Biofuel Production from Chinese Tallow Tree Seeds Using Microwave Technology

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BIOFUEL PRODUCTION FROM CHINESE TALLOW TREE SEEDS USING MICROWAVE TECHNOLOGY

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science

in

The Department of Biological & Agricultural Engineering

by
Mohamad Barekati Goudarzi
B.Sc., University of Tehran, 2013
December 2015
Dedicated to

Mamani, Babaie

To My beloved parents
ACKNOWLEDGEMENTS

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ABSTRACT

In-situ transesterification (simultaneous extraction and transesterification) of Chinese tallow tree seeds into methyl esters using two microwave systems were investigated in this study. In the first part, utilizing a batch system, parameters tested were catalyst concentration (1-4 wt.%), solvent ratio (2-6 v/w), reaction time (15-60 min) and temperature (50-70°C). A high degree of oil extraction and efficient conversion of oil to biodiesel were found in the proposed range. The process was further optimized in terms of product yields and conversion rates using Dohlert optimization methodology. Based on the experimental results and statistical analysis, the optimal production yield conditions for this process were determined as: catalyst concentration of 1.74 wt.%, solvent ratio about 3 (v/w), reaction time of 20 min and temperature of 58.1°C. GC and H-NMR were used to profile the fatty acid methyl esters and reaction conversion, respectively. All methyl esters produced using this method met ASTM biodiesel quality specifications.

For the second part, a continuous In-situ transesterification of the seeds using a microwave-assisted CSTR system was investigated with determination of kinetic parameters. A high production yield of 90.02% with 97.53% conversion rate was obtained in 24 min CSTR residence time at a methanol/hexane/CTT seed ratio of 3:3:1 (v/v/w), a microwave heating power of 290 W and 14 sec exposure time, reaction temperature of 60°C and sodium hydroxide catalyst loading of 4% wt. of oil. The experimental data fits the first order reaction kinetics. The values of rate constants at different temperatures and the corresponding activation energy were found out to be 0.083-0.087 min⁻¹ and 1987.82 J/mol, respectively. The thermodynamic parameters values such as Gibbs free energy (ΔG), enthalpy (ΔH) and entropy of activation (ΔS) were also
determined. The positive values of $\Delta G$ and small negative value of $\Delta H$ indicated that the reaction has an unspontaneous/endergonic nature and is slightly exothermic.
CHAPTER 1
INTRODUCTION

1.1. Introduction

Energy sustainability and the development of frameworks for an effective application of energy technologies in both local and global setting is still a major challenge for all developed and developing countries, mostly due to the continually increase in transportation fuel consumption for economic development. In 2013, total primary energy consumption increased by 2.3%, while the global oil consumption reached 91.3 million barrels per day, a 1.4% rise compare to previous years. In 2013, it is estimated that a total of only 1687.9 billion barrels remained in the oil reserves worldwide, sufficient for only 53.3 years of global production (Su, Zhang et al. 2015). The consequences of the current increase in global energy demand, as well as the fossil fuels negative environmental impacts, has led to a renewed attraction for renewable energy resources.

Energy sources can be divided into two main categories, renewable and non-renewable. The non-renewable sources of energy are mainly fossil fuels and nuclear energy, which can be replaced by other renewable sources like solar, wind, modern biomass, geothermal etc. The reason behind this replacement is the many positive effects of renewables. The local or domestic nature of renewable energy improves the energy supply security by minimizing the risk of energy supply disruptions (Dincer 2000, Panwar, Kaushik et al. 2011). Besides that, the abundant availability of renewable resources compared to(Zeng, Wang et al. 2008, Suganya, Kasirajan et al. 2014) fossil fuels scarcity, cleanness of renewable energies, minimal environmental impacts and reduced waste generation, such as pollutant gas emissions, are their main advantages. Although fossil fuels are still the major contributor to the world’s energy supply chain, the proportion of biofuels is raising rapidly with the development of science and technology.
The U.S. Energy Information Administration (EIA) estimates that renewable energy will comprise 15 percent of total energy consumption by 2040. Amongst all the mentioned alternative sources of energy, biomass based renewable energy attracted the most attention as it has been at the top of the renewable energy source list. In addition to being the world largest industrial producer and agricultural product supplier, the United State is also the biofuel global developer (Quinn and Davis 2015). Energy security, reduction of dependence on oil imports, the promotion of sustainable economy, development of employment opportunities in agricultural field, and new industrial explorations in order to implement new technologies for development of wide sources of energy are the main driving forces of biomass development in the United States (Su, Zhang et al. 2015).

Most literature reports show a significant increase in renewable energy supplies. In 2013, biofuel productions increased by 71,782 million L from 2006 and reached 117,715 million L in 2013 (Koizumi 2015). 75 percent of total biofuel production was allocated to bioethanol in 2013, and the remaining was attributed to biodiesel. Bioethanol production increased to 83,353 million L in 2012 in comparison to 39,187 million L in 2006. The United State (as the world’s largest producer) and Brazil (as the second producer) produced 50,397 million L and 25,530 million L, respectively, in 2013. These two countries are accounted for 86 percent of world-wide bioethanol production. Following them, China, France, Canada are the other large producer of bioethanol in the world. Biodiesel production, as the second renewable energy source, increased from 6,746 million L in 2006 to 29,545 million L in 2013. The EU is the largest producer of biodiesel by production rate of 12,103 million L in 2013, which was followed by USA, Argentina, Brazil, and Indonesia.
The direct combustion of vegetable oils as fuel in diesel engines proved to be impractical, due to high acid content, high free fatty acid composition, as well as gum formation due to oxidation and polymerization. Carbon sedimentation and thickening of lubricating oil are the other obvious problems (Fukuda, Kondo et al. 2001). In order to overcome these problems, researchers have developed methods to convert oil into more environmentally and technically suitable fuel. Microemulsion, thermal cracking, and transesterification are the most established methods. Amongst them, transesterification is the most popular and preferred (Ma and Hanna 1999). Transesterification is the reaction of oil with an alcohol to form methyl esters and glycerol. The reaction accelerates by catalyst in presence of primary or secondary monohydric aliphatic alcohols (having 1–8 carbon atoms) (Demirbas 2005). Excess amount of alcohol can shift this equilibrium reaction to the right side to produce more methyl esters, with methanol and ethanol being most commercially used. Even though the ethanol is more renewable and biologically friendly and can be produced energy from agricultural crops, methanol is preferable due to economical, physical and chemical advantages (Wen, Jiang et al. 2009). The reaction is catalyzed by alkali and acid catalyst, as well as enzymes (Fukuda, Kondo et al. 2001, Wang, Liu et al. 2011). The use of both batch and continuous process has been reported. However, high cost of investment to build large volume reactors to run batch systems is main challenge and make continuous process preferable (Maçaira, Santana et al. 2011).

Transesterification occurs either with homogeneous or heterogeneous catalysts. In homogeneous form, the usage of catalyst is in liquid/dissolved form, and it is mainly acid or alkali catalysts. The protonation of the carbonyl group in triglycerides is the basic factor in the acid catalysis where the alcohol attacks the protonated carbon to create a tetrahedral intermediate. However, creating nucleophilic alkoxide from the alcohol to attack the
The electrophilic part of the carbonyl group of the triglycerides is the important factor in a homogeneous-base catalyzed reaction (Schuchardt, Sercheli et al. 1998). The first conventional method applied in the biodiesel production industry was the use of homogeneous catalysts. Even though, its industrial application has been decidedly proven, recent investigations are focusing on the application of heterogeneous catalysis with a view to improve productivity. The application of heterogeneous catalysts, which are in form of a solid, in biodiesel production lessens the issues contributed to homogeneous catalysis. The catalyst can be recycled and reused for several times with better separation of final product due to high productivity and reduced cost of operation and production. This method is proven to be environmental friendly and can be utilized in both batch and continuous process without any further purification steps (Yan, DiMaggio et al. 2010, Endalew, Kiros et al. 2011).

The first objective in this work is to develop an in-situ method for direct production of biodiesel from Chinese tallow tree seeds through a homogeneously catalyzed reaction. In order to facilitate the reaction pace, the application of microwave technology as a fast source of heat was investigated. Doehlert optimization methodology was used to optimize the process in term of reaction operation factors like catalyst concentration, reaction time and temperature, and solvent ratio. The second objective was to apply the optimized condition in a continuous process and study the kinetic of the reaction as well as the thermodynamic parameters with important impacts on the process.

1.2. References


CHAPTER 2

IN-SITU TRANSESTERIFICATION OF SEEDS OF INVASIVE CHINESE TALLOW TREES (TRIADICA SEBIFERA L.) IN A MICROWAVE BATCH SYSTEM USING HEXANE AS CO-SOLVENT: BIODIESEL PRODUCTION AND PROCESS OPTIMIZATION

2.1. Introduction

Considering the increasing nature of global energy demand, volatile oil price, and recent concerns regarding side-effects of fossil fuels on environment, such as general health problems, air pollution and consequently global warming, green energy resources have attracted major research interests (Lynd and Cushman Jr 1991, Gnansounou, Dauriat et al. 2009, Costa and de Morais 2011). Economic competitiveness, environmental acceptability, and technical reliability are the essential characteristics of green energy resources (Meher, Vidya Sagar et al. 2006). Biodiesel derived from vegetable oil of either food or non-food material has acquired a growing interest as a promising alternative to mentioned concerns. The mitigation of carbon dioxide and being an identical substitute for petroleum diesel without requiring further modification on engines are two major advantages of biodiesel (Chisti 2008).

Biodiesel consists of monoalkyl esters of long chain fatty acids produced by reversible esterification reaction of vegetable oil or animal fat with mostly short chain alcohols such as methanol or ethanol which can be performed either in alkaline or acidic catalyst (Ma and Hanna 1999). Using less expensive and non-edible feedstock is a way of decreasing the biodiesel production costs (Goudarzi and Boldor 2015). Chinese tallow tree seeds are a good source of saturated and unsaturated non-food oil for biodiesel production (more than 40% lipids in the seed mass) due to the trees fast growth rate, salt and drought tolerance, and ability to resprout (Boldor, Kanitkar et al. 2010, Terigar, Balasubramanian et al. 2010). Its resistance against terse conditions makes it desirable for cultivation in vacant lands and abandoned agricultural fields, although
encroachment on native lands can increase invasive pressure (Scheld and Cowles 1981, Carrillo, Wang et al. 2012). Lipid presents in seeds consists mostly of palmitic acid, oleic acid and linoleic that are almost evenly distributed in external white vegetable tallow and kernel (Gunstone 2005, Terigar, Balasubramanian et al. 2010). Protein and amino acids extracted from kernel residual can also be used as a value-added product after oil separation (Bolley and McCormack 1950). Moreover, stems and branches leftover from harvesting can be used as a woody source of fuel.

In addition to the extraction process, degumming, deacidification, dewaxing, dephosphorization, dehydration, etc. are additional refining steps which contribute to oil extraction and purification cost using conventional methods of biodiesel production from various types of oil feedstock. Therefore, establishment of a direct method which excludes the extraneous unit operations mentioned above, and developing a reactive extraction method (in-situ transesterification) has the potential to decrease processing cost by up to 70% of the total biodiesel production cost (Haas, Scott et al. 2004, Velasquez-Orta, Lee et al. 2012). A key role in oil extraction process is choosing an effective solvent. Several studies reported in literature regarding mass transfer limitations in transesterification reactions due to low oil solubility in the alcohol phase (confirmed by our initial screening experiments with methanol only that resulted in low biodiesel yields), suggested the use of co-solvents such as benzene, hexane, THF, chloroform, petroleum ether and dichloromethane in the process (Boocock, Konar et al. 1998).

In general, a strong alkali catalyst can improve in-situ transesterification process in terms of shortening reaction times and reducing the amount of catalyst required in the commercial scale process (Wyatt and Haas 2009, Shahbazi, Khoshandam et al. 2012). However, using sodium hydroxide lowers triglycerides conversion to biodiesel (low product yield) and pushes
downstream separation cost higher due to an increase in the undesirable saponification reactions caused by presence of water and acting as a surfactant between the two final immiscible products (Mendow, Veizaga et al. 2011, Mazubert, Taylor et al. 2014).

