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Experimental and numerical investigation of pilot scale microwave assisted transesterification process for biodiesel production

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EXPERIMENTAL AND NUMERICAL INVESTIGATION OF PILOT SCALE MICROWAVE ASSISTED TRANSESTERIFICATION PROCESS FOR BIODIESEL PRODUCTION

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 Biological and Agricultural Engineering in The Department of Biological & Agricultural Engineering

by
Pranjali D. Muley
B. Tech., Dr. Babasaheb Ambedkar Technological University, 2008
May 2012
Dedicated to

Aai, Pappa
ACKNOWLEDGEMENTS

I am thankful to God for his blessings.

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# TABLE OF CONTENTS

**ACKNOWLEDGEMENTS**........................................................................................................... ii

**LIST OF TABLES**.................................................................................................................. vi

**LIST OF FIGURES** ................................................................................................................ vii

**LIST OF SYMBOLS** ................................................................................................................. ix

**ABSTRACT**............................................................................................................................. xi

CHAPTER 1. INTRODUCTION ....................................................................................................... 1
  1.1. References ............................................................................................................................. 7

CHAPTER 2. INVESTIGATION OF MICROWAVE DIELECTRIC PROPERTIES OF
Biodiesel Components .................................................................................................................... 9
  2.1. Introduction ............................................................................................................................ 9
  2.2. Materials and Methods ........................................................................................................ 15
  2.3. Results and Discussions ....................................................................................................... 17
    2.3.1 Soybean Oil ...................................................................................................................... 17
    2.3.2 Alcohol ............................................................................................................................. 20
    2.3.3 Alcohol-Catalyst ................................................................................................................. 25
    2.3.4 Oil, Alcohol and Catalyst Mixture .................................................................................... 29
  2.4. Conclusions .......................................................................................................................... 36
  2.5. References ............................................................................................................................ 37

CHAPTER 3. SCALE UP OF A CONTINUOUS MICROWAVE ASSISTED
TRANSESTERIFICATION PROCESS OF SOYBEAN OIL FOR PRODUCTION OF
Biodiesel ......................................................................................................................................... 40
  3.1. Introduction ............................................................................................................................ 40
    3.1.1. Transesterification Reaction Mechanism ......................................................................... 41
    3.1.2. Factors Affecting the Base Catalyzed Transesterification Reaction ................................. 43
  3.2. Materials and Procedure .................................................................................................... 49
  3.3. Results and Discussion ........................................................................................................ 53
    3.3.1. Rate of Conversion .......................................................................................................... 53
    3.3.2. Fatty Acid Ethyl Ester Composition ................................................................................. 56
    3.3.3. Quality Analysis .............................................................................................................. 57
  3.4. Conclusions .......................................................................................................................... 61
  3.5. References ............................................................................................................................ 62

CHAPTER 4. NUMERICAL MODELING OF TEMPERATURE PROFILES DURING
CONTINUOUS FLOW MICROWAVE ASSISTED TRANSESTERIFICATION
PROCESS ..................................................................................................................................... 66
  4.1. Introduction ........................................................................................................................... 66
4.2. Experimental Methods and Procedure for Numerical Simulation .......................... 75
  4.2.1. Experimental Measurements .................................................................. 75
  4.2.2. Governing Equations .............................................................................. 77
  4.2.3. Model Development ............................................................................... 79
    4.2.3.1. Geometry Building ........................................................................... 80
    4.2.3.2. Boundary Conditions ....................................................................... 81
    4.2.3.3. Material Properties .......................................................................... 82
    4.2.3.4. Mesh Generation .............................................................................. 84
    4.2.3.5. Solver Used and Convergence Criteria ........................................... 84
    4.2.3.6. Post Processing ................................................................................. 85
  4.3. Results and Discussion ................................................................................ 85
    4.3.1. Electric Field Intensity ......................................................................... 85
    4.3.2. Electromagnetic Power Density .......................................................... 87
    4.3.3. Velocity Profile and Temperature Distribution ....................................... 89
      4.3.3.1. Temperature Distribution in Cross Axial (Vertical $xy$ and $yz$ Plane) .... 91
      4.3.3.2. Temperature Distribution ($xy$-Plane) ........................................... 93
    4.3.4. Experimental Validation ....................................................................... 99
  4.4. Conclusions ................................................................................................. 101
  4.5. References ................................................................................................. 101

CHAPTER 5. SUMMARY AND FUTURE WORK ......................................................... 106
  5.1. Conclusions .................................................................................................. 106
  5.2. Future Work ................................................................................................ 108

VITA ................................................................................................................... 109
LIST OF TABLES

Table 2.1 Relaxation time and viscosity of ethanol and methanol at different temperatures...........25

Table 2.2 Values for dielectric constant and dielectric loss of pure components and alcohol-catalyst mixture at 915 MHz and 2450 MHz.................................................................29

Table 2.3 Values for dielectric constant and dielectric loss at 915 MHz and 2450 MHz for oil alcohol catalyst mixture (scenario 1 & 2).................................................................36

Table 3.1 Free and total glycerin content and percent conversion of soybean oil fatty acid esters studied at varying reaction temperatures and times..............................................56

Table 3.2 Fatty acid ethyl ester yield of soybean oil biodiesel..................................................57

Table 3.3 Qualitative analysis of soybean oil biodiesel...............................................................59

Table 4.1 Dielectric and thermo-physical properties (temperature dependent equations) of oil and ethanol mixture .........................................................................................84

Table 4.2 Numerical and experimental temperature values at different locations .................100
LIST OF FIGURES

Figure 2.1 Dielectric constant of soybean oil at 30ºC and 75ºC .............................................18

Figure 2.2 Dielectric loss factor of soybean oil at different temperatures and frequencies ..........20

Figure 2.3 Dielectric properties of alcohol: a) Dielectric constant of methanol and ethanol; b) Dielectric loss factor of ethanol; c) Dielectric loss factor of methanol ..................................23

Figure 2.4 First order derivative of dielectric loss with respect to frequency: a) Ethanol; b) Methanol ..................................................................................................................24

Figure 2.5 Dielectric properties of alcohol-catalyst mixture: a) Dielectric constant of alcohols + NaOH; b) Dielectric loss factor of ethanol + NaOH; c) Dielectric loss factor of methanol + NaOH ..................................................27

Figure 2.6 Dielectric properties of oil ethanol and catalyst mixture: a) Dielectric constant for scenario one; b) Dielectric constant for scenario two; c) Dielectric loss factor for scenario one; d) Dielectric loss factor for scenario two ..........................................................31

Figure 2.7 Dielectric properties of oil methanol-catalyst mixture a) Dielectric constant for scenario one b) Dielectric constant for scenario two c) Dielectric loss factor for scenario one d) Dielectric loss factor for scenario two ..................................................35

Figure 3.1 Continuous flow microwave applicator and tuning system used for the pilot scale production of biodiesel .........................................................................................................48

Figure 3.2 Change in temperature with respect to time at 4000W power input .........................51

Figure 3.3 Change in temperature with respect to time at 4700W power input ..........................51

Figure 3.4 Flow chart of pilot scale microwave assisted process ..................................................52

Figure 3.5 Chromatogram showing glycerol and biodiesel peaks .............................................58

Figure 4.1 Experimental temperature measurement locations .....................................................76

Figure 4.2 Geometrical rendering of continuous flow microwave heating system .....................80

Figure 4.3 Thermo-physical temperature dependent properties of fluid mixture (oil and ethanol) based on mass fraction: (a) thermal conductivity, W/m·K; (b) density, kg/m³; (c) dynamic viscosity, Pa·s; (d) specific heat capacity, J/kg·K; (e) relative dielectric constant; (f) dielectric loss factor .................................................................83

Figure 4.4 Electric field distribution in the microwave (a) xy-plane (b) xz-plane (c) yz-plane ...86
Figure 4.5 Electromagnetic power density (W/m$^3$) for $P_{in} = 4000\text{W}$ and $4700\text{W}$; (a) and (b) at pipe entrance; (c) and (d) at a distance of 0.065 from the entrance of pipe; (e) and (f) at a center of pipe (g) and (h) at a distance of 0.195 from the entrance of pipe and (i) and (j) at the pipe exit.

Figure 4.6 Average temperature vs time at the exit of pipe for $4000\text{W}$ and $4700\text{W}$

Figure 4.7 Velocity profile (m/s) for (a) $P_{in} = 4000\text{W}$ and (b) $P_{in} = 4700\text{W}$

Figure 4.8 Temperature distributions ($^\circ\text{C}$) in cross axial $xz$-plane for fluid mixture for $P_{in} = (a) 4000\text{W}$; (b) $4700\text{W}$

Figure 4.9 Temperature distributions ($^\circ\text{C}$) in cross axial $yz$-plane (microwave facing) for fluid mixture in (a) $4000\text{W}$ (b) $4700\text{W}$

Figure 4.10 Temperature distribution($^\circ\text{C}$) in $xy$-plane for $P_{in} = 4000\text{W}$ and $4700\text{W}$ at $t = 60\text{ sec}$; (a) and (b) at pipe entrance; (c) and (d) at a distance of 0.065 from the entrance of pipe; (e) and (f) at a center of pipe (g) and (h) at a distance of 0.195 from the entrance of pipe and (i) and (j) at the pipe exit.

Figure 4.11 Temperature distribution ($^\circ\text{C}$) in $xy$-plane for $P_{in} = 4000\text{W}$ at the center of the tube for (a) oil, ethanol catalyst mixture (b) water

Figure 4.12 Temperature distribution($^\circ\text{C}$) in $xy$-plane for $P_{in} = 4000\text{W}$ and $4700\text{W}$ at $t = 1\text{ sec}$; (a) and (b) at pipe entrance; (c) and (d) at a distance of 0.065 from the entrance of pipe; (e) and (f) at a center of pipe (g) and (h) at a distance of 0.195 from the entrance of pipe and (i) and (j) at the pipe exit.

Figure 4.13 Temperature distribution in radial direction ($x$-axis) for $P_{in} = (a) 4000\text{W}$ and (b) $4700\text{W}$

Figure 4.14 Experimental Validation and Temperature Distribution
LIST OF SYMBOLS

$A$ - pre-exponential factor, $s^{-1}$

$\alpha$ - spread of relaxation times; $\alpha \in [0,1]$  

$B$ - magnetic flux density; V·s

$c$ - speed of light in vacuum; m/s

$C_p$ - specific heat; J/kg·K

$D$ - electric displacement; C/m$^2$

$D_p$ - penetration depth; m

$\delta$ - loss angle

$E$ - electric field intensity; V/m

$Ea$ - activation energy; KJ/mole

$\varepsilon'$ - relative dielectric constant S/m

$\varepsilon''$ - relative dielectric loss factor

$\varepsilon$ - complex relative permittivity

$\varepsilon_{\infty}'$ - relative dielectric constant as ($\omega \rightarrow \infty$)

$\varepsilon_s'$ - relative static dielectric constant (at $\omega = 0$)

$\varepsilon_0$ - dielectric constant of the vacuum (value = $8.854 \times 10^{-12}$ S/m)

$F$ - force; N

$f$ - frequency; Hz

$g$ - acceleration due to gravity; m/s$^2$

$H$ - magnetic field intensity; A/m

$J$ - electric current; A
$k$ - rate constant

$K$ - thermal conductivity; W/m·K

$k_b$ - Boltzmann’s constant; $1.3806504 \times 10^{-23}$ J/K

$\lambda$ – wavelength; m

$\lambda_0$ - wavelength in free space; m

$\mu$ - viscosity; Pa·s

$\mu'$ - relative permeability of material; H/m

$\mu_0$ - magnetic permeability of material; $4\pi \times 10^{-7}$ N/A²

$P$ – pressure; Pa

$P_{abs}$ - power absorbed; W/m³

$Q_{gen}$ - power generated; W/m³

$R$ - gas constant; 8.314J/mole.K

$r$ - radius; m

$\rho$ - electric charge density

$\rho_m$ - density of material; kg/m³

$\sigma$ - conductivity; Siemens/m

$\sigma_e$ - electrical conductivity; Siemens/m

$T$ - absolute temperature; Kelvin

$t$ - time (sec)

$\tau$ - relaxation time; sec

$u$ - fluid velocity; m/s

$\nu_2$ - volume fraction of dispersed phase.

$\omega$ - angular frequency; rad/sec
ABSTRACT

The goal of this study was to design and test a pilot scale process for biodiesel production using advanced microwave technology and develop a numerical model for investigating various parameters affecting this process.

Dielectric properties of materials play a major role in microwave design of a process. The dielectric properties (dielectric constant $\varepsilon'$ and dielectric loss $\varepsilon''$) of biodiesel precursors: soybean oil, alcohols and catalyst and their different mixtures were measured at four different temperatures (30°C, 45°C, 60°C and 75°C) and in the frequency range of 154 MHz to 4.5 GHz. Results indicate that the microwave dielectric properties of almost all components depend on both temperature and frequency. Addition of catalyst changed the properties of solvent due to the strong ionic nature.

A scaled up version of a continuous microwave transesterification process was designed, built and tested. Experimental parameters were set based on previous laboratory scale results. Experiments were performed in a well controlled continuous pilot scale microwave reactor at temperatures of 60°C and 75°C and processing times of 5 to 15 minutes. Microwave power required to achieve the temperature of 60°C was 4000W and for 75°C was 4700W. Ethanol was used as a solvent with NaOH as a catalyst (< 0.2% by weight of oil). The conversion obtained was >99% for all experimental conditions.

The final objective was to develop a basic numerical model of continuous electromagnetic heating of biodiesel precursors. A finite element model was built using COMSOL Multiphysics 4.2 software. High frequency electromagnetic problem was coupled with the non-isothermal flow problem. The model was tested for the two different power levels.
The electric field, electromagnetic power flow and temperature profiles were studied. Resulting temperature profiles were verified by comparing to the experimental data.

The presented study assists in understanding microwave heating application for biodiesel production. The dielectric property analysis gives a clear picture of interaction of biodiesel components with microwave irradiation, numerical model aids in understanding temperature distribution while experiments validate the results. This study can be applied to optimize the microwave assisted continuous biodiesel production process.
CHAPTER 1

INTRODUCTION

A steady and reliable supply of energy is the requirement of a modern lifestyle. From the basic necessities of living (cooking) to comfort (heating) and transportation, having a sustainable source of energy is critical. Energy sources can be broadly divided into three categories; 1) chemical energy which is mainly energy derived from fossil fuels, 2) nuclear energy and 3) thermo-mechanical energy which is in the form of geothermal energy, wind, hydro etc. (Dresselhaus and Thomas, 2001). They can be further categorized into renewable and non-renewable sources of energy. The renewable sources of energy are solar, wind, tides, biomass etc. The non-renewable sources of energy are mainly fossil fuels and nuclear energy.

Although fossil fuels are generally believed to have been formed naturally, they require millions of years to form and the current rate of consumption of fossil fuel is very high, thus making them a non-renewable source. Fossil fuels includes coal, petroleum, and natural gas (Bertine and Goldberg, 1971). They are relatively readily available, and were an abundant source of energy until it was exploited on a large scale to produce variety of primary (transportation fuel) and secondary need products to meet the ever increasing demand of population. Secondary need products include coke, asphalt, polymers, specialty chemicals, detergents, cosmetics, lubricants, solvents, waxes, pharmaceuticals, synthetic fibers, plastics, etc. Nuclear energy requires a source of radioactive material such as uranium (Naik et al., 2010), but it presents several challenges in terms of safety and handling; as well as a risk of proliferation of nuclear weapons.

Currently, the major contributors to the world’s energy supply are fossil fuels and nuclear energy. According to the Energy Information Administration (EIA) statistic for 2007, 86.4% of
the primary energy source was supplied through fossil fuel, while nuclear energy supplied 8.5% of the total energy, ranking second, followed by hydropower (6.3%). Fossil fuel is also the largest supplier of transportation fuel (Annual, 2007).

Fossil fuels are convenient to use but have several disadvantages (in addition to being non-renewable) in terms of their utilization as an energy source. Any operation with fossil fuel emits carbon dioxide and other harmful gases such as sulphur oxides, nitrogen oxides, carbon monoxide, and ash deposition. Burning of fossil fuels produces 21.3 billion tonnes of carbon dioxide per year (Annual, 2007). Crude oil and natural gas prices are unstable for various economical and political reasons. The predicted increase in worldwide population adds to increased demand over the available supply, and therefore, crude oil prices are estimated to rise in the future. In addition, fossil fuel reserves are not uniformly distributed across the planet. Countries with large petroleum reserves are politically unstable leading to large uncertainties in crude oil prices.

Nuclear plants produce nuclear fission products and other nuclear wastes, but remain second largest source for production of electricity next to fossil fuels. Some of the concerns related to use of nuclear energy involve various safety aspects during storage and handling radioactive materials, and disposal of nuclear waste. It takes thousands of years for nuclear waste to decay. Recycling of nuclear waste is expensive and only a few countries have the infrastructure and resources for nuclear fuel waste reprocessing. Renewable sources also have certain limitations. Hydropower plants require large water bodies and large dam structures. In places such as Louisiana which lack cliffs and elevations, hydrothermal energy is not feasible. Hydrothermal energy is capital intensive and may lead to environmental issues related to aquatic life. Geothermal energy resources are scarce and unevenly distributed across the planet. Heat and
solar energy requires large areas for operation (Dresselhaus and Thomas, 2001). In spite of above mentioned drawbacks, these energy sources have been developed and used in various part of the world. However, there is a need to develop a reliable and renewable source for transportation fuel. Major problem persists with renewable transportation fuel, as, it should be capable of being operated in currently used motor vehicles, should be cleaner with lower emission of harmful gases and posses high energy density.

Although the first diesel engine developed by Rudolf Diesel in 1900 operated on vegetable oil, in a short time, the fuel was replaced by the more readily available diesel from petroleum. It was not until the first energy crisis of 1970’s and 80’s that the research on alternatives for transportation fuel was undertaken (Knothe et al., 2005). Since straight vegetable oil has a several limitations such as gum formation, high viscosity and acid content etc. (Ma and Hanna, 1999; Srivastava and Prasad, 2000), other options such as transesterification of vegetable oil with alcohol into biodiesel were considered for compression engines, while, bioethanol derived from sugarcane, sorghum, corn, sugar beet, to be used in ignition engines, were developed (Naik et al., 2010). Transesterification is a general term that describes an organic reaction where an alcohol from an ester is displaced by another alcohol (Schuchardt et al., 1998). This displacement reaction is similar to hydrolysis reaction except alcohol is employed instead of water (Fukuda et al., 2001). The first-generation biofuels (biodiesel from vegetable oil) have many advantages, including being carbon dioxide neutral, reducing green house gases emissions, having an energy content similar to petroleum diesel, possibility of use as direct diesel replacement without engine modification, and being domestically produced, therefore easing the dependence on foreign imports.
However, first generation biofuels have some drawbacks. They present a serious moral dilemma, as biofuel is produced either from food crops (corn, sugarcane, and soybean) or use prime agricultural land for non food crops (rapeseed oil, pal oil etc.) as such they directly interfere with the human food needs. To solve these issues, some researchers have come up with ideas such as production of biodiesel from iols obtained from non edible seeds that grow on marginal lands such as *jatropha crucias*, chinese tallow trees, algae etc.

