized form of isopropoxide rendered better

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ester yields as compared to titanium dioxide but lesser in comparison to monomeric

titanium isopropoxide.
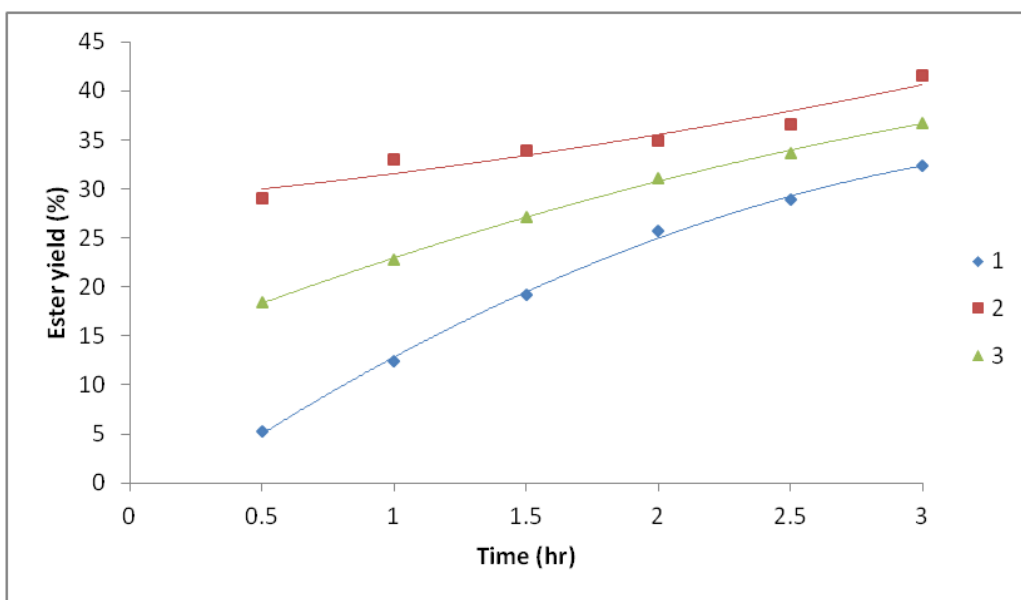
Figure 21: Ester yield w.r.t different catalyst type. (1- TiO$_2$, 2- Ti(OC$_3$H$_7$)$_4$, 3- Ti(OC$_3$H$_7$)$_4$ treated with 1:2 titanium isopropoxide: water.

It is likely that the higher number of alkoxide active sites per unit weight of catalyst

combined with the more active basic pathway contributed to the better performance

when titanium isopropoxide monomer was used. When water was added in the ratio

given, it is likely that a majority of the alkoxide groups disappeared via water

condensation leaving TiO$_2$ behind contributing to comparatively lower ester yields. In

the case of pure titanium dioxide (rutile), the reduced ester yields can be attributed to

switching to the acidic pathway (as described in Chapter 3).

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The next set of studies was carried out to elucidate the spatial distribution of the alkoxide

catalysts in the oil/alcohol system. The experiments were designed to test the premise

that was made during Chapter 2 that the amphiphilic catalysts would position themselves

at the oil/alcohol interface of the emulsion droplets to stabilize the emulsion as well as

lend active sites for the reaction between molecules in the opposing phases to occur.

An initial study was carried out to enumerate the excitation behavior of pyrene when

mixed with the components of the system. Pyrene was used as the fluorescent agent

based on previous studies on titanium-alkoxide based systems.[83] Excitation wavelengths

of different components are presented in figure 22.
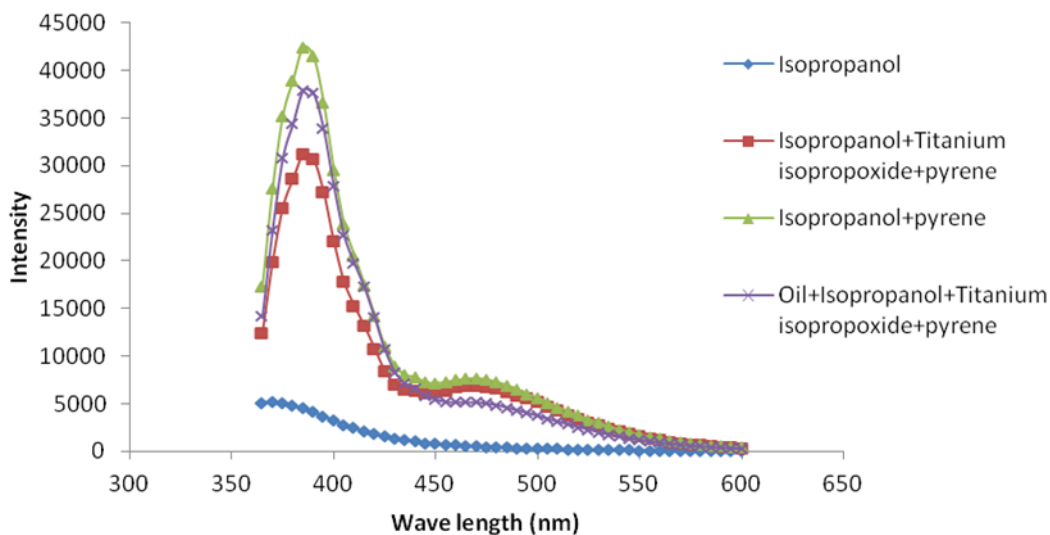
Figure 22: Excitation wavelength for different materials tested

