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Investigations of transesterification of canola oil with methanol and ethanol for a new efficient method of biodiesel production

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A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemical and Biochemical Engineering
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INVESTIGATIONS OF TRANSESTERIFICATION OF CANOLA OIL WITH
METHANOL AND ETHANOL FOR A NEW EFFICIENT METHOD FOR
BIODIESEL PRODUCTION

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Abstract

Transesterification of vegetable oil to biodiesel is a multistep process affected by mass transfer, mixing and chemical reaction equilibrium. Attempts have been made in this study to overcome these limitations by gradually feeding oil into a pool of alcohol. This approach provided large excess of alcohol to allow reaction to proceed further as well as allowed easy dispersion of oil into the alcohol. As a result improved conversion of feed, higher yield and better product quality were achieved. Comparisons have been made with other methods to show the differences and highlight improvements. Reactions were conducted at various reaction conditions for transesterification of canola oil with both methanol and ethanol using potassium hydroxide as a base catalyst. Reaction progress was followed by analysing samples collected at regular intervals from one liter reactor using Gas Chromatography Technique. The quality and yield of biodiesel obtained with the Gradually Fed method (G-Fed Method) were significantly improved, compared to conventional method. Detailed comparison studies are included for methanolysis and ethanolysis in G-Fed method. Methanolysis gives better yield over ethanolysis in G-Fed method. In addition kinetic studies have been conducted in detail and a kinetic model is developed to predict reaction rate constants of the transesterification reaction in batch as well as G-Fed method. The kinetic model following second order was used to determine the kinetics of canola oil in ethanolysis reaction at different temperature in batch runs. For the kinetic study of G-Fed method appropriate reaction rate equations are formulated including the mass transfer effects for different cases of order of reaction. Methanolysis

and ethanolysis in G-fed method follow pseudo first order with higher rate constant with methanol.

Key Words: Biodiesel, Transesterification, Alcoholysis, Kinetics, Mass Transfer, Gradual Feeding Method

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Chapter 1

1   Introduction

1.1   General Introduction

A large part of energy consumed in the world today comes from fossil sources such as petroleum, coal and natural gas. In 2010, the energy consumption ratio in G20 nations rapidly increased by more than 5% than the consumption ratio reported in previous year [1]. The demand is increasing day by day in the countries like India and China. The sources of energy are limited and the rising demand will make them perish in the coming future. Currently all over the world, research work is being carried out to develop alternative sources of renewable energy. These include: biomass, solar, wind, hydro and geothermal. The alternatives developed should have potential to combat issues like pollution, global warming and most important of all should be environment friendly [2]. BIODIESEL is one such alternative to replace fuel obtained from fossil sources in future. It is a promising renewable fuel whose importance is growing steadily. It can be easily blended with petroleum based diesel fuel to offset some of the environmental problems associated with petro-diesel. However feedstock costs and their availability have restricted large scale production and usage of biodiesel. There is also ongoing need to improve efficiency of biodiesel production processes, reduce losses during production, and minimize energy consumption. Such improvements would lead to lower cost of production and make biodiesel more competitive in the future.

Biodiesel is defined as mono-alkyl esters obtained from transesterification of vegetable oils and alcohols. Vegetable oils are not used directly as the fuel due to their high viscosity and poor fuel characteristics during combustion. Transesterification or alcoholysis is the common method to produce biodiesel from reaction of vegetable oils and alcohol to produce liquid fuel of acceptable quality. It is a sequence of three reversible reactions: the triglycerides present in vegetable oils react with alcohol to produce diglycerides; these diglycerides form monoglycerides in second step; and monoglycerides form glycerol in third step. With each reaction step one mole of alkyl esters (Biodiesel) is formed. The reaction is termed as 'methanolysis' when the transesterification is carried out using methanol as precursor and is called 'ethanolysis' if ethanol is used. Base or acid catalyst is used to accelerate the reaction. The base catalyst is preferred over acid catalyst as it is 4000 times faster as compared to acid catalyst. However the base catalyzed reaction is reported to have slow reaction rates in the initial and final stages. The mass transfer limitation is due to the low solubility of methanol/ ethanol in oil in the initial phase of the reaction [4]. Liu et al. [5] developed a model which proved that the reaction is mass transfer and kinetic controlled. To overcome this issue methods like co-solvent enabled method [6-10], low frequency ultra-sonication [11-13] are applied to obtain homogenous single phase to increase the reaction rate and reduce mass transfer limitation. A better understanding of alcoholysis could be achieved if the phase behavior is related to the mass transfer and kinetics during the progress of the reaction.

1.2   Scope and Objectives

In our study, novel cost effective and compact method is develop on a laboratory scale to produce biodiesel using canola oil and methanol/ethanol in the presence of potassium hydroxide as a base catalyst. The kinetic and mass transfer studies are investigated for the biodiesel produced with the application of this method.

This thesis has seven chapters including chapter 1 on introduction. Chapter 2 presents a detail literature review on biodiesel, biodiesel testing methods, current methodologies of biodiesel production and its advantages and disadvantages. Chapter 3 presents the development of new G-Fed (Gradually Fed) method. This concept is introduced in order to reduce the mass transfer limitations observed in transesterification reaction. Reactions were carried out at various conditions using canola oil as feedstock and methanol in a reactor designed at laboratory scale. The chapter highlights the differences and improvements in conversion of feedstock. Comparisons have been made with other methods investigated so far in literature. Chapter 4 reports on the application of G-Fed method for transesterification of canola oil and ethanol. Comparison studies have been carried out to highlight differences with fuel obtained with application of G-Fed method for methanolysis of canola. Batch runs are conducted for ethanolysis and methanolysis of canola oil to point out distinctions in the two systems and fuel quality. Chapter 5 presents investigations on kinetics of canola oil using ethanol as precursor. A kinetic model is developed to obtain the rate constants for the ethanolysis of canola oil. Chapter 6 presents the development of kinetic rate equations for G-Fed method. The kinetic models are developed with the assumptions for different order of the reaction and obtain the best fit. Finally Chapter 7 presents the conclusions obtained as a result of this study. The

summary of this work with recommendations and scope of future work is included in this chapter.

1.3   Thesis Format

This thesis is written in the format of 'Integrated Article thesis' as specified by the Faculty of Graduate Studies of the University of Western Ontario. Individual chapters are presented as technical papers without an abstract. Each chapter has its own conclusions and references with symbols and abbreviations listed at the end. Appendices are presented at the end of the individual chapters.

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Chapter 2

2 Literature Review

World market is concerned with issues of the increasing cost of the diesel fuels, the negative effect of greenhouse gas emissions, the depleting sources of petroleum products. It has made the need for an alternative fuel a necessity. BIODIESEL is an answer to all these major issues and in recent times it is being considered as the 'fuel of future'. Some of the early biodiesel initiatives took place in 1981 in South Africa and then in 1982 in Austria, Germany and New Zealand. In 1985, a small pilot plant was built in Austria using rapeseed oil for production of methyl esters, and in 1990 the first farmers' cooperative was started for commercial production of biodiesel. Soon there were fleet tests that lead to engine warranties by most tractor producers such as John Deere, Ford, Massey-Ferguson, and Mercedes. The following year in 1991 saw the introduction of the first fuel standard ON C 1190 for biodiesel by the Austrian Standardization Institute to ensure quality control for the fuel. Subsequently, biodiesel plants were installed in other parts of the European Union, East europe, Malaysia and the USA [1]. In 2006, Canada announced the commissioning of the first commercial scale biodiesel plant with a production capacity of 35 million litres per year [2].

2.1 Basic Definitions and Fuel Properties

Biodiesel is the mono alkyl esters of long chain fatty acids derived from renewable feed stocks, such as vegetable oil or animal fats, for use in compression ignition engine. Biodiesel is commonly composed of fatty acid (m)ethyl esters that can be prepared from

triglycerides in vegetable oils by transesterification with (m)ethanol. The resulting biodiesel is quite similar to conventional diesel fuel in its main characteristics. Besides offering similar power to diesel fuels, and having a higher flash point than diesel, biodiesel is less toxic, and provides significant lubricity improvement over petroleum diesel. Table 2.1 shows the comparison of the physical properties of diesel fuel and biodiesel.

Table 2.1 Properties of Diesel Fuel and Biodiesel [3]

Properties	Diesel fuel	Biodiesel
Viscosity (cP)	2.7 at 38^0C	4.41 at 40^0C
Cetane Number	47	51.7
Heat of Combustion (MJ/kg)	453	407
Flash Point (^{0}C)	52	185
Cloud Point (^{0}C)	-15	-3
Pour Point (^{0}C)	-33	-7
Specific Gravity	0.85	0.88

The density and viscosity difference are acceptable and the higher flash point of biodiesel makes it a safer fuel. Biodiesel has low cloud point which makes it unfit for use in extremely cold weathers. The problem can be overcome by use of certain additives, by blending with petro-diesel, and also by employing branched chain alcohols for the synthesis of biodiesel. Lee and coworkers investigated the use of branched alcohols for production of biodiesel, and compared the crystallization properties with those of the un-branched one. It was proposed that branched chain alcohols would not pack together

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easily, thereby lowering the melting points and improving low temperature properties. A decrease in cloud point was recorded; however the increase in the production cost due to the use of expensive branched chain alcohols for the reaction is a hindrance to commercial feasibility [4].