Second generation biofuels are produced from plant biomass, mainly lignocellulosic material. These are argued to be environmentally beneficial compared to first generation biofuels (Gomez et al., 2008). However the second generation biofuel production technology is currently not cost efficient and hence is not commercialized (Naik et al., 2010).

The first generation biodiesel is produced on a large scale with 50 billion liters produced annually in the United States (Naik et al., 2010). The production process is still relatively energy inefficient and it requires long reaction times (one to four hours). Although a few of the problems regarding biomass and production have been addressed, there is still a need for technology that will increase the overall production of biodiesel fuel.

Use of microwave energy to enhance the reaction process and ultimately the yield of biodiesel is a relatively new technology. It has been tested on a laboratory scale and the results were encouraging (D Boldor, 2010; Leadbeater and Stencel, 2006; Terigar et al., 2010b). Since 1940’s, microwave and radio frequency (RF) heating has been extensively used in a variety of industries for multiple purposes. Domestic microwave appliances are used for home cooking and thawing, and industrial microwave systems for applications such as drying, pasteurizing, extraction, baking and heating (Metaxas and Meredith, 1993). Microwave and RF heating has been extensively used in agricultural industry, mainly for drying and insect control. Recent
studies have demonstrated the successful use of microwave for the extraction of oil from oilseeds (Balasubramanian et al., 2011; Terigar et al., 2011). Use of microwaves in chemical industry has been growing recently because of the fact that microwave heating increases the rate of reaction (Lidstrom et al., 2001). Microwaves penetrate into the sample and cause molecular level heating throughout the volume of the material. Emerging technologies such as single and dual mode focusing cavity, continuous flow microwave systems, multi frequency operation etc. have taken this technology to a new level in terms of flexibility and applicability. With well defined material properties and specifications, a microwave system can be designed to optimize heating (Salvi et al., 2011).

Microwave heating depends on factors such as material properties (dielectric and thermophysical), frequency of operation and system design. These parameters should be studied in depth in order to obtain optimum heating with microwave technology. Numerical modeling helps by predicting heating and temperature profiles that could be obtained with different parameters. The process can be studied for optimization without actually performing the experiments, once certain geometrical parameters and material properties are known.

The goal of this research project was to test and develop advanced microwave technology for the production of biodiesel on pilot scale. Based on the above criteria, the following specific objectives were designed and investigated: 1) Determining dielectric properties of biodiesel components such as oil, alcohol and catalyst; 2) Designing and operating a continuous scale microwave assisted pilot plant for production of biodiesel and testing for the influence of reaction parameters on performance; 3) Developing a numerical model for continuous microwave heating for biodiesel production based on experimental parameters and validating it experimentally.
The first step in this research was to measure the dielectric properties of the components required to produce biodiesel. As to our knowledge, this data was not readily available in literature. We measured dielectric constant and the dielectric loss of pure components that are vegetable oil (refined soybean oil) and alcohol (200 proof ethanol and methanol), alcohol-catalyst mixture (Ethanol+ NaOH and Methanol+ NaOH) and the mixture of all the three components oil, alcohol and catalyst. The measurements were performed as a function of frequency at different temperatures. The results obtained were studied carefully and compared to available literature data for pure alcohol and oil.

The second objective was to carry out the transesterification reaction for biodiesel production on a pilot scale which has not been undertaken before in a focusing resonant cavity operating at 915 MHz. The solvent used was ethanol and two power levels were studied at one flow rate to obtain two temperatures of 60°C and 75°C. The biodiesel samples collected at different residence times were analyzed for the fatty acid ethyl ester content, transesterification yield and sample quality according to existing biodiesel standards.

The amount of energy utilized and the amount of sample used to produce biodiesel was rather large as the process was carried out on a pilot scale. To optimize the microwave assisted transesterification reaction it is usually desirable to test other process parameters such as optimum temperature, required residence time and power levels. However, carrying out extensive experiments at this scale is not feasible due to material and man power requirement. Numerical analysis approach was employed to test these parameters investigated in the second objective. Hence, using the dielectric properties of biodiesel components measured (objective 1), and the experimental parameters used in pilot scale transesterification reaction (objective 2), a finite element model was built using COMSOL Multiphysics 4.2 software. High frequency
electromagnetic problem was coupled with the non-isothermal flow problem. The model was tested for the two different power levels that were used to perform experiments. The electric field, electromagnetic power density, flow, and temperature profiles were studied. Resulting temperature profiles were verified by comparing to the temperatures obtained during the experimental part of the project. The results obtained were in good agreement with the experimental results.

Overall the present project assists in better understanding of microwave heating application for biodiesel production. This study can be applied to optimize the microwave assisted continuous biodiesel production process.

1.1 References


CHAPTER 2

INVESTIGATION OF MICROWAVE DIELECTRIC PROPERTIES OF BIODIESEL COMPONENTS

2.1 Introduction

Microwave dielectric heating is a well-established procedure used in industrial processing of food and other materials as well as for home cooking and heating. On the electromagnetic spectrum, microwaves fall in the transitional region between the infrared and the radiofrequency wavelengths. The frequency range is generally considered to be between 300 MHz to 300 GHz, with wavelengths between 1.0 cm and 1.0 m (Kappe, 2008). Applications of microwave technology include drying, cooking, thawing, heating, baking, extraction, and sterilization in food, bio-processing and agricultural industries, as well as many applications in the ceramic, rubber and plastic industry (Meredith, 1998; Metaxas and Meredith, 1993). Major advantages of microwave dielectric heating include rapid heating, safety and, in certain applications, improved energy efficiency.

Conventional heating methods are relatively slow and inefficient as the transfer of energy is by conduction and convection mechanisms, unlike microwave heating were the heating occurs at a molecular level. In order to understand how the microwave heating takes place, one needs to look at the specific interaction of electromagnetic fields with a material. Being of an electromagnetic origin, microwave radiation has two active fields, the electric field component (causing dielectric heating) and the magnetic field component. The interaction of electromagnetic waves with matter are characterized by two physical quantities – complex dielectric permittivity, $\varepsilon$ and complex magnetic susceptibility, $\mu$ (Stuerga, 2008). For significant interactions with magnetic field, a material needs to have a relatively important magnetic
susceptibility. This is not the case for most biological and agricultural materials and hence, will not be further discussed here. Dielectric heating induced by the electric field is produced by two mechanisms: dipolar rotation and ionic conductance.

For the first mechanism, a dipole (two equal and opposite charges separated by a finite distance), when exposed to an electric field, will try to align itself with the corresponding polarity of the field. If the field is rapidly changing its own polarity, the dipolar molecules try to realign to the new direction (also rapidly). If the frequency and the dipole size are appropriately matched, the dipole ends up spinning around very fast. In this effort of alignment, the molecules rasp with each other causing friction and subsequent heating.

In ionic conductance, charged ions oscillate through the solution under the influence of the applied electric field. As the electric field direction changes, the ions slow down and change direction. In the process, this motion causes collisions resulting in conversion of kinetic energy into heat energy.

The interaction phenomena induced between the electromagnetic waves and a dielectric substance can be divided into two major factors: dielectric constant – the storage of electromagnetic energy in the irradiated material, and dielectric loss factor – the thermal conversion of electromagnetic energy occurring via dipolar rotation and ionic conduction as explained above. The relation between permittivity $\varepsilon$ and dielectric constant $\varepsilon'$ and dielectric loss factor $\varepsilon''$ is given by the complex equation (Gabriel et al., 1998):

$$
\varepsilon = \varepsilon' - j\varepsilon''
$$

[2.1]

Where real part (or dielectric constant) $\varepsilon'$ represents the electromagnetic storage capability of a material and the imaginary part (or the dielectric loss factor) $\varepsilon''$ stands for the ability of material to convert the electromagnetic energy into heat. Dependence of dielectric permittivity on
frequency and temperature is a complex phenomenon. Frequency dependence of pure polar substances can be expressed using Debye’s equation (Hipel, 1954):

\[
\varepsilon = \varepsilon'^{'} + \frac{\varepsilon_s^{'}-\varepsilon_{\infty}^{'}}{1+j\omega\tau} \\
\varepsilon^{'} = \varepsilon_s^{'} + \frac{\varepsilon_s^{''} - \varepsilon_{\infty}^{''}}{1+\omega^2\tau^2} \\
\varepsilon^{''} = \frac{(\varepsilon_s^{''} - \varepsilon_{\infty}^{''})\omega\tau}{1+\omega^2\tau^2}
\]

[2.2]

Debye’s equation can be adapted for non-polar pure materials using Cole-Cole equation (Nelson, 1973):

\[
\varepsilon = \varepsilon^{'} + \frac{\varepsilon_s^{'}+\varepsilon_{\infty}^{'}}{1+(j\omega\tau)^{1-\alpha}}
\]

[2.3]

Where, \(\varepsilon\) is the complex relative permittivity, \(\varepsilon_{\infty}^{'}\)' stands for relative dielectric constant as \(\omega\) goes to infinity, \(\varepsilon_s^{'}\) is the relative static dielectric constant (at \(\omega = 0\)), \(\tau\) is relaxation time for a polar molecule (sec), \(\omega\) is the angular frequency, \(\alpha\) stands for spread of relaxation times; \((\alpha \in [0,1])\) and \(j = (-1)^{1/2}\).

At low frequencies, the electric field components is reversed at a slower pace giving enough time for the molecules to align and to store the applied charge in the dipoles. At the same time, frequency is high enough to create friction between adjacent molecules as they try to align themselves with the changing field. This phenomenon causes dielectric heating. Thus the dielectric constant at low frequencies is higher. However, with the increase in frequency, the field oscillation is rapid, not giving enough time for the molecules to rotate. The field polarity is reversed before the response of molecules to the previous field is fully received. Hence even the smallest molecule does not respond to the oscillating field causing a marked decrease in dielectric permittivity. The relaxation spectrum depends on various other material parameters such as temperature, viscosity, molecular weight and concentration.

Equations [2.2] and [2.3] are valid only for pure substances, hence cannot be used for mixtures. Therefore, several mixing rules have been derived to calculate the dielectric properties of heterogeneous as well as homogenous mixtures. Some of the more effective equations are
Landau and Lifshitz, Looyenga equation [2.4] (Dube, 1970; Landau and Lifshits, 1960) and Bottcher Equation [2.5] (Bottcher, 1945)

$$\varepsilon_2 = \left(\frac{\varepsilon_1^{1/3} + v_2^{-1}}{v_2}\right)^3 \quad [2.4]$$

$$\varepsilon_2 = \frac{\varepsilon_1[3v_2^2 + 2(\varepsilon_1^{-1})]}{3v_2\varepsilon_1-(\varepsilon_1^{-1})} \quad [2.5]$$

An important equation was developed by Bruggeman (Bruggeman, 1935; Yang et al., 2010) as follows;

$$\left(\frac{\varepsilon - \varepsilon_2}{\varepsilon_1 - \varepsilon_2}\right) \left(\frac{\varepsilon_1}{\varepsilon}\right)^{1/3} = 1 - v_2 \quad [2.6]$$

Where, $\varepsilon$ is complex permittivity of mixture, $\varepsilon_1$ is permittivity of component 1 (medium), $\varepsilon_2$ is permittivity of component 2 (dispersed phase), $v_2$ is the volume fraction of dispersed phase.

The above-mentioned mixing rules are simple volume fraction based mixing rules. They are most commonly applied to non-reacting and powdered mixtures. Thus, in case of liquids mixtures with reactions, these mixing rules cannot be directly applied (Sihvola, 2002). In case of reacting mixtures, the volume, density, temperature and concentration of reactants and products, as well as that of intermediate products should be taken into account, since these parameters tend to change as the reaction proceeds. The process of analytically calculating the dielectric properties of reacting mixtures at various temperatures is complex as too many parameters have to be taken into consideration. Some studies attempted to calculate the dielectric properties of liquid mixtures, which mainly involve modifying the above mentioned mixing rules with respect to the component properties. An important study, that was not specific to the reacting components was performed by Harvey et al., (Harvey and Prausnitz, 1987). Harvey et al., presented a modified and improved equation for estimating the dielectric constant of fluid mixtures. This expression was a function of temperature, density and composition of the fluid.
mixture. The limitation of this expression is that it cannot be used for mixtures containing nonpolar components. Also its application to our study requires too much data in terms of dielectric constant of pure components as a function of density and temperature and hence will not be included here.

Another factor that can be used to explain the dielectric heating is the loss tangent. Loss tangent or loss angle $\delta$ takes into account both the factors affecting dielectric heating: absorption ($\varepsilon'$) and conversion to heat energy ($\varepsilon''$). It is defined as;

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad [2.7]$$

Loss tangent depends on relaxation time. The torque exerted by the electric field induces rotation in the polar molecules, but the rate at which molecules orient could be slower compared to applied electric field. This delay between electromagnetic stimulation and molecule response, also known as relaxation time, is responsible for the dielectric loss. An increase in dielectric loss is observed when the equation $\omega = 1/\tau$ is satisfied, where $\omega = 2\pi/T$ (Stuerga, 2008). If the relaxation time of a solvent is higher than about 65ps (at 2450 MHz), there is an increase in loss tangent with temperature, resulting in higher conversion of electromagnetic energy into thermal energy (Baghurst and Mingos, 1992). Therefore the heating rate rises. This phenomenon is responsible for the localized superheating of organic solvents in the microwave region (Baghurst and Mingos, 1992). If the relaxation time $\tau$ is many times greater than the period $T$ of the alternation of the applied field, polarization is barely able to develop and the dielectric loss is very small. At low frequencies, where the relaxation time $\tau$ is considerably smaller than the period $T$, the polarization follows (lags behind) the field and the dielectric loss is also small because the number of reorientations per unit time is small. Loss tangent for methanol and ethanol are 0.659 and 0.941 respectively at 915 MHz, and the relaxation times for methanol and
ethanol are 51.5 ps and 170 ps respectively (Kappe, 2008; Pace et al., 1968b). Relaxation time is temperature dependent and decreases as the temperature is increased; it is also viscosity dependent. The relation between the viscosity and relaxation time is given by the following equation (Metaxas and Meredith, 1993);

\[ \tau = \frac{4 \pi r^3 \mu}{k_b T} \]  

Where; \( \tau \) is relaxation time (s), \( r \) is radius of the molecule (m), \( \mu \) is the viscosity of solution (Pa·s), \( T \) is absolute temperature (K) and \( k_b \) is Boltzmann’s constant (1.3806504 \times 10^{-23} \text{ J/K}). Longer relaxation times indicate low heat absorption due to slower response of molecules to the changing electric field.

Although the advantages of microwave heating are long known, it was employed in organic chemistry only starting in mid 80’s (Palacios et al., 1996). The application has now gained momentum in the chemical industry because of its rapid and targeted heating capabilities. Microwaves are introduced to the reaction site remotely and can pass through the vessel wall without heating the vessel. As such, microwaves interact volumetrically only with the reactants and solvents, and, for a well-designed apparatus, heating can be uniform without causing the decomposition of reactants or products.

One promising application of this technology in the bio-energy area is production of biodiesel, a promising alternative for petroleum fuel, via transesterification of vegetable oil in the presence of catalyst. As transesterification reaction requires energy input in the form of heat, microwave dielectric heating can be effectively used to carry out the transesterification reaction. The use of alcohols as a solvent and sodium hydroxide as a catalyst gives a unique combination, with the presence of both polar and ionic components in the mixture speeding up the heating process. Variables affecting the performance of microwave heating are microwave operation
frequency, design of cavity, power level, initial temperature, and dielectric properties of reacting materials (Terigar et al., 2010a). Whereas the other parameters are independent of the reacting material and can be selected for each specific application, dielectric properties are material specific. Therefore knowledge of dielectric properties of material is beneficial for process design calculations, execution and control of microwave heating. Dielectric properties help in predicting electromagnetic field distribution, heating rates, temperature profiles for the reactions and overall understanding of the mechanism of microwave dielectric heating.

Dielectric properties play an important role in calculating energy efficiency of the reaction process. The amount of energy absorbed and dissipated as heat can be given as (Nelson, 1992):

\[ P_{\text{abs}} = \sigma E^2 = 2\pi f \varepsilon_0 \varepsilon'' E^2 \]  

Where, \( P_{\text{abs}} \) is power absorbed (W/m³), \( \sigma \) is the conductivity (Siemens/m), \( f \) is frequency (Hz), \( \varepsilon_0 \) is the dielectric constant of the vacuum, \( \varepsilon'' \) is relative dielectric loss, \( E \) is electric field intensity (V/m).

The objective of this study is to understand the interaction of biodiesel components and its mixtures with the electromagnetic field by determining their dielectric properties at different temperatures.

### 2.2 Materials and Methods

Soybean oil was purchased from a local grocery store whereas ethanol (200 proof, ACS/US grade) and methanol (200 proof, ACS/US grade) were purchased from Pharmco-AAPER (Brookfield, CT). Anhydrous sodium hydroxide flakes were supplied by Fisher Scientific (Pittsburgh, PA).
Dielectric properties of the mixtures were determined using an Agilent ENA series E5071C Network Analyzer and Agilent 85070E dielectric probe kit (Agilent Technologies, Inc. Santa Carla, CA) using a slim form open-ended probe method in a 201-point frequency sweep from 280 MHz to 4500 MHz. The network analyzer was controlled by Agilent 85070E dielectric kit software (Agilent Technologies, Inc. Santa Carla, CA) and calibrated using the 3-point method (short-circuit, air and water at 25°C).

As biodiesel can be produced using either alcohols (methanol or ethanol) it was important to study the dielectric nature of both as well as their different mixtures with oil and catalyst. The dielectric properties of pure components: soybean oil, ethanol and methanol, and their various mixtures (including those with basic catalyst) were measured at four different temperatures of 30°C, 45°C, 60°C and 75°C. The temperature was maintained using a constant temperature water bath. Since methanol has a boiling point of 68°C, its dielectric properties were not measured at 75°C. Second step involved measurement of dielectric properties of solvent with basic catalyst. Anhydrous sodium hydroxide (0.18% by the weight of oil) was mixed with ethanol and methanol (Kanitkar et al., 2011). The NaOH pellets were allowed to dissolve completely by stirring the mixture with a magnetic stirrer prior to measurements. Third and final step involved measurements of dielectric properties of mixture of oil with solvent and the catalyst, as this is the mixture from which biodiesel is prepared. The oil to ethanol ratio was maintained at 1:9, while the oil to methanol ratio was 1:5 (Kanitkar et al., 2011). These measurements were performed for two different scenarios. In each scenario the catalyst was fully premixed with the alcohols.