Microwave processing is an effective technique to improve functional components extraction such as oil from plant raw material and to improve the transesterification reaction itself (Terigar, Balasubramanian et al. 2010, Balasubramanian, Allen et al. 2011, Terigar, Balasubramanian et al. 2011, Nde, Boldor et al. 2015). Microwave radiation plays a role both as heat source and thermal pre-treatment (Boldor, Sanders et al. 2005, Boldor, Kanitkar et al. 2010). On one side, rapid generation of heat and pressure build-up within plant cells significantly affects microstructure, while on the other side the rapid increase of temperature above boiling point leads to a supercritical state of the solvent. Both phenomena are driving forces that move compounds out of biological matrices (Terigar, Balasubramanian et al. 2011, Mazubert, Taylor et al. 2014).

The two major microwave-based mechanisms that cause these effects are dipolar rotation and ionic conduction. The frictional and collision forces between dipolar molecules and surrounding media due to electric field oscillation, and kinetic energy dissipation of the charged dissolved particles generate high amount of heat (Mazubert, Taylor et al. 2014, Fennell, Bourgeois et al. 2015). These heating effects are strongly dependent on the dielectric properties of the mixture undergoing microwave heating (Boldor, Sanders et al. 2004, Terigar, Balasubramanian et al. 2010, Fennell and Boldor 2013, Muley and Boldor 2013). Thus, rapid and selective extraction, low energy consumption and solvent usage, and reduced by-product formation are microwave-assisted processing advantages over conventional methods (Kanitkar, Sabliov et al. 2011, Terigar, Balasubramanian et al. 2011).
This chapter demonstrates the implementation of a microwave-based batch process for biodiesel production via \textit{in-situ} transesterification of Chinese tallow tree seeds using methanol and hexane as alcohol of reaction and co-solvent, respectively. In order to evaluate the effect of catalyst concentration, solvent ratio, reaction time and temperature on product yield, Doehlert optimization methodology was used. Reaction conversion was analyzed via H$^+$ NMR to ensure the occurrence of oil extraction along with transesterification. The obtained product yields were used to obtain a polynomial equation to predict the optimum process parameters. The predicted point was examined afterward experimentally to ascertain the reliability of the proposed model. Finally, the FAME composition was profiled using gas chromatography and the results compared with ASTM standards for further required specifications.

2.2. Materials and methods

2.2.1. Materials

Lab Grade methanol alcohol and reagent grade ACS (99.5\%) hexane used in the reactions were purchased from Fisher Scientific (Pittsburg, PA) and Mallinckrodt Chemical Inc. (St. Louis, MO), respectively. The catalyst sodium hydroxide was supplied by Pharmco-AAPER (Brookfield, CT).

2.2.2. Methods

2.2.2.1. Sample Preparation

Tallow tree seeds were manually harvested from near Baton Rouge, LA between October-November 2012 (30°23'22.3"N 91°11'57.2"W). Adhering leaves and branches were separated out from seeds manually. These seeds were winnowed further to remove any foreign material and dried for 24 hr at 103°C in a conventional hot air oven. The processed seeds were
then ground using a blade-type coffee grinder and stored in sealed plastic bags in the freezer at -4 °C to avoid moisture gain until further use.

2.2.2.2 Determination of Moisture Content

In order to determine the moisture content, conventional drying was performed using a conventional hot air oven set to 103°C. Three samples of 10 g CTT seeds were weighed and placed in the oven. After a given period of time, the samples were removed from the oven and weighed again. This weighing procedure was repeated for over 72 hours until all moisture was removed from the samples. This data was then used to determine the moisture content of the samples using following formula:

\[
Moisture\ content = \frac{X_1 - X_2}{X_1} \times 100
\]  

[2.1]

Where \(X_1\) is the initial weight of samples and \(X_2\) is the weight at the end.

2.2.2.3 Soxhlet solvent extraction

The theoretical maximum oil yield in the seeds was measured using a Soxhlet extraction (ASTM D5369-93(2008)e1) apparatus, where 20 g of ground CTT seed was weighed into a cellulose thimble (30 mm × 77 mm, Whatman, Maidstone, UK) and placed in a Soxhlet extractor. One hundred and fifty milliliters of hexane and methanol mixture were used as the solvent and the extraction was performed for 15 h. After solvent evaporation on a rota-vapor (BUCHI R-124) and drying in a vacuum dryer (Isotemp Vacuum Oven Model 285A) for 15 h, the crude oil weight was measured and used as the maximum recoverable oil in yield using Equation 2.2.

\[
Oil\ Content = \frac{Extracted\ oil\ weight\ (g)}{Biomass\ weight\ (g)} \times 100
\]  

[2.2]

2.2.2.4 In-situ transesterification procedure
In-situ transesterification were performed in an Ethos E batch microwave system (Milestone Inc., Monroe, CT), having a maximum power output of 1.6 kW. The system consisted of 270 mL sealed high-pressurized TFM (Tetrafluoromethane) vessels with magnetic stirrers and a built-in optical fiber temperature sensor for process monitoring and control. Twenty grams of ground CTT seeds (1% > moisture content) were placed in vessels with 60 ml of hexane along with calculated amount of sodium hydroxide dissolved in methanol. This mixture was subjected to microwave treatment at different desired temperatures and reaction times. Heating ramp-up time was 3 min with a cooling time of 10 min.

2.2.2.5. Separation of by-products

After each experimental run, the reaction mixture was centrifuged at 3600 rpm for 10 min to separate suspended solid biomass from the liquid mixture. The solid biomass residues were washed and pooled to liquid mixture further by re-suspension in recovered methanol, to recover traces of the ME (methyl esters) product. The obtained liquid phase was transferred into a separating funnel where 50 ml hexane and 50 ml distilled water were added to accelerate separation of phases. The lower layer containing extra methanol, water, glycerin, sodium hydroxide and soap was drained off from upper hydrophobic layer consisting of hexane, FAME (fatty acid methyl esters) and unreacted oil. In order to ensure complete removal of impurities, the upper layer was washed further three times with warm distilled water. Hexane was recovered to be reused in a rota-vapor, and residual product was then vacuum dried for 15 h.

2.2.2.6. Analytical methods

NMR spectroscopy and Gas chromatography (GC) are commonly used as analytical methods for biodiesel analysis. Due to their high accuracy, GC and NMR spectroscopic analyses have been the most reliable technique for the quantification of minor components and monitoring
the transesterification reaction, respectively. FAME produced from CTT biomass by the *in-situ* method, was analyzed by H$^+$ NMR and GC. The fatty acid methyl ester composition of the biodiesel was profiled by GC using a DB5-HT column. H NMR spectra were obtained using a BRUKER 500 MHz AVANCE III NMR analyzer with CDCl$_3$ as solvent and TMS as an internal standard.

A simple formula (Equation 2.3) (Gelbard, Brès et al. 1995) for reaction conversion (%) is

\[
C = \left(\frac{2A_{ME}}{3A_{CH_2}}\right) \times 100
\]  

[2.3]

Where C is conversion percentage of CTT oil to ME. A$_{ME}$ and A$_{CH_2}$ are integration value of the methoxy protons of the ME (3.6-3.7 ppm) and methylene protons of unreacted oil (2.3 ppm), respectively. Coefficients 2 and 3 were derived since the methylene carbon possesses two protons, while the methanol alcohol carbon has three protons.

2.2.2.7. Statistical Analysis

The effect of the four factors and their interactions were studied using Doehlert experimental design. Along with fewer experimental runs, flexibility towards assigning different levels for various factors, and higher efficiency in comparison to Box-Behnken central composite design, this approach also allows to study optimization via response surface methodology (Nde Bup, Abi et al. 2012). The factors studied were catalyst concentration, solvent ratio, reaction time, and temperature and they ranged from 1-4 wt.%, 2-6 v/w, 15-60 min, and 50-70°C, respectively. Twenty five experimental runs, including five replications for central point, were performed. Coded and un-coded values for Doehlert experimental design are presented in Table 2.1.
Table 2.1 The experimental parameters, experimental ($Y_{\text{exp}}$) and theoretical product yields ($Y_{\text{mod}}$), and corresponding standard deviation

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</tr>
<tr>
<td>15</td>
<td>0.5</td>
<td>-0.289</td>
<td>-0.204</td>
<td>-0.791</td>
</tr>
<tr>
<td>16</td>
<td>0</td>
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<td>-0.791</td>
</tr>
<tr>
<td>17</td>
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<td>0</td>
<td>0.612</td>
<td>-0.791</td>
</tr>
<tr>
<td>18</td>
<td>-0.5</td>
<td>0.289</td>
<td>0.204</td>
<td>0.791</td>
</tr>
<tr>
<td>19</td>
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<td>0.204</td>
<td>0.791</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>0</td>
<td>-0.612</td>
<td>0.791</td>
</tr>
<tr>
<td>21</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>23</td>
<td>0</td>
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<td>24</td>
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</tr>
<tr>
<td>25</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$X_1$: Catalyst Concentration, $X_2$: Solvent Ratio, $X_3$: Reaction Time $X_4$: Reaction Temperature, $Y_{\text{exp}}$: Experimental Product Yield, $Y_{\text{mod}}$: Predicted Product yield, RSE: relative standard error of the estimate
The results of experiment helped the regression analysis to fit the data for the following polynomial equation (Equation 2.4) with interaction.

\[
Y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j>i}^{k} b_{ij} x_i x_j 
\]

[2.4]

Where \(b_0, b_i, b_{ii}, \text{and } b_{ij}\) are model coefficients for intercept, linear, quadratic and interaction terms, respectively, and \(x_i\) and \(x_j\) are coded independent variables. The regression coefficient of determination or relative standard error (RSEE) observed between the experimental and predicted results are the criteria for reliability evaluation of the model. Regression coefficient (\(R^2\)) more than 0.7 and 0.8 for biological and chemical, respectively, are acceptable (Lundstedt, Seifert et al. 1998). The RSEE<10% is preferable and it is calculated from the equation (Equation 2.5) below:

\[
\text{RSEE\%} = \sum_{i=1}^{n} \left| \frac{Y_{\text{exp}} - Y_{\text{mod}}}{Y_{\text{exp}}} \right| \times \frac{100}{n} 
\]

[2.5]

where, \(Y_{\text{exp}}\) and \(Y_{\text{mod}}\) are the values obtained from experiments and from the model, correspondingly, and \(n\) is the number of experimental results.

