

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231272449>

Response of Titanium–Isopropoxide–Based Heterogeneous Amphiphilic Polymer Catalysts for Transesterification

ARTICLE *in* ENERGY & FUELS · JULY 2010

Impact Factor: 2.79 · DOI: 10.1021/ef100479q

CITATIONS

8

READS

279

3 AUTHORS, INCLUDING:



Gayan Ivantha Nawaratna

Texas A&M University

8 PUBLICATIONS 18 CITATIONS

SEE PROFILE



Sandun D Fernando

Texas A&M University

71 PUBLICATIONS 2,952 CITATIONS

SEE PROFILE

Response of Titanium-Isopropoxide-Based Heterogeneous Amphiphilic Polymer Catalysts for Transesterification

Gayan Nawaratna,[†] Sandun D. Fernando,^{*,†} and Sushil Adhikari[‡]

[†]Department of Biological and Agricultural Engineering, Texas A&M University, College Station, Texas 77843, and

[‡]Department of Biosystems Engineering, Auburn University, Auburn, Alabama 36849

Received April 15, 2010. Revised Manuscript Received June 4, 2010

Transesterification is a widely used reaction in the chemical industry. Currently, industrial-scale transesterification is primarily performed via homogeneous catalysts. Because of downstream separation issues, there is a need for effective heterogeneous catalysts. However, heterogeneous catalysts introduce the drawback of mass-transfer limitations into the reaction system. The substrates associated with transesterification form a three-phase system that is inherently immiscible in each other with liquid/liquid/solid (L/L/S) interfaces. This study was conducted to ascertain the behavior of a solid catalyst that has amphiphilic properties in the transesterification system. It was hypothesized that the amphiphilic catalyst, depending upon its degree of polymerization, would orient itself at the interface of the two immiscible liquids, forming an emulsion. The catalytic active site, in the mean time, would catalyze the transesterification reaction. In this study, the catalytic aspects of the titanium-isopropoxide-based inorganic dendritic polymers were investigated. Titanium isopropoxide catalysts with varying degrees of polymerization were developed by sol–gel water condensation. The degree of polymerization was controlled by the amount of water addition. Five forms of catalysts with varying degrees of polymerization were subjected to transesterification at varying temperatures and time intervals. In this experiment, soybean oil was used as the triglyceride. Isopropanol and titanium isopropoxide were used as the catalyst precursors. The highest yield of 41.56% of propyl esters was obtained at 200 °C after 3 h with 1% (w/w) of the monomeric form of the catalyst. The behavior of the dimeric and higher forms was highly correlated with reaction temperatures and residence times.

Introduction

Background. Increasing effectiveness of liquid/liquid/solid (L/L/S) ternary catalytic reaction systems, where two immiscible liquids come in contact with a solid-phase catalyst, is challenging because of limitations associated with the unavailability of sufficient interfacial area and mass-transfer limitations. Although the L/L incompatibility could be ameliorated by introducing a liquid surfactant, this causes downstream product separation problems, which wanes the effectiveness of such a system for practical applications.¹ The goal of this study was to address these limitations by developing a heterogeneous (solid) catalyst that acts as an emulsifier (amphiphile), which will essentially 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, because of the emulsification properties of the catalyst, stabilizes the emulsion. In the mean time, 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

because of its use in the biodiesel industry.^{2,3} Fatty acid methyl (or ethyl) esters commonly known as biodiesel are a renewable alternative fuel for compression ignition engines.^{4–7} Typical raw materials used are triglycerides of either plant or animal origin.⁷ Direct use of triglycerides as diesel fuel is not feasible because of 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 triglycerides to lower its viscosity close to that of petroleum diesel.

Transesterification is an acid or alkaline catalytic reaction between triglycerides and alcohols (methanol, ethanol, etc.).⁸

(3) Bray, R. Biodiesel via Axens heterogeneous catalysis Esterfip—H process. In *PEP Review*; SRI Consulting: Menlo Park, CA, 2005.

(4) Gerpen, J. V.; Shanks, B.; Pruszko, R. *Biodiesel Production Technology*; National Renewable Energy Laboratory (NREL): Golden, CO, July 2004.

(5) Hancsok, J.; Kovacs, F.; Krar, M. Production of vegetable oil fatty acid methyl esters from used frying oil by combined acidic/alkali transesterification. *Pet. Coal* **2004**, 46 (3), 9.

(6) Rothermel, J. Investigation of transesterification reaction rates and engine exhaust emissions of biodiesel fuels. Master's Thesis, Iowa State University, Ames, IA, 2003.

(7) Zappi, M.; Hernandez, R.; Sparks, D.; Horne, J.; Brough, M.; Arora, S. M.; Motsenbocker, W. D. *A Review of the Engineering Aspects of the Biodiesel Industry*; Mississippi State University (MSU) E-TECH Laboratory: Mississippi State, MS, August 2003.