In the first scenario, oil and the alcohol- catalyst mixture were heated separately and were mixed only when the desired temperature was attained. The dielectric properties were measured immediately after adding oil and ensuring sample homogeneity via stirring. As the data was
collected immediately, it gives insight into the dielectric properties of oil solvent mixture before the transesterification reaction was started.

The second scenario involved mixing of oil with the solvent-catalyst mixture at room temperature, followed by heating in a controlled temperature water bath at different temperature with continuous stirring. Measurements were collected as the temperature reached each of the value prescribed above. This methodology provided the dielectric properties at different temperature for a sample undergoing transesterification. The two type of heating methods (while undergoing transesterification and prior to it) will help in understanding the microwave dielectric heating for the biodiesel precursor components and will be useful in designing and optimizing a microwave-based transesterification process.

The data, collected in triplicate, was imported into Microsoft Excel® 2007 (Microsoft Corp., Redmond, WA). Data for each sample was averaged across each replicate measurement and replicate sample, and standard deviations of each sample and standard error across all samples were calculated. The results were imported into Sigma Plot® 10 (Systat Software Inc., San Jose, CA) for plotting graphs.

2.3 Results and Discussions

2.3.1 Soybean Oil

• Dielectric Constant

The dielectric constant measured for soybean oil is essentially unchanged throughout the frequency range; however a very slight decrease is observed as the frequency increases (Figure 2.1). The dielectric constant values are relatively low (the highest being 3.2), the main reason being the non-polar nature of oil. For comparison, the dielectric constant for a polar solvent such as water is 80.10 (Deshpande et al., 2010). Similar results are found in literature where the
Dielectric properties of soybean oil were measured at varying frequency and temperatures. For example, the value at 915 MHz and 30°C of 2.91 obtained in this study compares well to the 2.64-3.00 range presented in literature (Elshami et al., 1992; Pace et al., 1968b; Sorichetti, 2011).

For a frequency range much lower than investigated here, (10⁻⁵ MHz to 1 MHz) the decrease in the dielectric constant values as the frequency increases can be substantial (Hu et al., 2008). As resistance from the viscosity of the medium impedes the process of reorientation, with the rise in frequency the alignment becomes even harder due to inertial effects, causing the decrease in dielectric constant (Pace et al., 1968b). Fatty acid composition of oil is another determining factor of ε’. Soybean oil belongs to the linoleic acid class of fatty acids. Dielectric constant for this class of fatty acid noted by Hu et al 2008., at low frequency (10⁻⁴ MHz to 0.5 MHz) was 3.104 – 3.127 and decreased as the frequency was increased to 1 MHz. Dielectric constant ε’ increases with the increase in degree of unsaturation as the electron rich double bond has a negative charge and oscillates with the changing electric field (Hu et al., 2008). However

Figure 2.1 Dielectric constant of soybean oil at 30°C and 75°C (For clarity of data, only the values obtained at lowest and highest temperature is shown in the graph. Other temperature values essentially overlapped.)

For a frequency range much lower than investigated here, (10⁻⁵ MHz to 1 MHz) the decrease in the dielectric constant values as the frequency increases can be substantial (Hu et al., 2008). As resistance from the viscosity of the medium impedes the process of reorientation, with the rise in frequency the alignment becomes even harder due to inertial effects, causing the decrease in dielectric constant (Pace et al., 1968b). Fatty acid composition of oil is another determining factor of ε’. Soybean oil belongs to the linoleic acid class of fatty acids. Dielectric constant for this class of fatty acid noted by Hu et al 2008., at low frequency (10⁻⁴ MHz to 0.5 MHz) was 3.104 – 3.127 and decreased as the frequency was increased to 1 MHz. Dielectric constant ε’ increases with the increase in degree of unsaturation as the electron rich double bond has a negative charge and oscillates with the changing electric field (Hu et al., 2008). However
as it can be observed in our study, the decrease with frequency is relatively small at the higher frequency investigated here (280 – 4500 MHz).

Dielectric constant of oils decreases with the increasing temperature (Elshami et al., 1992; Sorichetti, 2011). This observation was prominent in literature compared to our results (virtually constant with respect to temperature). A possible explanation is that literature data covered a frequency range at much lower frequencies (from $10^{-5}$MHz to $10^{3}$MHz) than those investigated here. As the temperature rises, density decreases; molecular motion increases as well as molecule-to-molecule interaction (Elshami et al., 1992; Pace et al., 1968b). These phenomena oppose the polarization process as associated with the orientation of molecules with respect to the changing applied electric field (Sorichetti, 2011), therefore reducing dielectric constant.

- **Dielectric Loss**

  Dielectric loss of oil for the overall frequency range and at all the temperatures was negligible (max. 0.366 at 468 MHz) at least when compared to polar solvent such as water (6.0 at 460 MHz). The results indicated a clear decrease with the increase in frequency and slight variations with respect to temperature (Figure 2.2). For a constant temperature, with the changing frequency, there is sharp decrease in dielectric loss; the high viscosity and inertial effects prevent the molecules (which are non-polar, non ionic and therefore weakly interacting with the field) from reorientation at such high frequency values. In literature, data for low frequency (10 MHz to 1000 MHz.) shows an increase in loss factor and loss tangent with increasing frequencies (Sorichetti, 2011)
Figure 2.2 Dielectric loss of Soybean oil at different temperatures and frequency

At a constant frequency, with the increase in temperature, the loss factor varied slightly. As the temperature was increased from 30°C to 45°C and further to 60°C the $\varepsilon''$ increased; however as the temperature was further increased to 75°C, the dielectric loss decreased. This particular behavior of dielectric loss with respect to temperature was observed by other researchers and it was reported in literature (Pace et al., 1968b). At lower temperatures (30°C in this case), the viscosity is high and so the relaxation time is long, resulting in increased values of dielectric loss.

2.3.2 Alcohol

- **Dielectric Constant**

  **Ethanol**: Ethanol is a polar solvent; it has a permanent dipole moment. The dielectric constant of polar solvents is frequency dependent (Pace et al., 1968a) and shows a distinct decrease as the frequency increases. The data shows a decrease in the dielectric constant with the increase in frequency. Similar results were found in the literature where the trend of dielectric constant is similar to the one indicated by our experiments (Pace et al., 1968a). The decrease in
dielectric constant with frequency is confirmed by Debye’s equation explaining the dependence of dielectric constant with increasing frequency (Equation 2.2).

In our case, we studied the changing temperature parameter. It is observed that the rate of decrease of dielectric constant is smaller at higher temperature (Figure 2.3(a)). This could be because at high temperatures the kinetic energy of molecules is high; hence the response to the changing electric field is faster and the viscosity is smaller (molecules are further apart), which enhances the realignment process, increasing the dipolar rotation of molecules and ultimately the dielectric constant of the material compared to lower temperature. As temperature increases, a shift in frequency at which dielectric constant starts dropping was observed. A peculiar characteristic of a polar molecule; as the temperature rises, dipolar rotation is more prominent causing a shift in the location of where dielectric constant decreases (Terigar et al., 2010a).

Similar trends were observed for methanol. The graph shows a decreasing trend for dielectric constant. However, methanol had higher dielectric constant values for a given frequency compared to that of ethanol, ranging between the highest values of 31.0 at a frequency of 512 MHz to almost half (18.0) for the highest frequency of 4500 MHz (Figure 2.3(a)). The difference between the highest and lowest value of dielectric constant (31 to 18) is again highest for the lowest temperature of 30°C. By comparison, at 60°C the decrease is from 28 to 23 for the same frequency range. The rate of decrease of dielectric constant with frequency was smaller for methanol compared to ethanol because, as the number of CH₂ groups in R-OH chain increases, the dielectric constant decreases. When a hydrogen atom bonds with an oxygen atom, the electron distribution in the newly formed molecule alters and induces a dipole moment that changes the polarization. But a combination of carbon and hydrogen in the hydrocarbon portion of a molecule is always non-polar. On the other hand, methanol is more polar because of the
shorter distance between the poles and its smaller molecular size, which allows it to rotate and realign faster (smaller molecules also have a higher dipole moment).

- **Dielectric Loss**

  Dielectric loss for both the alcohols was frequency and temperature dependent. Loss factor increased with increasing frequency until it reached a peak, and then a gradual decrease was observed. With the increasing temperature, the loss factor peak shifted towards the higher frequency value. For ethanol, the loss factor peak at 30°C is observed around 1000 MHz (Figure 2.3(b)), whereas for methanol at 30°C the peak falls between 3000 and 4000 MHz (Figure 2.3(c)). At the higher temperatures, the peak seems to fall outside the range measured in this study for methanol. This trend is consistent with the data reported in literature, in which the loss peak for methanol measured at 20°C is observed at 3000 MHz (Gabriel et al., 1998).

  The highest value of dielectric loss factor for both alcohols was observed at lowest operating temperature of 30°C. At lower frequencies (< 1000 MHz), dielectric loss values for methanol were lower than those of ethanol. As the frequency increased, the decreasing values for ethanol became smaller than those of methanol, which, for the most part, did not reach their peaks in the frequency range investigated here.

  Relaxation frequency is defined as the frequency at which the dielectric loss for a given substance is highest. In order to calculate a more precise value of the relaxation frequency, we plotted the first derivative of dielectric loss factor of alcohol with respect to the frequency \( (d\varepsilon''/df) \) (Figure 2.4 (a), (b)). At lower temperature (30°C) the relaxation frequency of ethanol is 1005.6 MHz and that for methanol is 3463 MHz. As the temperature increases, the relaxation frequency rapidly increases [Table 2.1]. Hence, at a lower working frequency (below 2000 MHz), the dielectric heating will be higher for ethanol at lower temperatures.
Figure 2.3 Dielectric properties of alcohol. a) Dielectric constant of methanol and ethanol b) Dielectric loss of ethanol c) Dielectric loss of methanol
At higher working frequency (above 2000 MHz), the thermal conversion of electromagnetic energy is predominant at higher temperatures. Also, at frequencies below 1500 MHz, the dielectric loss is higher for ethanol that for methanol. Thus, ethanol causes better heating at 915 MHz compared to methanol.

![Figure 2.4 First order derivative of dielectric loss with respect to frequency (a) Ethanol, (b) Methanol.](image)

Similar results have been reported in the literature confirming the dependence of loss factor on temperature (Liao et al., 2001) and on frequency (Pace et al., 1968a). As Federal Communications Commission (FCC) allows certain microwave frequencies of operation (915 MHz and 2450 MHz), it is impractical to build a system with variable frequency in order to match the temperature behavior of material undergoing processing. Therefore, in order to design a process, one needs to choose an optimum frequency of operation from among those permitted in regulations. The data collected during this study provides the exact behavior of alcohols at different temperatures in order to optimize the heating process and select the most suitable frequency at which high heating rates are maintained throughout the temperature range. For a practical purpose, this selection is between 915 MHz and 2450 MHz as equipment is usually built only for these frequencies.
Relaxation frequency depends on viscosity of the material. In order to confirm our results, we calculated the viscosity of ethanol and methanol [Eq. 2.8] based on the relaxation frequency that was obtained from the first order derivative of dielectric loss factor. Viscosities obtained at different temperatures are given in table 2.1. The results are in close agreement with the standard viscosity data for ethanol but varies for methanol (Lide, 2000).

Table 2.1 Relaxation time and viscosity of ethanol and methanol at different temperatures

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Ethanol (r= 4.8 \times 10^{-10} \text{m})</th>
<th>Methanol (r=2.65 \times 10^{-10} \text{m})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Relaxation Frequency (MHz)</td>
<td>Relaxation time (s)</td>
</tr>
<tr>
<td>303.15</td>
<td>1005.6</td>
<td>1.58x10^{-10}</td>
</tr>
<tr>
<td>318.15</td>
<td>1540</td>
<td>1.03x10^{-10}</td>
</tr>
<tr>
<td>333.15</td>
<td>2378</td>
<td>6.69x10^{-11}</td>
</tr>
<tr>
<td>348.15</td>
<td>3749</td>
<td>4.24x10^{-11}</td>
</tr>
</tbody>
</table>

2.3.3 Alcohol-Catalyst

The dielectric behavior of any electrolytic solution (such as alcohol and basic catalyst) is complicated. Ions have a strong electric field; hence ions affect the molecular interaction of solvents. Although the amount of NaOH added was very low (0.18% by the weight of oil for transesterification, corresponding to 0.066gm catalyst in 19.3ml ethanol and 0.091gm catalyst in 10.235 ml methanol), its effect on the dielectric properties was quite spectacular.

- **Dielectric Constant**

The dielectric constant for alcohol-catalyst mixture decreased with increasing frequency, following a similar trend with what is observed for pure alcohols (Figure 2.5(a)). For a fixed
frequency, the dielectric constant increased with a rise in temperature. Overall dielectric constant is smaller for the alcohol-catalyst mixture than for pure alcohol by approximately 20%.

Depending on factors such as ion concentration, solvent properties and the association and dissociation of ions, dielectric constant may stay constant or decrease. In this case the decrease in dielectric constant compared to pure alcohol is primarily due to ion solvation (Hasted and Roderick, 1958). Solvation of ions takes place when the polar solvent molecules orient towards the ion as a response to the electrostatic attraction. This association with ions causes the system to stabilize by forming a molecular solvation shell around each ion. The solvent molecules that are bound in this shell cannot orient as easily by the applied electric field; therefore they do not generate effective dipole moment, decreasing polarization and hence reducing the dielectric constant. Interactions between ions and solvent dipoles lead to dielectric saturation of solvent molecules in the ion’s electric field by inhibiting the free rotation of the solvent molecules (Hasted and Roderick, 1958).

• Dielectric Loss

The influence of added ions was even more pronounced on the dielectric loss factor, which not only increased significantly, but also changed the frequency dependence (Figure 2.5(b), 2.5(c)). There was an asymptotic decrease in the dielectric loss as frequency increased. Significant difference was observed with the changing temperature for ethanol+ NaOH and methanol+ NaOH. Unlike pure alcohol (for which a peak was observed), the dielectric loss for alcohol-catalyst mixture decreased monotonously with frequency. For a particular frequency, the individual dielectric loss value was much higher for the mixture when compared with pure alcohols. Addition of small amount of electrolyte increases the conductivity (especially at lower frequencies) and ultimately increases the dielectric heating. Generally, solutions with higher
Figure 2.5 Dielectric properties of alcohol-catalyst mixture. a) Dielectric constant of alcohol + NaOH b) Dielectric loss of ethanol + NaOH c) Dielectric loss of methanol + NaOH
alkali concentration are more effective in absorbing microwave energy and converting the stored energy into heat. Since the conduction of ions is a major factor for thermal effects in microwave processes, a system with a higher concentration of NaOH should exhibit more ionic conduction in response to microwave energy. In our study, in spite of the very low NaOH concentration (0.066gm catalyst in 19.3ml ethanol and 0.091gm catalyst in 10.235 ml methanol), there was a significant increase in loss factor with its addition. While some studies have been performed on dielectric properties of alcoholic electrolytic solution, we did not find any literature data describing the dielectric properties of alcohol- NaOH solution (Hasted and Roderick, 1958). When compared to literature data on NaOH dielectrics in different solvents (generally water), the trends for dielectric constant were similar to those presented here. But for dielectric loss, literature data reported a rise in values with increase in frequency and increased concentration of NaOH (Kelly and Salomon, 1969; Kessler and Mariani, 1967).

Determining the temperature dependence behavior of an electrolyte solution is a very complicated process. For ethanol-catalyst mixture, a decrease in dielectric loss with temperature was observed at lower frequencies (up to 2450 MHz). As the frequency increased above 2450 MHz, the dielectric loss increased with temperature. The dielectric constant and loss values at 915 MHz and 2450 MHz, which are the frequencies allocated by the FCC for industrial, scientific and medical application are tabulated (Table 2.2). At 915MHz, the loss tangent for methanol-catalyst mixture is higher than that for ethanol-catalyst mixture. Higher loss tangent values ensure higher heating rates as higher conversion of microwave energy to thermal energy is obtained (Pace et al., 1968a).
Table 2.2 Values for dielectric constant and dielectric loss of pure components and alcohol-catalyst mixture at 915 MHz and 2450 MHz.

<table>
<thead>
<tr>
<th>Component</th>
<th>Temperature</th>
<th>915 MHz</th>
<th></th>
<th>2450 MHz</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ε′</td>
<td>εʺ</td>
<td>Tan δ</td>
<td>ε′</td>
</tr>
<tr>
<td>Soybean oil</td>
<td>30°C</td>
<td>2.90</td>
<td>0.23</td>
<td>0.079</td>
<td>2.86</td>
</tr>
<tr>
<td></td>
<td>45°C</td>
<td>2.97</td>
<td>0.28</td>
<td>0.096</td>
<td>2.85</td>
</tr>
<tr>
<td></td>
<td>60°C</td>
<td>2.99</td>
<td>0.28</td>
<td>0.094</td>
<td>2.95</td>
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<tr>
<td></td>
<td>75°C</td>
<td>2.85</td>
<td>0.21</td>
<td>0.075</td>
<td>2.81</td>
</tr>
<tr>
<td>Ethanol</td>
<td>30°C</td>
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<td>9.54</td>
<td>0.602</td>
<td>8.21</td>
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<tr>
<td></td>
<td>45°C</td>
<td>17.68</td>
<td>7.57</td>
<td>0.428</td>
<td>10.02</td>
</tr>
<tr>
<td></td>
<td>60°C</td>
<td>18.22</td>
<td>5.06</td>
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<tr>
<td></td>
<td>75°C</td>
<td>18.35</td>
<td>3.63</td>
<td>0.198</td>
<td>14.98</td>
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<tr>
<td>Methanol</td>
<td>30°C</td>
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<td>6.55</td>
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<td>28.34</td>
<td>4.63</td>
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<td></td>
<td>60°C</td>
<td>26.84</td>
<td>3.30</td>
<td>0.123</td>
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<tr>
<td></td>
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<td>-NA-</td>
<td>-NA-</td>
<td>14.98</td>
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<tr>
<td>Ethanol+ NaOH</td>
<td>30°C</td>
<td>13.57</td>
<td>11.04</td>
<td>0.814</td>
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<tr>
<td></td>
<td>45°C</td>
<td>15.76</td>
<td>10.25</td>
<td>0.650</td>
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<td></td>
<td>60°C</td>
<td>16.50</td>
<td>8.41</td>
<td>0.509</td>
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<tr>
<td></td>
<td>75°C</td>
<td>16.32</td>
<td>6.92</td>
<td>0.424</td>
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<td>Methanol+ NaOH</td>
<td>30°C</td>
<td>23.34</td>
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<td>30.42</td>
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<td>34.18</td>
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<tr>
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<td>75°C</td>
<td>-NA-</td>
<td>-NA-</td>
<td>-NA-</td>
<td>13.04</td>
</tr>
</tbody>
</table>

2.3.4 Oil, Alcohol and Catalyst Mixture

- **Oil Ethanol Catalyst (Scenario One)**

  - **Dielectric Constant**

    The dielectric constant was observed to decrease with increasing frequency and temperature for both scenarios. However, the value of dielectric constant at an individual frequency for scenario one was higher compared to scenario two for all temperatures (Figure 2.6(a), 2.6(b)). These higher values were due to mixing the components already at the ascribed temperatures. As such, there was little time for the transesterification reaction to undergo completion and a higher amount of ethanol was available, which increased the polarity of the
solution. At the lowest temperature of 30°C, the chances of reaction were extremely small, thus higher dielectric constant values are observed compared to other temperatures (Table 2.2).