When excited with a laser of 335nm wavelength with intensity 80%, it is evident that

pyrene responded with an excitation wavelength of 385 nm. The isopropanol control did

not get excited. However, it was evident that titanium isopropoxide – bound pyrene gets

excited at 385 nm even in the presence of isopropanol though with a lesser intensity than

pure pyrene in isopropanol. The next requirement for imaging this system was to

identify if the isopropoxide-bound pyrene fluorescence once excited. The emission

spectrum of pyrene is shown in figure 23 when excited with 420 nm laser.
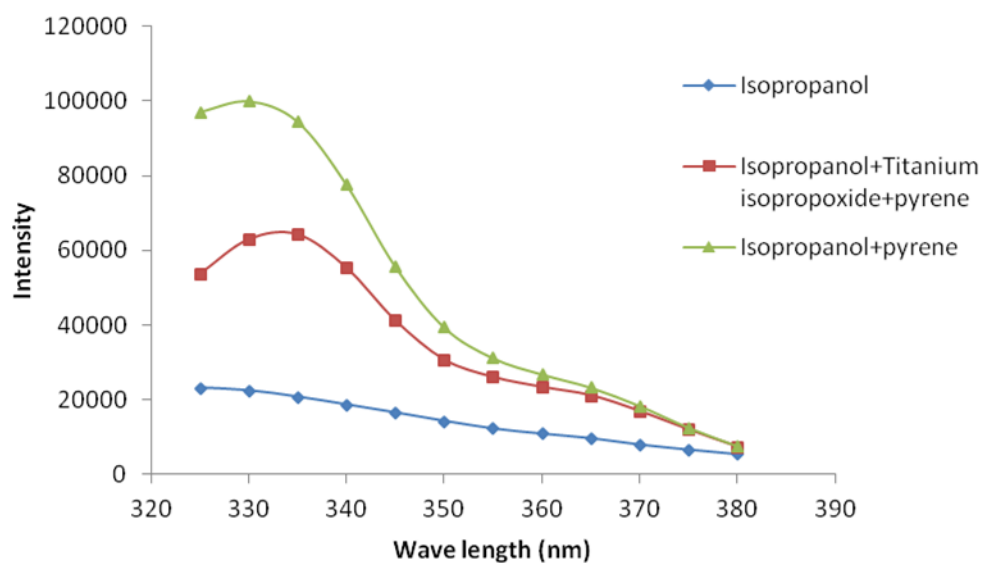
Figure 23: Emission wavelength of pyrene when excited with 420 nm laser

It was evident that although the isopropanol (control) did not contribute to any

emissions, the titanium-isopropoxide-bound-pyrene-in-isopropanol contributed to

emissions at 335 nm (with a lower intensity than pyrene-in-isopropanol) with this laser.

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There was also a peak shift between the two solutions (which could be used to differentiate the solution systems if necessary).

A Zeiss Axiovert microscope was used to image the solution systems. Figure 24 shows a set of images taken with different (oil/alcohol) component ratios. Figure 24-1 shows the background image taken with just oil and alcohol without any pyrene. In the background figure, the boundary of the sample is visible as a dark tangential line running across from top-right to bottom-left of the picture. Absence of any lighter-colored specs confirm the absence of fluorescence and thus absence of any pyrene.