(8) Wenzel, B.; Tait, M.; Módenes, A.; Kroumov, A. Modelling chemical kinetics of soybean oil transesterification process for biodiesel production: An analysis of molar ratio between alcohol and soybean oil temperature changes on the process conversion rate. *Bioautomation* **2006**, 5, 10.

*To whom correspondence should be addressed. E-mail: sfernando@tamu.edu.

(1) Nandi, A.; Mehra, A.; Khakhar, D. V. Coalescence in a surfactant-less emulsion under simple shear flow. *AIChE J.* **2005**, 52 (3), 10.

(2) Zhang, Y.; Dubé, M. A.; McLean, D. D.; Kates, M. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresour. Technol.* **2003**, 89, 16.

Because of superior activity and favorable economics, the most commonly used industrial catalysts are sodium and potassium hydroxides. However, alkaline hydroxides often produce saponifiable matter,⁹ which originates from the free fatty acid neutralization. The soap formation is undesirable because 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.^{10–12} 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 because of mass-transfer limitations in the L/L/S interface corresponding to triglyceride/alcohol/catalyst phases, respectively.¹³ 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 hydrophilic and hydrophobic liquids are necessary to be reacted in the presence of solid catalysts. Such a system includes but is not limited to esterification^{14–16} (and transesterification^{17–20}), etherification,^{21,22} and steam reform-

ing^{23–25} systems. Specifically, amphiphilic catalysts could potentially be used in L/L catalytic environments, such as hydrolysis of the propionic anhydride catalyzed with sulphuric acid,^{26,27} oxidative desulfurization of dibenzothiophene with molecular oxygen,²⁸ oxidation of hydrophobic alcohols using aqueous hydrogen peroxide,²⁹ hydroamination reactions in a L/L two-phase catalytic system,³⁰ and reforming of hydrophobic substrates, for instance, 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, provide the required amphiphilicity for emulsifying the originally biphasic 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 toward the continuous triglyceride phase, while the polar oxide would orient inward toward 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 because there is no driving force (other than mechanical agitation) to drive catalyst molecules toward the nonpolar lipid phase for the reaction to occur.

Heterogeneous Catalysts in Transesterification. Heterogeneous catalysts that have been used in biodiesel-production-related transesterification include metal oxides, such as $\text{ZrO}_2\text{--SiO}_2$, $\text{KOH/ZrO}_2\text{--SiO}_2$, $\text{Co}_2\text{O}_3\text{--SiO}_2$, $\text{Mo}_2\text{O}_5\text{--SiO}_2$, and $\text{Na}_2\text{O--SiO}_2$,^{31,32} metals, such as nickel powder, palladium powder, cast iron shavings, and steel shavings,^{32,33} zeolites,^{34–36} ion-exchange resins,^{31,37,38} and salts, such as sulfated zirconia.^{39,40} Literature suggests that the heterogeneous catalysts that showed the best performance

(9) Zhou, W.; Boocok, D. G. B. Phase distributions of alcohol, glycerol, and catalyst in the transesterification of soybean oil. *J. Am. Oil Chem. Soc.* **2006**, *83* (12), 6.

(10) Thompson, J. V.; He, B. B. Characterization of crude glycerol from biodiesel production from multiple feedstocks. *Appl. Eng. Agric.* **2006**, *22* (20), 5.

(11) Pachauri, N. He, B. Value-added utilization of crude glycerol from biodiesel production: A survey of current research activities. *Proceedings of the American Society of Agricultural and Biological Engineers (ASABE) Annual International Meeting*, Portland, OR, 2006.

(12) Nouredini, H.; Dailey, W. R.; Hunt, B. A. Production of ethers of glycerol from crude glycerol—The byproduct of biodiesel production. *Adv. Environ. Res.* **1998**, *2* (2), 12.

(13) Vicente, G.; Martinez, M.; Aracil, J. Integrated biodiesel production: a comparison of different homogeneous catalysts systems. *Bioresour. Technol.* **2004**, *92*, 9.

(14) Sejidov, F. T.; Mansoori, Y.; Goodarzi, N. Esterification reaction using solid heterogeneous acid catalysts under solvent-less condition. *J. Mol. Catal. A: Chem.* **2005**, *240* (1–2), 186–190.

(15) Zhao, Z. H. Studies on esterification reaction over aluminophosphate and silicoaluminophosphate molecular sieves. *J. Mol. Catal. A: Chem.* **2001**, *168* (1–2), 147–152.