2.3. Results and discussion

2.3.1. Modeling and optimizations

2.3.1.1. Product yield

The experimental factors in form of coded and real values, experimental (\(Y_{\text{exp}}\)) and Theoretical product yields (\(Y_{\text{mod}}\)), and their relative standard errors under different treatment conditions are presented in Table 2.1. The model coefficients for the polynomial equations, and P-values for both product yield are given in Table 2.2. Table 2.3 shows a summary of the ANOVA for the product yield.
Table 2.2 Model constants and P values for product yield and reaction conversion

<table>
<thead>
<tr>
<th></th>
<th>Product Yield</th>
<th></th>
<th>Reaction Conversion</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coefficient</td>
<td>P-value</td>
<td>Coefficient</td>
<td>P-value</td>
</tr>
<tr>
<td>b₀</td>
<td>84.4077</td>
<td>0.000</td>
<td>94.5850</td>
<td>0.000</td>
</tr>
<tr>
<td>b₁</td>
<td>-2.3461</td>
<td>0.019</td>
<td>9.3163</td>
<td>0.042</td>
</tr>
<tr>
<td>b₂</td>
<td>-4.4191</td>
<td>0.000</td>
<td>1.8334</td>
<td>0.520</td>
</tr>
<tr>
<td>b₃</td>
<td>-0.8176</td>
<td>0.352</td>
<td>-0.2210</td>
<td>0.937</td>
</tr>
<tr>
<td>b₄</td>
<td>0.1501</td>
<td>0.861</td>
<td>-0.1050</td>
<td>0.970</td>
</tr>
<tr>
<td>b₁₁</td>
<td>-4.7907</td>
<td>0.012</td>
<td>-80.8445</td>
<td>0.000</td>
</tr>
<tr>
<td>b₂₂</td>
<td>-3.6509</td>
<td>0.042</td>
<td>24.1109</td>
<td>0.023</td>
</tr>
<tr>
<td>b₃₃</td>
<td>-2.0899</td>
<td>0.186</td>
<td>11.5122</td>
<td>0.167</td>
</tr>
<tr>
<td>b₄₄</td>
<td>-4.6275</td>
<td>0.008</td>
<td>1.0348</td>
<td>0.887</td>
</tr>
<tr>
<td>b₁₂</td>
<td>0.3949</td>
<td>0.859</td>
<td>-4.1815</td>
<td>0.568</td>
</tr>
<tr>
<td>b₁₃</td>
<td>-9.9052</td>
<td>0.002</td>
<td>2.0800</td>
<td>0.797</td>
</tr>
<tr>
<td>b₁₄</td>
<td>-1.2215</td>
<td>0.637</td>
<td>2.0749</td>
<td>0.805</td>
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<tr>
<td>b₂₅</td>
<td>10.1582</td>
<td>0.002</td>
<td>37.5272</td>
<td>0.006</td>
</tr>
<tr>
<td>b₂₄</td>
<td>-2.3005</td>
<td>0.381</td>
<td>14.2779</td>
<td>0.142</td>
</tr>
<tr>
<td>b₃₄</td>
<td>4.0108</td>
<td>0.141</td>
<td>10.3273</td>
<td>0.258</td>
</tr>
</tbody>
</table>

Table 2.3 Analysis of variance for product yield and reaction conversion

<table>
<thead>
<tr>
<th></th>
<th>Product Yield</th>
<th></th>
<th>Reaction Conversion</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DF</td>
<td>SS</td>
<td>MS</td>
<td>F</td>
</tr>
<tr>
<td>Regression</td>
<td>14</td>
<td>335.981</td>
<td>23.999</td>
<td>6.855</td>
</tr>
<tr>
<td>Residual</td>
<td>10</td>
<td>35.011</td>
<td>3.501</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>24</td>
<td>370.993</td>
<td>15.458</td>
<td></td>
</tr>
</tbody>
</table>

Regression coefficient of determination and average RSEE calculated for product yield were 0.9056 and 1.19%, respectively. The results of P-value for the linear effects of catalyst concentration ($X₁$), solvent ratio ($X₂$), the quadratic effects of catalyst concentration ($X₁^2$), solvent ratio ($X₂^2$), and reaction temperature ($X₃^2$), and the interaction effects of catalyst concentration and reaction time ($X₁×X₃$), solvent ratio and reaction time ($X₂×X₃$) (P-value<0.05) show that they significantly influenced the product yield, whereas the other factor combinations did not, as indicated by their high P-values. Comparing the results presented in Table 2.2 with
corresponding values of study reported by Hailegiorgis, Mahadzir et al. (2013), some contradictions were observed. The linear effect of temperature, quadratic effect of time, and interaction effects of catalyst concentration and solvent ratio, catalyst concentration and temperature, and solvent ratio and time were significant for their study. These contradictions could be due to the effects of microwave on oil extraction and transesterification efficiency in comparison to conventional method as microwave interacts directly with the biomass microstructure as previously described (Terigar, Balasubramanian et al. 2010, Balasubramanian, Allen et al. 2011, Fennell and Boldor 2014). The differences could also be linked to the nature of the vegetable material (Jatropha curcas in their case and the CTT in this work).

2.3.1.2. Reaction conversion

The experimental factors, experimental (obtained by H-NMR analysis) and theoretical (calculated by model) reaction conversion, $C_{exp}$ and $C_{mod}$, under different treatment conditions are presented in Table 2.4 while model coefficients and P-values are given in Table 2.2. Table 2.3 shows a summary of ANOVA for reaction conversion (lower rows).

The residual plot (Figure 2.1) for regression analysis showed an unacceptable deviation for obtained conversion in row 1 and 2 (observation 1 and 2). Even though the repetition of NMR analysis proved the same degree of conversion for both data, datum in row 1 was treated as an outlier and eliminated in favor of higher regression coefficient, as previously described in literature (Welham, Gezan et al. 2014). The improvement of residual plot can be seen after elimination of first datum in Figure 2.1, see B. Regression coefficient of determination and average RSEE calculated for product yield were 0.9799 and 2.62%, respectively.
Table 2.4 The experimental parameters, the experimental ($C_{\text{exp}}$) and theoretical reaction conversion ($C_{\text{mod}}$)

<table>
<thead>
<tr>
<th>Exp’t No</th>
<th>Experimental matrix (Real values)</th>
<th>Responses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$X_1$(wt.%) $X_2$(v/w) $X_3$(min) $X_4$(°C)</td>
<td>$C_{\text{exp}}$ (%) $C_{\text{mod}}$ (%)</td>
</tr>
<tr>
<td>1</td>
<td>4 4 37.5 60</td>
<td>94.52 23.05</td>
</tr>
<tr>
<td>2</td>
<td>1 4 37.5 60</td>
<td>4.42 4.42</td>
</tr>
<tr>
<td>3</td>
<td>3.25 6 37.5 60</td>
<td>94.37 96.89</td>
</tr>
<tr>
<td>4</td>
<td>1.75 2 37.5 60</td>
<td>86.91 84.39</td>
</tr>
<tr>
<td>5</td>
<td>3.25 2 37.5 60</td>
<td>94.44 97.33</td>
</tr>
<tr>
<td>6</td>
<td>1.75 6 37.5 60</td>
<td>94.08 91.19</td>
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<td>7</td>
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<td>95.85 98.15</td>
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<tr>
<td>8</td>
<td>1.75 3.33 15 60</td>
<td>90.44 88.13</td>
</tr>
<tr>
<td>9</td>
<td>3.25 3.33 15 60</td>
<td>93.97 96.96</td>
</tr>
<tr>
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<td>2.5 5.33 15 60</td>
<td>94.47 93.84</td>
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<tr>
<td>11</td>
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<tr>
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<td>94.95 90.14</td>
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<td>75.21 80.02</td>
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<tr>
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<td>74.09 79.97</td>
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<tr>
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<td>2.5 2.67 43.13 70</td>
<td>94.29 93.28</td>
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<tr>
<td>20</td>
<td>2.5 4 20.63 70</td>
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<tr>
<td>21</td>
<td>2.5 4 37.5 60</td>
<td>94.58 94.58</td>
</tr>
</tbody>
</table>

RSEE: relative standard error of the estimate

Figure 2.1. The regression analysis residual of reaction conversion (Lower residual values in B)

The results of P-value show that the factors that significantly affect reaction conversion were catalyst concentration ($X_1$), quadratic effects of both catalyst concentration ($X_1^2$) and solvent ratio ($X_2^2$), and the interaction effect of solvent ratio and reaction time ($X_2 \times X_3$) (P-value<0.05). A
similar set of results, 90% of in-situ conversion calculated from H-NMR spectrum analysis, was already reported by (Suganya, Kasirajan et al. 2014), however for a different processing method (ultrasonic based) and feedstock (marine macroalgae), thus direct comparisons cannot be objectively performed.

2.3.1.3. Optimization

To optimize the product yield, first partial derivatives of Equation 2.4 were calculated and written as Equation 2.5.

\[
\text{Yield (\%)} = 84.4077 - 2.3461 \times X_1 - 4.41911 \times X_2 - 0.817647 \times X_3 + 0.150129 \times X_4 - 4.7907 \times X_1^2 - 3.65092 \times X_2^2 - 2.0899 \times X_3^2 - 4.62747 \times X_4^2 + 0.394916 \times X_1 \times X_2 - 9.90523 \times X_1 \times X_3 - 1.22154 \times X_1 \times X_4 + 10.1582 \times X_2 \times X_3 - 2.30054 \times X_2 \times X_4 + 4.01084 \times X_3 \times X_4
\]

The optimum points (minimum or maximum point) for each factor was obtained by equating the system to zero and then solving for each factor using the matrix method on Microsoft Excel. This gave the optimum points in coded values, which were then transformed to real values. The mathematical optimum values obtained were \( X_1 = 1.74 \) (% catalyst), \( X_2 = 2.98 \) (v/w methanol per seed mass), \( X_3 = 43 \) (min), \( X_4 = 58.1 \) (°C). Optimum conditions for the production yield fell inside of the experimental range. Since minimizing time is one of the primary goals of this study, two experiments were conducted at the optimum point mathematically obtained, with different reaction time at 20 and 43 min to determine optimal conditions and the results were 89.19% and 85.77%, respectively. This shows that the experimental production yield at 20 min was not only higher than that for 43 min but the microwave system also used 36 Watt energy for 23 min more (corresponding to 49680 J). However, the predicted results from model showed that the production yield for 43 min is slightly better (85.91% and 84.47%). This conflict could be attributed to the reliability of the model in prediction. The other possible reason could be the reverse transesterification reaction
from 20 to 43 min, or to some water being extracted at the longer time, which favored formation of soap to the detriment of biodiesel (Eevera, Rajendran et al. 2009, Kafuku, Lam et al. 2010).

These experimental obtained yields verify the optimum conditions and suggested that 20 min is more efficient in terms of time and energy. Nevertheless, the reaction conversion is the other important objective that should be taken into consideration. The result of H-NMR for experimental conversion at 20 min was 96.62%. Both experimental yield and conversion proved that the optimum point was highly efficient.

2.3.2. Parametric study of reaction factors on product yield and reaction conversion

The results of main plot effect for each individual factor are provided for product yield and reaction conversion. This was obtained by maintaining all other factors constant at the central point ($X_1=0, X_2=0, X_3=0, X_4=0$) and varying one as a function of the response. In order to investigate the interaction effect of factors on product yield, 3D surface curves were plotted by maintaining two factors constant while varying the others. Only interactions effect that had a significant effect on the response have been considered in this part of the study.

2.3.2.1. Effect of catalyst concentration on product yield and reaction conversion

The effects of catalyst concentration on the product yield and reaction conversion are shown in Figure 2.2. As catalyst concentration increases, the product yield starts to improve (very slightly by almost 2%) where it reaches a maximum. However, overloading the system with catalyst decreases product yield (final product weight). This is due to the fact that moisture traces imported by oil, catalyst and methanol (highly hygroscopic) can also significantly reduce the effectiveness of catalyst by saponification (Canakci and Van Gerpen 1999). Saponification is the dominant side-reaction of transesterification in which sodium hydroxide is preferentially binding with water instead of alcohol. Thus, the resultant ester chain has no methyl group and
remains in aqueous solution with the sodium forming soap and consequently lowering the production yield (Komers, Skopal et al. 2002). Similar behavior was reported by Kumar, Ravi Kumar et al. (2011) for *Pongamia pinnata* oil.

![Figure 2.2. Catalyst concentration main effect plots of reaction conversion and product yield](image)

The irreversible saponification reaction occurrence at higher catalyst concentration competes with the desired transesterification reaction and produce undesirable soap. Formation of soap in form of a gel (gel which was observed during washing with deionized-water for experiments with high catalyst concentration) can also elevate the viscosity of biodiesel phase. Some authors reported similar phenomena relate to gel formation previously for *in-situ* transesterification of other feedstock (Dorado, Ballesteros et al. 2003, Kumar, Ravi Kumar et al. 2011).

From Experiment #2 in Table 2.1, it can be observed that even though the reaction conditions led to high oil extraction yields (81.96%), lower concentration of the catalyst did not efficiently advance the production of FAME as the presence of other reactants may have
impeded the catalyst contact with extracted oil. Thus, conversion was only 4.42% (Table 2.3). In in-situ biodiesel production processes, higher experimental product yields may not necessarily be correlated with higher transesterification yields because extraction conditions may not necessarily favor the transesterification reaction. This emphasizes the need for supplemental measurements such as GC or H-NMR analysis, as performed in this work, to verify the degree of conversion of the extracted oil into biodiesel. Figure 2.2 buttresses the fact that product yield and the degree of conversion may not show the same trends in in-situ transesterification reactions, though the two values may approach each other under the right optimum conditions.