- **Dielectric Loss**

  Decrease in dielectric loss was observed with the rise in temperature at lower frequencies (Figure 2.6(c)). As explained earlier, with the increase in frequency, the polar molecules lag behind in response to the applied electric field. Temperature dependence was not as strong as frequency increased; mainly due to reduction in mobility of molecules. As the reaction proceeds, polar components (in this study alcohol) are utilized and form intermediate (mono and diglycerides) and final products. Some of the intermediate products formed during transesterification reaction are non polar compounds. These can be termed as inactive components for microwave heating, with unreacted ethanol acting as an active component. Thus dielectric loss value at individual frequencies was higher for scenario one than scenario two because of the presence of active polar molecules which were the result of incomplete reaction.

- **Oil, Ethanol and Catalyst (Scenario Two)**

- **Dielectric Constant**

  As mentioned earlier, ethanol-catalyst solution was well mixed with oil in the ratio of 1:9. The dielectric constant was observed to decrease with the increasing frequency and temperature especially at 30°C. At other temperatures, the decrease in dielectric constant $\varepsilon'$ was less pronounced compared to 30°C (Figure 2.6(b)).

  As a function of temperature, this is in contrast with the results obtained for pure solvents and the ethanol-catalyst solution. For the pure solvents the dielectric constant increased with the increase in temperature (Table 2.1 and 2.2). The decrease in dielectric constant with temperature for this mixture was mainly due to low values of $\varepsilon'$ for oil and, secondary to the fact that as the
Figure 2.6 Dielectric properties of oil, ethanol and catalyst mixture a) Dielectric constant $\varepsilon'$ for scenario one; b) Dielectric constant $\varepsilon'$ for scenario two; c) Dielectric losses $\varepsilon''$ for scenario one; d) Dielectric loss $\varepsilon''$ for scenario two.
temperature increases, oil is converted into biodiesel. At lower temperature the transesterification reaction is not started, thus polarity of ethanol remains dominant. As the temperature is increased, the reaction proceeds and the concentration of polar components are significantly reduced. The product formed, which is essentially either biodiesel (esters of free fatty acids) or the reaction intermediates (monoglycerides and diglycerides) are less polar in nature. As the polarity of the solution is decreased, the dielectric constant decreases.

- **Dielectric Loss**

  At the lower temperatures of 30°C and 45°C, a peak of the dielectric loss was observed at lower frequencies; a peak was not observed as the temperature was further increased (Figure 2.6(d)). As the frequency increased, dielectric loss decreased. At lower temperatures the solution is still polar and the ions are free to move about in the solution, hence the higher dielectric loss. Once the reaction proceeds, Na\(^{++}\) ions participate in the reaction and thus are not as free to move about. The peak at 30°C is similar to the peak of ethanol at 30°C observed at a lower frequency of 1000 MHz but with a lower value of 5.0 compared to 9.5 for pure ethanol. The value of dielectric loss at that particular frequency is lower for this mixture compared to pure ethanol; this is because of the presence of non-polar components (oil) in the mixture. The stoichiometric ratio for the reaction is 1:3 oil to alcohol, however as the reaction is reversible, excess alcohol is added to ensure the completion of reaction. The molar ratio we used for oil to ethanol was 1:9. Stoichiometrically, 6.0 moles of ethanol remain unreacted. This excess ethanol gives the solution a polar nature and hence the loss is increased with the increase in temperature. For the higher temperatures of 60°C and 75°C, conductivity (which is another representation of dielectric loss factor, see eq. 1.9) remained constant throughout the frequency range as the reaction was close to completion. The decrease in dielectric loss could be because of the less effective dipole moment
of the polar molecules (alcohol) due to their association with the non-polar molecules (oil, reaction intermediates) (Kappe, 2008).

- **Oil Methanol Catalyst (Scenario One)**

  - **Dielectric Constant**

    Dielectric constant for oil and methanol + catalyst mixture was relatively constant at lower frequency but decreased gradually as the frequency was increased (Figure 2.7(a)). Dielectric constant also changed with temperature as for ethanol-oil mixture. This difference was apparent at 60°C as with the increasing temperature, the reaction proceeded towards completion.

  - **Dielectric Loss**

    For oil-methanol mixture in scenario 1, a spectacular decrease in the dielectric loss factor values from a very large value was observed at lower frequencies (until the frequency reached 1500 MHz – 1600 MHz) after which the decrease is much less pronounced (Figure 2.7(b)). This behavior is observed for any given temperature. Similar trends were observed for methanol-catalyst solution but the overall values were lower with the addition of oil. Separate heating of oil and methanol-catalyst solution reduces the probability of the mixtures undergoing transesterification reaction. Nevertheless, at high temperature there could be a possibility of reaction taking place hence, a decrease in dielectric loss was noticed as the temperature was increased.

- **Oil, Methanol Catalyst (Scenario Two)**

  - **Dielectric Constant**

    The dielectric constant changed with temperature for oil-alcohol+ catalyst mixture (Figure 2.7 (c)). This was true for ethanol-oil at all the temperatures and also for methanol- oil mixture except at 30°C. This exception could be because at 30°C, ion solvation stakes place,
reducing the dielectric constant of the mixture. As the temperature rises to 45°C, the catalyst ions participate in the reaction reducing the effect of ion solvation; hence the rise in dielectric constant is observed. These results can be compared with the results obtained by (Sorichetti, 2011) et al., for FAME (Fatty acid methyl esters) before and after washing. They noted that as the temperature increases, more and more methanol reacts with the oil molecules; the new product obtained is a non polar product with lower dielectric constant. Thus, the concentration polar impurity in the form of methanol reduces with temperature and the dielectric value decreases. It should be noted that the frequency range (400 Hz to 10,000 Hz) at which the dielectric constant values were measured were much lower for Sorechetti et al., than in present study.

- **Dielectric Loss**

For the oil-methanol-catalyst mixture, the values for dielectric loss decreased asymptotically with increasing frequency at all the temperatures (Figure 2.7(d)). The dielectric loss is lower at 30ºC compared to 45ºC and 60ºC (which were very close to each other). These results can be compared to the FAME results by (Sorichetti, 2011). For an unwashed FAME product, the dielectric loss decreased with an increase in temperature. Unwashed FAME product contained unreacted methanol which increases the polarity and ultimately the dielectric loss. However, with an increase in temperature, more and more methanol undergoes reaction and the amount of unreacted methanol decreases, decreasing the dielectric loss. When the product was washed and was free of any polar impurities, the dielectric loss increased with temperature as expected.
Scenario 1

Scenario 2

(a) Frequency (Hz)

(b) Frequency (Hz)

(c) Relative Dielectric Constant

(d) Relative Dielectric Constant

Figure 2.7 Dielectric properties of oil methanol- catalyst mixture a) Dielectric constant for scenario one, b) Dielectric constant for scenario two, c) Dielectric losses for scenario one, d) Dielectric loss for scenario two
Table 2.3 Values of dielectric constant and dielectric loss at 915 MHz and 2450 MHz for oil alcohol catalyst mixture (Scenario 1 & 2)

<table>
<thead>
<tr>
<th>Component</th>
<th>Temperature</th>
<th>915 MHz</th>
<th>2450 MHz</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>ε’</td>
<td>ε''</td>
</tr>
<tr>
<td>Oil+ EtOH-NaOH</td>
<td>30°C</td>
<td>15.78</td>
<td>11.55</td>
</tr>
<tr>
<td>Scenario 1</td>
<td>45°C</td>
<td>12.23</td>
<td>6.90</td>
</tr>
<tr>
<td></td>
<td>60°C</td>
<td>11.19</td>
<td>3.38</td>
</tr>
<tr>
<td></td>
<td>75°C</td>
<td>8.13</td>
<td>1.58</td>
</tr>
<tr>
<td>Oil+ EtOH-NaOH</td>
<td>30°C</td>
<td>9.13</td>
<td>5.00</td>
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<tr>
<td>Scenario 2</td>
<td>45°C</td>
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</tr>
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<td></td>
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<td>5.88</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>75°C</td>
<td>6.20</td>
<td>0.72</td>
</tr>
<tr>
<td>Oil+ MeOH+NaOH</td>
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<td>21.03</td>
</tr>
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<td>Scenario 1</td>
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</tr>
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<td></td>
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<td></td>
<td>60°C</td>
<td>14.38</td>
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</table>

2.4 Conclusions

The dielectric properties of the constituents used in the production of biodiesel were studied. The measurements were carried out for pure components (vegetable oil, ethyl alcohol and methyl alcohol) and for the mixtures. The dielectric constant and the dielectric loss were both temperature and frequency dependent. The dielectric constant as well as the dielectric loss for oil was unaffected by the variations in frequency and temperature because oil is a non polar component. The dielectric constant was higher for methanol than that for ethanol throughout the frequency range. The dielectric loss values for ethanol at higher frequencies (above 1000MHz) were higher than ethanol at lower frequencies (below 1000MHz). Ion solvation effect was observed for the alcohol-catalyst mixture. The dielectric constant and loss values were higher for methanol-catalyst mixture than that for ethanol-catalyst mixture throughout the frequency range. Two methods of heating oil and alcohol-catalyst mixture were proposed. Scenario one required that the oil be heated separately and added to the alcohol-catalyst mixture and other
required that the components be heated together. The dielectric loss was much higher for the first scenario compared to the second scenario.

2.5 References


Stuerga D. (2008) Microwave-material interactions and dielectric properties, key ingredients for mastery of chemical microwave processes Wiley-VCH Verlag GmbH.


CHAPTER 3

SCALE UP OF A CONTINUOUS MICROWAVE ASSISTED TRANSESTERIFICATION PROCESS OF SOYBEAN OIL FOR PRODUCTION OF BIODIESEL

3.1 Introduction

Diminution of petroleum reserves worldwide, unstable crude oil prices, impact on environment due to combustion of fossil fuels, and large scale dependency on foreign resources have encouraged the search for alternative fuel sources (Clark et al., 1984; Meher et al., 2006; Srivastava and Prasad, 2000). While there are numerous sources of renewable energy (wind, solar, hydro-power, biological), the only suitable source for transportation fuels are liquid fuels derived from biomass. Major challenge lies in production of an alternative fuel which is economically feasible, environmentally friendly, meets the required ASTM standards, and is readily available (Meher et al., 2006).

Use of vegetable oil as direct fuel seems the most obvious option as vegetable oil has high heat content, is readily available, and is a renewable source of energy. In 1900, Rudolf Diesel demonstrated the use of vegetable oil as fuel for engines (Shay, 1993). However there are several technical disadvantages of direct use of straight vegetable oil (SVO). High viscosity, gum formation, high acid content, oxidation and polymerization during storage and combustion are among the major problems associated with it (Ma and Hanna, 1999; Srivastava and Prasad, 2000). In order to overcome these problems, techniques such as pyrolysis, micro-emulsions, transesterification, etc. have been proposed and tested. Pyrolysis produced an acceptable product in terms of viscosity, sulphur content, cetane number, and copper corrosion value; however the ash content, carbon residue and pour point were beyond the tolerable value (Ma and Hanna, 1999). Product obtained from micro-emulsion showed incomplete combustion, carbon deposits,
and increased viscosity (Ma and Hanna, 1999). Among the non-technical disadvantages, the most glaring one is the fact that currently vegetable oils are derived either from food feedstock or from non-food feedstock grown on prime agricultural land. As such, these feedstock compete with the food market and have a good potential to drive up the cost of food. Alternative oil feedstock that grows on non-agricultural land needs to be identified and developed. Some of the non-edible feedstock that has been investigated for biodiesel production are Jatropha (Lu et al., 2009), algae (Behzadi and Farid, 2007), and Chinese tallow tree seeds (Boldor et al., 2010; Gao et al., 2009). Regardless of their source, all vegetable oils are generally suitable for conversion into biodiesel; challenges still remain in improving the efficiency of the production process.

Biodiesel is a long chain fatty acid alkyl esters derived by transesterification of triglycerides with short chain alcohols (usually methanol and ethanol, but also propanol and butanol) in the presence of a catalyst (homogenous or heterogeneous). Vegetable oil and animal fat is a source of these triglycerides. Vegetable oil is preferred over animal fat as the presence of short chain saturated fatty acids in animal fat leads to problems such as carbon deposit and lubricating oil contamination (Ma and Hanna, 1999). Additionally, short chain fatty acids have higher melting point and easily form the quasi-crystalline structure leading to poor cold weather performance.

3.1.1 Transesterification Reaction Mechanism

Transesterification is a general term that describes an organic reaction where an alcohol from an ester is displaced by another alcohol (Equation 1) (Schuchardt et al., 1998). This displacement reaction is similar to hydrolysis reaction except alcohol is employed instead of water (Fukuda et al., 2001). The reaction is reversible and hence excess alcohol is used to ensure the equilibrium shift on right hand side (product side of the reaction) (Kanitkar et al., 2011).
Most commonly employed alcohols are methanol and ethanol. Methanol is readily available, and, because of its low cost and more favorable economics, it is widely used. Ethanol is sometimes preferred over methanol because it offers better solubility for oil, can be obtained from renewable agricultural resources and the ethyl esters formed have higher heat content and cetane number. A disadvantage is the hydrophilic nature of ethanol, which requires proper storage (Demirbas, 2008; Terigar et al., 2010b). Though methanol can also be obtained from renewable sources, a major problem associated with it is its safety as methanol is highly toxic.

\[
\begin{align*}
\text{Vegetable oil} & \quad \text{Alcohol} & \quad \text{Esters} & \quad \text{Glycerol} \\
\text{(Lipids)} & & & \text{(Biodiesel)}
\end{align*}
\]

The forward reaction becomes a pseudo first order reaction because of the excess alcohol (Zhou et al., 2006). Otherwise, transesterification is a three step reaction where a triglyceride is converted to diglyceride and ultimately to monoglyceride followed by the formation of 1mole of ester in each step and glycerol formation as a by-product.

\[
\begin{align*}
\text{Triglyceride (TG)} + R'OH & \quad \xrightleftharpoons[K]{\text{Catalyst}} \quad \text{Diglyceride (DG)} + R'\text{COOR}_1 \\
\text{Diglyceride (DG)} + R'OH & \quad \xrightleftharpoons[K]{\text{Catalyst}} \quad \text{Monoglyceride (MG)} + R'\text{COOR}_2 \\
\text{Monoglyceride (MG)} + R'OH & \quad \xrightleftharpoons[K]{\text{Catalyst}} \quad \text{Glycerol (GL)} + R'\text{COOR}_3
\end{align*}
\]
Where, $K$ is the reaction rate constant. The rate of reaction is enhanced by the catalyst (acid, base or enzymatic). Acid catalysts used for the transesterification include sulphuric, hydrochloric, phosphoric, and sulphonic acids (Canakci and Van Gerpen, 1999). Acid catalysts are slower than the base catalysts; however, they are suitable when the oil is a low grade material with a large content of free fatty acids and water (Freedman et al., 1984).

Alkali catalysts used for transesterification are sodium hydroxide (NaOH), potassium hydroxide (KOH), carbonates, and other alkoxides. The rate of reaction with base catalyst is almost 4000 times faster than that with acid catalyst (Fukuda et al., 2001) and the catalysts are less corrosive, reducing capital investments (Pinto et al., 2005). Oils and fats being generally immiscible in NaOH-alcohol solution, proper mixing is required. Oil is generally preheated to 45-50°C for better mixing. The temperature of generally 60°C and a reaction time up to one hour can be required for the reaction to complete if methanol is used (Ma and Hanna, 1999).

### 3.1.2 Factors Affecting the Base Catalyzed Transesterification Reaction

- **Moisture Content**
  
  The reaction should be carried out in completely anhydrous conditions. Presence of water causes saponification reaction (Wright et al., 1944). The soap formed consumes the catalyst, thus reducing its efficiency. It causes an increase in viscosity, forms gel and makes it difficult to separate out the glycerol.

- **Free Fatty Acid Content**
  
  Free fatty acids reduce the ester yield and trigger the soap formation. Free fatty acid content of less than 3% should be used for alkali-catalyzed reaction (Ma and Hanna, 1999). If the feedstock contains large amount of free fatty acids, a two step conversion process is employed. In the first step, the free fatty acid is reduced to fatty acid methyl esters by an acid catalyzed
reaction and the rest of the reaction proceeds in presence of alkali catalyst leading to complete biodiesel formation (Canakci and Van Gerpen, 1999).

- **Effect of Temperature**

  Temperature has a significant effect on the rate of reaction and the quality of product. Transesterification reaction can be carried out at room temperature; however the process is time consuming. Due to slow reaction rate, the amount of by-products formed is higher and, as the reaction may not undergo completion, the yield of product can be low. Low reaction rate also leads to poor product quality (K. Kapilakarn, 2007). Thus, transesterification reaction is carried out at higher temperatures (usually below alcohol boiling point). The conversion to biodiesel is higher and the product obtained is of superior quality. Many conventional ways of heating are implemented to perform the reaction. Some of the commonly used heat sources are heat exchangers, electric heaters, heat through pyrolysis, gasification etc. New techniques such as microwave heating, ultrasound etc. have been developed to increase the energy efficiency and reduce the reaction time.

- **Effect of Type of Alcohol**

  Methanol is the commonly employed alcohol due to its low price, availability, and physical and chemical advantages such as polarity and being the shortest chain alcohol (Sanli and Canakci, 2008). Methanol readily dissolves the catalyst and easily reacts with the triglycerides. The activity of long chain alcohols such as ethanol is lower compared to methanol. These long chain alcohols form a more stable emulsion as the triglyceride-alcohol mixture is immiscible, thus interfering with the separation and purification of esters. In case of methyl esters these emulsions break easily and separate into two layers, an upper methyl ester and a lower glycerol layer.
Ethanol advantages over methanol include better solubility with the oil, its renewable and agricultural origin, and higher heat content and cetane number of the ethyl esters formed (Demirbas, 2008; Terigar et al., 2010b). There are fewer safety issues related with ethanol than with the methanol as the latter is extremely toxic to human and animals.

- **Effect of Molar Ratio of Alcohol: Oil**

  Stoichiometrically, three moles of alcohol are needed for one mole of triglyceride to yield three moles of ester and one mole of glycerol. However, in practice, higher molar ratio is needed for maximum conversion and reaction stability. The molar ratio depends on the feedstock quality, temperature of reaction, and the type of catalyst used. For acid catalysts, ratios of as high as 30:1 had been used while in case of base catalysts ratios as low as 6:1 are noted to achieve good conversion rate (Freedman et al., 1986). On the other hand, if too high alcohol to oil ratio is used, it may lead to an increase in glycerol solubility in the alcohol and thus the reaction equilibrium can shift to left, reducing the yield of esters (Meher et al., 2006). In the prior work performed at Louisiana State University, the ethanol to oil ratio used was 9:1 in a batch microwave system and 5:1 in a continuous scale microwave assisted transesterification reaction (Kanitkar et al., 2011; Terigar et al., 2010b).