(16) Hu, C. W.; Hashimoto, M.; Okuhara, T.; Misono, M. Catalysis by heteropoly compounds. XXII. Reactions of esters and esterification catalyzed by heteropolyacids in a homogeneous liquid-phase effects of the central atom of heteropolyanions having tungsten as the addenda atom. *J. Catal.* **1993**, *143* (2), 437–448.

(17) Li, E.; Xu, Z. P.; Rudolph, V. MgCoAl-LDH derived heterogeneous catalysts for the ethanol transesterification of canola oil to biodiesel. *Appl. Catal., B* **2009**, *88* (1–2), 42–49.

(18) Benjapornkulaphong, S.; Ngamcharussrivichai, C.; Bunyakit, K. Al_2O_3 -Supported alkali and alkali earth metal oxides for transesterification of palm kernel oil and coconut oil. *Chem. Eng. J.* **2009**, *145* (3), 468–474.

(19) Chen, H.; Peng, B.; Wang, D.; Wang, J. Biodiesel production by the transesterification of cottonseed oil by solid acid catalysts. *Front. Chem. Eng. China* **2007**, *1* (1), 11–15.

(20) Pang, X.-Y.; You, T.-T. Preparation of biodiesel through transesterification of animal oil and alcohol under the catalysis of SO_4/TiO_2 . *E-J. Chem.* **2009**, *6* (1), 189–195.

(21) Kim, J. W.; Kim, D. J.; Han, J. U.; Kang, M.; Kim, J. M.; Yie, J. E. Preparation and characterization of zeolite catalysts for etherification reaction. *Catal. Today* **2003**, *87* (1–4), 195–203.

(22) Yadav, G. D.; Krishnan, M. S. Etherification of β -naphthol with alkanols using modified clays and sulfated zirconia. *Ind. Eng. Chem. Res.* **1998**, *37* (8), 3358–3365.

(23) Haryanto, A.; Fernando, S.; Murali, N.; Adhikari, S. Current status of hydrogen production techniques by steam reforming of ethanol: A review. *Energy Fuels* **2005**, *19* (5), 2098–2106.

(24) Adhikari, S.; Fernando, S. D.; To, S. D. F.; Bricks, R. M.; Steele, P. H.; Haryanto, A. Conversion of glycerol to hydrogen via a steam reforming process over nickel catalysts. *Energy Fuels* **2008**, *22*, 1220–1226.

(25) Borekov, G. K. *Heterogeneous Catalysis*; Zamaraev, K. I., Khasin, A. V., Eds.; Borekov Institute of Catalysis: Novosibirsk, Russia, 1992.

(26) Molga, E.; Cherbanski, R. Catalytic reaction performed in the liquid–liquid system at batch and semi-batch operating mode. *Catal. Today* **2001**, *66* (2), 9.

(27) Molga, E.; Cherbanski, R. Catalytic reaction performed in the liquid–liquid system: Comparison of conventional and neural networks modelling methods. *Catal. Today* **2003**, *79–80*, 7.

(28) Lü, H.; Gao, J.; Jiang, Z.; Yang, Y.; Song, B.; Li, C. Oxidative desulfurization of dibenzothiophene with molecular oxygen using emulsion catalysis. *Chem. Commun.* **2007**, 3.

(29) Choi, K.-M.; Ikeda, S.; Ishino, S.; Ikeue, K.; Matsumura, M.; Ohtani, B. Oxidation of hydrophobic alcohols using aqueous hydrogen peroxide over amphiphilic silica particles loaded with titanium(IV) oxide as a liquid–liquid phase-boundary catalyst. *Appl. Catal., A* **2005**, *278* (2), 6.

(30) Bodis, J.; Mueller, T. E.; Lercher, J. A. Novel hydroamination reactions in a liquid–liquid two-phase catalytic system. *Green Chem.* **2003**, *5* (2), 5.

(31) Pinto, A. C.; Guarieiro, L. L. N.; Rezende, M. J. C.; Ribeiro, N. M.; Torres, E. A.; Lopes, W. A.; Pereira, P. A. de P.; de Andrade, J. B. Biodiesel: An overview. *J. Braz. Chem. Soc.* **2005**, *16* (6B), 1313–1330.

(32) Suppes, G.; Dasari, M. A.; Doskocil, E. J.; Mankidy, P. J.; Goff, M. J. Transesterification of soybean oil with zeolite and metal catalysts. *Appl. Catal., A* **2004**, *257*, 11.

(33) Dasari, M.; Goff, M.; Suppes, G. Noncatalytic alcoholysis kinetics of soybean oil. *J. Am. Oil Chem. Soc.* **2003**, *80* (2), 189–192.