Images 2-4 are with pyrene shown on the image as cyan-colored spots. It is evident that pyrene was attached only to the titanium isopropoxide and alcohol since clear cyan spots are being seen from the confocal microscope. Literature has stated that pyrene can be attached to the titanium isopropoxide.[83] Figure 24-2 shows an initial picture of a small alcohol bubble in oil while 24-3 shows a bigger propagated bubble.
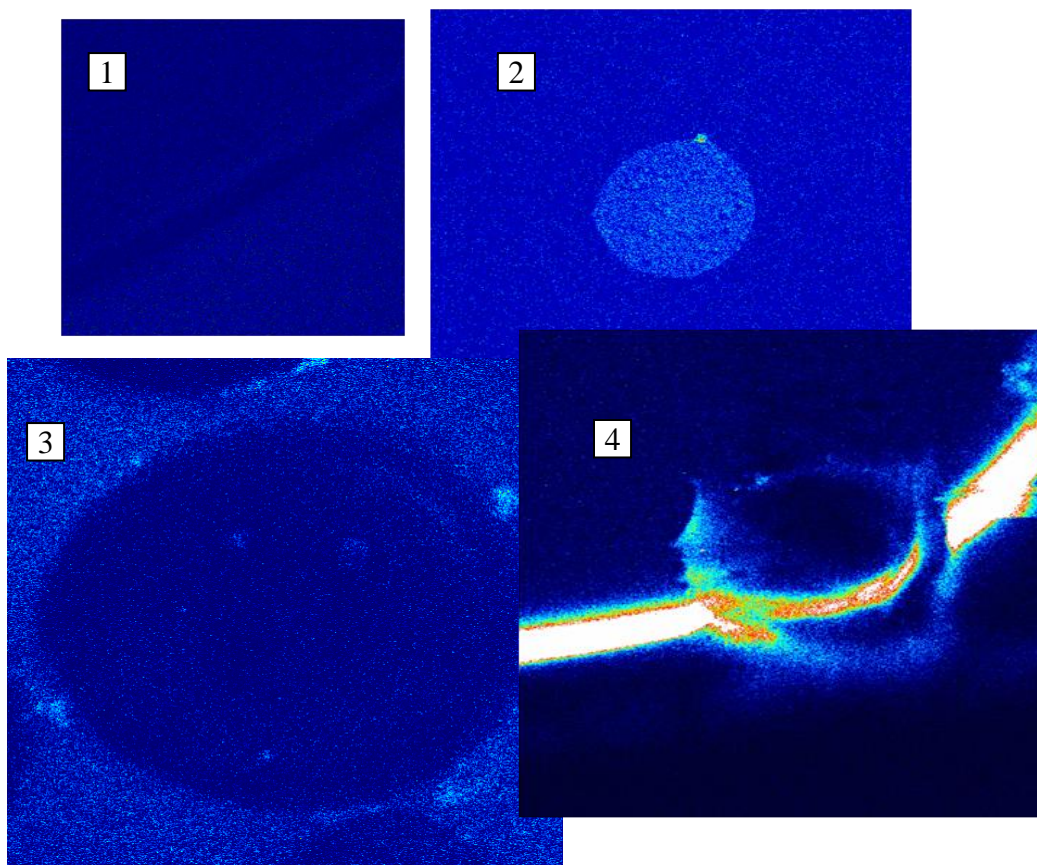
Figure 24: 1- Background image; 2- alcohol+surfactant (20%) in oil (80%) emulsion (the lighter specs show distribution of pyrene-bound titanium isopropoxide in the inner alcohol phase); 3- oil 20% in alcohol+surfactant 80% emulsion (showing amphiphile distributed in the outer alcohol phase). 4- oil (20%) in alcohol+surfactant (80%) emulsion (showing amphiphile accumulation at the oil/alcohol interface after some time has elapsed) (images are 200 um x 200 μm).

Figure 24-2 shows an alcohol-in-oil emulsion with pyrene clearly distributed in the discontinuous alcohol phase. It is clear that from this image that titanium isopropoxide preferentially resides in the alcohol phase in the presence of oil. Image 24-3 depicts the counter situation where oil is dispersed in a continuous pyrene-bound alcohol phase. It is evident that still, titanium isopropoxide preferentially resides in the alcohol phase.

However, image 24-4 depicts what happens after the system is allowed to equilibrate for some time. It is evident that the isopropoxides are now residing at the oil/alcohol interface. This experiment confirms that titanium isopropoxides can act as amphiphile that eventually contribute to stabilization of the phases as observed in phase diagrams in Figure 19 at component concentrations given. It should be noted that the component concentrations used for the microscopic imaging study did not stabilize the emulsions and coalescence was observed throughout the imaging process. The component concentrations were selected to form large enough micelles to allow imaging with light microscopy

Specific Conclusions

Ternary phase diagrams were developed for alcohol/oil/catalytic-surfactant systems. It was observed that the emulsifying ability of titanium alkoxides increased with the increase in carbon number of the hydrocarbon tail group. Higher C-4 alcohols were miscible in oil even in the absence of a surfactant. It was noticed that oligomerization or polymerization of titanium isopropoxide reduced its surface active properties – reducing the phase stability of the ternary system. It was noticed larger carbon numbered alcohols were more miscible in oil than the smaller counterparts. Accordingly, the amount of smaller alkoxide needed to stabilize the alcohol/oil system was also comparatively higher. Also, n-propanol was more miscible in oil than iso-propanol: thus, the amount of n-propoxide needed to stabilize that system was much less than isopropoxide.

The amphiphilic nature of the catalyst had a substantial impact on the performance of the catalyst. It was observed that introducing adequate amount of amphiphilic catalyst that can bring the system to a single phase triggered the reaction to progress at room temperature at the same rate the reaction progressed at 200°C.

An imaging study confirmed that titanium isopropoxide catalyst preferentially stays in the alcohol medium and migrates toward the alcohol-oil interface with time. This behavior likely contributes to the remarkable catalytic activity of the titanium isopropoxide catalyst at room temperature.

CHAPTER VI

KINETICS AND REUSABILITY STUDY FOR TITANIUM ISOPROPOXIDE

CATALYZED TRANSESTERIFICATION

Introduction

The objective of this study was to enumerate kinetic aspects of the transesterification

reaction in the presence of select transition metal alkoxide amphiphilic catalysts. A

parallel study on the reusability of spent metal alkoxide catalyst is also presented.

There are a number of kinetic studies in the literature on the transesterification of esters

with alcohol.[84-88] However, almost all these studies have relied on base catalysts such as

sodium and potassium hydroxides (or alkoxides) and inorganic acids (such as sulfuric

acid[84,85,89-93]). Also, only a handful of studies have looked at kinetic aspects of

heterogeneous catalysts.[88,91,93] In contrast, this study will look at kinetic aspects of

transition-meal alkoxides as transesterification catalysts. The studies on the

transesterification kinetics for fatty esters typically include determination of the reaction

rate constants, the equilibrium constant, and the activation energy for the

transesterification reaction. Such parameters help in predicting to what extent the

reaction occurs under a particular set of conditions.