2.1.1 Physiochemical Properties of Biodiesel

The redox characteristics of biodiesel make it a reducing agent for materials, such as brass, bronze, copper, lead, tin and zinc. For this reason; contact of biodiesel with these materials must be avoided [5]. Materials such as aluminum, steel, fluorinated polymers and Teflon do not react with biodiesel and can be used to handle it. In addition, biodiesel shows mild solvent properties; hence contact of biodiesel with painted or varnished surfaces as well as rubber devices, such as hoses, seals and gaskets, may cause problems. The storage stability of biodiesel is adversely affected by the presence of unsaturated alkyl components. The olefinic moieties in biodiesel fuel can undergo oxidative degradation via exposure to air with deleterious results, including formation of solids and gums [5]. Biodiesel can be used neat and when used as a pure fuel it is known as B100. However, it is often blended with petroleum-based diesel fuel and when this is done the blend is designated as "BXX" where XX is the percentage in volume of biodiesel in the blend. For instance, B20 is a blend of 20% volume biodiesel and 80% volume petro-diesel. In USA blends of 20% (B20) and lower are approved, but there is also some interest to utilize biodiesel blends over 20% [6].

2.1.2 Advantages and Disadvantages of Biodiesel

Biodiesel is renewable in nature and posses environmentally benign character. Biodiesel synthesis from biomass offers an option to produce a transportation fuel that is

biodegradable and provides a pathway for the recycling of carbon dioxide emissions. The biodegradability has been reported to be more than 90% within 3 weeks, thereby alleviating potential hazards in the case of spills or other accidents. It was reported that biodiesel has significant contribution to the reduction of green house gases by at least 3.2 kg CO_2 equivalent per 1 kg biodiesel, thereby greatly reducing the emission of green house gases [7]. The biodiesel emissions for net CO_2 are lower than petro-diesel emissions, and even for the biodiesel blends those emissions are reduced depending on the blend used [8]. Fig 2.1 compares the net CO_2 life cycle emissions of petro-diesel, pure biodiesel and the blend B20, and it is obvious that there is a considerable reduction of those emissions. The net CO_2 emissions were reduced by 16% and 79% by using the blend of B20 and B100 respectively. Engine and emission tests demonstrate that biodiesel is superior to its petroleum counterparts. The decrease in emissions especially of carbon monoxide by 20%, hydrocarbons by 32%, soot by 50% and particulate matter 39% are now well-established facts.

In addition, the fuel is essentially sulfur free so the sulfur oxide emissions are almost eliminated. The NO_x emissions have been reported to increase, when unsaturated methyl esters are used, while they decrease with the use of saturated methyl esters. This slight increase, in the NO_x emissions when using unsaturated methyl esters can be altered by adjusting the injection timing in the engine [9]. Biodiesel also has a high lubricity so blending it with the low-sulfur diesel solves the problem of lubricity losses when the sulfur is removed. The addition of biodiesel, even in small amount greatly enhances the lubricity of the fuel. It has been shown that the addition of 1.5wt% biodiesel to diesel with a 15 ppm sulfur concentration can change the lubricity from an unacceptable level to

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an acceptable level [8]. It was reported in a study that the lubricity of ethyl ester is better than methyl ester. It was also stated that lubricity of mixed fuel is better than the lubricity of methyl ester [10].
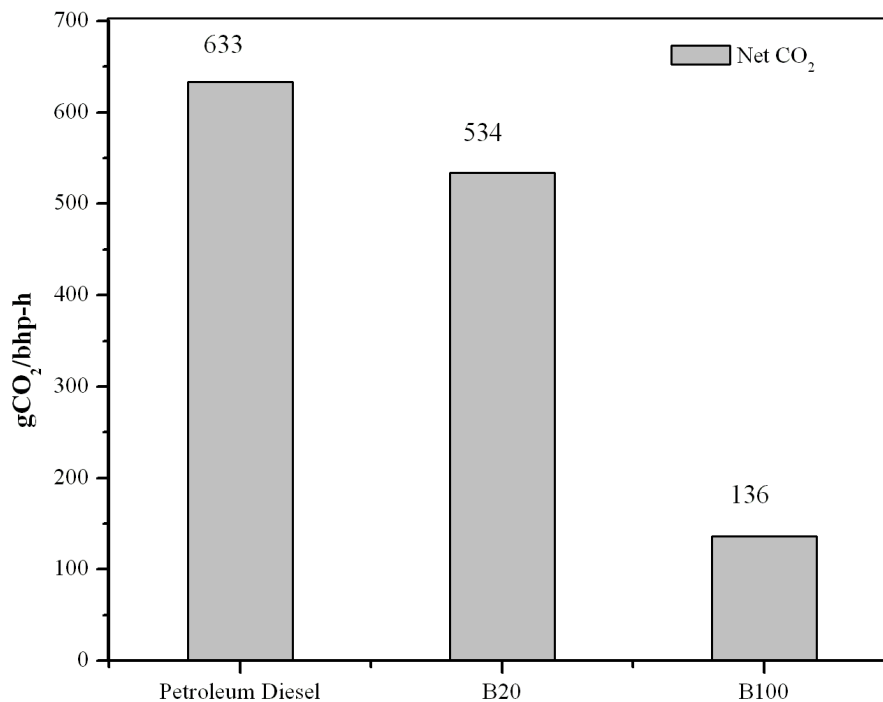
Figure 2.1 Comparison of Net CO$_2$ Life Cycle Emissions for Petroleum Diesel and Biodiesel Blends [11].

2.2   Chemical Reactions and Thermodynamics

Transesterification

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis. The applicability of transesterification is not restricted to laboratory

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scale. Several relevant industrial processes use this reaction to produce different types of compounds. The transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. The presence of catalyst accelerates the reaction to the product side. In order to achieve high yield of esters the alcohol has to be used in excess. The reaction consists of transforming triglyceride into fatty acid alkyl esters, in the presence of an alcohol and a catalyst with glycerol as the major by product. As the reaction is reversible, excess alcohol is used to push reaction to product side. The stoichiometric ratio of the reaction is 3:1. The reaction is inherently exothermic and is accompanied by a temperature rise of nearly 1 to 2 degrees, immediately after catalyst addition. The molar masses of the esters are approximately one third that of the triglycerides which in turn leads to significant reduction in the viscosity. Thus it is therefore a good process to make petro diesel substitutes from vegetable oils. The overall reaction scheme can be shown in fig 2.2:

$CH_2 - OOC - R_1$

$CH - OOC - R_2 \quad + \quad 3R'OH \xrightleftharpoons[]{Catalyst} \quad R_2 - COO - R'$

$R_1 - COO - R'$ $CH_2 - OH$

$R_3 - COO - R'$ $CH_2 - OH$ $CH_2 - OOC - R$

Alcohol   Esters   Glycerol   Glyceride
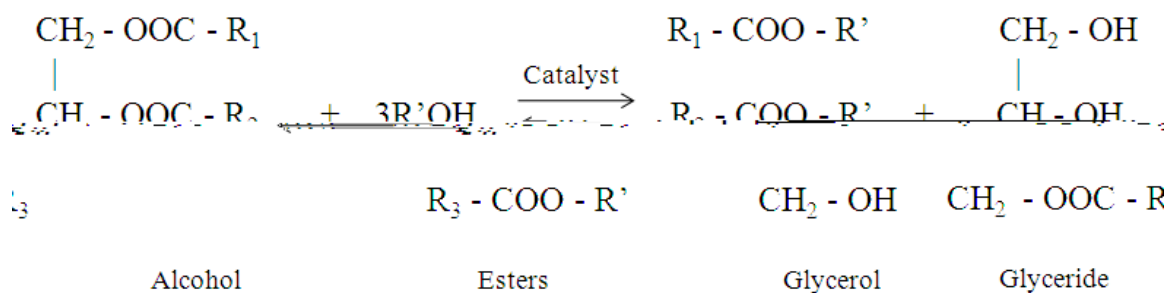
Figure 2.2 Transesterification reaction [3, 12].

The transesterification is a three step reaction as shown below in fig 2.3

Triglyceride + Alcohol ⇌ Diglyceride + Alkyl Esters

Diglyceride + Alcohol ⇌ Monoglyceride + Alkyl Esters

Monoglyceride + Alcohol ⇌ Glycerol + Alkyl Esters
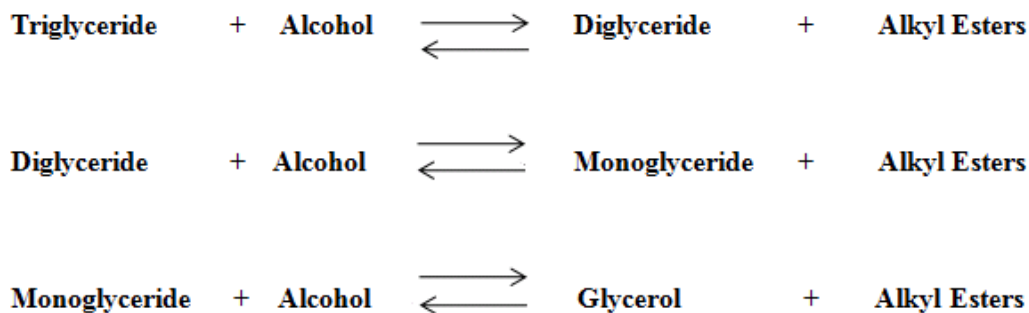
Figure 2.3 Stepwise reaction of transesterification [12].