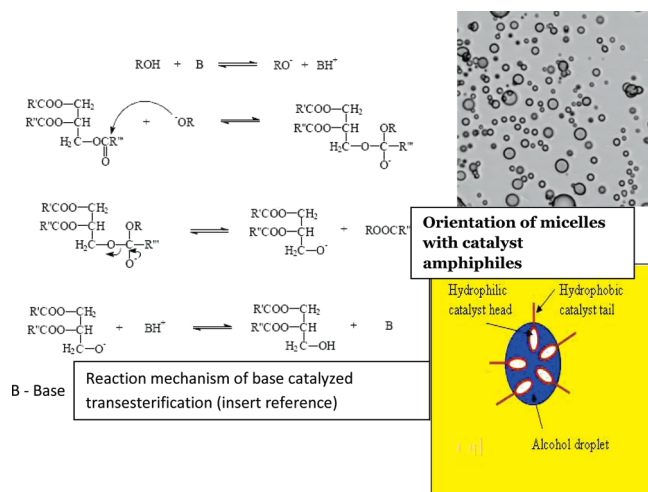


Figure 1. Reaction mechanism of base-catalyzed transesterification along with the orientation of the catalyst amphiphiles.

are zeolites, mainly the ETS-10 group.⁴¹ ETS-10 with a catalyst loading of 11 wt % in a 1 mL vial reactor gave a conversion of 95.8% in 24 h at 150 °C with a 6:1 molar ratio of methanol/soybean oil.³² However, “Esterfip–H” offered by Axens is the only commercial process available that uses a heterogeneous catalysts.^{3,42,43} This process uses a mixture of zinc oxide, aluminum oxide, and zinc aluminates as the catalysts and requires a temperature between 170 and 250 °C, a pressure of approximately 100 bar, and a two-stage reaction. In contrast, homogeneous basic catalysts give conversions near 100% at temperatures at or below 65 °C in less than 3 h.¹³ 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 trade-off between solubility and basicity.

(34) Serio, M.; Ledda, M.; Cozzolino, M.; Minutillo, G.; Tesser, R.; Santacesaria, E. Transesterification of soybean oil to biodiesel by using heterogeneous basic catalysts. *Ind. Eng. Chem. Res.* **2006**, *45*, 6.

(35) Leclercq, E.; Finiels, A.; Moreau, C. Transesterification of rapeseed oil in the presence of basic zeolites and related solid catalysts. *J. Am. Oil Chem. Soc.* **2001**, *78* (11), 5.

(36) Cantrell, D. G.; Gillie, L. J.; Lee, A. F.; Wilson, K. Structure–reactivity correlations in MgAl hydrotalcite catalysts for biodiesel synthesis. *Appl. Catal., A* **2005**, *287*, 8.

(37) Shibasaki-Kitakawa, N.; Honda, H.; Kuribayashi, H.; Toda, T.; Fukumura, T.; Yonemoto, T. Biodiesel production using anionic ion-exchange resin as heterogeneous catalyst. *Bioresour. Technol.* **2007**, *98*, 416–421.

(38) dos Reis, S. C. M.; Lachter, E. R.; Nascimento, R. S. V.; Rodrigues, J. A., Jr.; Reid, M. G. Transesterification of Brazilian vegetable oils with methanol over ion-exchange resins. *J. Am. Oil Chem. Soc.* **2005**, *82* (9), 5.

(39) Kim, H.; Kang, B.-S.; Kim, M.-J.; Kim, D.-K.; Lee, J.-S.; Lee, K.-Y. Development of heterogeneous catalyst system for esterification of free fatty acid contained in used vegetable oil. *Stud. Surf. Sci. Catal.* **2004**, *153*, 4.

(40) Furuta, S.; Matsushashi, H.; Arata, K. Biodiesel fuel production with solid superacid catalysis in fixed bed reactor under atmospheric pressure. *Catal. Commun.* **2004**, *5* (12), 3.

(41) Philippou, A.; Rocha, J.; Anderson, M. W. The strong basicity of the microporous titanosilicate ETS-10. *Catal. Lett.* **1999**, *57*, 3.

(42) Sapienza, R.; Johnson, A. Processes for production of esters from oilin-containing hydrocarbon streams and vegetable or animal oils. U.S. Patent Application 20060270866, 2006.

(43) Stern, R.; Hillion, G.; Rouxel, J.-J.; Leporq, S. Process for the production of esters from vegetable oils or animals oils alcohols. Patent 5,908,946; Institut Français du Pétrole (IFP): Rueil-Malmaison, France, 1999.

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 di-, tri-, tetra-, and polymeric/dendritic or mixtures of these forms) by the sol–gel synthesis method. The focus of this study was to evaluate the catalytic aspect of the inorganic polymer for transesterification ability. In this case, soybean oil was used as the triglyceride and isopropanol was used as the alcohol.