Mass transfer limitations play an important role on the rate of reaction and conversion and product formation, particularly in catalytic systems. In a homogeneous catalytic reaction in which all substances (reactants, products, and catalyst) are in the same phase, the effect of mass transfer between phases is nonexistent. In a heterogeneous catalytic reaction, however, the catalyst is usually in a different phase from the reactants. Commonly the catalyst is in the solid phase dispersed in the reacting species which usually are in the liquid or gaseous phase.[87] Consequently, the reaction rate principally relies on mass transfer or diffusion between these phases. In our approach, the catalyst is initially in same phase as the reactants making the system homogeneous. This is expected to alleviate mass transfer issues, at least during the initial phase of the reaction. However, as observed during previous studies, transition-metal alkoxide catalysts undergo a phase transformation during the reaction via condensation and the kinetics of such a system is of significant interest.

Materials and Methods

Transesterification Reaction Kinetics with Titanium Isopropoxide and Monoolein

To elucidate the transesterification kinetics with titanium isopropoxide catalyst, isopropyl alcohol was used as the alcohol. The glycerol monooleate was used as the model glyceride. Oleate was used since this is a commonly found fatty acid in vegetable oils and the ease of deciphering the kinetic data. As monooleate has only one fatty acid chain, the reaction stoichiometry is 1:1 with isopropanol.

The development of an accurate kinetic model requires that external and internal mass transfer resistances be minimized in reaction. To ensure that there were no external mass transfer resistances, the transesterification reaction was carried out with lipid/alcohol/surfactant ratios such that the reaction mixture was in a single phase (as described in the previous chapter). A ratio of lipid:alcohol:surfactant of 3:2:1 that proved to be in the single phase was selected for this study. Since the system was a single phase, transport limitations were expected to be minimal.

The transesterification reaction was carried out in high pressure reaction tubes (10 ml, glass) with continuous stirring by magnetic stirrer. Monoolein(rac-Glycerol 1-monooleate) was purchased from Sigma-Aldrich Corp. Isopropanol was purchased from

EMD chemicals Inc. Titanium isopropoxide catalyst was purchased from Sigma-Aldrich Corp.

The monoglyceride was heated to 70 ^{o}C on a standard hot plate stirrer while stirring continuously with the reaction vial closed with high pressure septum. Alcohol and the catalyst (titanium isopropoxide) were added as soon as monoglyceride reached the reaction temperature. A temperature of 70 ^{o}C was chosen so that the reaction occured below the boiling point of isopropanol.

Samples were drawn from the reaction mixture at 10 min intervals. Samples were weighted and analyzed via gas chromatography (GC-6850 Agilent Technologies, Santa Clara, CA USA) for ester composition. The gas chromatograph was calibrated with the respective alkyl ester standard (oleate isopropyl ester, Nu-Chek Prep Inc., Elysian MN 56028, USA) prior to obtaining quantitative yields. Three replicates were carried out and the results were analyzed using statistical software, design expert (Stat-ease Inc.). Kinetic data were calculated assuming batch reactor conditions and a homogeneous phase.

Yield Optimization

Yield optimization and catalyst re-usability studies were carried out as a part of the final phase of this series of experiments. In the yield optimization study, titanium

isopropoxide concentrations of 1%, 2%, 3%, 4%, 6% and16% (w/w) were tested as the transesterification catalyst.

Catalyst Reusability

The once spent catalyst was isolated from the medium using centrifugation. The catalyst was dispersed in isopropyl alcohol prior to use in the reaction. The re-used catalyst was also used at a 1% (w/w) level. However, since catalysts were separated from the products by centrifugation, the catalysts had significant amounts of liquid (isopropanol + unreacted triglyceride +glycerol) associated with them, thus the weights were approximate.

The catalyst reusability studies were carried out in a high pressure reactor that had a magnetic drive stirrer with maximum RPM of 2000 and a tachometer module with an accuracy of ± 10 rpm. The stainless steel reactor vessel is capable of handling 500 ml of reactants. The reactor was used in the batch mode. Degummed soybean oil was purchased in bulk from STE Oil Company, San Marcos, TX USA. In order to initiate the transesterification reaction the catalyst was infused into the reaction chamber containing triglyceride immediately after the contents reached the designated temperature (200 ^{o}C) through a high pressure liquid pump (Eldex 5790, Eldex laboratories Inc. Napa, CA). Alcohol to oil ratio of 3 : 1 (molar basis) was used for the transesterification reaction. The GC method utilized (for Oleate esters) detection is as in table 7.

Table 7 GC method for oleate ester detection

Inlet Temperature	250 ^{o}C
Split ratio	50:1
Injection volume	1 µl
Column flow (Helium)	1.6 ml/min (constant flow)
FID temperature	280 ^{o}C
H$_2$ Flow	40 ml/min
Air flow	450 ml/min
Makeup gas (Nitrogen)	30 ml/min
Oven program	75 ^{o}C hold 1min, to 200 ^{o}C at 50 ^{o}C/min, hold 3 min, to 230 ^{o}C at 20 ^{o}C/min, hold 10 min.
Column	30m x 0.25mm x 0.25µm (DB-Wax Column)

The amount of fatty acid alkyl esters yield was calculated via Chemstation software (Agilent technologies). The area under the peak from the FID chromatogram corresponded to the concentration of that component. These concentrations were determined using calibrations with pure ester standards along with an internal standard (C-12 ester).