Mostly base catalyst is used for the process and thus it is very important to understand the mechanism of base catalyst with the alcohol during the process. The base catalyzed mechanism is shown in Fig 2.4

$$ROH + B \rightleftharpoons RO^- + BH^+ \qquad [1]$$

$$\text{R'COO–CH}_2 \\ \text{R''COO–CH} + {}^-OR \rightleftharpoons \text{R''COO–CH} \\ \text{H}_2\text{C–OCR'''} \qquad \text{H}_2\text{C–OCR'''} \qquad [2]$$

[3]

[4]
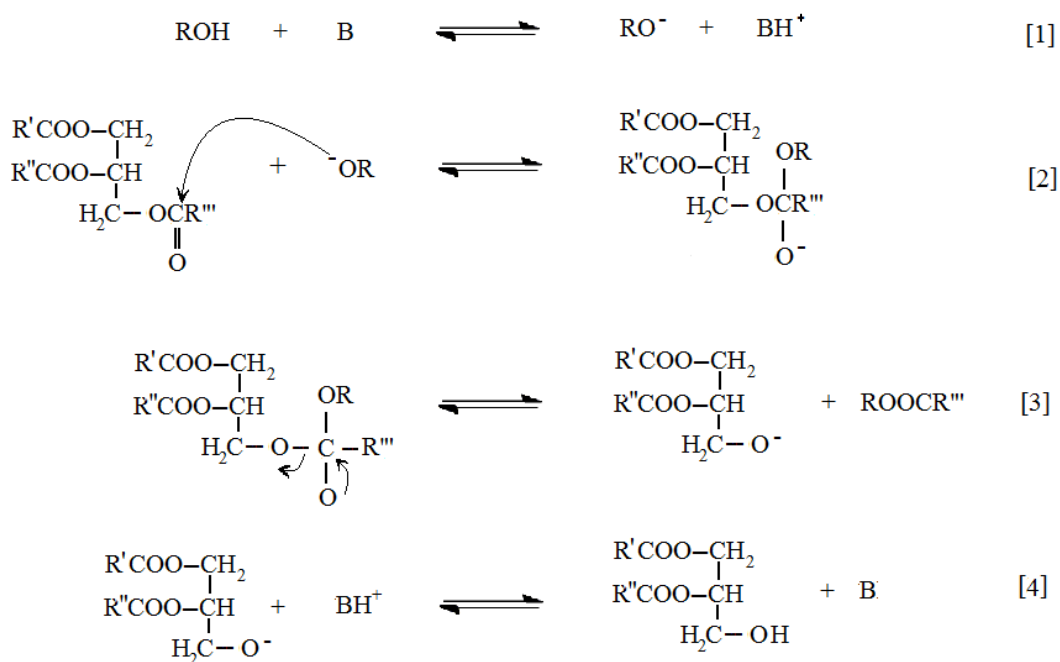
Figure 2.4 Mechanism of base catalyst in the reaction of transesterification of vegetable oil [13].

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The first step (Eq. 1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq. 2), from which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq. 3). The latter deprotonates the catalyst, thus regenerating the active species (Eq. 4), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol [12]. Many scientists have worked on the transesterification process and many papers are available in the scientific and patent literature [14-23].

Saponification

The production of soap sometimes called alkaline hydrolysis, converts tri-acyglycerols to glycerols and a mixture of salts of long chain carboxylic acids. As seen in fig 2.5 and 2.6, the reaction can be carried out with an ester (i.e. triglycerides) or with carboxylic acids (i.e. free fatty acids). However the production of fatty acids is an intermediate step when triglycerides are directly used for saponification.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \quad + \quad NaOH \quad \xrightarrow{\text{Heat}} \quad R-\overset{\overset{\displaystyle O}{\|}}{C}-O^-Na^+ \quad + \quad H_2O$$
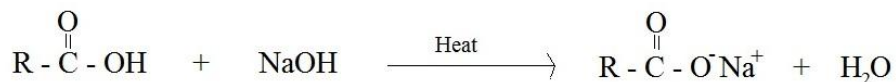
Figure 2.5 Saponification from free fatty acid

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR \quad + \quad NaOH \quad \xrightarrow{\text{Water}} \quad R-\overset{\overset{\displaystyle O}{\|}}{C}-O^-Na^+ \quad + \quad R-OH$$

Figure 2.6 Saponification from ester.

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2.3 Biodiesel Standards

For commercialization and market penetration of fuels, certain standards for fuel performance and characteristics need to be established and followed. Many countries have their independent standards for biodiesel fuel. ASTM standards are the most significant ones in order to determine the quality of the fuel. With the increasing number of studies in further detail on fuel production, chemistry and performance, these standards are being revisited and significant changes remain on going. Table 2.2 shows the North American Standards for Biodiesel, ASTM (American Society for Testing and Materials) requirements for biodiesel.

Table 2.2 North American Biodiesel-standard ASTM D6751-03 [24].

Property	Limits	Units	Test Method
Water and sediment	≤ 0.050	% Volume	D2709
Kinematic Viscosity @ 40^{0}C	1.9-6	mm^2/s	D445
Flashpoint	≥ 130.0	^{0}C	D 93
Sulfur (15)	≤ 0.0015	%	D5453
Sulfated Ash	≤ 0.020	% mass	D 874
Carbon Residue	< 0.050	% mass	D4530
S 500	< 0.050	% mass (ppm)	D5453
Copper Strip Corrosion	< No. 3		D 130
Cetane number	> 47		D 613
Cloud Point	Report	^{0}C	D2500
Acid Number	< 0.80	Mg KOH/g	D 664
Free glycerine	0.020	% mass	D 6584
Total Glycerine	0.240	% mass	D 6584
Phosphorous Content	< 0.001	% mass	D 4951
Distillation T, 90% recovery	< 360	^{0}C	D 1160

The ASTM initiated the development of a standard for biodiesel by designating a task force and the first provisional biodiesel specification was released in 1999 known as the ASTM PS 121-99. After this the refining procedures for the standards continued and several precision and bias tests for the analytical methods were conducted. Finally in March 2002 the ASTM published its first full biodiesel standard, ASTM D6751 [25]. Table 2.3 shows the ASTM standards of maximum allowed quantities in diesel and biodiesel.

Table 2.3 The ASTM standards of maximum allowed quantities in diesel and biodiesel [24].

Property	Diesel	Biodiesel
Standard	ASTM D975	ASTM D6751
Composition	HC[a] (C10-C21)	FAME[b] (C12-C22)
Kinematic Viscosity at 40^0C (mm^2/sec)	1.9 to 4.1	1.9 to 6.0
Specific Gravity (g/ml)	0.85	0.88
Flash Point (^{0}C)	60 to 80	100 to170
Cloud Point (^{0}C)	-15 to 5	-3 to 12
Pour Point (^{0}C)	-35 to -15	-15 to 16
Water, vol%	0.05	0.05
Carbon, wt%	87	77
Hydrogen, wt%	13	12
Oxygen, wt%	0	11
Sulfur, wt%	0.05	0.05
Cetane number	40 to 55	48 to 60
HFRR[c], microns.	685	314
BOCLE[d], scuff (g)	3,600	> 7,000

[a] Hydrocarbons. [b] Fatty Acid Methyl Esters. [c] High Frequency Reciprocating Rig. [d] Ball-on-cylinder Lubricity Evaluator.

2.3.1 Total and free Glycerol

The total and free glycerol content in the biodiesel is a crucial and very important parameter for the quality analysis. The ASTM limit for free glycerol is 0.02 mass % and the total glycerol (free and chemically bound glycerol (CBG)) is limited to 0.240 mass %. The total glycerol in the system is related to the free glycerol and CBG in the following manner:

$$G_{total} \quad = G + [(MG \text{ X } 0.25) + (DG \text{ X } 0.15) + (TG \text{ X} 0.10)] \ = G + CBG$$

Where the G represents the free glycerol and the MG, DG and TC refer to the mono, di and triglycerides, their concentration being multiplied by the respective glycerol moiety, which is collectively referred to as CBG or chemically bound glycerol in this study. Gas chromatography (D 6584) is the reference analytical method used to determine the total and free glycerol content in biodiesel by measuring the levels of glycerol and the individual glycerides [24]. The solubility of glycerol in methyl esters is 0.028 ± 0.003 wt %, measured higher amounts of free glycerol suggest that incomplete separation has taken place [26]. In addition, increased levels of free and chemically bound glycerol in biodiesel are associated with carbon deposits in the engine due to incomplete combustion. It has been also been reported that combustion of glycerol produces acrolein, a known carcinogen. But it was reported that increase in biodiesel concentration usually reduces acrolein emissions but by an amount too small to be quantified [11].

2.4 Analytical Methods

Gas Chromatography (GC) has to date been the most widely used method for the analysis of biodiesel due to its generally higher accuracy in quantifying minor components [27].