- **Effect of Microwave Irradiation**

  Microwave irradiation offers short reaction times and an expanded range of reaction (Anan and Danisman, 2007; Azcan and Danisman, 2008; Barnard et al., 2007). The reaction time is low (< 1min), in contrast with the conventional heating techniques such as water/oil baths and heating jackets. The latter methods are slow and a temperature gradient may develop within the sample, causing local overheating near the heat source. In case of organic and medicinal chemistry, local overheating could lead to damage of the product (Lidstrom et al., 2001). For a
sample to heat upon microwave exposure, it should be either ionic or polar, that is, it should possess a dipole moment. A dipole tries to align itself in the direction of the applied electric field, as the field polarity changes rapidly in microwave, dipolar molecules rotate. The neighboring molecules, that also rotate, hinder the instantaneous rotation generating a phase difference between orientation of field and the dipole. As a result, the energy provided by the applied field is lost to molecular friction and collisions and converted into heat (Kappe, 2008). Presence of ions also gives rise to dielectric heating. Ions tend to move under the influence of an electric field and collide with other molecules, converting kinetic energy acquired from the applied field into heat energy. These phenomena causes efficient molecular mixing, the probability of an alcohol molecule to collide with a molecule of oil increases, ultimately increasing the rate of reaction and yield of biodiesel. The unique combination of presence of both polar and ionic components in the mixture of oil, alcohol, and sodium hydroxide speeds up the heating process. This heat generation can be transitory, but higher than the temperature of bulk reaction mixture causing local superheating.

In relevance with the chemical reactions, another important aspect of microwave dielectric heating is the increased rate of reaction. Rudimentary explanation of the observed increase in rate of reaction is due to local superheating and increased molecular movement and subsequent molecular level interaction (Terigar et al., 2010b). A number of studies have been conducted to understand the mechanism behind these rapid reaction rates; however the lack of reliability in measuring reaction temperature has hindered the development of this research area (Inoue et al., 2002). Most of the researchers note an increase in the rate of reaction while a few claim that the rate of reaction proceeds similar to that in conventional heating. One of the theories explaining the reason for this increase is related to Arrhenius equation.

46
Where, $K$ – Rate constant, $E_a$ – Activation energy, $R$ – Gas constant, $T$ – Temperature, $A$ – Pre exponential factor

The frequency factor $A$ represents molecular mobility and depends on the frequency of vibration of reacting molecules at the reaction interface. As mentioned above, microwave radiation increases the frequency and rate of collision, affecting the frequency factor $A$. Increase in frequency factor indicates increased rate of collision, thus, increases the rate of reaction (Lidstrom et al., 2001). Another theory put forth is that the microwave energy affects the activation energy thus affecting the exponential factor increasing the rate of reaction (Lidstrom et al., 2001).

One of the major problems with base catalyzed formation of ethyl esters is the formation of stable emulsions (Meher et al., 2006). In case of methyl esters with higher polarity groups, the emulsions are unstable and easily break down into glycerol and esters. However, ethanolysis gives rise to more stable emulsions that are mainly intermediates mono and diglycerides having more non-polar hydrocarbon chain and hydroxyl group with lower polarity. Therefore, in order to avoid emulsions, the reaction should be as complete as possible. With conventional heating, completion of reaction means longer reaction times and high temperatures to break emulsions. Microwave radiation assists in addressing this problem. High heating rates, and subsequently completion of reaction can be obtained with small quantity of polar solvents having high loss tangent. The energy transfer is rapid between polar molecule that combine with the microwave radiation and the non-polar molecules. Ethanol has a higher loss tangent of 0.941 compared to methanol 0.659 at 915 MHz frequency (Kappe, 2005). Higher loss tangent compensates for the higher non-polar group responsible for emulsion formation, drawing the reaction to completion.
Microwave applicators play an important role in the heating process. Commonly used applicators are single-mode and multimode applicators. Multimode cavity applicators support large number of resonant modes for a given frequency. It is widely used in domestic microwave ovens because of their low cost and simple construction. These designs can process a wide range of samples of different dielectric properties. However, there are certain drawbacks of multimode cavity applicators. Lack of uniformity in temperature distribution and difficulty in analysis of electric field distribution for materials of different sizes, shapes and composition are some of the major disadvantages (Sun et al., 2005). Single mode applicators, on the other hand, support only one resonant mode hence results in high localized heating. As single-frequency systems can be tuned for maximum throughput, it can efficiently provide high electric field strength. Thus, single mode cavities are more focused, and highly efficient compared to multimode cavities. The heating profile can be more uniform and reliable (Asmussen et al., 1987). Thus, for most of the industrial heating processes where uniform heating is desired, single-mode applicator is used. In this study, a single mode focusing cavity applicator was used for the pilot scale production of ethyl ester biodiesel.

Figure 3.1 Microwave system (915 MHz, 5 kW) used for the pilot scale production of biodiesel

So far, use of microwaves for heating was demonstrated to increase the efficiency of reaction, to reduce the reaction and separation times, and to reduce the energy consumption; it
also enhances the product recovery by making the separation of biodiesel from alcohol and glycerin easier in the post reaction mixture (Refaat et al., 2008). Refaat et al., showed that the time of separation was reduced from 480 min to 30 min when microwave heating was used compared to conventional heating. Thus, microwave heating is more efficient than conventional heating options, offering energy efficiency, high reaction rates, and easy separation and purification of the product (Azcan and Danisman, 2008; Leadbeater and Stencel, 2006).

- **Objective**

The objective of this study was to scale up the microwave assisted biodiesel production to a pilot scale and to compare the results to those previously obtained at laboratory scale in both batch (Kanitkar et al., 2011) and continuous (Terigar et al., 2011) modes. Different parameters such as type of alcohol, alcohol to oil ratio, catalyst percent and temperature were previously studied and the optimum parameters were chosen for the current scale up system.

### 3.2 Materials and Procedure

- **Materials**

Vegetable oil used for this process was commercial grade soybean (SB) oil purchased from a local grocery store (Wal-Mart Stores, Inc. Bentonville, AR). The solvent, 200 proof, ACS/US Grade ethanol was purchased from Pharmco-AAPER (Brookfield, CT). The testing standards of fatty acid ethyl esters (FAEE) were purchased from Sigma Aldrich (St. Louis, USA). Other chemicals, sodium hydroxide flakes and hydrochloric acid were obtained from Fisher scientific (Pittsburgh, PA, USA).

- **Procedure**

Prior to reaction, an alcohol catalyst mixture was prepared by thoroughly mixing anhydrous NaOH (0.18% by the weight of oil) and ethanol in a feed tank equipped with an
industrial stirrer. Immediately prior to reaction, oil was added to the ethanol-catalyst mixture and continuously stirred. Though methanol was cheaper and gave better results as compared to ethanol, we chose ethanol because it can be fermented from the renewable agriculture resources (Silva et al., 2007). Ethanol had higher loss tangent too (refer chapter 2), an important factor for microwave assisted transesterification process, which makes ethanol a suitable choice compared to other organic solvents. Based on prior lab scale studies, the oil to ethanol molar ratio was maintained 1:9. For a continuous laboratory scale process, oil to alcohol molar ratio was maintained at 1:5 (Terigar et al., 2010b). However, in that case, the catalyst amount used was 0.6% by the weight of oil. For a pilot scale we chose a lower catalyst amount (0.18% by the weight of oil), hence the oil to ethanol ratio was increased to 1:9 to ensure the completion of reaction (Kanitkar et al., 2011). A Seepex® progressive cavity pump (BCSB 05-12, Seepex GmbH, Bottrop, Germany) coupled with a NEMA 1 HP motor (Baldor Electric Company, Fort Smith, AR) and controlled by a AC Tech MC Series controller was used to pump the process mixture at a flow rate of 0.840 L/min through a 5 kW, 915 MHz continuous microwave system (Industrial Microwave Systems, Morrisville, NC). This flow rate was selected to obtain the desired residence time when combined with the length of the holding tubes (diameter 1.5 in, total length 295 in). Preliminary trials established that in order to achieve the target temperature of 60°C and 75°C microwave power levels of 4000 W and 4700 W, respectively were needed and further used throughout this study (Figure 3.2, 3.3). The experiments were first performed for 75°C. With the maximum pump capacity, the microwave power supply required to achieve a temperature of 75°C was 4700W.
Since oil and ethanol are essentially immiscible, oil was pre heated to ensure proper mixing. The inlet temperature of the oil ethanol catalyst mixture entering the microwave was 45°C. The second set of reaction was carried out at 60°C. This experiment could be performed in two different ways; 1) by increasing the flow rate of the fluid mixture so as to allow lower residence time in the tube, decreasing the temperature or 2) reducing the power level while
maintaining the same flow rate. We opted for the second method as it was more energy efficient and the amount of material required for testing would be less. Without pre heating the oil, the inlet temperature was 30°C. With the flow rate of 840ml/min, which is obtained with maximum pump capacity, the power input required to obtain the temperature of 60°C was 4000W.

The pipes between the feed tanks and the pump were equipped with an inline pipe mixer so as to avoid separation of oil and alcohol- catalyst mixture. Another inline pipe mixer was used between the pump and the microwave-heating unit. The samples of treated mixtures were obtained at various holding times (0, 5, 10, 15 minutes) through the panel of pipes arranged accordingly (Figure 3.4). The pipes were insulated so as to minimize heat losses.

For the scale up process, the total amount of solution required was between 60 and 80 liters per run. The total amount of time to perform one experimental run was approximately 6-7 hours including dissolving catalyst in alcohol, set up and reaction time, and clean up. Due to these practical limitations, in this study we investigated only one molar ratio for oil to alcohol (1:9) and one catalyst type and concentration (0.18% by the weight of oil) which were established in previous studies in our group for a laboratory scale process. All experiments were performed in triplicates.

Figure 3.4 Flow chart of pilot scale microwave assisted transesterification process
• **Separation, Washing and Quality Analysis on Biodiesel Samples**

A flow rate of 840 ml/min was maintained to assure the microwave exposure time of 1 min. The reaction was then maintained at that temperature for different holding times before stopping the reaction by quenching with water (5% of the total sample) and the sample was allowed to settle overnight. The lighter biodiesel phase and the denser glycerol phase were separated. Biodiesel was washed with lukewarm water several times to ensure the removal of impurities such as catalyst, and alcohol and intermediate products. The ethyl esters formed was analyzed by gas chromatography as described in ASTM standard D 6584. The results obtained were analyzed in terms of yield, conversion obtained, separation of glycerol and quality analysis for testing other specifications of the biodiesel standards such as cloud point (ASTM D 2500), viscosity (ASTM D 445), flash point (ASTM D 93), and acid number (ASTM D 664).

**3.3 Results and Discussions**

**3.3.1 Rate of Conversion**

The main factors affecting conversion to ethyl esters are temperature, catalyst amount, and molar ratio. The results obtained were compared to the laboratory scale batch and continuous transesterification processes previously performed by our group (Kanitkar et al., 2011; Terigar et al., 2010b). In these prior studies, temperatures investigated at laboratory batch scale were 60°C, 70°C and 80°C (Kanitkar et al., 2011). The highest conversion obtained was 98.18% at 80°C and 15 min; with the lowest conversion of 96.62% obtained for the combination of 60°C and 5 min (Kanitkar et al., 2011). Subsequently, a lower temperature of 50°C was studied in a continuous process; while the highest temperature was limited to 73°C (Terigar et al., 2010b). The conversion at 50°C in a continuous process was approximately the same to that obtained at 60°C.
for the batch scale. However, higher conversion (99%) was achieved at 73°C in the continuous process (Terigar et al., 2010b) compared to 80°C in the batch process (Kanitkar et al., 2011).

Based on these studies, the operating temperatures of 60°C and 75°C were maintained for the pilot scale process described herein. No measurable difference was observed in the rate of conversion for both the temperatures. The conversions obtained were greater than 99% for all time and temperature combinations (table 3.1). The lowest conversion obtained was 99.93 for 60°C and a residence time of 1 minute. The study parameters were initially selected so as to obtain the reaction kinetics data, however, this was deemed impossible as virtually all of the conversion took place within the first few seconds after the exposure to microwave.

It can be concluded that the process efficiency increases as the scale is increased and the system geometry is varied. Major reasons for this significant increase include the use of single mode resonant cavity at the pilot scale versus a multimode cavity on the laboratory scale (the single mode cavity applicator is more efficient than the multimode applicator) and the microwave frequency of 915 MHz used at pilot scale vs. 2450 MHz at laboratory scale. As frequency decreases, penetration depth for the reactants increases resulting in latter volumetric heating and molecular mixing. This increase in performance at pilot scale was also observed for the microwave- assisted oil extraction process from different feedstock (Terigar et al., 2011). The results accomplished are also supported by other data presented in the literature. A 99% conversion was achieved at 50°C and 1min (at a laboratory scale) by methanolysis of used refining oil (Leadbeater and Stencel, 2006; Leadbeater et al., 2008). Hernando et al., confirmed the efficiency of a laboratory scale microwave technology for production of biodiesel by microwave (97% conversion) vs. conventional heating (84% conversion) (Hernando et al.,
2007). Note that both these processes were carried out at 2450 MHz, in multimode cavity microwave systems.

Literature data (and current commercial practice) indicate that using conventional heating leads to longer reaction times. A conversion of about 94.1% was obtained by De Oliveira et al., for 70°C and soybean oil/ethanol ratio of 1:9 with catalyst concentration of 0.5 % by weight and a reaction time of 1.0 hr (de Oliveira et al., 2005). Freedman et al., obtained similar results (98% conversion) for the temp of 60°C and 1.0 hr residence time with methanol (Freedman et al., 1984). Using conventional heating, ethyl ester yield of 80% were obtained, however the molar ratio was as high as 1:40 (Silva et al., 2007). This literature data clearly indicates that microwave heating is highly efficient compared to conventional heating in terms of heating rates and yield of biodiesel.

It is important to obtain the reaction kinetics data for complex reactions in order to optimize the reaction process. Reaction kinetics data gives a clear picture of the dependence of reaction on various parameters affecting the rate of reaction. As mentioned earlier, transesterification reaction is a three step reaction with a number of sub-steps. The major factors influencing the rate of transesterification reaction are reaction steps, temperature, and catalyst activity. However, with the use of microwave heating, the conversion obtained was always greater that 99% which made it difficult to obtain the data for calculating the reaction kinetics for pilot scale. Kinetics data was obtained for the continuous laboratory scale results (Terigar et al., 2010b) but could not be obtained for the pilot scale.
Table 3.1 Free and total glycerin content and percent conversion of soybean oil fatty acid esters studied at varying reaction temperatures and times.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Time (Min)</th>
<th>Soybean oil Ethyl Esters</th>
<th>Batch Scale&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Continuous Scale&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Pilot Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Free Glycerin (%Mass)</td>
<td>Total Glycerin (%Mass)</td>
<td>Conversion (%)</td>
<td>Free Glycerin (%Mass)</td>
</tr>
<tr>
<td>50</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.03±0.01</td>
</tr>
<tr>
<td>50</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.02±0.01</td>
</tr>
<tr>
<td>50</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>0.01±0.01</td>
<td>0.18±0.01</td>
</tr>
<tr>
<td>50</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>5</td>
<td>Tr. 0.101±0.004</td>
<td>96.62±0.431</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>10</td>
<td>Tr. 0.084±0.007</td>
<td>96.95±0.085</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>15</td>
<td>Tr. 0.064±0.004</td>
<td>97.3±0.141</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>70</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>70</td>
<td>5</td>
<td>Tr. 0.079±0.001</td>
<td>97.04±0.056</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>70</td>
<td>10</td>
<td>Tr. 0.076±0.002</td>
<td>97.36±0.113</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>70</td>
<td>15</td>
<td>Tr. 0.068±0.004</td>
<td>97.46±0.098</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>75</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.02±0.01*</td>
</tr>
<tr>
<td>75</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.02±0.01*</td>
</tr>
<tr>
<td>75</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>0.01±0.00*</td>
<td>0.16±0.01*</td>
</tr>
<tr>
<td>75</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>80</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>80</td>
<td>5</td>
<td>Tr. 0.056±0.001</td>
<td>97.0±0.311</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>80</td>
<td>10</td>
<td>Tr. 0.059±0.011</td>
<td>98.11±0.12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>80</td>
<td>15</td>
<td>Tr. 0.015±0.001</td>
<td>98.18±0.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ASTM D 6584 limits</td>
<td>Max. 0.02</td>
<td>Max. 0.24</td>
<td>Max. 0.02</td>
<td>Max. 0.24</td>
<td>Max. 0.02</td>
</tr>
</tbody>
</table>

<sup>a</sup>: Batch scale results (Kanitkar et al., 2011)

<sup>b</sup>: Continuous laboratory scale (Terigar et al., 2010b)

*: Reaction carried out at 73°C

### 3.3.2 Fatty Acid Ethyl Ester Composition

The fatty acid ethyl ester composition was in accordance with the type of oil used. No significant changes in the composition were observed between the reaction temperatures of 60°C and 75°C (Table 3.2). Similarly for all reaction times, the composition for a given temperature was approximately the same.
### Table 3.2 Fatty acid ethyl esters of soybean oil biodiesel.