Results and Discussion

Transesterification Reaction Kinetics with Titanium Isopropoxide and Monoolein

Figure 25 depicts the glyceride conversion vs time graph. It was noticed that it took up to one hour to detect any initial products. The reasons for this observation may be due to the detection limits of the gas chromatograph or the system not being able to overcome the activation energy.
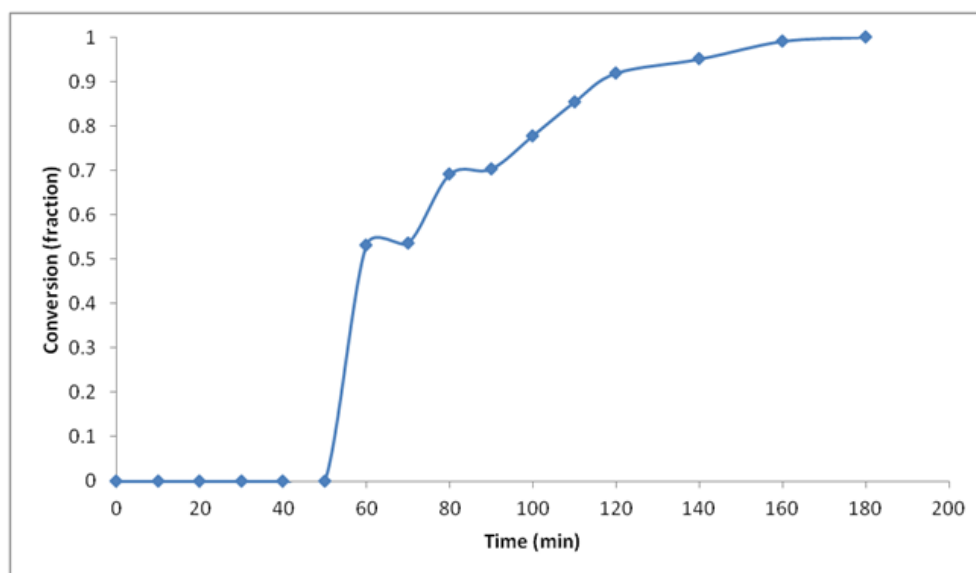
Figure 25: Conversion of oleate mono glycerol with time

It was observed that the reaction was completed after 180 minutes. Samples were taken at 20 minute intervals after 120 minutes. Kinetics of this system were calculated with conversion factors as obtained via the GC analysis.

The transesterification reaction is a reversible. Therefore, excess isopropanol was used to drive the reaction forward. Eq. (1) shows the generalized reaction, where A is the monoglyceride, B is isopropanol, C is isopropyl oleate ester and D is glycerol. The equation also shows the stoichiometric relationship between the reactants and the products.

$$A + B \overset{Heat}{\Longleftrightarrow} C + D \tag{1}$$

We can write the general rate equation for the above reaction,

$$-\frac{dC_A}{dt} = k C_A^\alpha C_B^\beta \tag{2}$$

where,

$\frac{-C_A}{t}$ is the consumption of reactant A per unit time, k is the rate constant, C_A and C_B are the concentrations of reactant A and B at time t respectively, α and β are the order of the reaction with respect to A and B components. Then we can write the following equations for species A and B.

$$C_A = C_{A0}(1 - X) \tag{3}$$

$$C_B = C_{B0}(1 - X) \tag{4}$$

$$\theta = \frac{C_{B0}}{C_{A0}} \tag{5}$$

where,

C_{A0} and C_{B0} are initial concentrations of species A and B respectively. θ is the ratio of initial concentrations of species B and A, while X is the conversion. Finally we can conclude to a generalized equation for conversion as follows:

$$\frac{dX}{dt} = kC_{A0}^{(\alpha+\beta-1)}(1-X)^{\alpha}(\theta-X)^{\beta} \qquad (6)$$

In this study, nine different cases for reaction order were looked at. Since most of the literature stated transesterification has 0, 1, or 2 order, the nine different cases were considered. For each case, equation 6 was integrated from t=0 to t=t with conversion X=0 to X=X. Finalized equations are listed below:

Case1: (α=0, β=0)

$$C_{A0}X = kt$$

Case 2: (α=1, β=0)

$$\ln\frac{1}{(1-X)} = kt$$

Case 3: (α=0, β=1)

$$\ln\frac{(\theta-X)}{\theta} = kt$$

Case 4: (α=1, β=1)

$$\frac{1}{(\theta-1)}\ln\frac{(\theta-X)}{(1-X)\theta} = kC_{A0}t$$

Case 5: (α=2, β=0)

$$\frac{X}{(1-X)} = kC_{A0}t$$

Case 6: (α=0, β=2)

$$\frac{X}{\theta(\theta-X)} = kC_{A0}t$$

Case 7: (α=2, β=1)

$$\frac{1}{(\theta-1)}\left\{\frac{1}{(1-X)} - \frac{1}{(\theta-1)}\ln\frac{(1-X)}{(\theta-X)}\right\} = kC_{A0}^2 t$$