However the accuracy of GC analysis can be influenced by factors such as baseline drift, overlapping signals, etc. It is not always clear that such factors are compensated for in such reports on biodiesel analysis. The first report on the use of capillary gas chromatography discussed the quantification of esters as well as mono-, di-, and triacylglycerols [28]. High Performance Liquid Chromatography (HPLC) has a general advantage compared to GC, the reagent consuming derivatizations are not necessary, which reduces analysis time. However there are few works done of HPLC applied to biodiesel than GC analysis. This system allowed for the detection of mono-, di-, and triacylglycerols as well as methyl esters as classes of compounds. The system was useful for quantifying various degrees of conversion of the transesterified reaction [29]. Gel Permeation Chromatography (GPC) is very similar to HPLC in instrumentation except for the nature of the column and the underlying separation principle, namely molecular weight of the analysis for GPC. The use of GPC for the analysis of transesterification products was investigated. Refractive index detector and tetrahydrofuran as mobile phase was used. Mono-, Di-, and triacylglycerols as well as the methyl esters and glycerol could be analyzed with this technique. The method was tailored for palm oil and the standards were selected accordingly [30]. However; in general GC analysis is used for the analysis of the biodiesel samples in terms of products and intermediates.

2.5 Business and Cost Issues

The greatest hurdle to commercialization of biodiesel is the cost of production. Currently, the raw material costs and the cost of production are keeping the retail price of biodiesel too high for it to be an option for many users. The current method used for the production of biodiesel is with large batch reactors. Although the production is conducted on large

scale, there are still many problems with using crude feed stock [31]. Until this problem is resolved with measures such as a continuous process and the use of crude oils waste fats, such as used cooking oils and abattoir fats, the cost of production will remain relatively high. The recovery of high quality glycerol, a by-product which is required for many other processes, would also contribute to substantially reducing production costs

2.6   Process Variables

The reaction parameters affecting the extent and rate of completion include; the nature of the feedstock and alcohol, type of catalyst, molar ratio of alcohol to oil, reaction temperature and the in homogeneity of the reaction mixture (phase behaviour).

2.6.1   Feedstock

Vegetable oils are commonly used, besides that biodiesel can be produced from other feed stocks like animal fats and recycled greases. A material with high triglycerides and low free fatty acid content is preferred. The free fatty acid content of different feedstock is listed in Table 2.4. The feasibility of fats and oils as feedstock for biodiesel results from their molecular structure and high energy content. Thus long chain, saturated, un-branched hydrocarbon chains in fatty acids is fair well in this regard.

Table 2.4 Free fatty acid content of various feed stocks [32].

Feedstock	% FFA
Refined vegetable oils	< 0.05%
Crude vegetable oil	0.3-0.7%
Restaurant waste grease	2-7%
Animal Fat	5-30%
Trap Grease	40-100%

Restaurant frying oil is good source of biodiesel, this enables cheap production and provides a solution to the disposal problem especially after the onset of the Creutzfeldt - Jakob disease (CJD: technical name for Mad Cow Disease). Ma *et al*. (1998) investigated the transesterification of Beef Tallow [31]. Much research work is done on the alcoholysis of triglycerides, such as fish oils, tallow, soybean, rapeseed, cottonseed, sunflower, safflower, peanut, coffee oil and linseed oils [21, 31, 33-41]. The selection of feedstock depends on the vegetable oils available in the country. In North America canola oil, soybean oil and rapeseed oil is produced in abundance thus it could be a fair choice for the process. Table 2.5 shows the constituents of Canola, Rapeseed and Soybean oil.

Table 2.5 Constituents of different types of vegetable oil[8]

Component	Canola	Rapeseed	Soybean
Triglycerides (%)	94.4-99.1	91.8-99.0	93.0-99.2
Crude Oil	Up to 2.5	Up to 3.5	Up to 4.0
Water-degumed	Up to 0.6	Up to 0.8	Up to 0.4
Acid-degummed	Up to 0.1	-	Up to 0.2
Free Fatty Acids (%)	0.4-1.2	0.5-1.2	0.5-1.6
Unsaponifiables (%)	0.5-1.2	0.5-1.2	0.5-1.6
Tocopherols (ppm)	700-1200	700-1000	1700-2200
Chlorophylls (ppm)	5-35	5-35	Trace
Sulphur (ppm)	3-15	5-25	Nil

The vegetable oil mostly contains C 18 fatty acids, like stearic acid, oleic acid, linoliec acid. In particular canola oil mainly contains oleic acid (with one double bond) and

linoleic acid (with two double bonds) with traces of palmitic acid (C 16 group), stearic acid (C 18 group) and linolinic acid (C 18 group with three double bonds). Table 2.6 shows the fatty acid composition of canola oil. The major content of canola oil is oleic acid and linoleic acid.

Table 2.6 Composition of Canola Oil [42]

Fatty Acid	Formula[a]	M^b (g.mol^{-1})	% molar	% mass
Miristic	C14:0	228.38	0.0575	0.0469
Palmitic	C16:0	256.43	7.3757	6.7565
Palmitoleic	C16:1	254.41	0.1910	0.1736
Stearic	C18:0	284.48	2.0964	2.1305
Oleic	C18:1	282.47	48.0179	48.4533
Linoleic	C18:2	280.45	31.9683	32.0275
Linolenic	C18:3	278.44	9.2860	9.2365
Arachidic	C20:0	312.54	0.4809	0.5369
Behenic	C22:0	340.59	0.2960	0.3602
Erucic	C22:1	338.58	0.2303	0.2785

[a] In Cx:y, x= number of carbons, y= number of double bonds

M^b = Molecular weight

2.6.2 Types of Alcohols

Among the alcohols used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol. However; for the transesterification reaction methanol and ethanol are used more frequently. Methanol is produced from natural gas, while ethanol is obtained from ethylene. Ethanol can also be produced from renewable resources like wheat sugarcane, sugar beet and sweet sorghum etc. Ethanol is more

hygroscopic than methanol, therefore is more susceptical to soap formation. The research work so far reports excessive emulsion formation during the ethanolysis of vegetable oils [43-45]. An investigation was carried out on methanolysis of menhaden oil using straight chained and branched alcohols in single-phase system at 60^0C. The results suggested that the straight chain alcohols were more reactive than the corresponding branched ones. It was observed that the degree of oil conversion to fatty esters decreased with the increase in the carbon chain length [46].

2.6.3   Catalyst Types and Concentration

The transesterification reaction can be catalyzed by alkaline or acid catalysts. Enzymes are also used for transesterification but the use of lipase as biocatalyst is very expensive and so commercializing the process of biodiesel with the help of enzymes is still under research. The mechanism for acid and base catalyst reactions is similar; it differs with the type of feedstock used for reaction. However, the reactions with acid catalyst reduces by 4000 times [47, 48]. Further the acids are more likely to cause corrosion problems and thus commercially; base-catalyzed reactions are favored more as compared to acid-catalyzed reactions. The alkalis include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. Sulfuric acid, sulfonic acids and hydrochloric acid are usually used as acid catalyst. As disadvantages alkaline catalyst are unable to esterify free fatty acids and also require very rigorous anhydrous conditions. The moisture will interact with alkoxide to produce hydroxide ions and will increase the formation of hydroxide ions via the hydroxide-ethoxide equilibrium. The hydroxide ions react with the ester bonds to produce soap irreversibly. Alternatively in an anhydrous system, alkaline

catalyst can form soap with the free fatty acid present in the substrate. This soap consumes the catalyst, makes the alkyl esters soluble in glycerol and thus, reduces the efficiency of the system. These limitations makes alkaline catalyst unsuitable for transesterifying waste fats and oils where acid content and moisture level are high, but contrary to that can give good yields with refined oils in less reaction time. Sodium hydroxide and potassium hydroxide is most commonly used in industry as it is cheap and convenient [49]. Potassium hydroxide can be neutralized to produce artificial fertilizer decreasing the problem of waste water treatment, the washed water mixture can be neutralized using phosphoric acid [50].

Many researchers have studied the effects of catalyst concentration on the yield and rate of conversion. Nye and Southwell reported that no catalysis occurred before all FFA in the feedstock had been neutralized, which required about 0.2wt% NaOH [51]. It was reported ester conversion at 6:1 molar ratio of alcohol/oil for 1% NaOH and 0.5% NaOMe, it was also observed that for both the catalysts used in the study conversion was similar after 60 min [41]. As a catalyst in the process of alkaline alcoholysis mostly sodium hydroxide or potassium hydroxide has been used in concentration of 0.4% to 2% w/w of oil. Refined and crude oils with 1% either sodium hydroxide or potassium hydroxide catalyst resulted in successful conversion. Methanolysis of soybean oil with the catalyst concentration of 1% potassium hydroxide has given the best yields and viscosities of the esters [39]. Dorado and his coworkers reported that both excess as well as insufficient amount of catalyst may cause soap formation. The study stated that 2% of catalyst concentration produces emulsion, soap formation makes the separation of esters difficult from the glycerol phase [52]. Although no strong literature work is available

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with respect to the technical support. In most of the studies, 1% w/w catalyst concentration was stated as the optimum value for the transesterification of vegetable oils.