<table>
<thead>
<tr>
<th>FAEE</th>
<th>Soybean Oil Fatty Acid Ethyl Esters (%)</th>
<th>60°C</th>
<th>75°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1min</td>
<td>5min</td>
<td>10min</td>
</tr>
<tr>
<td>Lauric</td>
<td>5.03±0.002</td>
<td>5.58±0.002</td>
<td>5.15±0.003</td>
</tr>
<tr>
<td>Palmitic</td>
<td>7.99±0.01</td>
<td>7.72±0.003</td>
<td>7.57±0.005</td>
</tr>
<tr>
<td>Stearic</td>
<td>4.36±0.006</td>
<td>3.41±0.003</td>
<td>3.71±0.0003</td>
</tr>
<tr>
<td>Oleic</td>
<td>18.6±0.009</td>
<td>20.92±0.006</td>
<td>19.32±0.005</td>
</tr>
<tr>
<td>Linoleic</td>
<td>55.46±0.075</td>
<td>54.55±0.009</td>
<td>56.35±0.001</td>
</tr>
<tr>
<td>Linolenic</td>
<td>7.17±0.009</td>
<td>7.17±0.004</td>
<td>6.95±0.007</td>
</tr>
<tr>
<td>Eicosenoic</td>
<td>0.18±0.003</td>
<td>0</td>
<td>0.36±0.000</td>
</tr>
<tr>
<td>Lignoceric</td>
<td>0</td>
<td>0.09±0.009</td>
<td>0.15±0.0045</td>
</tr>
<tr>
<td>Docosenoic</td>
<td>1.18±0.006</td>
<td>0.52±0.003</td>
<td>0.41±0.002</td>
</tr>
</tbody>
</table>

### 3.3.3 Quality Analysis

- **Free and Total Glycerol Content in Biodiesel**

  The amount of free and total glycerol content in biodiesel reflects both the quality and the conversion rate of biodiesel. Major drawback of fuel with high content of free glycerol is formation of viscous mixtures that plug the fuel filters in engine, causing combustion problems. Settling in storage tanks is another common problem with such fuels. The ASTM specification for the permissible amount of free and total glycerol content in biodiesel is max 0.25%. As indicated in table 3.1, biodiesel obtained from all sets of temperature and time combination met the ASTM standard. Maximum free glycerol of 0.07% was obtained at a combination of lowest temperature and shortest time. No measurable difference in free and total glycerin contents was observed at both the temperatures. Gas chromatography analysis showed no free and total glycerol peaks (Figure 3.5). This indicates more complete transesterification reaction and an efficient washing procedure. As stated earlier, microwave assisted transesterification reaction leads to completion of reaction in much shorter times, resulting in the production of excellent quality biodiesel as compared to conventional heating techniques.
Kinematic Viscosity

Kinematic viscosity is a measure of resistance to flow of liquid due to friction. It is a major factor affecting the lubricity of fuel. Highly viscous fuel can cause problems such as poor atomization of fuel in fuel, thus leaving deposits in the combustion chamber causing coking which could damage the engine (Demirbas, 2009). It is an important factor influencing the optimization of storage and operation conditions of the fuel. According to the ASTM specifications, the acceptable range of viscosity is 1.9-6.0 mm²/sec. Biodiesel obtained from both the reaction temperature conditions fall within this specified range (table 3.3). Viscosity decreased with the increase in reaction temperature but remained unchanged at each temperature among the different times. Moreover, biodiesel obtained at the higher reaction temperature of 75°C had a kinematic viscosity in the ASTM specified range of petro-diesel (1.9-4.1 mm²/sec).
Table 3.3. Qualitative analysis of soybean oil biodiesel

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Holding Times (Min)</th>
<th>Kinematic Viscosity (mm²/sec)</th>
<th>Acid number (Mg of KOH/gm.)</th>
<th>Cloud Point (°C)</th>
<th>Flash Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>1</td>
<td>4.26±0.001</td>
<td>0.26±0.0016</td>
<td>4.0±0.01</td>
<td>146±0.05</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.36±0.0068</td>
<td>0.34±0.0088</td>
<td>4.5±0.005</td>
<td>155±0.01</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>4.14±0.0001</td>
<td>0.34±0.0088</td>
<td>4.0±0.01</td>
<td>153±0.01</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>4.45±0.0074</td>
<td>0.30±0.0052</td>
<td>4.5±0.02</td>
<td>157±0.015</td>
</tr>
<tr>
<td>75</td>
<td>1</td>
<td>3.83±0.0079</td>
<td>0.34±0.0088</td>
<td>4.5±0.02</td>
<td>166±0.02</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3.98±0.0090</td>
<td>0.34±0.0087</td>
<td>5.0±0.00</td>
<td>171±0.02</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3.97±0.0039</td>
<td>0.43±0.0066</td>
<td>6.0±0.005</td>
<td>154±0.00</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>3.86±0.0089</td>
<td>0.39±0.0024</td>
<td>5.0±0.00</td>
<td>158±0.015</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ASTM standard</th>
<th>D 445</th>
<th>D 664</th>
<th>D 2500</th>
<th>D 93</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.9 – 6.0</td>
<td>Max. 0.5</td>
<td>Max. 10°C</td>
<td>Min 130°C</td>
</tr>
</tbody>
</table>

• **Acid Number**

It is the measure of quantity of acids (free acids and mineral acids) present in biodiesel. High fuel acidity is directly associated with the corrosion of engine parts, such as fuel injector. ASTM standard requires that acid value is less than 0.5 mg of KOH/gm of oil. Acid values for all the samples tested fall under this ASTM specified standard (table 3.3). No measurable difference was found, however the values increased slightly with the increase in temperature.

• **Cloud Point and Flash Point**

Cloud point is a measure of flow properties of fuel in cold environment. The requirement of ASTM standard of the maximum cloud point temperature is 10°C. However, even lower values are desired as this quality is directly associated with the low temperature performance of fuel. Cloud point of all the biodiesel samples tested were in this acceptable range. No significant difference in the cloud point temperature was observed for different times and temperature.

• **Flash Point**

It is defines as the minimum temperature at which the fuel self-ignites. A higher flash point value indicates low fuel volatility and ensures safety in handling, transportation and storage.
of fuel (Demirbas, 2009). In the biodiesel samples tested, there was significant difference in the values of flash point for different reaction temperatures and times. Biodiesel obtained at higher reaction temperatures had significantly high flash point values, which further increased with the reaction times. The lowest value obtained was still well above the ASTM specification (>130ºC).

- **Scale-Up Performance**

  The pilot plant scale up experiments described here were 184 times than those of laboratory scale. Assuming near 100% conversion, with two shifts operating for 8.0 hrs each (16 hrs a day), about 1476 litres/day of biodiesel can be produced. We note here that the bottlenecks in these production scenarios would stem from the purification stages. Since no significant difference was observed in the conversion rate at two different temperatures, an operating temperature of 60ºC could be used to successfully perform the transesterification process. The required molar ratio is 1:3 (oil: ethanol), however to drive the reaction to completion, excess ethanol is added (1:9 molar in this case). This excess ethanol can be recovered, purified and reused. The system can further be scaled up to an industrial level where per day production can be even higher which guarantee efficiency of the system.

  The net energy balance for biodiesel from soybean oil is higher than petroleum diesel (Hill et al., 2006; Wesseler, 2007). Soybean produce long chain triglycerides, which reduce the energy intake for the production of biodiesel thus providing 93%, more energy than the total energy input required for its production (Pradhan et al., 2008). These advantages of biodiesel from vegetable oil encourage the production of biodiesel. One of the major steps in industrial scale production of biodiesel is the economic evaluation of overall process. Production cost estimated in 2006 for soybean biodiesel was $0.35 per diesel energy equivalent liter (EEL) after subsidies (Hill et al., 2006). Two important factors responsible for the high production cost of
biodiesel are 1. Cost of feed and 2. Operating cost (utilities) (Deshpande et al., 2010). Cost of feedstock can be significantly reduced by the use of non-edible oil seed that can grow on unfertilized land or by the use of waste cooking oil from households and restaurants. Operating cost per unit of biodiesel produced can be significantly reduced by the use of microwave technology. Use of microwave irradiation makes the process more energy efficient in comparison with the conventional heating methods. In a study of energy consumption, a microwave with 60% efficiency was found to be much more energy efficient than the conventional heating technique (45% efficiency of fired heaters) (Deshpande et al., 2010; Leadbeater et al., 2008). Energy consumed by microwave at 6.1L/min of flow rate was 26.0 kJ/L of biodiesel produced, whereas that for the conventional heating was 94.3kJ/L (Leadbeater et al., 2008). Use of a high volume capacity microwave would be more energy efficient. Also, as the reaction is faster, the amount of production is much higher in a microwave assisted biodiesel production, making it economically viable.

3.4 Conclusions

The scale up study for a continuous microwave-assisted transesterification process for biodiesel production was performed. Based on prior laboratory scale performance, the oil to alcohol molar ratio was 1:9, while the catalyst amount used was 0.18% by the weight of oil. The results of this study demonstrated the feasibility of using microwave technology at a larger scale for the production of biodiesel. Microwave technology is a promising tool in terms of reaction time, temperature and energy efficiency. Reactions were performed under atmospheric pressure conditions. Percent conversion of 99% obtained does not differ significantly at 60°C and 75°C. Thus, we suggest that the optimum temperature used should be 60°C. The results also demonstrated that the processing efficiency increased compared to the laboratory scale. Use of
single mode cavity applicator increases the efficiency of process, a more uniform heating is obtained. Quality analysis shows that the biodiesel produced meets all the ASTM standards. The reaction time allotted was 1 min, which is significantly low compared to conventional heating. The energy efficiency of microwave technology is higher, thus it can be scaled up for an industrial scale production.

3.5 References


CHAPTER 4

NUMERICAL MODELING OF TEMPERATURE PROFILES DURING CONTINUOUS FLOW MICROWAVE ASSISTED TRANSESTERIFICATION PROCESS

4.1 Introduction

The consumption of fossil fuels at an alarming rate and the impact of combustion of these fuels on environment have resulted in a critical need to develop clean sources of renewable fuels. The impact of crude oil, natural gas and coal combustion on the environment is tremendous. Transportation fuels such as diesel and gasoline largely consists of aliphatic hydrocarbons containing 10-25 carbon atoms. When these fuels undergo combustion, are thermally altered and emitted in the atmosphere in the form of polycyclic aromatic hydrocarbons (PAH’s) (Schauer et al., 1999), green house gases such as CO$_2$ and sulphur emission. PAHs are carcinogenic in nature and could prove fatal to living organisms (Schauer et al., 1999).

The domestic and industrial need of energy can be met by various renewable resources such as solar energy (Glaser, 1968), wind energy (Karki and Billinton, 2004), hydropower energy (Demirba, 2002), geothermal energy (Wohletz and Heiken, 1992), etc. These renewable sources are well developed and have been successfully applied in various fields but mostly as standalone facilities. On the side of transportation fuels, satisfactory alternatives are limited and still under development. Although there are a few commercially developed vehicles operated on alternative sources such as solar or electricity, these modifications are not compatible with the existent infrastructure. For instance, cars that could be operated on electricity need frequent charging as they do not have a very large range. Since 2/3$^{rd}$ of the electricity production is from fossil fuel, these cars ultimately utilize energy from fossil fuels.
Development of a reliable renewable transportation fuel also has its limitations. The fuel has to be in liquid state to be operated in combustion engines (spark ignition gasoline or compression ignition diesel engines). It should have chemical and physical properties such as cetane number, octane number, viscosity, flash point, cloud point etc. similar to those of petroleum derived fuels. It should be competitively priced, and it must be able to operate in the engine without requiring too many modifications. The triglycerides existent vegetable oils have been investigated and marked as suitable for use in diesel engines (Fukuda et al., 2001). However they cannot be directly used in the current engines due to the problems such as gum formation, polymerization, and high viscosities (Fukuda et al., 2001). To overcome these constraints, these oils are treated with different processes such as pyrolysis (Demirbas, 2008), micro-emulsion (Lin and Lin, 2007), dilution and transesterification.

Amongst the first generation alternative fuels are bioethanol and biodiesel. Bioethanol can be used as a blend with gasoline as it has higher octane number than gasoline and is environment friendly; yet bioethanol has a few disadvantages such low heat content compared to gasoline, corrosiveness, low vapor pressure, and low flame luminosity (making ignition difficult during cold weather). Additional problems related to feedstock availability for production of bioethanol from cornstarch, competition with food market and technological hurdles for lignocellulosic-based bioethanol have led to its limited use. (Balat et al., 2008). Biodiesel produced from renewable vegetable oil or animal fat meets most of the liquid fuel requirements and it is a practical alternative. Biodiesel has lower emission compared to petroleum based diesel. The net green house gases produced by biodiesel are minimal and the amount of sulphur exhaust in the atmosphere is negligible (Azcan and Danisman, 2007).
Biodiesel is produced by transesterification reaction of vegetable oil (or animal fat) with alcohol in presence of catalyst and heat. Among the edible oils that can be used for biodiesel production are soybean (Liu et al., 2008), rice bran (Einloft et al., 2007), canola (Leung and Guo, 2006), palm (Noiroj et al., 2009), and sunflower oil (Antolin et al., 2002). Non edible oils proposed for production of biodiesel include those derived from Chinese tallow tree seeds, castor oil, *jatropha curcas* (Zhou et al., 2006) and algae (Behzadi and Farid, 2007). Transesterification for biodiesel production has been proved efficient and it is the most widely used method (Van Gerpen, 2005). Transesterification or alcoholysis is a chemical reaction in which one alcohol is displaced from the ester by another alcohol in the presence of catalyst. The overall reaction is in three consecutive reversible reaction steps, with diglycerides and monoglycerides as intermediate products (Pinto et al., 2005). In order to design an efficient reaction system, it is important to know the parameters affecting the reaction process.

Transesterification reaction is affected by moisture content; the reaction has to be free of moisture to avoid saponification process. Catalyst type used can affect the rate of reaction, with the base and acid catalysts being the most commonly used catalysts. Free fatty acids in the oil reduces the ester yield and enhances soap formation, hence the quality of oil plays an important role in the reaction process. Transesterification is also known as alcoholysis, with ethanol and methanol being used most commonly for the reaction. Since the reaction is reversible, excess alcohol should be added to drive the reaction towards completion, so the alcohol to oil molar ratio is also an important factor affecting the rate of reaction. Lastly, the rate of reaction is also improved by addition of heat (higher temperature increases the conversion rate).

Microwave heating is a process that has been widely used as an alternative to conventional heating in industrial processes with applications in chemical engineering, food
engineering and environmental fields since mid 20\textsuperscript{th} century (Metaxas and Meredith, 1993; Oliveira and Franca, 2002). The major advantages of microwave heating are lack of an intermediate heat transfer medium and their direct interaction with the medium (Zhu et al., 2007). Thus volumetric heating is achieved by microwave processing of materials as the microwave energy is transferred directly to the solution. Microwave heating takes place at molecular level due to friction between adjacent molecules which is the result of dipolar rotation and/or migration of conducting ions under the effect of electric field (Stuerga, 2008; Zhu et al., 2007) which increase heat transfer rates and thus reduce the processing time (Salvi et al., 2011). Use of microwave as a source of heat makes biodiesel production more efficient, faster, and safer than conventional heating technique (Kanitkar et al., 2011; Leadbeater and Stencel, 2006; Terigar et al., 2010b). The reaction and separation time is considerably reduced (Hernando et al., 2007).

Microwave heating of fluids has many advantages over conventional heating including high energy efficiency, rapid heating, short ramp up time (sometimes even instantaneously) and the ability to provide a more uniform heating in case of a continuous process if the system is properly designed (Boldor et al., 2008). An added advantage is the ease of control of energy transfer (near instantaneous) by turning the microwaves on and off. However, a major drawback of conventional microwave systems is the uneven heating of the material due to the different dielectric properties (in case of heterogeneous materials) and the standing wave patterns in multimode heating cavities (Zhang et al., 2000). This drawback is mainly associated with the batch-microwave heating systems. The development of continuous microwave heating systems in single mode cavities has significantly reduced this problem as the electric field is applied such that it is more uniformly distributed (i.e. maximum electric field is applied at the center where
there is maximum velocity, whereas minimum at the walls where the flow rate is minimum) (Falqui-Cao et al., 2001).

Microwave heating depends on the physical properties of components undergoing heating including dielectric properties (dielectric constant and dielectric loss factor), thermal properties (conductivity, specific heat) and rheological properties (viscosity). One of the important factors that affect microwave heating is penetration depth. Penetration depth is defined as the depth at which 63% (e⁻¹) of the incident energy is dissipated (Smith and Hui, 2004). Penetration depth depends on material dielectric properties and frequency of operation, hence is unique for every component. Since the frequencies set by Federal Communications Commission (FCC) for industrial, scientific and medical microwave heating are 915 MHz and 2450 MHz, the penetration depth becomes mostly a function of dielectric properties of material. Penetration depth is given as (Mujumdar, 2007)

\[
D_p = \frac{\lambda_0}{\pi \sqrt{2} \varepsilon'} \sqrt{\frac{1}{1+\left(\frac{\varepsilon''}{\varepsilon'}\right)^2}} \quad [4.1]
\]

Where, \(D_p\) is the penetration depth \(\lambda_0\) is the wavelength of free space, \(\varepsilon'\) is the relative dielectric constant of material, and \(\varepsilon''\) is the dielectric loss of material.

A very large penetration depth (quartz glass penetration depth is 16000 cm) indicate that the energy is poorly absorbed; whereas a low penetration depth indicates predominantly surface heating which is a characteristic of high dielectric loss materials. Metals, which act as conductors have very low penetration depth (Aluminum \(Dp=1.7\times10^{-4}\) cm) (Gupta et al., 2007). Another important factor that affects penetration depth is the presence of ions. With the addition of ions, penetration depth significantly decreases; in this case heating again is dominant at the surface (Mudgett, 1986; Smith and Hui, 2004). For cylindrical objects, the penetration depth should be
two to three times higher than the diameter of the material for focused accumulation of electromagnetic density at the center (Smith and Hui, 2004). If the diameter is much larger than the penetration depth, the material acts as a semi infinite block where the heating is limited to the surface of the material (Smith and Hui, 2004).

In order to understand and account for the different phenomena occurring in microwave heating during transesterification, and to optimize the process, it is necessary to understand the effects various parameters have on the process. Among these parameters one can include flow patterns of the fluid, electromagnetic field distribution, temperature profile, heating effects, and reaction kinetics (Zhang et al., 2000). Although the experimental approach provides the most pertinent information for a specific product, adequate experimentation may be impractical as a large number of tests are usually required to obtain representative results. If the process is to be performed at relatively large scale, the costs could become prohibitive. For example, as discussed in the previous chapter, the amount of raw materials required to carry out one pilot scale data set of transesterification reaction is 60 – 80 liters of reacting solution. The time required is roughly 6-7 hours for experiments and another 6-8 hours for analysis of data. Experimental measurement of many of these parameters is not feasible as the measuring devices may interfere with the electromagnetic field and with the flow distribution in continuous processes.

In these cases, numerical analysis can be employed in order to estimate the effects these various operating parameters have on the process. For electromagnetic heating of a fluid, several equations need to be solved simultaneously. These equations include Maxwell’s equations to determine electromagnetic field distribution, Navier-Stokes equation solved for the flow pattern.
of the liquid, and Fourier’s equations of energy balance to calculate the heat transfer in the fluid and the power requirement.

Huge interdependency of one mechanism on the other makes it tedious to solve a problem of multiphysics. In the absence of a closed form solution, it is either extremely difficult to obtain a solution for anything than the most simple cases or impossible for multiple equations using different physics. Due to often impracticability of experimental approach, numerical analysis provides the most suitable compromise. Advancements in computer technology have made it possible to develop better numerical models. Computer simulation is a powerful alternative research tool that can be used to solve complex numerical iterations.

In order to optimize the microwave heating and transesterification process, the knowledge of fluid flow, three dimensional heating profile, chemical rate constant and electromagnetic field distribution as a function of input parameters such as initial flow, input microwave power etc. is necessary in order to evaluate the optimized condition for maximum yield (Romano et al., 2005; Sabliov et al., 2007; Zhang et al., 2000). Additional complexities are introduced if physical properties change with temperature. Once the numerical model is developed and validated, numerous simulations can be conducted to evaluate the effects of different parameters on the end product.