2.3.2.2. Effect of solvent ratio on product yield

The effect of solvent ratio on product yield is shown in Figure 2.3. There was a gradual rising in the product yield for low solvent ratio (almost 1% rise as shown on the Figure). However, as a methanol ratio increased further, the product yield decreased again. The probable reason could be explained in terms of methanol properties. Methanol, due to its high polarity, is an effective solvent in terms of microwave radiation absorption. Therefore, the effect of methanol in oil extraction even at low concentration is considerable. Moreover, keeping methanol ratio at the lowest possible amount is favorable in terms of reducing the downstream separation costs (Stiefel and Dassori 2008). However, using excess methanol may not be desirable to the extraction and transesterification. This could be attributed to a higher absorption of microwave irradiation by solvent, thereby preventing or limiting the absorption of radiation by seed biomass and consequently a reduction in the release of oil. The reduction in the amount of hexane (co-solvent) and sodium hydroxide (catalyst) concentrations due to excess methanol can also slow down the oil extraction and transesterification reaction. Considering the optimum point and behavior of solvent presented in Figure 2.3, very low methanol (2.98 vol/wt.) usage was
achieved in comparison to that reported by Patil, Gude et al. (2011) on microwave-assisted transesterification of dry algal biomass, where they used 12:1 (vol/wt.) ratio. This could be as a result of hexanes role in the present study as co-solvent in oil extraction from the biological matrix and reduction of oil viscosity when mixing in the additional hexane.

Figure 2.3. Solvent ratio main effect plots of product yield

2.3.2.3. Effect of reaction time on product yield

The effect of reaction time on the lipid yield, as shown in Figure 2.4, is negligible (82.5% vs. 84.5%). This is acceptable evidence, along with high P-value (0.352), to prove that changes in reaction times do not significantly affect the production yield. According to our previous work on CTT seed oil extraction only, microwave exposure can effectively decreases the extraction time to as little as 20 min (Boldor, Kanitkar et al. 2010). Thus, due to such an improvement in extraction and consequently transesterification, there is a residual amount of oil to be extracted and esterified for reaction times longer than 20 min, minimizing any observable improvements. A comparison to published data (Amalia Kartika, Yani et al. 2013) indicates that the system described here is more efficient with respect to time for in-situ transesterification (20 min vs. 4
hr). However, the data already reported in that study is based on a different feedstock, which make it difficult to perform a substantive comparison with the present study.

2.3.2.4. Effect of reaction temperature on product yield

The effects of reaction temperature on the product yields are given in Figure 2.5. Similar to trends observed with reaction time, the variation of product yield with reaction temperature was not significant, whereas they varied only between 81.5% and 84.5%. On the one hand, the batch microwave system used in this study maintained temperature constant by turning the magnetron on and off. Microstructural damages and most of the effective oil extraction is limited only to the duration of active microwave exposure (Boldor, Kanitkar et al. 2010). This means that the higher the temperature, the higher the oil extraction rate and subsequently transesterification. At higher temperatures on the other hand, increased solvent evaporation and saponification reaction led to less solvent-feedstock contact and product yield, respectively, which therefore neutralized the normally beneficial effects of higher temperature. For
temperature between 50°C and 60°C, a higher temperature increased oil extraction and reactants solubility, decreased viscosities of extracted oils, and consequently resulted in an increased reaction rate and a shorter reaction time. However, temperature higher than 60°C (above optimum temperature) favors saponification reaction over transesterification (Leung, Wu et al. 2010) and solvents evaporation.

![Reaction temperature main effect plots of product yield](image)

**Figure 2.5.** Reaction temperature main effect plots of product yield

2.3.2.5. Effect of catalyst concentration and reaction time on product yield

The effect of catalyst amount and total reaction time on product yield at a constant solvent ratio and temperature is shown in Figure 2.6. The biodiesel production yield was influenced significantly by the amount of catalyst and total reaction time (P-value = 0.002). By gradually increasing catalyst concentration, maximum product yield of the reaction started to move toward lower reaction time. This could be due to the higher catalyst concentration effect on reaction kinetics of both saponification and transesterification. According to a study published by Komers, Skopal et al. (2002), the increased catalyst concentration may increase the total reaction rate. This means that the triglycerides consumption rate increases but it could be favoring soap
formation. Moreover, saponification of triglycerides is slower than their methanolysis (Komers, Skopal et al. 2002). Thus, on the one hand, increasing catalyst loads promote product yield at shorter reaction time (saponification did not impact product yield). On the other hand, overloading catalyst concentration increases saponification reaction given enough reaction time with a decline in product yield being observed at reaction time higher than 50 min.

Figure 2.6. Surface plots of the product yield as affected by reaction time and catalyst concentration

2.3.2.6. Effect of solvent ratio and reaction time on product yield

The interaction effects of methanol concentration with reaction time on the product yield are shown in Figure 2.7. The yield of products at lower reaction time decreased with increasing the volume of alcohol, however further increasing of reaction time gradually change the product yield behavior as it tends to improves when solvent ratio increases at higher reaction time. In other words, the summit of the yield surface plot moves in direction of both solvent ratio and reaction time. This limitation could be due to the low solubility of oil in methanol. According to
a study on the transesterification of castor oil, low concentration of oil in methanol delay the reaction and causes an ignition period due to low dissolution rate of the oil in alcohol (Peña, Romero et al. 2008). The addition of a co-solvent greatly accelerates the reaction (Boocock, Konar et al. 1996). However, excess methanol can decrease the efficiency of the co-solvent and in consequence shift the summit to higher reaction time.

![Figure 2.7. Surface plots of the product yield as affected by reaction time and solvent ratio](image)

2.3.2.7. Effect of reaction time and temperature on product yield

The interaction effect between reaction time and temperature presented in Figure 2.8 is due to the low P-value and high equation coefficient ($b_{34} = 4.0108$). At lower temperatures, the product yield decreases with reaction time as expected (under the used reaction conditions). As the temperature increased the yield increased to an optimum value then decreased again at temperatures above the boiling points of the methanol and of the co-solvent, presumably due to reduced contact with the biomass resulting from evaporation and soap formation elevation as earlier described. The same trends as higher temperature are predicted for lower temperature by
growing the factorial domains for reaction time and temperature towards lower amounts.

However, the optimum time and temperature for maximum yield shifted in the direction of longer time and higher temperatures. The same behavior was observed by Abdullah, Razali et al. (2009) for palm oil transesterification. Even though it is on the contrary to the fact that higher temperature favors saponification reaction velocity (higher temperature increases saponification so that product yield must decrease by increasing time and temperature), in this case the negative effect of evaporation on solvent and co-solvent contact with biomass is dominant and slow down the extraction and esterification.

![Figure 2.8. Surface plots of the product yield as affected by reaction time and temperature](image)

**2.3.3. Fatty Acid Methyl Esters composition**

Principal fatty acid methyl esters (FAME) composition for CTT oil by *in-situ* transesterification using microwave are presented in Table 2.5. Palmitic and Linoleic acids are the major components as expected from waxy layer and kernel, respectively, according to our previous study (Picou and Boldor 2012).
Table 2.5 Fatty acid composition of Chinese Tallow Tree seeds

<table>
<thead>
<tr>
<th>Methyl Esters</th>
<th>Fatty acid</th>
<th>Molecular formula</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl butyrate</td>
<td>Butyric acid</td>
<td>C₄H₈O₂</td>
<td>0.001</td>
</tr>
<tr>
<td>Methyl hexanoate</td>
<td>Hexanoic acid</td>
<td>C₆H₁₂O₂</td>
<td>0.002</td>
</tr>
<tr>
<td>Methyl octanoate</td>
<td>Caprylic acid</td>
<td>C₈H₁₆O₂</td>
<td>0.005</td>
</tr>
<tr>
<td>Methyl decanoate</td>
<td>Decanoic acid</td>
<td>C₁₀H₂₀O₂</td>
<td>0.001</td>
</tr>
<tr>
<td>Methyl tetradecanoate</td>
<td>Myristic acid</td>
<td>C₁₄H₂₈O₂</td>
<td>0.005</td>
</tr>
<tr>
<td>Methyl pentadecanoate</td>
<td>Pentadecanoic acid</td>
<td>C₁₅H₃₀O₂</td>
<td>0.002</td>
</tr>
<tr>
<td>Methyl cis-9-hexadecenoate</td>
<td>Palmitoleic acid</td>
<td>C₁₆H₃₀O₂</td>
<td>0.01</td>
</tr>
<tr>
<td>Methyl hexadecanoate</td>
<td>Palmitic acid</td>
<td>C₁₆H₃₂O₂</td>
<td>55.789</td>
</tr>
<tr>
<td>Methyl cis,cis, cis-9,12,15-octadecatrienoate</td>
<td>Linolenic acid</td>
<td>C₁₈H₃₀O₂</td>
<td>28.553</td>
</tr>
<tr>
<td>Methyl cis,cis-9,12-octadecadienoate</td>
<td>Linoleic acid</td>
<td>C₁₈H₃₂O₂</td>
<td>9.135</td>
</tr>
<tr>
<td>Methyl cis-9-octadecenoate</td>
<td>Oleic acid</td>
<td>C₁₈H₃₄O₂</td>
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</tr>
<tr>
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<td>Stearic acid</td>
<td>C₁₈H₃₆O₂</td>
<td>0.547</td>
</tr>
<tr>
<td>Methyl cis-11-eicosenoate</td>
<td>11-Eicosenoic acid</td>
<td>C₂₀H₃₈O₂</td>
<td>0.028</td>
</tr>
</tbody>
</table>

2.3.4. Properties of biodiesel at optimum point

The properties of FAME produced at optimum values are presented on Table 2.6. The analysis of the biodiesel produced by *in-situ* transesterification of Chinese tallow tree seeds under optimal reaction conditions (1.74 wt.% catalyst, 2.98:1 methanol to seed ratio, 20 and 43 min reaction time, and 58.1°C temperature) indicated that the product met the ASTM standard specification for biodiesel fuel.

Table 2.6 Properties of fatty acid methyl esters

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>FAME value</th>
<th>Required by ASTM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CCT at 20 min</td>
<td>CTT at 43 min</td>
</tr>
<tr>
<td>Kinetic viscosity at 40°C</td>
<td>mm² s⁻¹</td>
<td>2.024 ± 0.0042</td>
<td>1.724 ± 0.0014</td>
</tr>
<tr>
<td>Density at 40°C</td>
<td>g cm⁻³</td>
<td>0.875 ± 0.0014</td>
<td>0.871 ± 0.0007</td>
</tr>
<tr>
<td>Acid value</td>
<td>mgKOH g⁻¹</td>
<td>0.34±0.0055</td>
<td>0.34±0.0078</td>
</tr>
<tr>
<td>Cetane number</td>
<td>---</td>
<td>62.7613 ± 0.0013</td>
<td>62.7513 ± 0.0023</td>
</tr>
<tr>
<td>Water content</td>
<td>Wt.%</td>
<td>0.0633 ± 0.001</td>
<td>0.13532 ± 0.002</td>
</tr>
<tr>
<td>Cloud point</td>
<td>°C</td>
<td>8-9</td>
<td>9-10</td>
</tr>
<tr>
<td>Pour point</td>
<td>°C</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>
2.4. Conclusion

Microwave-assisted extraction and transesterification of Chinese tallow tree seeds were demonstrated for optimum reaction conditions using a Doehlert optimization methodology. The microwave in-situ transesterification process proved to be an energy efficient and economical method to produce biodiesel compare to conventional route with the major advantages of considerable reduced amount of solvent and catalyst, reaction time and temperature. The single-step extractive transesterification process has the potential to use for inedible biomass biodiesel production. Obtaining optimum reaction condition in order to minimize the soap formation as a side reaction is a crucial part of this method. Based on the preliminary studies, further research studies could be focusing on the process scale up, reaction kinetics study, in-situ transesterification methods using a heterogeneous catalyst to avoid side reaction.