2.6.4 Alcohol to Oil molar ratio

The transesterification is an equilibrium reaction; it requires an excess of alcohol to drive the reaction towards completion. Thus the molar ratio of alcohol is one of the most critical variables in the experiment. The molar ratio for oil to alcohol by stoichiometry is 1:3. Some researchers have also reported the use of molar ratios up to 86:1. It was observed that as the molar ratio increased from the stoichiometry requirement of 3:1 to an excess of 6:1, the ester yield increased from 82% to 98% in an hour. It was also suggested that molar ratios in excess of 6:1, would interfere with the separation of glycerol through gravity settling and complicate the product recovery, thus molar ratio of 6:1 was considered to be optimum [49].

2.6.5 Moisture and Free fatty acid content

The glycerides and alcohol must be anhydrous for alkali-catalyzed transesterification as water causes a partial reaction change to saponification, which produces soap [53]. The soap consumes the catalyst and reduces the catalytic efficiency as well as causing an increase in viscosity, the formation of gels, and difficulty in achieving separation of glycerol. Methanol, being a solvent for both esters and alkali, facilitates saponification [54]. It was suggested that the free fatty acid content of the refined oil should be as low as possible, below 0.5% [31]. The conversion in refined oil is higher as compared to crude oil because of the presence of extraneous material in the crude [49]. Sodium hydroxide and Sodium alkoxide reacted with moisture and carbon dioxide in the air diminishing

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their effectiveness. Some researchers recommended the use of a nitrogen atmosphere for the reaction. This was however, deemed unnecessary by Freedman and his coworkers [41].

2.6.6 Temperature

The temperature is limited to the boiling point of the alcohol for atmosphere-pressure base catalyzed reactions. An increase in temperature would accelerate the conversion of triglycerides to methyl esters but at the same time would also increase the saponification reaction at a much higher rate. Saponification indirectly leads to deactivation of the catalyst affecting the reaction rate.

2.6.7 Non-homogeneity of the reaction mixtures

Mixing is very important in the transesterification reaction, as oils or fats are immiscible with sodium hydroxide-methanol/ethanol solution. Due to the immiscible properties, the transesterification reaction is mass transfer limited. Intensive stirring does not result in a satisfactory increase in the reaction rate due to the unavoidable separation of a glycerol phase, which results in the removal of the catalyst. Also high temperatures and pressure conditions forms emulsion increase in saponification associating to hazards. Various ways of mixing are applied to make these phases a homogeneous phase. Many methods processes have been developed to increase the miscibility of the phases and decrease the mass transfer lag observed in the initial stage of the reaction. The low frequency ultra-sonication [55-59] and co-solvent enabled systems [60-63] are available in literature and studied the most among the other processes developed so far.

2.7 Production processes

2.7.1 Low frequency ultra-sonication

Low frequency ultra-sonication is a useful tool for emulsification of immiscible liquids. Ultra-sonication processing technology can be used for various purposes. It can be used for reduction of the particle size in minerals, powders and emulsions for water treatment. Sonication can accelerate the mixing in heterogeneous reactions. Sono-chemistry has virtually developed in all the fields of chemistry and related chemical technology fields. Low frequency ultra-sonication is a useful tool for improving mass transfer of liquid-liquid heterogeneous system [58, 59, 64]. The process of ultra-sonication depends on four variables: 1. Diameter of the tip of the sonotrode. 2. Frequency. 3. Amplitude/Input Energy. 4. Duration of Sonication. An investigation was carried out to study the effect of ultra-sonication versus mechanical stirring at 45^0C. A conversion of 80-85% of yield was obtained in both the type of mixing methods after 30 min. The catalyst used was 0.5% w/w NaOH for the transesterification of rapeseed oil and methanol [65]. Later studies demonstrated a comparison of mechanical stirring and ultra-sonication. With the use of ultra-sonication (28KHz) 95% of methyl esters is achieved in 10 min at room temperature. In 10 min at room temperature 91% of yield was obtained by mechanical stirring (1800rpm). NaOH (1%w/w of feedstock) was used as the catalyst for this experimental studies [66]. Singh and his coworkers studied the effect of amplitude, pulse and input energy on rate of the transesterification of soybean oil. High yield was observed in the shorter duration of reaction time [67]. The effect of mechanical stirring (600rpm) and low frequency ultra-sonication (24kHz, 200W) was investigated for soybean oil and the mixture of soybean oil and cotton seed oil. Ultra-sonication was

shown to be more efficient process as compared to mechanical stirring. The conversion took place in less time while with mechanical stirring the time taken for conversion is more. The reaction was studied at high temperature of 60^0C. Studies were reported on the effect of drop size and its affect on biodiesel yield. It was reported in literature that with the use of low frequency ultra-sonication (30W), the droplet size reduced to 42% as compared to conventional mixing. The increase in the input energy decreases the droplet size of the biodiesel mixtures [68]. Recently methanolysis and ethanolysis of sunflower oil was investigated, homogenous reaction mixture was formed with the application of ultra-sonication (24kHz, 200 W, UP 200 S, England) and mechanical stirring (600 RPM). 95% of methyl esters were obtained in 20 min and 98% of ethyl esters in 40 min following the process of ultra-sonication. On the contrary mechanical stirring gave fewer yields even after 4 hours of reaction time. The mechanical stirring at 600rpm produced low yields in spite of high reaction temperature of 60^0C for methanolysis and 80^0C for ethanolysis [59]. Low frequency ultra-sonication can improve the mass transfer between alcohol and oil in the initial phase of reaction for small scale systems. However; implementing this process for larger systems increases the cost of equipment making the process not economically viable.

2.7.2 Co-solvent enabled processes

Another method applied was co-solvent enabled method (addition of THF or other co solvents), which improves the miscibility of feedstock and alcohol [60-63]. In this process one phase (homogeneous) oil rich system is formed, with the use of inert co-solvents the triglycerides and converted into esters. Investigations were carried out on the single phase system formed by methanolysis reaction; THF was used as the co-solvent to

in order to generate a single phase system. The reaction rate for methanolysis at 20^0C was reported as fast as that obtained with the conventional mixing for the butanolysis at 30^0C [60, 61]. Further Mao and coworkers reported fast conversion of triglycerides followed by the sudden fall with the decrease in the reaction rate producing two phase system. The study was conducted for the methanolysis of soybean oil at 23^0C using THF as a solvent to form one phase system. The conversion of triglycerides generates esters as well as glycerol, this glycerol tends to separate and settle down. The catalyst being in the glycerol phase affects the reaction rate by deceleration [63]. The team reported that the TG concentration was lower as compared to that of DG and MG concentration at the end of the reaction, similar studies were carried out incorporating this method [62, 69]. The separation of co-solvent from the biodiesel and glycerol phase is a necessary and crucial step for these processes. The reason for the removal of co-solvents is due to its possible hazards and toxic properties [60, 61]. THF has a property to form peroxide if stored for a longer time [70]. The boiling point of methanol and THF is similar and thus separation of co-solvent is an issue. This property of the co-solvent complicates the recovery of excess alcohol from the reaction system [32]. Other than THF, DME (dimethyl ether) was used as co-solvent for methanolysis of vegetable oil. It was reported that within 20 s the feedstock such as corn sunflower, rapeseed, soybean and palm oil forms one homogenous phase in methanol enrich with KOH as catalyst [70]. In recent times, the use of DME as the co-solvent for the transesterification of vegetable oils has gained a lot of interest. However the studies with DME as co-solvents are conducted in micro-reactors and the scale up of this system will take years to commercialize [71]. The toxic nature and hazardous property of co-solvents is a concern for its effect on health and environment.

On commercializing this process, extra processing equipment is required for the purification of biodiesel in order to remove co-solvent from the alkyl ester phase [72].

2.8   Kinetic and mass transfer studies

In the literature, there are number of kinetic studies on the transesterification of esters with alcohol. Kinetics is useful in describing the rate of chemical reactions, rate equations are typically written in terms of the concentrations of the reactants. These rate equations can be obtained by application of the law of mass action (LMA). This law relates the rate of reaction to the concentrations of reactants. The application of this law is only restricted to elementary reaction. Elementary reactions are the one which posses the mechanism at the molecular level and occurs in one event. Simplicity test are carried out by chemists to determine whether the reaction is elementary or not. These tests include number of collisions, number of bonds broken, number of bonds formed, integer reaction coefficients, and simplicity of reverse reaction. The study of kinetics will provide parameters that can be used to predict extend of the reaction at any time under particular conditions. So far, literature describes kinetic studies on methanolysis of various feed-stocks. So far in literature, the kinetic studies on the methanolysis of various feed-stocks have been carried out as methanol is used more commonly in the process [14, 15, 19, 22, 23, 35, 37, 41, 73]. Recently the kinetic study on ethanolysis of sunflower oil was carried out by Stamenkovic and his group [45]. Mainly the kinetics of the reaction depends on the degree of mixing between alcohol and triglyceride (TG) phases. Reaction temperature and the alcohol oil molar ratios are other criteria which are important in kinetic studies. The two phases (TG) and alcohol are two immiscible phases and thus they form two separate layers upon introduction into the reactor. All the kinetic studies carried out so far

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posses mixing as one of the criteria, yet the effect of mixing intensity are not fully addressed in all the studies.