• **Literature Survey**

A number of studies have documented numerical modeling of microwave heating (Zhu et al., 2007). In many cases, limited understanding of the power distribution, flow patterns in case of fluids, temperature profiles, and limitation with the computing power (memory, number of elements, long solution time etc.) have hindered the understanding of this technology. Recent advancements in computational technology allowed more studies to be published in this
particular area of study (Anantheswaran et al., 1994; Clemens and Saltiel, 1996; Evans and Evans, 1993; Jia et al., 1992). Jia et al., (1992) used the finite element method approach to develop a mathematical model in order to understand the microwave field and power distribution in a multimode cavity (Jia et al., 1992). This model had certain drawbacks; a major one was that it required long computational hours even for the simplest models such as the batch microwave (Zhang et al., 2000). In addition, a majority of the studies are limited to the heating of solids (Hansson et al., 2006; Lin et al., 1995); there are only a few papers available in literature that have looked at processes involving fluid flow (Jia et al., 1992; Patankar, 1980; Webb J. P, 1983; Zhang et al., 2000). One reason is that the analysis of fluid heating is challenging as it involves fluid motion which increases exponentially the computational requirements. A few of the studies involves numerical modeling of batch microwave for heating liquids (DATTA et al., 1992; Ohlsson and Bengtsson, 2001).

Even scarcer are the reports of studies investigating continuous flow microwave heating and many of these studies looked at the two-dimensional cases assuming symmetry (Le Bail et al., 2000; Mudgett, 1986; Ratanadecho et al., 2002; Sabliov et al., 2007; Salvi et al., 2011), Ratanadecho et al., (2002) was among the first studies to investigate the microwave heating of a liquid in a rectangular waveguide both experimentally and numerically. Zhang et al., studied the heating of a batch of liquid in a microwave with a three dimensional approach. Few models (Zhu et al., 2007) used finite difference time domain algorithm to solve Maxwell’s equations and finite volume method (FVM) to solve energy and mass balance equations using independent numerical codes. Coupling of different physics like fluid flow, electromagnetism and heat transfer has been only recently developed, as usually electromagnetic solution is obtained in the frequency domain whereas the other fields require solutions in the time domain.
The finite element method (FEM) has several advantages over finite difference method (FDM) and finite volume method (FVM) including the possibility of using irregular geometries, and being more accurate (Puri and Anantheswaran, 1993). This accuracy depends on several other factors, such as, time step, number and shape of the elements. The size of the element should be smaller (a fraction) than the smallest wavelength in the material (Lin et al., 1995).

Thus, numerical modeling helps in predicting the behavior of the systems under certain sets of parameters and can be used for the optimization of the continuous flow microwave heating process. Amongst the most important problem associated with the computational numerical solving of continuous flow microwave heating problem is coupling these different physics. The major inconvenience of the published numerical models is their independent coding; the complexity of solving tedious equations, grid generation, and post visualization. Due to limitations of experimental procedures and lack of dielectric data, validation of these models becomes difficult.

Computational solving of numerical problem is performed in two ways 1) writing your own code and 2) using commercial multiphysics software. Use of finite element method (FEM) or finite difference method (FDM), finite difference time domain method (FDTD) to develop a numerical model requires thorough knowledge of numerical analysis as well as complex programming skills. Engineers have limited knowledge when it comes to programming associated with mesh forming and mathematical modeling of the problem, thus use of commercial software is a feasible option. Commercial software packages circumvent many of the above mentioned problems. Various commercial simulators packages have been developed throughout the years that are capable of numerical modeling of microwave heating problems. These include COMSOL Multiphysics (former FEMLAB), ANSYS Multiphysics, QuickWave-
3D, MEFiSTo-3D, Microwave Studio and others (Rienen et al., 2001). Commercial multiphysics software packages such as ANSYS and COMSOL have built in fundamental equations which can be coupled; they also have options of building geometry, mesh generation and post processors which offers better visualization. COMSOL Multiphysics is a finite element software packages which can couple the various multiphysics such as high frequency electromagnetism, fluid flow, chemical engineering and heat transfer directly i.e. without reforming mesh. COMSOL Multiphysics offers variety of solvers for the different physical phenomenon, different grid options and post processing options for the visualization of the results, and it was selected for this particular study.

- **Goal and Objective**

The goal of this study was to develop a finite element model in COMSOL Multiphysics version 4.2 coupling a high frequency electromagnetism to fluid flow and heat transfer for microwave heating of biodiesel components. The corresponding objectives were to investigate the effect of two different power levels on the temperature profile for a pilot scale continuous flow microwave system and to validate the results experimentally by comparing with the temperatures obtained experimentally.

### 4.2 Experimental Methods and Procedure for Numerical Simulation

#### 4.2.1 Experimental Measurements

As described in chapter 3 in more detail, experiments were performed to test the efficiency of microwave assisted biodiesel production. Two power levels were tested at one flow rate to obtain the two target temperatures of 60°C and 75°C. With the flow rate of 840 ml/min, the microwave power supply required to achieve a temperature of 75°C was 4700W. Since oil and ethanol are essentially immiscible, oil was pre heated to ensure proper mixing. The inlet
temperature of the oil/ethanol-catalyst mixture entering the microwave was 45ºC. These experiments were performed in triplicates and the temperature of exiting fluid was measured at nine different locations. The experimental set up was reproduced from Salvi et al., (2008) the radial measurement was carried out at an angle of 120º at 3 different locations as shown (Figure 4.1). The experiments were performed in triplicates and the average temperature values at each location and each power level are tabulated (table 4.2).

The second set of reaction was carried out at 60ºC. The decrease in the temperature could be achieved either by increasing the flow rate of the fluid mixture so as to allow shorter residence time in the tube, or by reducing the power level while maintaining the same flow rate. In order to maintain the consistency with the first experiment, the second method was chosen. It did not require additional material to be used (higher flow rate also requires more feedstock). Without pre-heating the oil, the inlet temperature was 30ºC. With the flow rate of 840ml/min (lowest flow rate achieved by the pump), the power input required to obtain the temperature of 60ºC was 4000W.
The geometry of this particular microwave system was custom designed to heat salt water and fresh water. The diameter of the tube and other geometrical characteristics of the cavity were built considering the dielectric properties of water and salt water rather than less polar fluid like the one studied here. Hence, the efficiency of the microwave (amount of effective power absorbed) significantly decreased for the oil/ethanol-catalyst fluid mixture compared to that obtained by Salvi et al., 2008 for a water based feedstock.

The model was build considering the above parameters (existent geometry, flow rate, power levels, and initial temperature); temperature profiles obtained from the model were compared with the experimental temperatures obtained and validated.

### 4.2.2 Governing Equations

- **Electromagnetic Equation**

  Microwave heating is governed by two phenomena: electromagnetic wave propagation and heat diffusion. Electromagnetic interaction in a medium is given by Maxwell’s equations.

\[
\nabla \cdot \vec{D} = \rho \tag{4.2}
\]

\[
\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \tag{4.3}
\]

\[
\nabla \cdot \vec{B} = 0 \tag{4.4}
\]

\[
\nabla \times \vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t} \tag{4.5}
\]

\[
\vec{D} = \varepsilon \varepsilon_0 \vec{E} \tag{4.6}
\]

\[
\vec{B} = \mu \mu_0 \vec{H} \tag{4.7}
\]

\[
\vec{J} = \sigma \vec{E} \tag{4.8}
\]

where, $E$ is the electric field; $B$ is the magnetic flux density; $\rho$ is electric charge density; $J$ is the electric current; $\sigma$ is electrical conductivity; $D$ is electric displacement; $\varepsilon_0$ is the permittivity of free space ($8.854 \times 10^{-12}$) F/m; $H$ is magnetic field intensity; $\varepsilon'$ is the relative dielectric constant; $t$
is time (sec); $\mu'$ is relative permeability of material; $\mu_0$ is magnetic permeability of vacuum ($4\pi \times 10^{-7}$) N/A²

To determine the electric field distribution in a TE₁₀ rectangular waveguide (WR 975), a wave equation derived from Maxwell’s equations is solved,

$$\nabla \times \left(\frac{1}{\mu} \nabla \times \vec{E}\right) - \frac{\omega^2}{c} (\varepsilon' - j\varepsilon'')\vec{E} = 0$$ \hspace{2cm} [4.9]

Total volumetric power generation due to microwave is calculated by the following equation

$$Q_{gen} = \sigma_e E^2 = 2\pi f \varepsilon_0 \varepsilon'' E_{rms}^2$$ \hspace{2cm} [4.10]

$Q_{gen}$ is power absorbed from microwave, which is used as a heat generation term in Fourier equation (W/m³), $\sigma_e$ is the conductivity (Siemens/m), $f$ is the frequency (Hz),

• **Heat Transfer Equation**

The rate of change of temperature for the material heated by the electromagnetic waves is given by the Fourier’s thermal balance equation as;

$$\frac{\partial T}{\partial t} + \vec{u} \nabla T = \frac{k}{\rho_m c_p} \nabla^2 T + \frac{Q_{gen}}{\rho_m c_p}$$ \hspace{2cm} [4.11]

Where $\frac{\partial T}{\partial t}$ is the rate of change in temperature with time; $\vec{u} \nabla T$ is convective heat transfer term; $\frac{k}{\rho_m c_p} \nabla^2 T$ represents heat diffusion. Heat generation is calculated by equation 3.9; $\rho_m$ is density of material (kg/m³); $C_p$ is the specific heat (J/kg·K); $T$ is temperature (K); $u$ is fluid velocity (m/s); $k$ is the thermal conductivity (W/m·K); and $Q_{gen}$ is heat generation (W/m³)

• **Fluid Flow Momentum Balance Equation**

Navier-Stokes equation is used to describe the momentum balance in a fluid. The equation for incompressible flow is given by,
Continuity equation is

\[ \nabla \cdot \vec{u} = 0 \]  \[\text{(4.13)}\]

Where; \( u \) is velocity of fluid in (m/s); \( \mu \) is viscosity in (Pa·s); \( P \) is pressure (Pa); \( F \) is other forces such as gravity or centrifugal force per unit volume (N/m³)

- **Assumptions**

  High frequency electromagnetism module was coupled with heat transfer and laminar fluid flow in COMSOL Multiphysics version 4.2. To reduce the complexity of the problem the following assumptions were made:

  1) The oil-ethanol-catalyst mixture is a fully mixed, Newtonian, incompressible fluid flowing under laminar conditions.
  2) No phase change was considered.
  3) Convective heat transfer between the dielectric material and the air in the cavity.
  4) The PTFE tube carrying the fluid through the microwave was completely transparent to the microwaves.
  5) No chemical reaction is taking place.

### 4.2.3 Model Development

COMSOL Multiphysics software is a tool for solving complex numerical problems in a multi-disciplinary physics field. As COMSOL 4.2 does not have a module that directly couples microwave heating to fluid flow, we coupled the RF electromagnetic waves module to non-isothermal fluid flow module, which combines both heat transfer and fluid flow. Main steps in model development were geometry generation, defining boundary and subdomain settings, mesh generation, solver definition, solving and post processing. We developed model for two power
levels 4000 W and 4700 W. The power levels were decided based on experimental values described in chapter 3.

4.2.3.1 Geometry Building

A 3D geometry of a pilot scale 5kW, 915 MHz frequency continuous microwave system manufactured by Industrial Microwave Systems (IMS), Inc., Morrisville, NC was built in COMSOL Multiphysics version 4.2. The microwave consists of a waveguide, tuning coupler, an elliptical shaped single mode focusing resonant cavity and a cylindrical tube (3.2 cm diameter and 25.4 cm long) made of PTFE material through which the fluid mixture of soybean oil, ethanol and catalyst passes. As stated in the introduction, the cavity is designed such that the fluid passing through the center of the tube, which has the highest velocity, will be exposed to high energy compared to the fluid at the walls, which have longer residence time in the tube, which is exposed to lower energy. This concept, while generally true, does not apply to the case studied here as the focusing cavity is designed based on the material dielectric properties for water and salt water. The temperature profiles in this case were not expected to result in uniformity due to significantly different dielectric properties of this mixture compared to those of water.

Figure 4.2 5kW, 915 MHz microwave heating system
4.2.3.2 Boundary Conditions

- **Electromagnetic Waves**

  The microwave energy of 4000 W and 4700 W was supplied to the cavity at port one by the means of a TE$_{10}$ mode through a rectangular waveguide at a frequency of 915 MHz. All the exterior boundaries of the waveguide are assumed to be perfect conductors of electricity. The electromagnetic waves module was active in all the domains of the microwave system. As stated in the assumptions, the PTFE tube was assumed perfectly transparent to the microwaves. Temperature dependent fluid dielectric properties were defined in the tube domain. Heat transfer due to natural convection was defined between the air and fluid. Any sudden discontinuity in the waveguide perturbs the field and leads to undesired reflections; to avoid this phenomenon two important boundary conditions were set. First, continuity boundary condition was set by default for all the internal boundaries between the three domains, namely tube domain, cavity domain and the waveguide domain. Second, scattering boundary conditions for EM field was applied at the inlet and outlet of the pipe to avoid any sudden transition in the pipe dimensions. Application of scattering boundary condition at the outer boundaries of the pipe simulates an infinitely long pipe. Dielectric properties of fluid were temperature dependent.

- **Non Isothermal Fluid Flow**

  Non isothermal fluid flow module was used to define the heat transfer and fluid flow problem. This module was active only in the pipe domain. The constant initial flow rate was set at 840 ml/min which corresponds to an average velocity of 0.0177 m/s. This flow rate is the same flow rate that was used to carry out the experiments described in previous chapter. As the oil was pre heated to ensure proper mixing of ethanol and catalyst in the oil, the inlet temperature was maintained at 45ºC for 4700W, and 30ºC for 4000W power supply, while the outlet pressure
was set to atmosphere. No slip condition for fluid flow and natural convection boundary condition for heat transfer were considered at the walls, thermal insulation to all other boundaries was defined. Fluid properties (viscosity, density, specific heat and thermal conductivity) were temperature dependent. In order to couple the non isothermal application mode to the electromagnetic waves mode, the heat source in Fourier’s equation was defined as the electromagnetic power loss density from the electromagnetic wave module.

4.2.3.3 Material Properties

The thermo-physical properties of the fluid such as density, dynamic viscosity, specific heat, and thermal conductivity were obtained from literature (Noureddini et al., 1992; Petravic, 2005; Sawai et al., 2002; Turgut et al., 2009; Wang and Briggs, 2002). Temperature dependent linear equations were derived based on mass fraction of oil and ethanol (Figure 4.3a, 4.3b, 4.3c, and 4.3d). The density and thermal conductivity of fluid mixture is generally calculated using the volume fraction of components, however oil and ethanol have relatively similar density values (oil 0.92gm/ml, ethanol 0.79gm/ml) and hence mass fraction was used as an adequate approximation for calculations. The catalyst mass fraction was negligible; its physical properties (with the exception of dielectric properties) were not taken into consideration. The dielectric properties measured for biodiesel components (see chapter 2) were used to determine temperature dependent relationships between dielectric constant, dielectric loss and temperature (Figure 4.3e, 4.3f).
Figure 4.3 Thermo-physical temperature dependent properties of fluid mixture (oil and ethanol) based on mass fraction (a) Thermal conductivity, W/m·K (b) Density, kg/m³ (c) Dynamic viscosity, Pa·s (d) Specific heat capacity, J/kg·K (e) Relative dielectric constant $\varepsilon'$ (f) Dielectric loss $\varepsilon''$
Table 4.1 Dielectric and thermo-physical properties (temperature dependent equations) of oil and ethanol mixture

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
<th>R²</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative dielectric constant ε' at 915 MHz</td>
<td>-0.1562\times T+62.74</td>
<td>0.9627</td>
<td>Chapter 2</td>
</tr>
<tr>
<td>Dielectric loss ε'' at 915 MHz</td>
<td>2.18\times 10^6 \times e^{-0.04\times T}</td>
<td>0.9647</td>
<td>Chapter 2</td>
</tr>
<tr>
<td>Thermal conductivity, k (W/m·K)</td>
<td>-1.314\times 10^{-4}\times T+0.2092</td>
<td>0.9999</td>
<td>(Petravic, 2005; Turgut et al., 2009)</td>
</tr>
<tr>
<td>Density, ρ (kg/m³)</td>
<td>-0.7253\times T+1094</td>
<td>1.0000</td>
<td>(Noureddini et al., 1992)</td>
</tr>
<tr>
<td>Dynamic viscosity, μ (Pa·s)</td>
<td>5.53\times 10^{-4}\times T+0.2017</td>
<td>0.9495</td>
<td>(Wang and Briggs, 2002)</td>
</tr>
<tr>
<td>Specific heat capacity, C_p (J/kg·K)</td>
<td>4.854\times T+599.8</td>
<td>1.0000</td>
<td>(Sawai et al., 2002; Wang and Briggs, 2002)</td>
</tr>
</tbody>
</table>

4.2.3.4 Mesh Generation

The element size requirement for solving the electromagnetic problem is that the maximum grid element size ($S_{max}$) should be less than half the wavelength. This requirement is known as the Nyquist criterion and is defined as,

$$S_{max} < \frac{\lambda}{2} = \frac{c}{2f\sqrt{\varepsilon'\mu'}} \quad [3.14]$$

Where, $\lambda$ is the wavelength (m), $f$ is the frequency (Hz), $c$ is the speed of light in vacuum (m/s), $\varepsilon'$ is the relative dielectric constant, and $\mu'$ is the relative permeability. Based on this criterion, the maximum element size for the electromagnetic wave problem was set conservatively at 0.03m in the waveguide and microwave cavity. The maximum element size was set to 0.004 m in the applicator tube to solve for fluid flow.

4.2.3.5 Solver Used and Convergence Criteria

Wave equation was solved in the radio frequency (RF) module using frequency domain to calculate heat generation. Energy and momentum equations were solved in non-isothermal fluid flow module (laminar flow with heat transfer) using transient solver ranging from 0 to
60sec with a time step of 1sec to obtain velocity and temperature profiles. The two modules were coupled with the heat source for the non-isothermal fluid flow domain obtained from the electromagnetic power loss density. **MUltifrontal Massively Parallel sparse direct Solver** (MUMPS) was used to solve both the time dependent flow problem as well as the stationary frequency problem. MUMPS solver reduces the memory usage however, takes longer solution times compared to PARDISO or GMRES solvers.

### 4.2.3.6 Post Processing

The electric field, electromagnetic power density and temperature profiles were mapped out using the COMSOL 4.2 post processing tool. Parameters obtained and discussed include electric field in the waveguide, power density, flow profiles and temperature distribution. Volume average and surface average of the temperature and power density were obtained in this step too. The temperature profile was plotted in longitudinal \((xz-plane)\) and radial direction \((xy-plane)\). Actual values were also plotted as a function of distance from the entrance.