Case 8: (α=1, β=2)

$$\frac{1}{(\theta-1)}\left\{\frac{X}{(\theta-X)\theta} + \frac{1}{(\theta-1)}\ln\frac{\theta(1-X)}{(\theta-X)}\right\} = kC_{A0}^2 t$$

Case 9: (α=2, β=2)

$$X(1-\theta)\left[\frac{1}{(X-1)} + \frac{X}{(X-\theta)\theta}\right] + 2\ln\left\{\frac{(1-X)\theta}{(\theta-X)}\right\} = kC_{A0}^3 t$$

All these equations conform to $y=mx$ (linear) form and as the concentration is known, when conversion (X) plotted against time in each case, the resulting plot would be a straight line going through the origin. The gradient of the straight line gives the reaction rate constant (k). The correlation coefficient (R^2- value) of each plot was compared for discerning the best fit.

Figure 26 depicts plots of all scenarios along with the R^2- values. It is evident that three cases have a correlation coefficient around 0.8. It should be noted that case 3 and 8 have negative gradients and in a reaction engineering context, these are invalid.
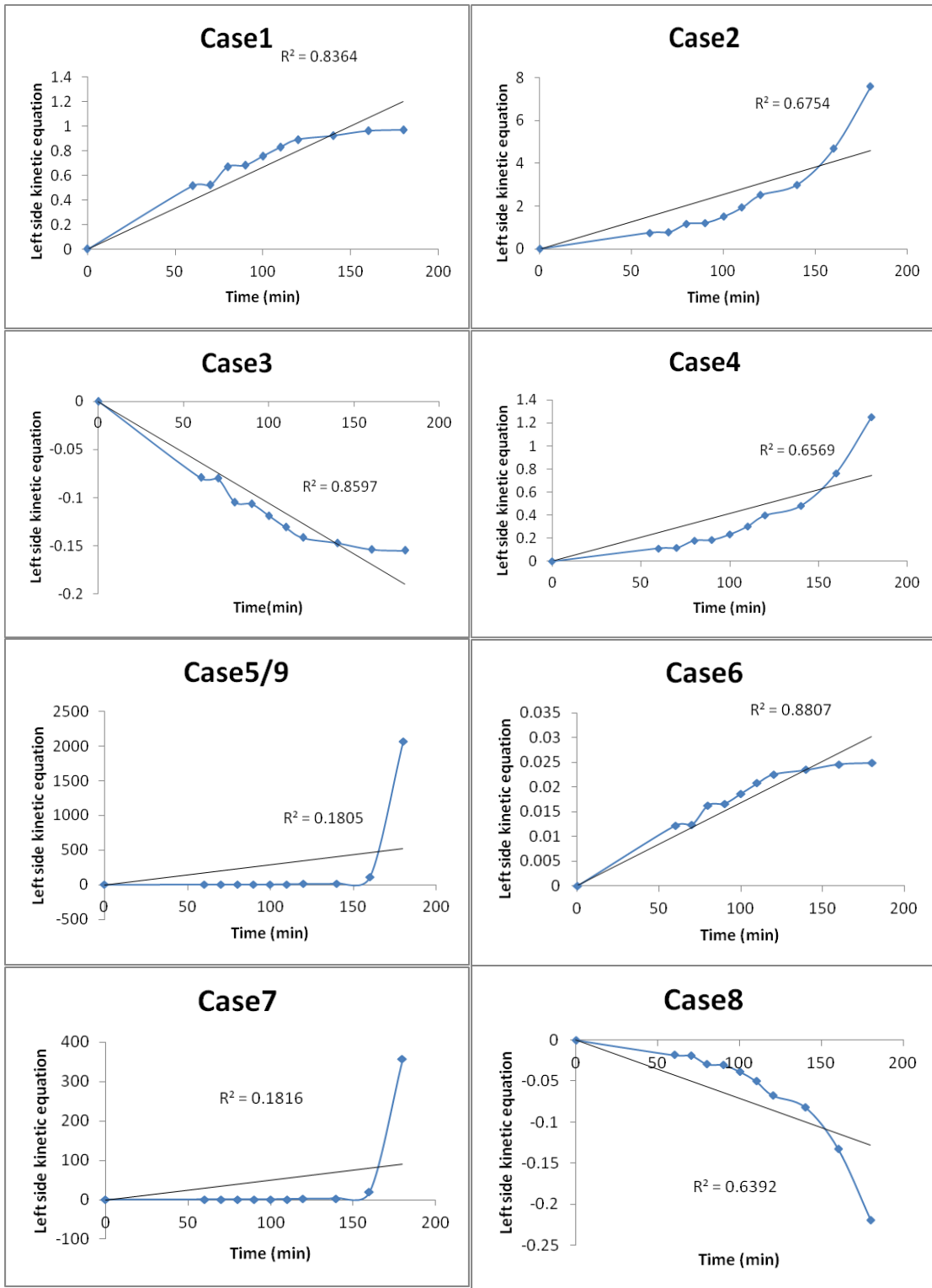
Figure 26: Kinetic equation plots for 9 cases studied

From case 1 and 6 it is clear that case 6 has significantly higher correlation coefficient of 0.88. So, we can conclude that the transesterification reaction behaves according to the case 6 scenario. Therefore, transesterification reaction of our interest has order of 2 with respect to alcohol in the system and zero order for triglycerides. This is in agreement with some of the literature (although the order of the transesterification reaction has been reported to vary depending on the situation and type of starting materials.[21,84,85,87]

From aforementioned information, the rate constant was calculated to be 0.0002 min^{-1}. If we consider case 1, rate constant calculated to be 0.0067 min^{-1}. Thus it can be concluded that this is a second order reaction with respect to isopropanol.