2.8.1   Factors affecting the kinetics and mass transfer

2.8.1.1   Mixing Intensity

The degree of mixing between the alcohol and triglyceride (TG) phases is of particular importance. In most cases mechanical mixing is applied to increase the contact between the reactants, this process increases the mass transfer rate. The influence of mixing on the reaction rate was observed in the eighties. Thus the change in mixing intensity in the reaction can alter the kinetics of the transesterification reaction. Understanding of mixing effects on the kinetics can be used in further scale up of the design [37]. Mixing intensity can be reported by Reynold's number. In fluid dynamics N_{Re} (dimensionless number) can be defined as the ratio of inertial forces to viscous forces as shown in equation 2.1.

$$N_{Re} = \frac{nDa^2}{\mu}\rho \tag{2.1}$$

Where n is the rotational speed of the impeller, D_a is the impeller diameter, and ρ and μ are the fluid density and viscosity. Noureddini and his team investigated on the effect of Reynolds number on the transesterification reactions. The study was carried out for the rotational speed of 150, 300 and 600 rpm. It was shown that the increase in Reynolds number decreases the viscosity of the biodiesel produced. Thus with the progress of the reaction, Reynolds number increases. The mass transfer region was short for higher mixing intensities. Ideally mechanical mixing is carried out for the reaction in a batch reactor [37]. Another team reported agitation as an important parameter in the study of kinetics of methanolysis of beef tallow. The study correlated drop size with the speed of

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mixing with mechanical agitation in the stirred reactor. It was stated that smaller size of droplet increases the rate of reaction with stable emulsion [74]. Similar results were obtained with other studies and investigations. Later it was proved with experimental results and evidence that agitation plays an important part in the transesterification of vegetable oil and has a strong impact on the kinetics of the reaction [75, 76]. Kinetic studies observed the mass transfer limitations in the initial stages of the reaction. This initial mass transfer regime was eliminated by increasing the mixing speed of the reaction. Vicente and his coworkers carried out a study for the kinetics of sunflower oil at high agitation to eliminate the mass transfer region. It was observed that the phase becomes homogenous due to the 'self enhancement' of the interfacial area [22]. The droplet breakage was vigorous as the mixing was carried out at high speed of 600 RPM. The study also confirmed the effect of temperature and catalyst concentration on the reaction. The increase in catalyst concentration or increase in temperature increases the rate of reaction. This was explained with the increase in the rate constant values. The intensity of the agitation speed was properly investigated by Stamenkovic and his team using sunflower oil as the feedstock. Mean Drop diameter and drop size distribution was studied at different mixing speeds. The reaction was carried out at low temperature of 20^0C in order to increase the mass transfer regime and decrease the reaction rate in the initial stages. Proper understanding of this regime can help to develop a better model for the kinetics. The agitation speeds of 60 and 200 RPM were selected and the corresponding values Reynolds numbers were in the range of 56 and 151. Thus it indicates that the agitated emulsions were in transition state, the flow was fully turbulent near the impeller and the behaviour became laminar away from the blade [77]. However;

Stamenkovic and his coworkers contradicted the results obtained from Noureddini and Zhu (1997). They showed the existence of two phases till the completion of the reaction unlike Noureddini and Zhu. It was also observed that the other products of monoglycerides, diglycerides and soaps act as emulsifying agents. This will enhance the stable emulsion of small drops leading to the progress of the reaction [23, 37]. Mixing effect was studied for beef tallow, the relationship between the droplet size and the speed was developed. It was shown that the droplet diameter was inversely proportional to the square of the rotation speed. But in the latter case, the droplet diameter was inversely proportional to $n^{1:2}$ [33]. Mass transfer region was not significant with increasing the mixing speeds to 600 rpm at 65^0C [22]. Slinn and Kendall confirmed their results with the results of the other developed models. The reaction was predicted to be mass transfer limited and the droplet size affected the end point of the reaction. Increasing the mixing intensity increased the conversion of methyl esters, although reaction time was stated as the controlling factor in terms of conversion [78]. Recently mixing model is developed which can demonstrate the relation between mixing speeds and its effect on the transesterification reaction. The models developed in past are specific and can be used only on the particular systems. This model has been validated by with the literature data and is claimed to be used on any transesterification systems [79].

2.8.1.2   Reaction Temperature

Temperature has always been an important parameter for the conversion of triglycerides into methyl/ethyl esters. It plays a role in affecting the kinetics of the transesterfication reaction. Many studies are carried out at different temperature (from 25^0C -200^0C) to analyse the optimum temperature for the reaction to take place. Noureddini and Zhu

(2007); investigated on the temperature dependency on the overall reaction rate. The study was carried out for the temperature of 30, 40, 50 and 60^0C. It was observed by the team that the increase in temperature decreases the mass transfer regime in the initial period of the reaction. The study on the activation energies concluded that the forward reaction rate increases with higher temperatures [37]. Similar results were confirmed by Darnoko and his team for the transesterification of palm oil. The rate of conversion increased with increasing the temperature [15]. The similar trend was observed by Vicente and his team; the experiments were carried out between 25^0C to 65^0C. Although, it was reported that mixing intensity is more important than temperature for the transesterification of sunflower oil as the conversion results were similar for 25^0C and 65^0C for the mixing intensity of 600rpm [22]. Klofular and his team investigated on the effect of temperature on the duration of mass transfer controlled regime and the TG mass transfer coefficient. The overall results stated that the rate of forward reaction dominated the rate of reverse reaction. Temperature was significantly reported as an important parameter for the reaction kinetics of waste sunflower oil and natural rapeseed oil [19]. Investigations have been carried out for the effect of low temperature on the kinetics for the methanolysis of sunflower oil. The study was carried out for the temperatures as low as 10^0C, 20^0C and 30^0C. It was stated that initial drop size of the dispersed phase reduced up to 10 times as the reaction proceeded. With increase in the reaction temperature, the droplet size decreases with the fast trend. The intermediates formed during the reaction were reported as emulsifying agents. Therefore the total interfacial area increased with formation of stable emulsions, leading to enhance TG mass transfer rate [23]. The kinetic behaviour for different systems with different reaction temperature is not same, thus it is

appropriate to consider the kinetic studies for each case separately. It can be concluded that, reaction temperature plays the role in the reaction kinetics. However; mixing intensity is a more important criterion than the temperature of the reaction.

2.8.1.3 Molar Ratios

In general a molar ratio of 6:1 for alcohol to vegetable oil is preferred. According to the literature, it is proved to be an optimum molar ratio for the conversion [13, 80, 81]. To drive the reaction towards the right, excess of alcohol is used. Moreover increasing the molar ratios to 12:1 has given a reasonable yield by increasing the conversion. In the study of transesterification of cynara oil, a range between 9:1 and 12:1 gave better results [82]. For higher molar ratio of 15:1, the separation of glycerin in the reaction becomes complicated as the solubility increases due to the higher alcohol concentration. Freedman reported on the transesterification of soy oil using butanol and methanol with varying molar ratios of alcohol to oil of 30:1 and 6:1. At higher molar ratios of 30:1, the order of the reaction becomes pseudo first order using both butanol and methanol. While at the molar ratios of 6:1, the order obtained was second and fourth order using butanol and methanol respectively [49]. As homogenous base catalyst, the studies were carried out using NaOH and KOH. Later the investigations were also carried out for the methoxides and ethoxides as the catalyst in the transesterification. Usually the catalyst and catalyst concentration is the least important factors to develop a model for the kinetics of methanolysis/ethanolysis. The molar ratios selected for almost all the studies were 6:1 for alcohol: oil. It was reported that the system follows a second order reaction rate for the ratios of 6:1. While for higher ratios of 10:1 and higher, pseudo first order reaction rate was observed.

2.8.2   Kinetic Models

The knowledge of kinetic data is a key factor in process assessment and development of large scale reactor systems. Kinetic models are essential in designing chemical reactors, in the study of chemical reactions and side reactions and in the catalyst development for the process. Many kinetic models have been predicted so far using feed stocks of soybean, rapeseed, sunflower and palm oils [14, 15, 19, 23, 35, 37, 73]. To our knowledge there is a lack of kinetic studies and kinetic model for transesterification reactions. No literature to our knowledge has been reported on the kinetic studies for canola oil as a feedstock. The first model for the transesterification of soybean oil was developed by Freedman and his coworkers [41]. Later the models were developed including only second order reaction and second order reaction with shunt reaction. Transesterification reaction progress is shown by three regimes. These regimes are:

(a) mass transfer controlled regime in the initial period of the reaction (slow).

(b) chemically controlled regime for almost the entire period of reaction (fast).

(c) equilibrium regime during the completion of the reaction (slow).