2.5. References


CHAPTER 3
CONTINUOUS IN-SITU TRANSESTERIFICATION OF SEEDS OF INVASIVE CHINESE TALLOW TREES (TRIADICA SEBIFERA L.) IN A MICROWAVE-ASSISTED CSTR USING HEXANE AS CO-SOLVENT: KINETIC AND THERMODYNAMIC STUDIES

3.1. Introduction

Human population growth and the increase in standards of living worldwide led to exponentially increasing global energy demands. The large demand applies pressures on the existing resources due to the uncertainty in petroleum supplies and its availability, which poses concerns for the sustainability of this approach (Terigar, Balasubramanian et al. 2010, Kanitkar, Balasubramanian et al. 2011).

Studies have shown that at the current rate of energy consumption, the petroleum-based fossil fuels reserves are expected to be depleted in the next 40 to 50 years (Nautiyal, Subramanian et al. 2014). Air pollution, as a direct consequence of the continuous combustion of fossil fuels, has reached dangerous limits for both human health and the environment (Nicoletti, Arcuri et al. 2015). Thus, the environmental concerns and the negative sustainability indices of fossil fuels have forced the society to find alternative energy sources and replace conventional fuels with clean and renewable fuels (Picou and Boldor 2012). Amongst the numerous alternatives available (e.g. wind, solar, biomass, etc.), biodiesel derived from biological materials has attracted much attention as a suitable replacement of transportation fuels. The advantages of biodiesel have convinced governments to develop strategies to expand biodiesel production. Statistics show significant annual increases in the global biodiesel production from 2005 to 2020 according to the OECD and FAO (Hosseini and Wahid 2012), with the main producers being USA, Canada, France, Brazil, India, Indonesia, Malaysia, and Australia (Atabani, Silitonga et al. 2012).
Biodiesel as an alternative source of fuel must be technically acceptable, economically competitive, and environmentally friendly. Regardless of the minor differences, most of the oils including animal fat, and waste oil are in general suitable for conversion into biodiesel. Multiple methods have been proposed by researchers in order to overcome the biodiesel production limitation related to productivity (yields), energy consumption, investment costs, and reaction time by adjusting various operational conditions. Many of these methods are covered in literature, including in an excellent review by (Ma and Hanna 1999). Fleisher employed a plug flow reactor operating at 180°C and 30 atm to produce biodiesel (Choedkiatsakul, Ngaosuwan et al. 2015). Although the operation time for this method was significantly shorter than other methods, it suffers from low productivity yields. Packed bed reactors operated at 140°C, and 2-5 atm were also investigated by Moritz, Faessler et al. (2009), with good yields (>99%), but its disadvantages include plugging and high investment cost. Other systems operating at different temperature and pressure conditions such as rotary packed bed, annular gap, membrane (circulation), or reactive distillation reactors are also discussed in literature (Chen 2008, Lichtenberger, Mcgrevy et al. 2008, Chen, Huang et al. 2010, Chen 2010, Tremblay 2013). High energy consumption, low productivity, high cost of investment or operation, and long operation time are the main drawbacks of these reported systems. It is generally accepted that, in addition to feedstock costs, the largest barrier in biodiesel production is scale up, which is also related to feedstock availability. A continuous system is a practical route to achieve this goal, and an abundant and low-cost feedstock is desirable (such as the one used in this study), which does not compete on the food market or affect land-use.

One of the earliest sources of energy with high heat content and wide availability is vegetable oil, which can be burned directly as a fuel. However, high acid content and viscosity,
oxidation and polymerization (gum formation) during storage and combustion are the major problems associated with its combustion. Several techniques such as transesterification (Ma and Hanna 1999) or hydroprocessing (Sharma, Adhvaryu et al. 2008) were developed to convert oil into better secondary, ready-to-use fuels with high heat content. Among the societal disadvantages of vegetable oil as an energy source, we can mention the fact that vegetable oils are either produced from edible food source, or from non-edible feedstock cultivated on prime agricultural land. Alternative feedstock that grows on non-agricultural lands is desirable and would constitute a feasible substitution for food-based vegetable oil in order to control the competition with the food market.

Microalgae, Jatropha, and Chinese tallow tree seeds are among the most abundant non-edible source of lipids that have been investigated. Some microalga species are able to produce and store up to 50–70% of oil or lipid per dry weight under suitable culture conditions which makes them a good source of oil for biodiesel production (Chen, Yeh et al. 2011). Apart from that, the tremendous oil production capacity of microalgae due to their high growth rate makes them one the most promising source of sustainable biofuel production (Goudarzi and Boldor 2015). However, high investment cost and technical obstacles to their mass production, and high moisture content prevents the commercially production of microalgae-based biofuels. Chinese tallow tree was first imported to the United States by Benjamin Franklin as an ornamental tree and as a potential source of oils for candles (Picou and Boldor 2012). A second introduction at the beginning of the 20th century, in order to be used as a wood fuel source, is generally considered the driver behind its current designation as an invasive species due to its habitats neutralizing abilities (Picou and Boldor 2012). However, the high lipid content (above 40%) of its seeds makes it one of the most prolific natural sources of oil for soap and potentially biodiesel
production (Fennell, Bourgeois et al. 2015). The utilization of its seeds as a feedstock for alternative fuels could be environmentally safe and provide ecologic benefits (by seed collection the invasiveness nature is controlled), be technically practical (its lipid composition is suitable for transesterification), and economically reasonable (there are little too no costs involved in its production), all of these being requirements for biodiesel as a transportation fuel (Meher, Vidya Sagar et al. 2006).

In organic chemistry, transesterification is described as a reaction where an alcohol from an ester is displaced by another alcohol (Schuchardt, Sercheli et al. 1998).

\[
\begin{align*}
\text{CH}_2\text{-OC-R}_1 & \quad \text{O} \quad \text{CH}_2\text{-OH} \\
\text{CH-OOC-R}_2 & \quad + \quad 3\text{R}^+\text{OH} \quad \text{Heat} \quad \text{R}_1\text{-OC-R}' \quad + \quad \text{CH}_2\text{-OH} \\
\text{CH}_2\text{-OC-R}_3 & \quad \text{O} \quad \text{R}_2\text{-OOC-R}'' \quad + \quad \text{CH}_2\text{-OH} \\
\text{O} & \quad \text{R}_3\text{-OC-R}''' \quad \text{O} \\
\text{Vegetable oil (Lipids)} & \quad \text{Alcohol} \quad \text{Esters (Biodiesel)} \quad \text{Glycerol}
\end{align*}
\]

In general, the reaction is consisted of three consecutive reversible steps, which produce diglyceride (DG), monoglyceride (MG), and finally glycerol (Gl) and biodiesel (R'CO₂R) out of triglyceride (TG) and alcohol (ROH) reaction in presence of catalyst. (Meher, Vidya Sagar et al. 2006) Since the overall reaction is reversible, excess amount of alcohol can shift equilibrium to the product side of the reaction (Kanitkar, Balasubramanian et al. 2011).

Microwave heating has been proven to accelerate and enhance the reaction time in terms of heat transfer (transferring energy directly to reactant), including for transesterification reactions. Unlike the conventional heating method, in which heat is transferred through conduction, convection, and irradiation from the surface of the reactor to the reaction bulk, in
microwave technology, electromagnetic irradiation in the wavelengths range of 0.01 to 1 m and corresponding frequency range of 0.3 to 300 GHz is used to heat up the reaction solution (Motasemi and Ani 2012). Dipoles tend to align themselves in the field of the applied electric field and consequently the transformation of electromagnetic energy to heat is the result of the dipoles rotation, friction, and collisions in solution. The magnitude of heating depends on the dielectric properties of the material (Terigar, Balasubramanian et al. 2010, Muley and Boldor 2013) including for the seeds of the tallow tree (Fennell and Boldor 2013). Apart from the molecules polarity, the presence of ions in the solution improves the dielectric properties of the solution, as ions will oscillate under the influence of the changing electric field. Thus, the collision amongst molecules and ions causes the kinetic energy conversion to heat energy. This phenomenon helps the reaction kinetic rates (thus the process yields) by providing efficient molecular mixing, increasing the alcohol and triglyceride collision probability in the homogeneous mixtures of oil, alcohol, and catalyst.

Besides the reaction rate improvement, in the case of extraction from solid biological matrices, microwave processing can also enhance the oil extraction (Boldor, Kanitkar et al. 2010, Biller, Friedman et al. 2013). Fast heating mechanism at the molecular level produces high pressure and temperature spots in the biological matrix and results in extensive physical damage and faster release of lipids from cells.

Numerous studies have been reported on the kinetics of reaction involved in biodiesel production from pure or refined lipids, but virtually none on the kinetics of in-situ transesterification in microwave fields as it is described in this paper. Kattimani (2014) investigated the reaction parameters and optimized the three stage transesterification process, including two esterification stages, for biodiesel production from rice bran oil resulting
in 90% yield at optimum conditions. Nautiyal, Subramanian et al. (2014) investigated the effect of stirring intensity, catalyst concentration, algae biomass:methanol ratio and algae drying duration on single stage extraction–transesterification of *Spirulina platensis* algae biomass and reported 75% maximum biodiesel yield. Kumar and Ali (2013) studied the effect of the Zn/CaO heterogeneous catalyst on biodiesel production from cotton seed oil and reported that the reaction follows pseudo first order kinetics. Darnoko and Cheryan (2000) reported that the kinetics of biodiesel production from palm oil follows the second order reaction mechanism. Kumar, Ravi et al. (2011) studied the kinetic of biodiesel production from jatropha and mahua oil, and they suggested that the reaction follows second and first order kinetic with respect to triglyceride and methanol concentration, correspondingly. Hidalgo, Ciudad et al. (2015) investigated the simultaneous *in-situ* esterification/transesterification of Botryococcus braunii microalgae kinetic and they also obtained 80.1% theoretical maximum fatty acid methyl esters (FAME) yield. Yin, Zeng et al. (2014) proposed the pseudo second order kinetics for dimethyl carbonate and phenol transesterification in the reactive distillation reactor and described the transesterification kinetic behavior with a semi-empirical kinetic model. Asakuma, Maeda et al. (2009) determined a various biodiesel feedstocks activation energies using quantum computational chemistry; these energies were further used to explain the alkyl esters (biodiesel) formation mechanism from triglycerides.

*In-situ* transesterification has been reported to be an efficient approach in biodiesel production (Haas, Scott et al. 2004, Haas and Scott 2007, Mondala, Liang et al. 2009). In this single stage process, lipids in the biomass convert directly into biodiesel through simultaneously combining the oil extraction with the transesterification reaction. This method addresses a variety of drawbacks in comparison to the conventional method of extraction → refining →
conversion. It has been reported that high yield of reaction products (up to 97%) were achieved for in-situ transesterification on soy flakes and wastewater sludge (Haas, Scott et al. 2004, Haas and Scott 2007, Mondala, Liang et al. 2009). However, higher alcohol to oil ratio of 1:300 in these works compared unfavorably with the two-stage conversion of pure oil (alcohol to oil ratio 6:1 to 12:1), along with longer reaction times.

The objective of this work is to obtain the highest reaction yield and conversion rate, in the shortest amount of time through a continuous in-situ transesterification process using resonant microwave cavities. The disadvantages related to the large amounts of alcohol for in-situ transesterification reported previously was overcome by using hexane as co-solvent. Hexane improves the mass transfer rate by increasing the solubility of oil in alcohol phase through lowering the oil viscosity. Microwave technology (Boldor, Balasubramanian et al. 2008) has been used as the heat source in this study where the feedstock heated up to the desired temperature in significantly shorter amount time and transferred to a secondary CSTR reactor. The reaction kinetic of single stage extractive transesterification reaction was further studied. From the kinetic study, the rate constant and the activation energy were determined using Arrhenius equation (Hill and Root 2014). The thermodynamic parameters like Gibbs free energy ($\Delta G$), enthalpy ($\Delta H$) and entropy ($\Delta S$) of activation were also investigated using the Eyring–Polanyi equation (Schaschke 2014).