Yield Optimization

Figure 27 depicts the ester yields for the different percentages of titanium isopropoxide catalyst used. Results show that 1% (w/w) catalyst has significantly lower ester yields than any other catalyst concentrations (note that we used 1% catalyst for most of our experiments). The highest ester yield was 71% with 16 % catalyst by weight after 2 hours of reaction time. Since titanium isopropoxide was added to the liquid phase and due to formation of the phase transformed gel, it was not possible to add more than 16 % of catalyst to the system.
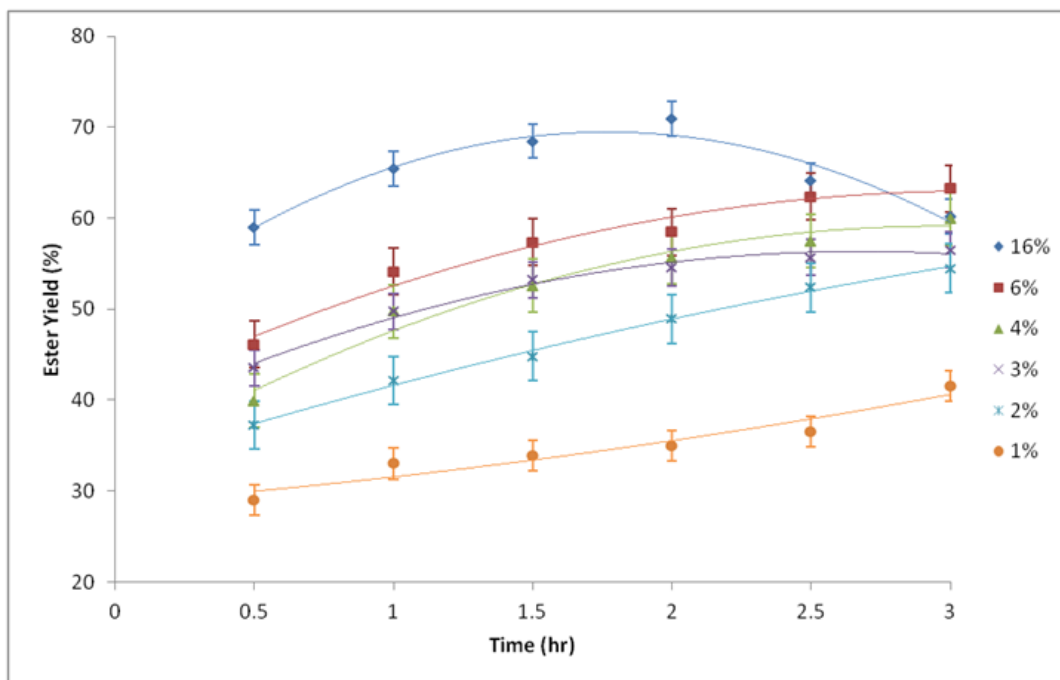
Figure 27: Ester yield % vs time plot for different % of catalyst by weight

Based on the results, it is likely that the optimal catalyst concentration would be somewhere in between the 6% and 16% levels.

Catalyst Reusability

The ester yields of the once used catalyst are depicted in Figure 28. As was expected, the ester yields from the fresh catalyst were significantly higher as compared to the reused catalyst. The maximum ester yield for reused catalyst was 34% while maximum for fresh catalyst was 41 %. The results are encouraging since more than 80 % from the original yield can be achieved from a once used catalyst.
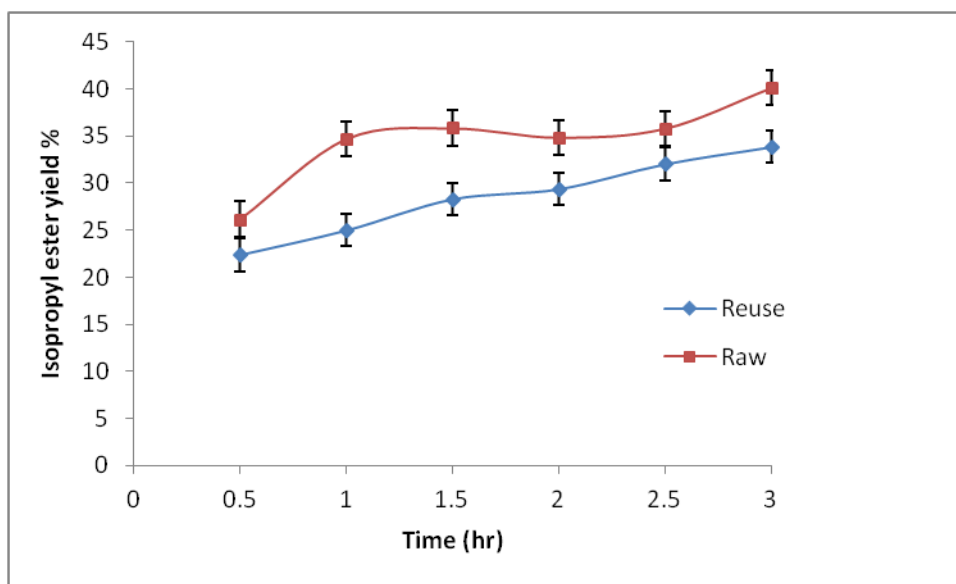
Figure 28: Performance comparison of raw catalyst vs reused catalyst