Fig 2.7 shows the general trend for Alcoholysis reaction at ambient reaction conditions. Many studies confirmed that the mass transfer controlled regime can be decreased by changing the other variables of the reaction [37, 77].
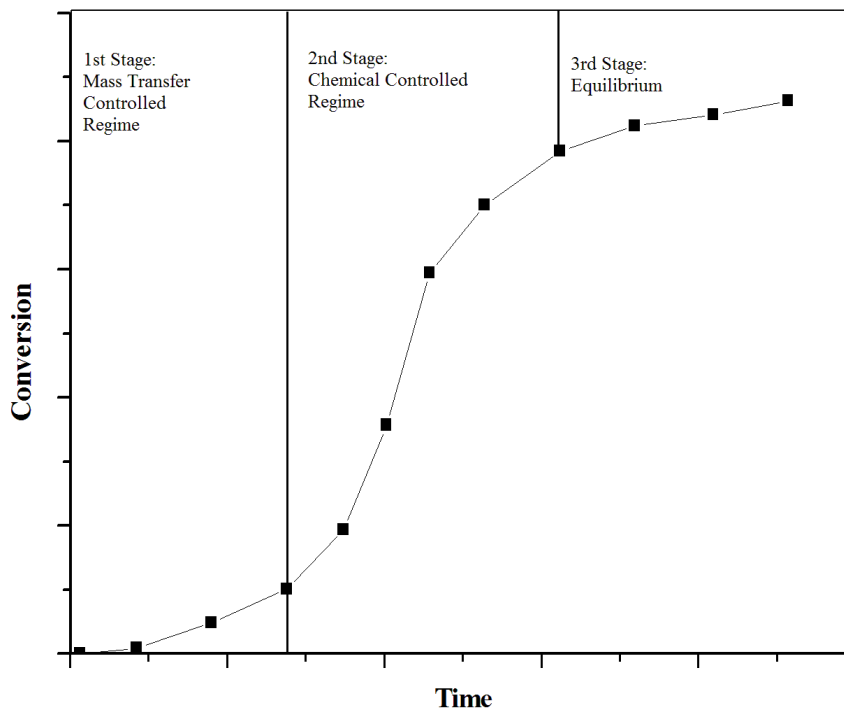
Figure 2.7 General trend of alcoholysis of vegetable oil.

The model with shunt reaction did not do any better to fit the experimental data. Thus, with these studies it was reported that considering shunt reaction in developing kinetic model was an unnecessary step. Later Mittelbach and Trathnigg discussed the parameters affecting the transesterification for sunflower oil using methanol. The work did not report on proposing the rate equations and deriving rate constants. Mittelbach and coworkers had contradictory results as compared to Freedman and team in terms of phase and order of the reaction. Mittelbach proposed that two phase of the system should be considered with formation of consideration amount of glycerin. Although complicating the kinetics, this fact should be considered for the kinetic model. The order of the reaction obtained by Mittelbach and his team contradicts to that of Freedman and coworkers. The work also showed that rate of the reaction is temperature dependent but temperature dependency of

the percent conversion is not a strong function if the reaction proceeds at least ten minutes [83]. Freedman et al. [41] used Arrhenius equation to relate reaction coefficients to temperature (Equation 2.2)

$$k = A \exp\left(-\frac{E_a}{RT}\right) \tag{2.2}$$

Where: A is the Arrhenius pre-factor and E_a is the activation energy of the reaction. In 1997 Noureddini and Zhu brought the concept of Reynolds number and modified the equation. They modified the equation by deriving a parameter 'n' with experiments (Equation 2.3). They also found the correlation between activation energy and Reynolds number. Using the concept of shunt reaction and using n=1, the rate constants obtained were very small and were neglected. The results obtained with their studies were interesting as the rate constant for the reverse direction for the first two reaction were larger than the rate constant for the forward reaction [37].

$$k = A\, T^n \exp\left(-\frac{E_a}{RT}\right) \tag{2.3}$$

Another work was carried out on the transesterification of cotton seed oil using ethanol. The third order was suggested with respect to ethanol for all the three reaction steps. The effect of the presence of water in the reaction was also studied. The direction of the reaction shifted to left for all the three reaction steps with the presence of water in it [84]. Later Saponification reaction was included in the kinetic model with the overall transesterification reaction. Soap production is the side reaction taking place during the transesterification. It takes place in the process of base catalysis, the alkaline (used as base catalyst) attacks the molecules of TG, DG, MG and alkyl esters. The soap

production reduces the yield of esters in the system. This is an unwanted reaction during the production of alkyl esters. The biodiesel industry and many researches has come up with ways to reduce soap production like using methoxides and refined oils. Thus taking saponification into the consideration to develop a kinetic model is not an important criterion. Further Vicente and his team introduced the affect of catalyst concentration into the kinetic model. The reaction rates were taken as the sum of the rates from un-catalyzed and catalyzed reaction. The catalyzed reactions were assumed to be first order with respect to the catalyzed concentration. Individual study of both catalyzed reactions and un-catalyzed reactions were carried out. But this model simplifies to the model as reported by Noureddini and his team; if the catalyst concentration stays constant during the reaction [22, 85]. Almost all the studies neglected the mass transfer regime in developing the model. Stamenkovic and his team worked on the development of the model for methanolysis reaction introducing both the mass transfer controlled regime and chemical controlled regime. The effort was made to simplify the model to avid the complex computation of kinetic constants. The fast irreversible second order reaction was followed by the slow reversible second order reaction close to the completion of the transesterification reaction [23]. The three regimes obtained in the overall methanolysis process behave differently in term of kinetics. Thus it was confirmed that the reaction kinetics for each phase should be carried out separately and in more details.

2.8.3 Mathematical model and simulation

Currently, to deal with complex reaction systems the computer programs has become essential. It helps to develop the kinetic model using a suitable numerical method [86, 87]. In order to increase the productivity and optimize the cost of the system, a successful

simulator is required for the kinetic models. So far many software tools and mathematical methods have be used to simulate the reaction kinetics [88, 89]. MATLAB and MLAB are the most important simulators so far used. More attention is focused to MATLAB due to its user friendly parameters. It is also one of the successful simulator, as it posses strong tools for the simulation process. The *Ordinary differential equation (ODE45) solver* build in function in Mat lab software is mostly used to solve the differential equations for the reaction to obtain the values of rate constant (k) of the reaction. There are number of built-in ODE functions in MATLAB to solve differential equations [89]. Scientist has used to determine the profiles of concentration vs. time for various specious in the transesterification reaction [37, 90, 91]. Recently the simulation for the transesterification of palm oil was carried out by Hamid and his team. They selected the ODE function named ode45, this function implement the nonstiff solutions of Runge-Kutte 4, 5 order method. The kinetic equations were defined in the terms of weight fraction. The data curve obtained by the simulator is used for curve fitting with experimental values [90].

2.9   Concluding Remarks

Biodiesel is a promising renewable fuel whose importance is steadily growing. It can be easily blended with petroleum based diesel to offset some of the environmental concerns with petro-diesel as well reduce the consumption of fossil fuel. However feedstock costs and their availability have restricted large scale production and usage of biodiesel. There is also ongoing need to improve efficiency of biodiesel production processes, reduce losses during production, and minimize energy consumption. Such improvements would lead to lower cost of production and make biodiesl more competitive.

2.10   References

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Chapter 3

3 New Cost-effective Method for Conversion of Vegetable Oil to Biodiesel

3.1 Introduction

There is growing demand for clean and renewable fuels due to increased environmental concerns, tougher regulations and depletion of conventional fossil feedstock. However, for alternative energy sources to be viable they must be readily available, sustainable, economically competitive, technologically feasible, and environmentally acceptable [1]. Thus for these developments, large amount of time and money is being invested in sources for renewable and eco-friendly fuels. Many governments are considering policies for establishing economies based on renewable fuels to alleviate environmental concerns. In Canada, the green house gas emissions are 33.8 per cent above its Kyoto commitment [2] thus there is a crucial need of an alternative biofuels. In recent years bio-fuels have become leading alternative to fossil fuels because they can be produced domestically. Biodiesel is one such renewable liquid fuel whose importance is growing in recent years. Biodiesel derived from vegetable oil or animal fats, is recommended for use as a substitute for petroleum based diesel. The term biodiesel is used here to describe the alkyl ester derived from the transesterification of a triglyceride with a short-chained alcohol in the presence of a catalyst. Currently, vegetable oils used for biodiesel production are produced by extrusion or solvent extraction followed by degumming and refining of the oil. Feedstock cost of the refined vegetable oil is a major contributor to the cost of biodiesel accounting for more than 70% of the cost of the product [3]. This bio-based fuel

could become more attractive by reducing the feedstock by either simplifying the oil production or esterification process. Vegetable oils have been considered as fuel for diesel engines since the earliest days of the compression-ignition engines. In 1900 Rudolph Diesel, the inventor of the compression-ignition engines, used peanut oil in a demonstration of his diesel engine at Paris Exposition [4]. Vegetable oils are economically not as viable as petro-diesel fuels because of several limitations. These include their high viscosity, poor atomization, fuel line and filter clogging, thermal cracking in diesel engine. In addition, long-term use can cause substantial engine damage due to fuel- nozzle fouling and carbon deposition. This problem is due to the high viscosity of the vegetable oils in comparison to that of the diesel fuel (10-20 times). The oils with high viscosity burn too slowly and unevenly in engines leading to several problems. Thus in order to reduce the viscosity, methods like micro emulsion, pyrolysis, dilution and transesterification has been suggested [5, 6].