We propose to name this approach for biodiesel production GREEN$^3$ (GREEN-Cubed), as microwave technology is considered a green chemistry process (GREEN 1) (Kappe, Dallinger et al. 2008, Kappe, Stadler et al. 2013), the feedstock used does not compete with the food markets, its utilization provides tremendous environmental and ecological benefits by controlling
the dispersion and invasiveness of this species (GREEN 2), and the end product is a green fuel (GREEN 3).

3.2. Materials and methods

3.2.1. Materials

The Lab Grade methanol and technical grade (55%) n-hexane used in the reactions were purchased from Fisher Scientific (Pittsburg, PA). The catalyst sodium hydroxide and hydrochloric acid were supplied by Pharmco-AAPER (Brookfield, CT).

3.2.2. Methods

3.2.2.1. In-situ transesterification procedure

In-situ transesterification were performed using a commercially available professional GMP 60KSM XTR microwave system (Sairem, France – Serial#103907), having a maximum power output of 6 kW and frequency of 2450 MHz. The system consisted of 173.75 mL (1.905 cm diameter and length 60.96 cm) PTFE tube placed vertically at the axial center of the resonant focusing cavity chamber in order to ensure the consistent flow rate and avoid phase separation. A Raytek® MI3 infrared temperature sensor was used in conjunction with a NI DAQ data acquisition board and a specially-designed “PID Auto-generator temperature controller” program in LabVIEW 8.6 (National Instruments Corporation, Texas, US) to control the power and temperature of the microwave system. The program was designed to adjust microwave power output based on the temperature feedback signals from IR sensor both manually and automatically. Thus, based on the operator experience, an initial output power was set to the program such that this value suited the desire temperature. In most cases, it was able to reach and maintain the desired temperature in less a minute. Once the temperature reached the set value,
the experiment started. The oscillations in temperatures used for the control system were less than ±2°C.

Ground CTT seeds (1% > moisture content) were weighed and continuously mixed in a 20 Liters, with the equivalent mixture of hexane and methanol (methanol/hexane/CTT seed ratio was 3:3:1 (v/v/w)) in a plastic tank for one minute to ensure a homogenous feedstock solution. The feedstock solution was further pumped through the microwave focusing reactor using a peristaltic pump working at 250 ml flow rate. 4 wt.% catalyst solution was added before the experiment start. After microwave irradiation, the processed reactants solution was dumped into a CSTR reactor. The CSTR reactor was a 15 Liters tank, insulated with 10 cm thick wool-glass insulation wrap, and equipped with a safety valve to release the extra vapor and prevent the pressure built-up. Due to the hexane high volatility at the reaction operation temperature, the stirrer inlet port had to be fully sealed, in order to keep hexane inside the tank. Thus, the stirrer was inserted through a PFA tube to the bottom of the tank and submerged into the solution to minimize vapor release. A vacuum suction venting system was placed at the top to evacuate any escaped volatiles. A T-type thermocouple was placed at the bottom of the CSTR to record the temperature throughout the experiment. Feedstock inlet port was connected to the bottom of the tank, using a plastic tube so as to inject the fresh processed feedstock directly into the reactor contents. This facilitated hexane vapor condensation and prevented pressure built-up in the tank. A metallic valve was installed at the tank bottom and used to collect samples.

3.2.2.2. Separation of by-products

For each experiment, 100 ml samples were taken at different time intervals. Samples were added with 100 ml distilled water and neutralized with hydrochloric acid to stop the reaction. Following 50 ml hexane addition, they were further centrifuged at 3600 rpm for 10 min
to separate suspended solid biomass from the liquid mixture. The top liquid phase (hydrophobic layer consisting of hexane, FAME and unreacted oil) of each centrifuge vessel was transferred into a separating funnel where 50 ml distilled water was added three times to ensure complete removal of impurities. The lower layers of vessels containing extra methanol, water, glycerin, sodium hydroxide, soap and solid biomass were stored and later disposed of. Hexane was evaporated on rota-vapor, and residual product was then vacuum dried for 10 h.

3.2.2.3. Kinetic model of transesterification

The overall transesterification reaction takes place into the CSTR following the microwave exposure according to following expression:

\[ TG + MeOH \xrightarrow{K_{L-i}} FAME + Gl \]

where TG, MeOH, FAME, Gl, and \( K_{L-i} \) are triglyceride, methanol, free fatty acid methyl esters, glycerol concentration and kinetic rate constants, respectively. The overall transesterification reaction follows a first order kinetic model as a function of FAME concentration (Kusdiana and Saka 2001, Shah, Parikh et al. 2014). Thus, the first order rate equation of the transesterification reaction is expressed by Equation 3.1.

\[ r = kC_{FAME} \]

[3.1]
k is the rate constant (min\(^{-1}\)).

Since the reaction is taking place through a continuous CSTR reactor, the mass balance for the CSTR reactor startup before reaching steady-state has been developed as the following:

\[ \text{Inlet} - \text{Outlet} + \text{Generation} = \text{Accumulation} \]

[3.2]

\[ 0 - 0 + r_{FAME}V = \frac{dN_{FAME}}{dt} \]

[3.3]

Substitution for \( N_{FAME} = C_{FAME}V \) and taking partial derivatives give Equation 2.8 as following:

\[ kC_{FAME}V = \frac{d(C_{FAME}V)}{dt} = V \frac{dC_{FAME}}{dt} + C_{FAME} \frac{dV}{dt} \]

[3.4]
\[ \frac{dv}{dt} = \dot{V} \rightarrow V = \dot{V}t \]  

[3.5]

Combining Equation 3.4 and Equation 3.5 give Equation 3.6 which was further simplified and expressed as Equation 3.8.

\[ V \frac{dC_{FAME}}{dt} + C_{FAME} \dot{V} = kC_{FAME}V \]  

[3.6]

\[ \frac{dC_{FAME}}{dt} = \left( kC_{FAME}V - C_{FAME}\dot{V} \right) \frac{1}{V} \]  

[3.7]

\[ \frac{dC_{FAME}}{C_{FAME}} = kdt - \frac{\dot{V}}{V} dt = kdt - \frac{dt}{t} \]  

[3.8]

Assuming the initial concentration of methyl esters as \( C_{FAME_0} \) at time \( t = 0 \) and concentration after time ‘t’ as \( C_{FAME_t} \), on integration the Equation 3.1 can be written as Equation 3.2.

\[ \int_{C_{FAME_0}}^{C_{FAME_t}} \frac{dC_{FAME}}{C_{FAME}} = \int_0^t kdt - \int_0^t \frac{dt}{t} \]  

[3.9]

\[ \ln C_{FAME} = kt - \ln t \]  

[3.10]

\[ \ln C_{FAME t} = kt \]  

[3.11]

Equation 3.12 is also introduced \( C_{FAME} \) as the following which gives the amount of FAME in a liter of solution (since our sample volume was 100 ml).

\[ C_{FAME} \left[ \frac{g}{litr} \right] = x_{gram\ product} \times conversion\ rate \times 10 \]  

[3.12]

Where: \( C_{FAME} \) is the weight of the pure product (FAME) in a liter of final solution from CSTR; conversion rate is found in table 3.1 to 3.5, and 10 is the conversion factor from 100 ml to 1 Lit. For all calculations involving Arrhenius and Eyring-Polanyi equations, the temperatures were converted to absolute values (K).
3.3. Results and discussion

3.3.1. Effect of operation temperature on yield and conversion

The results of in-situ transesterification for product yield ($Y_{exp,i}$), and reaction conversion ($C_{exp,i}$) for both replications, and their corresponding standard deviations under different time intervals are presented in Tables 3.1 to 3.5.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Product Yield</th>
<th>Reaction Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Y_1$</td>
<td>$Y_2$</td>
</tr>
<tr>
<td></td>
<td>Y_{1}</td>
<td>Y_{2}</td>
</tr>
<tr>
<td>0.4</td>
<td>1.038</td>
<td>0.967</td>
</tr>
<tr>
<td>2.4</td>
<td>2.893</td>
<td>2.965</td>
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<tr>
<td>4.4</td>
<td>3.636</td>
<td>3.542</td>
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<tr>
<td>6.4</td>
<td>4.268</td>
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</tr>
<tr>
<td>8.4</td>
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<td>12.4</td>
<td>4.495</td>
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<td>16.4</td>
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<td>20.4</td>
<td>5.055</td>
<td>5.407</td>
</tr>
<tr>
<td>24.4</td>
<td>5.716</td>
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</tr>
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<td>28.4</td>
<td>5.928</td>
<td>5.578</td>
</tr>
<tr>
<td>32.4</td>
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<td>6.224</td>
</tr>
<tr>
<td>36.4</td>
<td>6.145</td>
<td>6.225</td>
</tr>
<tr>
<td>40.4</td>
<td>6.402</td>
<td>6.224</td>
</tr>
</tbody>
</table>

$Y_{mean}$: Mean ($Y_1$, $Y_2$) ± SD, $Y_{mean}$ (%) is the product yield percentage calculated based on 6.333 gr of maximum productivity per 100 ml of sample
Table 3.2 Experimental data for 55°C

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Product Yield</th>
<th>Reaction Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Y&lt;sub&gt;1&lt;/sub&gt;</td>
<td>Y&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>Tank</td>
<td>1.104</td>
<td>1.037</td>
</tr>
<tr>
<td>0.4</td>
<td>2.537</td>
<td>2.658</td>
</tr>
<tr>
<td>2.4</td>
<td>3.597</td>
<td>3.505</td>
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<tr>
<td>4.4</td>
<td>3.51</td>
<td>3.838</td>
</tr>
<tr>
<td>6.4</td>
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<td>8.4</td>
<td>3.519</td>
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<td>12.4</td>
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<td>5.609</td>
</tr>
<tr>
<td>36.4</td>
<td>5.909</td>
<td>5.695</td>
</tr>
<tr>
<td>40.4</td>
<td>6.087</td>
<td>6.243</td>
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</table>

Y<sub>mean</sub>: Mean (Y<sub>1</sub>,Y<sub>2</sub>) ± SD, Y<sub>mean</sub> (%) is the product yield percentage calculated based on 6.333 gr of maximum productivity per 100 ml of sample.
<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Product Yield</th>
<th>Reaction Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Y&lt;sub&gt;1&lt;/sub&gt;</td>
<td>Y&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
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<td>Tank</td>
<td>1.078</td>
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<tr>
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</tr>
<tr>
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<td>8.4</td>
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<td>3.63</td>
</tr>
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<td>12.4</td>
<td>3.536</td>
<td>3.88</td>
</tr>
<tr>
<td>16.4</td>
<td>4.378</td>
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<td>20.4</td>
<td>4.271</td>
<td>4.275</td>
</tr>
<tr>
<td>24.4</td>
<td>4.729</td>
<td>4.579</td>
</tr>
<tr>
<td>28.4</td>
<td>5.106</td>
<td>5.232</td>
</tr>
<tr>
<td>32.4</td>
<td>5.252</td>
<td>5.028</td>
</tr>
<tr>
<td>36.4</td>
<td>5.637</td>
<td>5.471</td>
</tr>
<tr>
<td>40.4</td>
<td>5.666</td>
<td>5.746</td>
</tr>
</tbody>
</table>

Y<sub>mean</sub>: Mean (Y<sub>1</sub>,Y<sub>2</sub>) ± SD, Y<sub>mean</sub> (%) is the product yield percentage calculated based on 6.333 gr of maximum productivity per 100 ml of sample.
<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Product Yield</th>
<th>Reaction Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Y_1$</td>
<td>$Y_2$</td>
</tr>
<tr>
<td>Tank</td>
<td>11.621</td>
<td>11.621</td>
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<tr>
<td>0.4</td>
<td>47.535</td>
<td>47.535</td>
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<tr>
<td>2.4</td>
<td>88.445</td>
<td>88.445</td>
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<td>4.4</td>
<td>92.734</td>
<td>92.734</td>
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<td>6.4</td>
<td>93.602</td>
<td>93.602</td>
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<tr>
<td>8.4</td>
<td>94.473</td>
<td>94.473</td>
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<td>12.4</td>
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<td>16.4</td>
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<td>20.4</td>
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<td>95.845</td>
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<tr>
<td>24.4</td>
<td>97.89</td>
<td>97.89</td>
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<tr>
<td>28.4</td>
<td>97.599</td>
<td>97.599</td>
</tr>
<tr>
<td>32.4</td>
<td>97.253</td>
<td>97.253</td>
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<tr>
<td>36.4</td>
<td>98.44</td>
<td>98.44</td>
</tr>
<tr>
<td>40.4</td>
<td>98.888</td>
<td>98.888</td>
</tr>
</tbody>
</table>