### 4.3 Results and Discussion

#### 4.3.1 Electric Field Intensity

Electric field distribution influences the processing of material in a microwave. Electric field intensity is affected by factors such as magnetron frequency, dielectric properties of material, geometry etc. It is assumed that the incident wave has a transverse electric \((TE_{10})\) mode. Since the material in the waveguide is defined as air, a regular distribution of electric field is observed in the waveguide until it enters the applicator cavity. The impedance mismatch between the waveguide and cavity with tube and material generates higher values at domain transition boundary. The electric field intensity (Figure 4.4) varies from negligible to \(> 50000 \text{ V/m}\) for both the power inputs (4000W and 4700W).
Figure 4.4 Electric field distributions in the microwave. (a) \( xy \)-plane (b) \( xz \)-plane (c) \( yz \)-plane
4.3.2 Electromagnetic Power Density

Electromagnetic power density is defined as the electromagnetic energy absorbed by the material per unit volume of each element in the model. The electromagnetic power density at the center of the tube ranges from 0 to $4.7 \times 10^6$ W/m$^3$ for an input power of 4000W and from 0 to $3.6 \times 10^6$ for an input power of 4700W. At the inlet of the tube, a higher density region is observed near the pipe walls (this is undesired). As observed further up in the pipe, this higher density region moves towards the center (as desired).

Figure 4.5 Electromagnetic power density (W/m$^3$) for Pin = 4000W (left) and 4700W (right); (a) and (b) at pipe entrance ($z = -0.065$), (c) and (d) at a distance of 0.065 from the entrance of pipe ($z = 0$), (e) and (f) at a center of pipe ($z = 0.065$), (g) and (h) at a distance of 0.195 from the entrance of pipe ($z = 0.127$) and (i) and (j) at the pipe exit ($z = 0.189$)
(Figure 4.5 Continued)
The amount of absorbed microwave energy for the fluid was 19% at 4000W power input and 13% for 4700W power input approximately. This corresponds to the total power generation of 756W and 605W respectively.

This behavior is due to the high impedance mismatch as the cavity was designed for higher loss materials such as water. Even though tuning stubs were used to minimize the impedance mismatch, due to the extremely low dielectric properties, a poor coupling of microwave energy to the material was observed. As the fluid enters the tube, it is exposed to microwaves and is heated. The dielectric properties of the fluid are temperature dependent and changes as the fluid heats up. The electromagnetic power distribution in the microwave cavity also changes with the changing dielectrics of the fluid. Less power is absorbed in the upper tube region because as the fluid heats up, its dielectric properties change. As dielectric properties are temperature dependent, dielectric constant and dielectric loss decrease with temperature, leading to poor absorption of electromagnetic energy. Less power is absorbed for the higher power input of 4700W because with higher power higher temperatures are achieved faster. This leads to rapid changes in the dielectric properties of the material reducing the absorption of electromagnetic energy. Thus, as higher temperature is achieved with higher power input, a lower power density is observed for 4700W input power than for 4000W input power. Reaction rate is not considered in this study hence the effect of reaction is not known.

4.3.3 Velocity Profile and Temperature Distribution

Temperature distributions of fluid mixture as a function of distance from the entrance of the tube to tube exit (longitudinal distribution) in xz-plane and in yz-plane (facing the microwave) and also the radial temperature profile (radial xy-distribution) for the two power levels 4000 W and 4700 W were studied. Velocity profile in the longitudinal direction (xz-plane)
was plotted so as to understand the flow profile in $z$-direction (Figure 4.6a, 4.6b). Velocity profile observed was consistent with the boundary conditions and a fully developed laminar flow was observed. Highest velocity was observed at the center of the tube with lower velocity at the walls. Temperature ranged from 30ºC to 82ºC for 4000W power and 45 ºC to 89 ºC for 4700W power input. The maximum temperature values were above the boiling temperature of ethanol. However, this high temperature region was limited to the tube walls and the average temperature obtained was well below the boiling point of ethanol. Thus, no phase change was considered in solving the problem as the maximum temperature was only 6ºC and 12ºC higher than the boiling point of ethanol. Zero net energy change was assumed (once the ethanol boils up, it immediately condenses back in to liquid). Average exit temperatures obtained were 61ºC and 73ºC respectively, for the two power levels of 4000 W and 4700 W (figure 4.6). These averaged results as well as values were compared to the experimental results at specific locations to check for the accuracy of model. About 55 time steps (in seconds) were required for the temperature to reach steady state which is approximately the time required by the fluid to travel through the tube.

![Figure 4.6 Average temperatures at the exit of pipe at different times for 4000W and 4700W](image)

Figure 4.6 Average temperatures at the exit of pipe at different times for 4000W and 4700W
4.3.3.1 Temperature Distribution in Cross Axial (Vertical xz and yz-Plane)

A clear increase in temperature is observed from the entrance of the applicator tube towards the exit as the fluid mixture moved in the vertical direction for both power levels (Figure 4.8a, 4.8b). The temperature at the very entrance of the applicator tube is constant as the fluid is not exposed to microwave irradiation immediately on entering the applicator tube. For $P_{in} = 4000$W, lower temperatures are observed at the center of the tube along the z axis (Figure 4.9a, 4.9b) compared to that at the walls, especially away from the direction of incident microwaves. The penetration depth of the fluid mixture studied here is 3.79cm at 915 MHz and the diameter of pipe is 3.2cm. As a result, much of the power incident is absorbed by the fluid at the surface of the tube and the interior remains at low temperature. In order to obtain more uniform central heating, the diameter of the tube should be adjusted.

For a fully developed laminar profile, the velocity of fluid at the center of tube is higher (0.033 m/s) compared to the fluid at the tube walls (0.01 m/s) (Figure 4.7a, 4.7b). As such, the residence time for the fluid traveling at the center of the tube is much lower compared to that traveling at the walls. Lower residence time means less exposure to microwave irradiation and hence lower temperature is obtained at the center of the tube even though electromagnetic power density is larger than at the walls. A focusing cavity is designed to reduce this effect, however the geometry of the tube prove ineffective for our fluid mixture with lower relative dielectric permittivity as it was originally designed to heat water. As the power level is increased from 4000 W (Figure 4.8a) to 4700 W (Figure 4.8b), this cooler region narrows as the fluid moves higher up in the applicator tube. The temperature profile in xz- plane matches well with the electromagnetic power loss density profile in the xz- plane, where heating is observed at the pipe exit away from microwave waveguide (Figure 4.8a, 4.8b). Figure 4.9a and 4.9b shows the
temperature profile in yz-plane facing the microwave irradiation direction for the two power levels of 4000W and 4700W.

![Velocity profile](image)

Figure 4.7 Velocity profile (m/s) for (a) Pin = 4000W and (b) Pin = 4700W

![Temperature distributions](image)

Figure 4.8 Temperature distributions (°C) in cross axial xz-plane for fluid mixture in (a) 4000W (b) 4700W
4.3.3.2 Temperature Distribution (xy- Plane)

Temperature distribution in the $xz$- plane was obtained for both the models. The cross sectional plots were obtained at five different locations in the tube; with one slice at the entrance ($z = -0.0651$), three in middle of tube at three different locations ($z = 0$, $0.0651$ and $0.127$) and one at the exit of tube ($z = 0.1889$). In order to investigate the transient effects, the cross sectional plot was also obtained for the start of the microwave heating ($t=1$sec) and at the end of one minute ($t=60$sec). It was observed that there was no further increase in temperature and the temperature remained steady from $t=55$sec after microwave heating was started. Figure 4.10 (a, b, c, d, e, f, g, h, i, j) represent, the corresponding temperature profiles. In order to compare the temperature profile for two power levels, the scale of the figures was changed such that the color map is the same. For instance, starting temperature of figure 4.10a and 4.10b is 30°C, although for 4.10b, the minimum temperature value is 45°C. The maximum and minimum values are represented in the figures with the triangles above and below scale.
Figure 4.10 Temperature distribution (°C) in $xy$ - plane for $Pin = 4000W$ (left) and 4700W (right) at $t = 60sec$; (a) and (b) at pipe entrance ($z = -0.065$), (c) and (d) at a distance of 0.065 from the entrance of pipe ($z = 0$), (e) and (f) at a center of pipe ($z = 0.065$), (g) and (h) at a distance of 0.195 from the entrance of pipe ($z = 0.127$) and (i) and (j) at the pipe exit ($z = 0.189$)
The lower temperature region in the tube center and towards the incident microwave was noticeable even at the tube entrance (Figure 4.10a, b, c, d), but it became more defined as the fluid travelled longitudinally (Figure 4.10e, f, g, h). The lower temperature region at the center is still very evident at the exit of the tube, and it is smaller for \( P_{in} = 4700W \) than that for \( P_{in} = 4000W \) (Figure 4.10i, 4.10j). The distribution pattern is the same for 4000W and 4700W, but the values are higher for 4700W, making it more uniform. In the radial direction, highest temperature was achieved at the distance farthest away from the center of the tube. Heating occurred at the walls of the tube mainly due to lower fluid velocity, while the center of the tube had lower temperature compared to the walls for both the power levels.
Higher central heating and higher average temperature was observed for higher power levels. This pattern is opposite to what is observed for water or for materials with higher dielectric permittivity. For water, central heating is more prominent than surface heating. The average temperature achieved is higher for water than for the fluid mixture studied here at same power levels. Water is a more polar substance compared to the fluid mixture studied here whereas the fluid mixture studied here has non polar components such as oil. Non polar nature of fluid increases as the reaction proceeds. The dielectric permittivity for the fluid mixture is very low compared to water and other polar solvents, resulting in lower power absorption and lower average temperatures. The microwave power absorbed by water is 24% (Salvi et al., 2011) vs. 18% absorbed by the fluid mixture studied here. A comparison of microwave heating of water in the same geometry (Salvi et al., 2011) and with an input power of 4000W is shown in figure 4.10. At time t=1sec, where the heating had just begun, the profile shows a slight increase in temperature along surface on the right, away from the waveguide (Figure 4.12 (a), (b), (c), (d), (e), (f), (g), (h), (i), (j)).

Figure 4.11 Temperature distribution (°C) in $xy$ - plane for $P_{in} = 4000$W at the center of the tube for (a) Oil, ethanol and catalyst mixture (left) (b) Water (right)
Figure 4.12 Temperature distribution (°C) in xy - plane for Pin = 4000W (left) and 4700W (right) at t = 1sec; (a) and (b) at pipe entrance (z = -0.065), (c) and (d) at a distance of 0.065 from the entrance of pipe (z = 0), (e) and (f) at a center of pipe (z = 0.065), (g) and (h) at a distance of 0.195 from the entrance of pipe (z = 0.127) and (i) and (j) at the pipe exit (z = 0.189)
The lowest temperature region corresponds to lower electric field intensity and energy density. This heating pattern (heating away from waveguide) was observed for water (Salvi et al., 2011; Zhu et al., 2007), where the surface heating began along the surface on the right. The temperature distribution as a function of distance from the center was plotted for $P_{in} = 4000\,W$ (Figure 4.13a) and $P_{in} = 4700\,W$ (Figure 4.13b) for different times (1s, 5s, 10s, 15s, 25s, 30s, 45s and 60s) at the tube exit. Temperature decreases towards the center and surface heating to the right is evident.
Figure 4.13 Temperature distribution in radial direction (x-axis) for (a) Pin = 4000W and (b) Pin = 4700W

4.3.4 Experimental Validation

Experiments were performed as described in the previous chapter, at the two power levels of 4000 W and 4700W. The temperatures were measured only at the exit of the applicator tube at nine different locations. For $P_{in} = 4700W$, the measured temperatures and those derived from the model at the same locations are in good agreement with a maximum variation of 7.0°C. For $P_{in} = 4000W$, slight variations were observed between the measured values and the values that were
derived from the model, especially at the innermost region, the maximum difference in temperature was 10°C. The higher values of temperature in the model are likely due to conductive heat losses through pipe. The innermost locations (a1, b1, c1) have the lowest temperature in both the model and the experiments; while the highest temperature was recorded at the outermost location close to the surface of the tube (a3, b3 and c3).

Table 4.2 Numerical and experimental temperature values

<table>
<thead>
<tr>
<th>Location</th>
<th>Power input 4700W</th>
<th>Power input 4000W</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature from model (ºC)</td>
<td>Temperature experimentally (ºC)</td>
</tr>
<tr>
<td>a1</td>
<td>66.0</td>
<td>58.61</td>
</tr>
<tr>
<td>a2</td>
<td>70.20</td>
<td>67.47</td>
</tr>
<tr>
<td>a3</td>
<td>76.0</td>
<td>75.79</td>
</tr>
<tr>
<td>b1</td>
<td>63.5</td>
<td>60.69</td>
</tr>
<tr>
<td>b2</td>
<td>64.54</td>
<td>71.70</td>
</tr>
<tr>
<td>b3</td>
<td>69.40</td>
<td>76.13</td>
</tr>
<tr>
<td>c1</td>
<td>63.06</td>
<td>58.60</td>
</tr>
<tr>
<td>c2</td>
<td>63.18</td>
<td>63.15</td>
</tr>
<tr>
<td>c3</td>
<td>66.6</td>
<td>71.86</td>
</tr>
</tbody>
</table>

Figure 4.14 Experimental validation and temperature distribution
4.4 Conclusions

The aim of this study was to develop a model in COMSOL Multiphysics 4.2 based on the experimental procedure carried out for microwave assisted biodiesel production. A multiphysics model coupling high electromagnetic field, heat transfer and fluid flow was developed. The flow profile followed the laminar flow profile with maximum flow velocity at the center of the tube and minimum at the tube walls. Maximum electromagnetic power density observed was $4.7 \times 10^6$ W/m$^3$ and $3.6 \times 10^6$ W/m$^3$ for 4000W and 4700W power input. Total power absorbed was 19% (756W) for 4000W power input and 13% (605W) for 4700W power input. Increase in temperature was observed as the fluid moved up in the tube. Highest temperature was obtained at the distance farthest away from the center of the tube. Central heating was observed in the upper region. Temperature ranged from 30 °C to 82 °C and 45 °C to 89 °C with an average temperature of 61°C and 73°C for 4000W and 4700W power inputs respectively. The temperature results were in good agreement with the experimental results. Surface heating was dominant for the oil ethanol catalyst mixture as opposed to central heating for water especially at the surface, far away from the incident microwaves. One of the main reasons is high dielectric loss factor for the fluid mixture studied here which decreases the penetration depth. The geometry of this process can be modified to decrease the diameter of the tube in order to obtain uniform central heating. This remains the future scope of the project.

4.5 References

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CHAPTER 5
CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

The goal of this project was to scale up the transesterification process for biodiesel production to a pilot scale using microwave technology and to develop a numerical model to study microwave heating effects. In order to achieve these goals, dielectric properties of pure biodiesel components (soybean oil, Ethanol and Methanol) and their various combinations (Alcohol-catalyst and oil/alcohol-catalyst) were experimentally measured at different temperatures ($30^\circ$C, $45^\circ$C, $60^\circ$C and $75^\circ$C) and frequencies (250 MHz to 4500 MHz). Results indicated that dielectric constant decreases with the increase in frequency, and is strongly dependent on temperature. Dielectric loss values varied for each combination and were dependent on factors such as frequency, temperature, presence of ions and polarity of the material under investigation. Addition of catalyst significantly increased the dielectric constant as well as dielectric loss of material due to conductive effects. Non polar nature of oil affects the interaction of biodiesel precursors (oil/alcohol-catalyst mixture) with microwaves. This study was important to understand the behavior of biodiesel components when they undergo microwave heating. Temperature dependent equations of dielectric loss and dielectric constant were obtained from this study and were used to define the material properties required for the development of a numerical model.

Second goal of this study was to design and operate a pilot scale microwave assisted biodiesel production process. Based on laboratory scale results, previously achieved in other studies, a continuous pilot scale biodiesel production process was designed. Transesterification process was carried out at two different temperatures $60^\circ$C and $75^\circ$C. A 915 MHz, 5 KW
focused microwave system was used for heating. Power level of 4000W and 4700 W was required to achieve a temperature of 60°C and 75°C respectively. Ethyl alcohol was used as a solvent and the catalyst used was sodium hydroxide (NaOH). Based on the laboratory scale results, alcohol to oil ratio used was 9:1, and the catalyst amount used was 0.18% by the weight of oil. Conversion rates from oil to ethanol obtained by this process were near 100% for both the temperatures investigated here. Biodiesel samples were qualitatively analyzed for glycerol content, kinematic viscosity, acid number, flash point, and cloud point, and were found to meet the ASTM standards. The conclusion of this study was that microwave technology can be used for production of biodiesel on an industrial scale with some modification to the process. The lower temperature of operation of 60°C still achieved more than satisfactory conversion. Advantages of microwave heating over conventional heating include shorter operation time, higher conversion due to molecular level heating, faster recovery of excess alcohol, and low energy input.

The final goal of this project was to develop a numerical model to study temperature profiles of a continuous flow microwave assisted transesterification process. The model was developed by coupling high frequency electromagnetic heating with non-isothermal fluid flow in COMSOL Multiphysics 4.2. The dielectric properties studied in chapter one was used to define the material dielectric properties for the model. The model was validated with the experiments performed on the course of this project. Total energy absorbed by the mixture was 18% for an input power of 4000W and 13% for an input power of 4700 W. The average temperatures obtained by the model matched with those obtained from experiments. Surface heating was dominant for both the power levels. One of the important reasons for this is a relatively low penetration depth of the biodiesel precursor materials.
This project’s results will greatly aid in further developments of microwave technology for faster and efficient production of biodiesel from vegetable oil. The numerical model developed herein will help in understanding the effects of various parameters affecting the microwave heating.

5.2 Future Work

Experimental and numerical study performed in this research work provides a tool for further developments in the biodiesel production process. A pilot scale study demonstrated in this study can be applied for an industrial scale production of biodiesel. Advanced microwave technology could be used for commercial production of biodiesel. Extraction of oil by use of microwaves on a pilot scale has also been demonstrated by Terigar et al., (2009).

The model developed here can be modified to examine other processes. It would be a significant step to study the reaction kinetics of transesterification reaction and input those values in the model to obtain the conversion rate. Although the pilot scale plant results were promising, the microwave system used for this study was custom designed for ballast water heating. The geometry of the microwave system was build based on the dielectric properties and penetration depth of saline water. It would be significant to check for the optimum tube diameter so as to heat the oil/alcohol-catalyst mixture with maximum energy efficiency.

Addition of reaction kinetics to the model will help in obtaining the optimum operation temperature to carry out the reaction process. The overall biodiesel production process from oil extraction to transesterification can be made more energy efficient by studying different parameters affecting microwave heating.
VITA

Pranjali D. Muley was born in India in April 1986. She received her Bachelor of Technology degree in Petrochemicals in May 2008 from Dr. Babasaheb Ambedkar Technological University, India. Pranjali started her Master of Science in Biological and Agricultural Engineering program at Louisiana State University in August 2009 with a concentration in pilot scale biodiesel production. She expects to receive the degree of Master of Science in Biological and Agricultural Engineering at the spring 2012 commencement.