Materials and Methods

Materials. The transesterification reaction was carried out in a high-pressure thermal reactor (4570, Parr Instrument, Moline, IL). The reactor has a maximum operating temperature of 500 °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. 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).

Catalyst Preparation. Titanium isopropoxide (99%, Sigma-Aldrich) 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 propoxide 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. First, a water molecule hydrolyzes an alkoxide bond of the titanium isopropoxide, generating a hydroxyl group. Two such molecules having orthogonal hydroxyl groups give –Ti–O–Ti– via water condensation. The degree of polymerization could be controlled by changing the isopropoxide/water ratios. 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. To obtain the desired structures, water addition was performed, while the propoxide–alcohol mixture was subjected to ultrasonication, as indicated earlier. The sonication system (UP400S, Hielscher Ultrasound Technology), is capable of producing 24 000 kHz waves with a power output of 400 W.

Transesterification. 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 consists of a magnetic drive stirrer with a maximum of 2000 rpm and the tachometer module with an accuracy of ± 10 rpm. The stainless-steel reactor vessel is capable of handling 500 mL of reactants. To initiate the transesterification reaction, 1% (w/w) of the catalyst was added to the triglyceride immediately after preparation and the reactor was sealed. The initial pressure of the reactor was kept constant at atmospheric pressure. The reaction was carried out at six different temperatures, i.e., 50, 100, 150, 200, 250, and 300 °C. Samples were drawn from the reactor only after the reaction temperature reached the desired level for that experiment. However, ancillary data were collected to assess how much conversion had occurred from the onset of the reaction up until the desired temperature was reached (it was observed that during temperature ramping there was only slight conversion). After the temperature reached the reaction temperature, six samples were drawn from each experimental batch in 30 min intervals up to 3 h. The samples drawn were cooled immediately to cease the reaction from progressing further. Then, the samples were centrifuged with 10 000 rpm at 12 °C to separate propyl esters and glycerol. Catalyst and product separation was performed by a centrifuge system (Sorvall

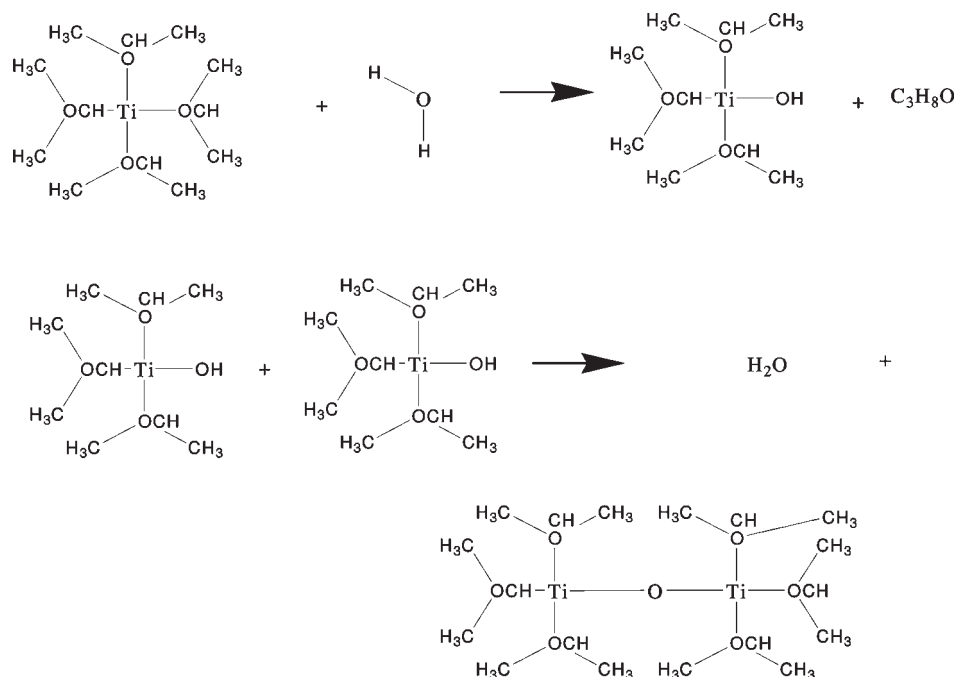


Figure 2. Hydrolysis and water condensation reactions of titanium isopropoxide.

Table 1. Corresponding Structures with the Degree of Polymerization

Water:Titanium isopropoxide ratio	Expected Resultant molecule
0	<p>monomer</p>
1:2 (0.5:1)	<p>Likely a dimer</p>
1:1	<p>based polymer with two propoxide groups residing per monomer</p>
3:2 (1.5:1)	<p>based polymer with one propoxide group residing per monomer</p>
2:1	<p>condensing to TiO₂ polymer</p>

Legend 23 R, Thermo Scientific) that could reach up to 24 000 rpm and was capable of cooling to -4°C .