$Y_{\text{mean}}$: Mean $(Y_1,Y_2) \pm \text{SD}$, $Y_{\text{mean}}$ (%) is the product yield percentage calculated based on 6.333 gr of maximum productivity per 100 ml of sample
Table 3.5 Experimental data for 40°C

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Product Yield</th>
<th>Reaction Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tank</td>
<td>Y&lt;sub&gt;1&lt;/sub&gt;</td>
<td>1.038±0.08</td>
</tr>
<tr>
<td>0.4</td>
<td>0.981</td>
<td>1.800±0.09</td>
</tr>
<tr>
<td>2.4</td>
<td>1.734</td>
<td>2.948±0.15</td>
</tr>
<tr>
<td>4.4</td>
<td>2.836</td>
<td>3.153±0.12</td>
</tr>
<tr>
<td>6.4</td>
<td>3.067</td>
<td>3.119±0.16</td>
</tr>
<tr>
<td>8.4</td>
<td>3.107</td>
<td>3.275±0.23</td>
</tr>
<tr>
<td>12.4</td>
<td>3.449</td>
<td>3.383±0.09</td>
</tr>
<tr>
<td>16.4</td>
<td>3.531</td>
<td>3.391±0.19</td>
</tr>
<tr>
<td>20.4</td>
<td>3.606</td>
<td>3.682±0.10</td>
</tr>
<tr>
<td>24.4</td>
<td>3.713</td>
<td>3.758±0.06</td>
</tr>
<tr>
<td>28.4</td>
<td>4.344</td>
<td>4.209±0.19</td>
</tr>
<tr>
<td>32.4</td>
<td>4.445</td>
<td>4.512±0.09</td>
</tr>
<tr>
<td>36.4</td>
<td>4.402</td>
<td>4.486±0.11</td>
</tr>
<tr>
<td>40.4</td>
<td>5.224</td>
<td>5.033±0.27</td>
</tr>
</tbody>
</table>

Y<sub>mean</sub>: Mean (Y<sub>1</sub>, Y<sub>2</sub>) ± SD, Y<sub>mean</sub> (%) is the product yield percentage calculated based on 6.333 gr of maximum productivity per 100 ml of sample.

Reaction temperature, alcohol/oil ratio, and catalyst amount are the main factors affecting the transesterification reaction (Muley and Boldor 2013). All the parameters except temperature are constant in this work. The results of the production yield (in % of maximum achievable) and the reaction conversion with error bars are also presented in Figures 3.1 and 3.2. The second data point in tables 3.1 to 3.5 correspond to time t=0.4 min, the time required for the mixture to travel from the endpoint of microwave exposure in the resonant cavity to the CSTR.
As it is shown in Figure 3.1, production yield is increasing throughout the operation time with the temperature rise. Similar production yield results for *in-situ* transesterification of
Cynara cardunculus L. seed was obtained by Koutsouki, Tegou et al. (2015) using an alkaline ultrasonic process. However, employing a CSTR in the current study helped to produce biodiesel with the same conversion rates and yields in a continuous mode with lower amount of alcohol and catalyst. The same trends were observed for the reaction conversion. The measurable changed in the reaction conversion is much faster than production yield, as the reaction conversion reached above 88% after only 2 min. This demonstrates that in all experiments the reaction is taking place with a higher pace than extraction, such that the extraction is the rate limiting step in this process.

These results were compared to the laboratory scale batch and continuous transesterification and in-situ transesterification processes published previously. In these studies, the highest conversion rate obtained for a continuous flow microwave reactor with oil only was 99.4% in 1.75 min residence time for an oil/alcohol ratio of 1:12 at 70°C (Choedkiatsakul, Ngaosuwan et al. 2015). The conversion rate reported by Choedkiatsakul et al. is almost the same to that obtained at 60°C in this study. For the continuous laboratory-scale process described previously, the oil:alcohol ratio was higher. However, in this case, a higher catalyst concentration was chosen which compensate for the lower alcohol ratio. Another study by Muley et al. reported a high 99.93% conversion rate after 1 min microwave irradiation with 0.18 wt. % catalyst concentration for transesterification of soybean oil with ethanol (Muley and Boldor 2013).

The slight differences in these works could be associated to the differences in configurations and operating parameters. As in this study, a smaller microwave cavity size led to a shorter irradiation time of 8.68 sec (36.2 cm³ for 250 ml). Apart from irradiation time, microwave power to inlet flow-rate ratio was higher (4000 watt for 840 ml at 60°C (Muley and
Boldor 2013) with the mixture being processed at more severe conditions compared to the present study (290 watt for 250 ml at 60°C). Higher power dissipation can improve FAME production yield and conversion by increasing the reorientation of the dipole moment of methanol (Patil, Reddy et al. 2012). This causes mass transfer enhancement between extracted oil and methanol. High conversion rate for a laboratory scale continuous-microwave transesterification of soybean oil was achieved in a study by Terigar et al., where feedstock was processed directly inside the reaction vessel (Boldor, Kanitkar et al. 2010). The advantages of the current work is lower alcohol consumption, lower microwave exposure time (energy efficient) which is associated to the hexane role as a co-solvent. Hexane can be finally separated and reused.

However, it is important to note that the accurate and objective comparison with previously published work cannot be made, as none of the mentioned studies used the proposed combination (*in-situ* transesterification with microwave extraction in continuous flow resonant focusing cavities). The most important advantage of this method was the lower CSRT reactor operating temperature compared to the previous studies. As it is shown in the Figure 3.3, the average temperature of CSTR reactor is slightly lower than the microwave processing set point due to thermal losses. The improvement in the production yield and conversion results as a function of time show that both oil extraction and transesterification reaction are taking place not only during the active microwave exposure period, but also afterward, with the processed feedstock mixture (with heavily damaged microstructure) still carrying the microwave-imparted heat energy to the CSTR reactor. Thus, the current approach is more efficient in terms of energy consumption as it is working on a lower temperature.
3.3.2. Transesterification kinetic model

A transesterification kinetic model for the transformation of CTT seed oil into FAME was developed from Equations 2.15) and 2.16. In Figure 3.4 to Figure 3.8, the experimental data of FAME production yield (from tables 3.1 to 3.5) were fitted to the obtained kinetic model.
Figure 3.5. Plot of $\ln(C_{\text{FAME}}t)$ vs. time for 55°C

Figure 3.6. Plot of $\ln(C_{\text{FAME}}t)$ vs. time for 50°C

Figure 3.7. Plot of $\ln(C_{\text{FAME}}t)$ vs. time for 45°C
The reaction rate constants found for transesterification of CTT seed at different temperatures, regression coefficients are presented in Table 3.6. The predictive model appropriately fit the experimental data with high coefficients of determinations for all temperatures. This correlation shows that the system follows the first order reaction kinetic and that the reaction rate is linearly related to production yield of methyl esters. The reaction rate constants for this study ranged between 0.0809-0.0846 min\(^{-1}\) (according to Equation 3.15) for all temperatures (Table 3.6). The values of rate constants obtained in this study were almost in the similar range for those of reported by Amish, Jaswant et al. (2011) for transesterification of Jatropha oil using a ultrasound assisted system.

### Table 3.6 Kinetic reaction rate constant and regression coefficient

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Rate Constant (min(^{-1}))</th>
<th>Regression Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.0846</td>
<td>0.9079</td>
</tr>
<tr>
<td>55</td>
<td>0.0839</td>
<td>0.9254</td>
</tr>
<tr>
<td>50</td>
<td>0.0824</td>
<td>0.9269</td>
</tr>
<tr>
<td>45</td>
<td>0.0816</td>
<td>0.9169</td>
</tr>
<tr>
<td>40</td>
<td>0.0809</td>
<td>0.9221</td>
</tr>
</tbody>
</table>
The reaction rate constant varies depending on the oil compositions, reaction operation conditions (temperature, catalyst type and amount, pressure, solvent and co-solvent ratio) and technology associated to biodiesel production, such as conventional heating, microwave, ultrasonic and supercritical systems. Nautiyal, Subramanian et al. (2014) reported lower reaction rate constant values of 0.001 min\(^{-1}\) for single stage extraction–transesterification of Spirulina platensis algae biomass. The values of reaction rate constant for a study by Ghoreishi and Moein (2013) on biodiesel production from waste vegetable oil in a supercritical batch reactor were reported to be in the range of 0.0019–0.0033 min\(^{-1}\). Hidalgo, Ciudad et al. (2015) investigated the kinetics of \textit{in-situ} esterification / transesterification of Botryococcus braunii microalgae resulting in a value of 0.0037 min\(^{-1}\) for rate constant. Most of the literature reported that the rate constant for a first order transesterification reaction varies from 0.001 to 0.006 min\(^{-1}\), mostly depending on temperature, technology, and operational parameters (Rathore and Madras 2007, Joelianingsih, Maeda et al. 2008, Cho, Kim et al. 2012). The higher reaction rate obtained in this study is due to the microwave irradiation and hexane usage as co-solvent.

The change in the reaction rate constant with respect to temperature is shown in Figure 3.9. The linear relation between rate constant and temperature along with the regression coefficient (\(R^2\)) value of 0.889 obtained also shows that reaction follows the first order kinetic.

![Figure 3.9. Plot of rate constant vs. temperature](image-url)
3.3.3. Activation energy determination

The Arrhenius equation can be written as Equation 3.17 (Hill and Root 2014):

\[ k = A e^{-\frac{E_a}{RT}} \]  \hspace{1cm} [3.17]

where \( A \) and \( E_a \) are the Arrhenius parameters which stand for the pre-exponential factor coefficient or the pre factor (min\(^{-1}\)) and activation energy (J mol\(^{-1}\), respectively. \( R \) is the molar universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and \( T \) is the absolute temperature (K). By taking the natural logarithm, Equation 3.17 is transformed to Equation 3.18 as:

\[ \ln k = \ln A - \frac{E_a}{RT} \]  \hspace{1cm} [3.18]

The activation energy and pre-exponential factor for the reaction were determined from the plot of \( \ln(k) \) with respect to \( 1/T \) (Figure 3.10). The activation energy and pre-exponential factor were found to be 2057.382 J mol\(^{-1}\) and 5.47 min\(^{-1}\) respectively. The value obtained for activation energy is lower than those corresponding to values published in literature while the pre-exponential factor, indicating the degree of molecular agitation is much higher. Ghoreishi and Moein (2013) and Nautiyal, Subramanian et al. (2014) reported values of 31710 J mol\(^{-1}\) and 3.37 min\(^{-1}\) and 14518 J mol\(^{-1}\) and 2.31 min\(^{-1}\) respectively. Besides employing different operational conditions and feedstock, the difference in the obtained results is reflecting the role of microwave technology on the efficiency of system in terms of lower activation energy and higher pre-exponential factor (Lewis, Summers et al. 1992, Binner, Hassine et al. 1995). Dipolar rotation and ionic movement, which both are the effects of microwave irradiation, improved the pre-exponential factor which represent the probability of molecular collisions in the system. The other effect of microwave irradiation is lowering the state of energy for the activated complex. In other words, it stabilizes the transition state to a more extended degree (lower energy state for
activated complex) which consequently decreases the activation energy (Lewis, Summers et al. 1992).