It should be noted here that the spirit of this catalyst technology is not to reuse the spent catalyst in its transformed (solid) form, but to regenerate via transforming it to the liquid isopropoxide form. The oligomerized/polymerized form of titania can be transformed to the isopropoxide form using the following reaction scheme.[79,94]

Scheme 3- Metal alkoxide produce from metal oxides

$$M^{I}OH + ROH \leftrightarrow M^{I}OR + H_2O$$

$$M^{III}O + 2ROH \leftrightarrow M^{III}(OR)_2 + H_2O$$
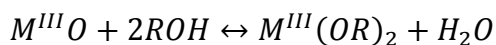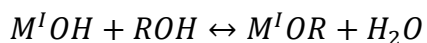
Both reactions are reversible, thus application of these methods is expedient in the case of alcohols with low boiling point.[94] This method is called alcoholysis of metal oxides.

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Specific Conclusions

The kinetic study revealed that transesterification of monoolein with titanium isopropoxide having a second order with respect to isopropyl alcohol. However zero order reaction is also plausible. The rate constant was evaluated to be 0.0002 min^{-1}.

Optimization studies revealed that this catalytic system can yield up to 71 % ester yields using 16% (w/w) of catalyst. However results suggest better yields may be plausible with a catalyst composition between 6% and 16%.

The separated (gel), likely having significant amounts of titania rendered a maximum yield of 34% ester yield. This depicts that the catalyst retained more than 80% of its activity after an initial use.

CHAPTER VII

OVERALL CONCLUSIONS

The study revealed several transition-metal based alkoxide catalysts that have

amphiphilic as well as catalytic properties toward transesterification. It was revealed that

monomeric forms of liquid-phase transition-metal alkoxides act as amphiphile and

would position (themselves) at the interface of the immiscible oil/alcohol interface of the

emulsion. The composition of the hydrocarbon ligand of the alkoxide catalytic

amphiphile significantly affected the amphiphilicity and thus the stability of the

oil/alcohol emulsion. Metal alkoxides with larger hydrocarbon groups favored

stabilizing alcohol-in-oil systems whereas smaller hydrocarbon groups favored oil-in-

alcohol emulsions. In terms of transesterification reaction where a smaller amount of

alcohol is dispersed in a larger continuous phase of oil, metal alkoxide ligands with

larger hydrocarbon groups seemed to favor formation of more stable emulsions. It was

noted that once the alcohol-oil-surfactant/catalyst system was brought to a single phase

by addition of appropriate amount of surfactant-catalyst, the transesterification reaction

occurred at room temperature. This was an unexpected and remarkable observation.

Of the many transition metal alkoxides tested, the early transition metals, Ti and Y, fared

well for the transesterification reaction. It was revealed that most monomeric forms of

liquid-phase transition-metal alkoxides, in addition to participating in the

transesterification catalysis, undergo an autonomous condensation

olygomerization/polymerization reaction (in the presence of alcohols) resulting in solid gels – affording the term "phase-transforming catalysts". Depending on the level of polymerization and the type of metal present in the metal alkoxide catalyst, the transesterification reaction proceeds via exterior alkoxide driven Bronsted basic pathway (monomeric forms) or interior metal center driven Lewis acidic pathway (polymeric forms). Ni, Ti and Yi isopropoxides displayed basic properties whereas Zr and Fe isopropoxides displayed acidic properties. The Bronsted basic catalytic pathway was superior (in terms of activity) to the acidic pathway.

The novelty of this catalytic process is the ability to introduce the catalyst in liquid-phase and the capability to cyclically remove the spent catalyst from the reaction medium as a solid and reintroduce to the reaction medium after regenerating as a liquid. Nevertheless, it was revealed that the spent (solid) catalyst retains about 80% of its activity after one cycle.

The kinetic study revealed that transesterification with titanium isopropoxide catalyst having second order with respect to isopropyl alcohol (although the possibility of zero order cannot be excluded). Reaction rate constant was evaluated to be 0.0002 min^{-1}.

Recommendations for Future Studies

- Elucidating the behavior of this phase transforming metal alkoxide catalysis with a broader range of metals, alkoxides and conditions to achieve industrially feasible ester yields (in excess of 90%).

- Understanding the effect of oligomerization on transesterification catalysis in a more controlled manner (ensuring that dimerization, trimerization etc. occurred as presumed).

- Evaluating the feasibility of the use of such phase-transforming catalysts to other reaction system that utilize immiscible liquid phase reactants.

- Studies on effective regeneration of spent catalysts.

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