The top fraction of the products was analyzed for ester yield. Samples were analyzed by gas chromatography (GC 6850, Agilent Technologies, Santa Clara, CA). Auxiliary analysis

was carried out on GC–mass spectroscopy (GC–MS 7890, Agilent Technologies, Santa Clara, CA).

The fatty acid propyl ester yield with respect to the degree of polymerization, time of reaction, and temperature are discussed in the following sections. The results were statistically analyzed

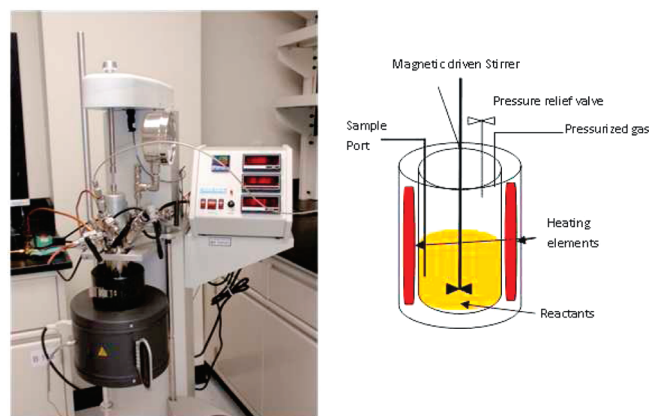


Figure 3. (Left) Actual setup of the reactor and (right) schematics of the reactor.

by Design Expert software. A response surface-reduced quadratic model was used to analyze the data.

The GC method used for isopropyl ester detection is given as follows: inlet temperature, 250 °C; split ratio, 50:1; injection volume, 1 μ L; column flow (helium), 1.6 mL/min (constant flow); flame ionization detector (FID) temperature, 280 °C; H₂ flow, 40 mL/min; air flow, 450 mL/min; makeup gas (nitrogen), 30 mL/min; oven program, 50 °C hold for 1 min, to 200 °C at 25 °C/min, hold for 3 min, to 230 °C at 3 °C/min, and hold for 18 min; column, 30 m \times 0.25 mm \times 0.25 μ m (DB-wax column).

Results and Discussion

To the best of our knowledge, this is the first time such an extensive study on the behavior of the titanium isopropoxide system on transesterification at varying temperatures, degrees of polymerization, and residence times has been performed. The suggested molecular arrangement is shown in Figure 4. The monomer titanium isopropoxide arranges itself with the polar headgroup orienting toward alcohol and the nonpolar hydrocarbon chain orienting toward the oil phase. It is expected that dimers, trimers, and polymers arrange in a similar manner, while Ti atoms stay primarily along the interface. The primary objective of the study was to identify the optimum combination of these parameters that maximize the transesterified product yield. To capture the correlation of all of 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 times, and yield at varying temperatures and reaction times.

The behavior of the titanium isopropoxide system with varying reaction times at increasing degrees of polymerization is depicted in Figure 5. In these graphs, the time begins after the reaction mixture reaching 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., 50–100 °C, it is clearly noticeable that, at lower residence times, the degree of polymerization does not have a significant effect (Figure 5A) on the ester yield. However, as residence time increases, the polymers tend to produce lower ester yields as opposed to smaller molecular (monomeric, dimeric, etc.) forms. It is also noteworthy that, as the residence times increase, the yields increase regardless of the degree of polymerization.

It was interesting to note that, as the temperatures increased beyond 150 °C, the trend reversed, i.e., lower residence times

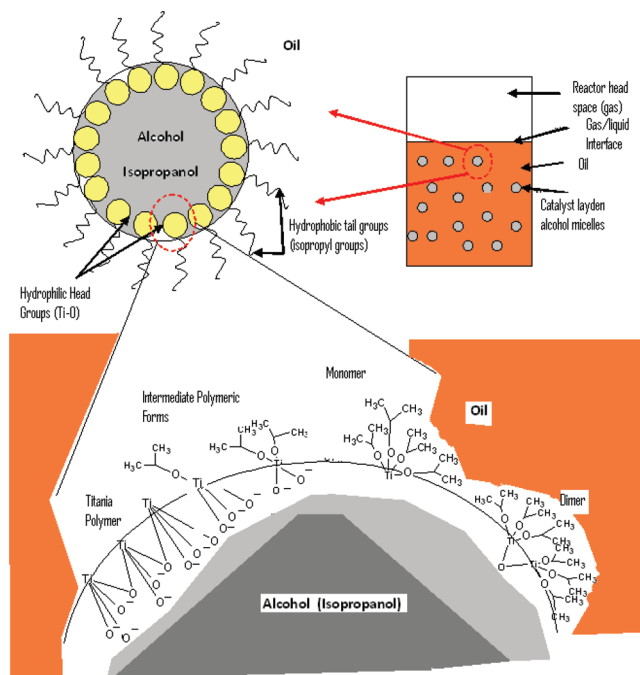


Figure 4. Orientation of titanium isopropoxide polymers in the oil/alcohol interface.