Figure 3.10. The Arrhenius equation plot of ln(k) vs. (1/T)

According to Arrhenius equation, higher activation energy is related to smaller reaction rate constant. With a lower activation energy, a reaction is more likely to proceed and the rate of reaction is faster (high reaction rate constant). The physical state and concentration of reactants, reactants dispersion rate (mass transfer pace), temperature and pressure, solvents, and the presence and concentration of a catalyst are the factors affecting the rate constant of a chemical reaction. Thus, the reason for the higher rate constant and accordingly lower value of activation energy in this work is due to the presence of the co-solvent, higher amount of catalyst, and more importantly, to the specific interactions of microwave irradiation with the system. The closest results for activation energy and pre-exponential factor found in literature was 2132.608 J mol\(^{-1}\) and 0.753 min\(^{-1}\) in a study by (Kanitkar, Balasubramanian et al. 2011) on microwave assisted biodiesel production from soybean oil using methanol at 60°C. Other low activation energy results were reported for transesterification of sunflower oil (4856.69 J mol\(^{-1}\)) in presence of KF
(10 wt%) supported on Al₂O₃, and soybean (11, 147 J mol⁻¹) and rice bran oil (6,334 J mol⁻¹) with ethanol in a continuous-flow microwave-assisted system were also reported (Terigar, Balasubramanian et al. 2010, Calero, Cumplido et al. 2014).

3.3.4. Thermodynamic parameters

In order to calculate Gibbs free energy, the Eyring-Polanyi equation was written as

Equation 3.19:

\[ k = \frac{k_bT}{h} e^{\left(-\frac{\Delta G}{RT}\right)} \]  

[3.19]

Taking the natural logarithm of Equation 3.19 and substituting \( \Delta G = \Delta H - T \Delta S \) where \( \Delta H \) and \( \Delta S \) are the enthalpy and entropy of activation respectively, Equation 3.19 was written as

Equation 3.20:

\[ \ln\left(\frac{kT}{T}\right) = -\left(\frac{\Delta H}{RT}\right) + \left[\ln \kappa + \ln \left(\frac{k_b}{h}\right) + \frac{\Delta S}{R}\right] \]  

[3.20]

where \( k \) is the rate constant (min⁻¹), \( T \) is the absolute temperature (K), \( R \) is the universal gas constant (8.314 J mol⁻¹ K⁻¹), and \( k_b \) and \( h \) are Boltzmann (1.38×10⁻²³ J K⁻¹) and Planck's (6.63×10⁻³⁴ J s) constants, respectively. \( \kappa \), which is taken as unity, is the transmission coefficient.

Employing Equation (3.20), the values of rate constant and temperature, the slope and intercept of the Eyring plot of \( \ln(k/T) \) vs. \( 1/T \) (Figure 3.11) gave the values of \( \Delta G, \Delta H \) and \( \Delta S \). The values of \( \Delta H \) and \( \Delta S \) were found out to be -574.83 J mol⁻¹ and -267.85 J mol⁻¹ K⁻¹, respectively. These values were used in order to calculate the value of \( \Delta G \) as 85579.12 J mol⁻¹ at 321.65 K. The small negative value obtained for \( \Delta H \) shows that the reaction is slightly exothermic. This result is consistent with the theory stating that increasing temperature decreases equilibrium constant (Jiang, Zhang et al. 2010, Tsai, Lin et al. 2013, Martinez-Guerra and Gude 2014, Zeng, Li et al. 2014). A negative value of \( \Delta S \) indicates that the activated complex has a
lower entropy (disorder or chaos) or a better degree of ordered geometry/alignment as compare to the reactants in their ground state.

Finally, the obtained positive value of $\Delta G$ indicates that the reaction was not spontaneous and has endergonic nature. Different results were found for parametric thermodynamic studies of biodiesel production due to the variation of the methods which consequently changes the reaction parameters. Ahmad, Yasin et al. (2013) obtained $\Delta S = -180.190 \, J \, mol^{-1}$ and $\Delta G = 96128 \, J \, mol^{-1}$ for study of two step oil extraction and transesterification of Chlorella oil at 333.15 K.

![Figure 3.11. The Eyring-Polanyi equation plot of ln(k/T) vs. 1/T](image)

3.3.5. Energy consumption per kg of biodiesel produced

Overall energy consumption was measured by a plug-in power meter. The consumed energy for all equipment used in this experiment was used in these measurements, including for the feedstock tank overhead stirrer, peristaltic pump, and CSTR reactor overhead stirrer. The power consumption rate for pre-mixing (feedstock tank), post mixing (CSTR reactor) and
pumping were 35, 32 and 12 Watt, respectively, for all experiments. The microwave input power was set using the LabVIEW program. The other energy consumptions such as hexane evaporation and heat loss were not considered here. The power consumption rate for the microwave at the steady state operation was 290 Watt for 60°C. However, a small portion of it reflected back and was absorbed by the built-in water cooling system.

The estimated heat energy demand, calculated by heat capacities of mixture (2.5762 J g\(^{-1}\)°C based on 2.720, 2.293 and 2.8339 J g\(^{-1}\)°C (Picou and Boldor 2012) for methanol, hexane, and CTT whole seed, respectively), in order to heat up the mixture from 24°C to 60°C was 17.268 KJ min\(^{-1}\). This value is slightly lower than the energy consumption by microwave which is 17.4 KJ min\(^{-1}\). The difference is associated to the reflected power or unabsorbed irradiation which is referred as the microwave energy efficiency. The total energy consumption for this system was 22.14 KJ min\(^{-1}\) (369 w) at 60°C.

The production capacity at system steady state was 13.87 g min\(^{-1}\) of biodiesel (90% production yield, 97.5% conversion rate at 60°C after 24 min). Thus, the total actual energy consumption is 1596.2 J g\(^{-1}\) of biodiesel. Energy consumption for a microwave-assisted extraction of microalgae in a study by (Bermudez Menendez, Arenillas et al. 2014) was reported 3240 J per gram of dried and treated microalgae (0.9 W.h/g\(_{DM}\)), which means that even more energy is needed for a single stage extraction-transesterification process, as proposed here. The values reported in the Bermundez et al. study did not include the energy used for drying either. In the other recent studies by Choedkiatsakul, Ngaosuwan et al. (2015) and (Muley and Boldor 2013) on continuous production of biodiesel from palm oil and soybean oil using microwave-assisted flow reactor, the total actual energy consumption was found to be 488.5 and 430.13 J g\(^{-1}\) of biodiesel, respectively. Even though it is significantly low, those results are not comparable to
what was obtained in this study due to the *in-situ* nature of the described transesterification process.

3.3.6. Biodiesel Properties

The properties of the produced biodiesel i.e., the kinetic viscosity, density, acid value, cetane number, water content, cloud and pour points were determined according to the ASTM standard methods. The results of all property analyses are summarized in Table 3.7. These results indicate that the obtained product met ASTM standards.

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>FAME property value</th>
<th>Required by ASTM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic viscosity at 40°C</td>
<td>mm² s⁻¹</td>
<td>2.186 ± 0.0023</td>
<td>D 445 (1.9 – 6.0)</td>
</tr>
<tr>
<td>Density at 40°C</td>
<td>g cm⁻³</td>
<td>0.861 ± 0.0011</td>
<td>0.850–0.890</td>
</tr>
<tr>
<td>Acid value</td>
<td>mgKOH g⁻¹</td>
<td>0.33±0.0082</td>
<td>D 664 (Max. 0.5)</td>
</tr>
<tr>
<td>Cetane number</td>
<td>---</td>
<td>61.2734 ± 0.0013</td>
<td>D 613 (47 minimum)</td>
</tr>
<tr>
<td>Water content</td>
<td>Wt.%</td>
<td>0.14279 ± 0.003</td>
<td>D 2709 (0.050%)</td>
</tr>
<tr>
<td>Cloud point</td>
<td>°C</td>
<td>9-10</td>
<td>D6751 (-3_12)</td>
</tr>
<tr>
<td>Pour point</td>
<td>°C</td>
<td>2</td>
<td>D6751 (-15_10)</td>
</tr>
</tbody>
</table>

3.4. Conclusion

Microwave-assisted extraction and transesterification of Chinese tallow tree seeds were demonstrated for a continuous production process in a CSTR. The microwave *in-situ* transesterification process followed by a fully isolated CSTR showed to be an efficient and economical method to produce biodiesel compare to conventional path in terms of energy consumption. The single-step extractive transesterification process has the potential to use for inedible biomass biodiesel production. The proposed first order kinetic model showed to be a good fit for the overall simplified transesterification reaction. Based on the preliminary studies, further research studies could be focusing on the process scale up for pilot scale and commercialization, and employing a heterogeneous catalyst to prevent side reaction for *in-situ* transesterification methods.
3.5. References


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CHAPTER 4
CONCLUSIONS AND FUTURE WORK

4.1. Conclusions

The objective of this study was to investigate the in-situ transesterification process for biodiesel production from Chinese tallow tree seeds using microwave technology. For the first step, a batch in-situ system was used to study the effects of parameters in the process. The parameters chosen were catalyst concentration (1-4 wt.%), solvent ratio (2-6 v/w), reaction time (15-60 min) and temperature (50-70°C). In order to optimize the process, Dohlert optimization methodology was used in terms of product yields and reaction conversion rate. For further clarifications, the effects of each individual parameters along with their interaction effects were studied. Results indicate that all the parameters are playing important roles and in order to minimize the soap formation and maximize production yield and conversion rate, obtaining the optimum reaction conditions is essential. This study was important to understand the behavior of parameters, in order to apply them to a continuous system, and further on process scale up.

Second goal of this study was to design and operate a lab scale continuous microwave assisted biodiesel production process. Based on laboratory scale results a continuous biodiesel production process was designed. In-situ ransesterification process was carried out at different temperatures to study the kinetic of the reaction. Production yields and reaction conversion rates obtained by this process were significantly high. Biodiesel samples were qualitatively analyzed for density, kinematic viscosity, acid number, cloud and pour point, and were found to meet the ASTM standards.

The conclusion of this study was that microwave technology has the potential to be used for production of biodiesel through in-situ process. The microwave irradiation not only helps the reaction to carry on with an extremely faster pace but it also improves the oil extraction from
biological matrix. The other advantages of microwave heating system over conventional heating are shorter operation time, greater reaction conversion rate due to molecular level heating, faster recovery of excess alcohol and low energy input. Finally, the study proved that microwave technology opened up a new route for faster and efficient production of biodiesel from vegetable oil.

4.2. Future work

Experimental study performed in this research work provides a tool for process sale up to commercialization. A pilot scale continuous process would be the next step toward scaling up. The kinetic model developed here can be modified to examine other processes. It would be a significant step to study the reaction kinetics of a pilot scale in-situ transesterification reaction. Although the results of laboratory scale in-situ transesterification process was satisfying, the overall biodiesel production process from oil extraction to transesterification can be optimized in terms of energy efficiency by studying different parameters affecting microwave heating. Employing tools to deliver the highest portion of consumed energy to the reaction components such as microwave auto-tuner can improve the process in terms of energy consumption. Moreover, a magnetic heterogeneous catalyst can also avoid the side reaction (soap formation) and lower the cost of separation units. Implementing heterogonous catalyst into the continuous process could be a feasible future work.
VITA

Mohamad Barekati Goudarzi, a native of Boroujerdi, Lorestan, Iran. He went to school in the same city as he was born. After finishing elementary school, he started his middle school (also known as orientation cycle) in National Organization for Development of Exceptional Talents school, where highly intellect students were accepted to pursue education after taking a national entrance exam. He passed his middle and high school successfully in the field of mathematics and physics and became qualified for sitting on the national public university comprehensive exam in the field Engineering and construction. Around 300,000 students participates in this national exam on the same day where only less than 10% of them can be awarded free higher education. His rank was below 1% and made him qualified to enter the best Iranian engineering college, University of Tehran, Tehran, Iran (#56 in 2015 Best Global Universities for Engineering based on U.S. News & World Report website). He chose Chemical Engineering as his major of study and after 5 years, 2013, graduated with rank 10th amongst nearly 80 students in the same class. He started graduate school at Louisiana State University in Biological Engineering Department and he is a candidate to receive his degree on December 2015.