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 (panels C and D of Figure 5) 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 because of 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 GC–MS 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^{44,45}).

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

(44) Brunner, H.; Müller, J.; Spitzer, J. Enantioselective catalysis, C. Decarboxylation of malonic acids in the presence of copper(I) compounds—Not a copper(I) catalysis but a base effect. *Monatsh. Chem.* **1996**, 127 (8), 845–858.

(45) Rajadurai, S. Pathways for carboxylic acid decomposition on transition metal oxides. *Catal. Rev.—Sci. Eng.* **1994**, 36 (3), 385–403.

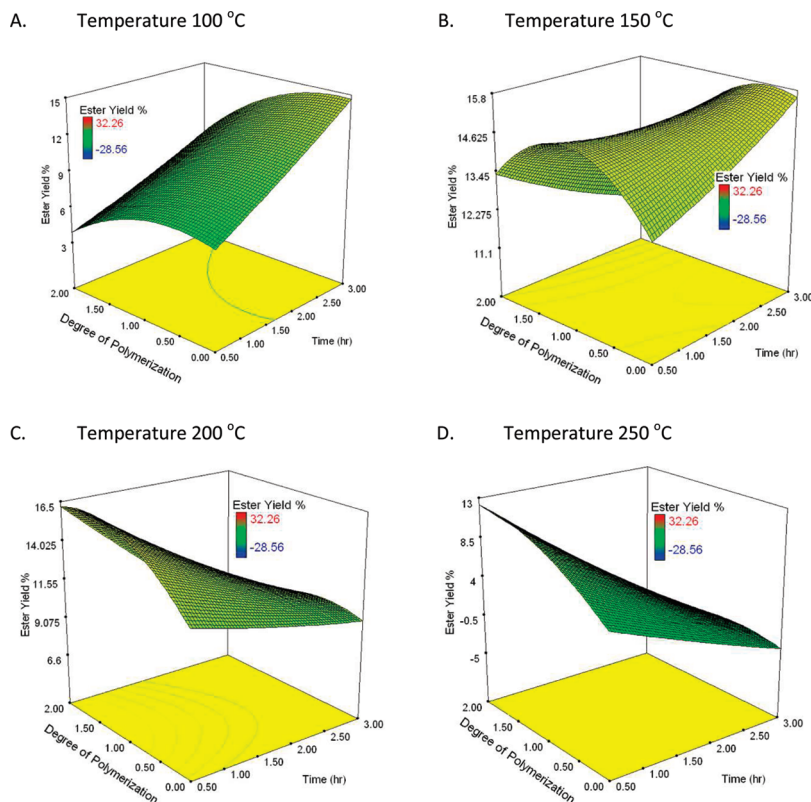


Figure 5. Time and degree of polymerization variation with the ester yield at different temperatures.

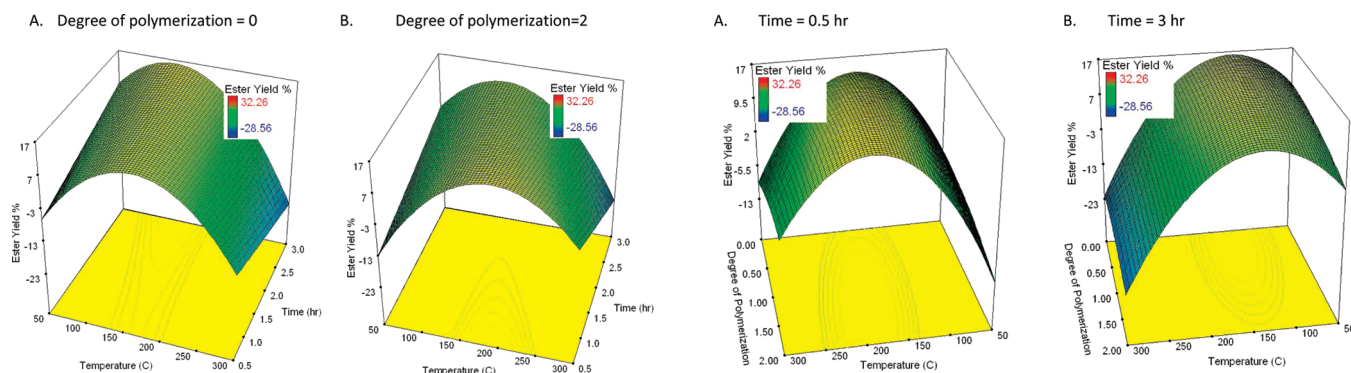


Figure 6. Effect of the temperature and time on ester yield at (A) 0% and (B) 100% polymerization.

optimum temperature for the reaction was between 150 and 200 °C. Notice that regardless of the degree of polymerization or the residence time, the maximum ester yields were obtained between these temperatures. The statistical analysis predicted the optimum temperature for maximizing ester yields to be 181 °C, regardless of the other variables.

To determine the optimum residence time for the reaction, we did an analogous analysis to that above, where the response of the system at 150 and 200 °C was compared at different degrees of polymerization and residence times. Again, in reference 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 h. This means that, by the time the reactor reached 200 °C, the maximum ester yield had already been reached. To further analyze the yield behavior at these temperatures, the responses of the system for varying residence times were compared (Figure 8). To make the comparison easy, the ester yields were adjusted to zero after the

reaction medium reached the desired temperature. The resultant maximum ester yield was 32.3% at 150 °C after 2 h of reaction with the monomeric catalyst. According to Figure 8, it could be noted that most of the system had reached equilibrium by 2 h of reaction time.

Subsequent to identification of 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 TiO₂ inorganic polymer. Although statistically insignificant, the intermediate complexes had intermediate activity. For example, at 0.5 h residence time, the best catalytic activity was displayed by the 1:1 dimer (Figure 8).

At higher temperatures, there can be thermal contribution to the transesterification reaction. To determine this, we analyzed samples (collected at 30 min intervals during 3 h of reaction time) from experiments conducted at 150 and 200 °C

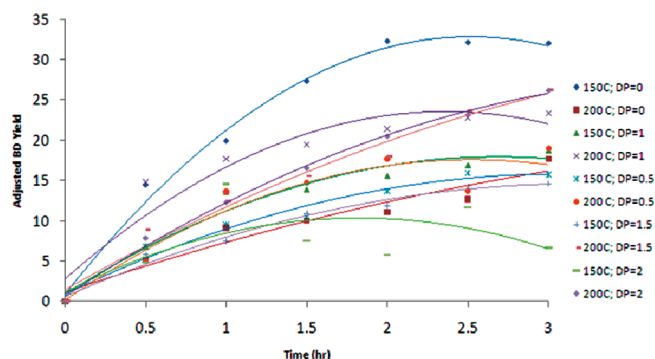


Figure 8. Time versus adjusted biodiesel yield at 150 and 200 °C, at various degrees of polymerization.

without any catalyst. It was evident that there were no esters produced in any of the samples. This denotes that no esterification occurred because of thermal homogeneous phenomena.

There is only a limited amount of literature available to compare these findings to analogous works.^{20,46–48} All of

(46) Cozzolino, M.; Tesser, R.; Di Serio, M.; Ledda, M.; Minutillo, G.; Santacesaria, E. Preparation, characterization and catalytic performances of highly dispersed supported $\text{TiO}_2/\text{SiO}_2$ catalysis in biodiesel production. *Stud. Surf. Sci. Catal.* **2006**, 299–306.

(47) Bonelli, B.; Cozzolino, M.; Tesser, R.; Di Serio, M.; Piumetti, M.; Garrone, E.; Santacesaria, E. Study of the surface acidity of $\text{TiO}_2/\text{SiO}_2$ catalysts by means of FTIR measurements of CO and NH_3 adsorption. *J. Catal.* **2007**, 246 (2), 293–300.

(48) Di Serio, M.; Tesser, R.; Pengmei, L.; Santacesaria, E. Heterogeneous catalysts for biodiesel production. *Energy Fuels* **2007**, 22 (1), 207–217.

these works cite the efficacy of titania as a transesterification catalyst. For instance, Pang and You²⁰ reported a yield of 79.6% with 0.3:1 catalyst/oil after an 8 h experimental run. Our observations suggest that, although much weaker than the propoxide counterparts, titania has a lower but respectable activity for transesterification at temperatures above 150 °C and at a much shorter time span. However, there are no literature data available to compare the performance of other titanium oligomers.

Conclusions

The study confirms that mono-, di-, tri-, 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 °C after 3 h of reaction with the monomeric titanium isopropoxide. However, polymerization reached equilibrium yields after approximately 2 h. It was observed that the reaction reached its optimum at temperatures between 150 and 200 °C after 2–3 h of reaction time. The statistical analysis concluded that only temperature and time had a significant effect on ester yields. The temperature has the most profound effect. The interaction between the temperature and degree of polymerization and the interaction between the 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 catalysts performed slightly better than the polymeric forms. Further experiments should be carried out to elucidate the kinetic behavior of the reaction.