Micro emulsions with solvents like methanol have been studied, as diesel fuel substitutes. However heavy carbon deposits, incomplete combustion and increase of lubricating oil viscosity was observed. Also the high alcohol content of the fuel results in flash point lower than that allowed for diesel fuel. *Pyrolysis* is the method to convert one substance into another by means of heat or by heat with the aid of catalyst. It involves heating in absence of air or oxygen and cleavage of chemical bonds to yield small molecules. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and alkyl esters of fatty acids. The equipment for thermal cracking and pyrolysis is expensive and the product quality posses many issues which are not solved yet. Alcoholysis or transesterification of triglycerides in vegetable oils has emerged as the most common

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method for converting vegetable oils into biodiesel of acceptable quality. This process consists of three sequential reversible reactions: the triglyceride (TG) is converted stepwise to di-glyceride (DG), then to mono-glyceride (MG) and finally to glycerol with alkyl esters formed in each step as shown in Figures 3.1 and 3.2. The conversion of the vegetable oils to alkyl esters lowers the molecular weight by one third, which reduces the viscosity significantly [7].

$$
\begin{array}{ccccccc}
 & \text{H} & & & \text{H} & & \\
 & | & & & | & & \\
\text{H}-\text{C}-\text{OOR}_1 & & & \text{H}-\text{C}-\text{OH} & & \text{ROOCR}_1 & \\
| & & \xrightleftharpoons{\text{catalyst}} & & | & & \\
\text{H}-\text{C}-\text{OOR}_2 & + & 3\text{ROH} & & \text{H}-\text{C}-\text{OH} & + & \text{ROOCR}_2 \\
| & & & & | & & \\
\text{H}-\text{C}-\text{OOR}_3 & & & \text{H}-\text{C}-\text{OH} & & \text{ROOCR}_3 \\
 & \text{H} & & & \text{H} & & \\
\text{Triglyceride} & & \text{Alcohol} & & \text{Glycerol} & & \text{Alkyl Ester}
\end{array}
$$
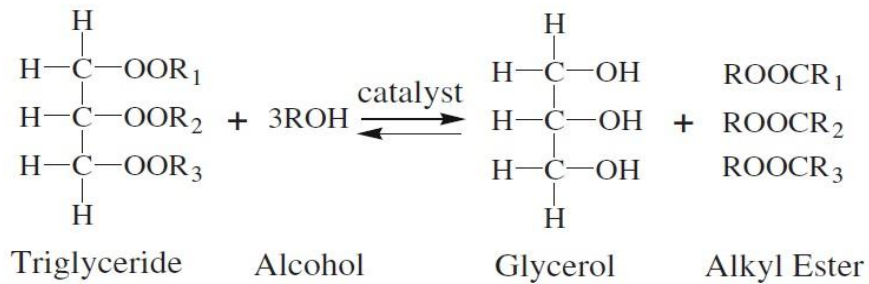
Figure 3.1 Overall Transesterification Reaction

$$
\begin{array}{ccccccc}
\text{Triglyceride} & + & \text{Alcohol} & \rightleftharpoons & \text{Diglyceride} & + & \text{Alkyl Esters} \\
\\
\text{Diglyceride} & + & \text{Alcohol} & \rightleftharpoons & \text{Monoglyceride} & + & \text{Alkyl Esters} \\
\\
\text{Monoglyceride} & + & \text{Alcohol} & \rightleftharpoons & \text{Glycerol} & + & \text{Alkyl Esters}
\end{array}
$$
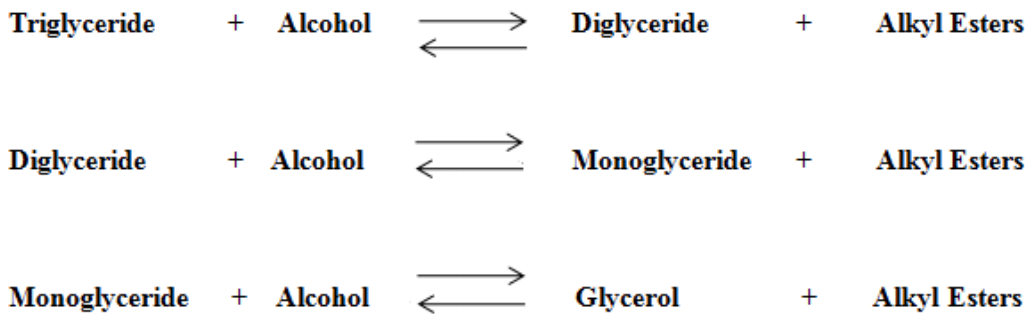
Figure 3.2 Stepwise Transesterification Reaction

The fuel derived by this process is known as biodiesel. It is biodegradable, non-toxic and possesses low emission profiles. It contains 90% of the energy of the petro-diesel fuel

and has very similar physical and chemical attributes as well as combustion properties [8]. Due to this reason biodiesel can be used in existing diesel engine with few or no modifications and can be blended with diesel in any proportions. In order to establish commercial viability of biodiesel, international standards such as ASTM and European standards have been adopted for quality control. The biodiesel properties can be specified by ASTM D 6751 [9]. Alcohol and vegetable oil phases are nearly immiscible in the transesterification and the reaction mixture is heterogeneous especially in the initial stages of the reaction. The mass transfer of the triglycerides from the oil phase to the alcohol oil interface is of critical importance. In spite of mixing the two phases, the initial mass transfer controlled region results in a slow reaction rate which affects the conversion of triglyceride [7, 10-12]. Due to this, longer reaction times are required for the complete conversion of triglycerides to alkyl esters. In order to overcome this limitation different approaches have been tried in literature studies. These include high intensity agitation, sonication and use of a solvent to achieve homogeneous phase.

Low frequency ultra-sonication is a useful tool for emulsification of immiscible liquids. The sound frequencies most commonly applied is 20-40 KHz. Power ultrasound is able to produce chemical effects through the phenomena of 'cavitation'. When large negative pressure is applied to a liquid, micro-bubbles are produced in the liquid. This process of formation of the micro-bubbles is termed as cavitation which can take place if sufficiently high tension is generated in a liquid. This can be obtained by fluid flow (hydrodynamic cavitation) or by ultrasound (acoustic cavitation) [13, 14]. Literature studies have shown significant improvements in reaction rate with sonication [15, 16]. Mostly the ultra-sonication experiments were conducted with small volumes (usually less

than 200 ml) and the scale up effects have not been studied systematically. Both energy costs and equipment costs are expected to be high for a large scale unit compared to conventional systems [16].

In their attempt to overcome mass transfer limitations, literature studies have also used solvents added to reaction mixture to convert the initial heterogeneous phase into homogeneous mixture. Boocock et al. used THF (Tetrahydrofuran) as the solvent for the methanolysis of oil and obtained a better conversion of triglycerides [17]. The studies on methanolysis of soybean were conducted at 23^0C with an alcohol oil molar ratio of 6:1. The concentrations of TGs were reported less than DGs and MGs at the end of the reaction. Ataya et al. compared the agitated single phase (with solvent) and agitated two phase reaction (c*onventional method*) wherein 20ml of THF was added in the reaction medium to obtain homogenous phase system. It was shown that the agitated single phase reaction gave remarkable high conversion of triglycerides as compared to the conventional two phase reaction system [18]. However, in the solvent enabled method it is necessary to remove the co-solvents from the glycerol and biodiesel phase after separation. This is important to reduce solvent costs and to avoid possible hazard and toxic properties [17, 19].   This additional step increases the cost of purification of biodiesel, and co-solvent removal from the alkyl ester phase requires extra processing equipment [20].   The recovery of excess alcohol is difficult when co-solvent enabled method is applied as the boiling point of methanol and THF is very close to each other [21].

In order to overcome the limitations of the above processes, an effort was made to develop a new technique for the transesterification process. The novel approach is developed in order to increase mixing rate and efficiency, eliminating the mass transfer controlled regime. The initial mass transfer regime is reduced by increasing the diffusion of the triglyceride into alcohol phase at low reaction temperature. The characteristics of the reactants, final product and intermediates are studied in the experiments. The biodiesel obtained from the novel approach has been characterized by measuring the total glycerol content of the fuel. The total glycerol content of the fuel is an important parameter to categorize the fuel properties. So far in literature it has not been studied in co-solvent enabled processes and ultra-sonication [14-22]. Also an effort has been made to predict the physical properties: Cetane number, fuel density and kinematic viscosity with the application of modified correlations. The expressions available in literature have a limitation of predicting the properties for pure biodiesel fuel [22-25]. In this study, the approximation of the fuel physical property is carried out in terms of its intermediate content in the fuel.

3.2 Experimental Details

Materials: Refined and edible Canola oil was purchased from Metro, Canada. Potassium hydroxide, anhydrous ethanol, methanol and aqueous HCl (1N) were purchased from VWR (Canada). The reference (ASTM) standards required for the GC analysis were purchased from Sigma Aldrich. The standards were solution of glycerol, 1- mono-olein, 1,3-di-olein (1% 1,2 isomer) and triolein. *n*-Hexane (HPLC grade) was used as a solvent to dilute the samples for GC analysis. N-methyl-N-trimethylsilyl trifloroacetamide (MSTFA) was used as a derivatizing agent.

Initial experiments to compare effects of sonication and mechanical stirring were conducted in 100ml, 200ml and 400 ml conical flasks on a hot plate stirrer. For sonication runs, ultrasonic horn from Hiescher (model # UP 400S) was used. Canola oil and ethanol were feedstock in presence of potassium hydroxide as catalyst (1%). Figure 3.3 below shows schematic of experimental set up used.
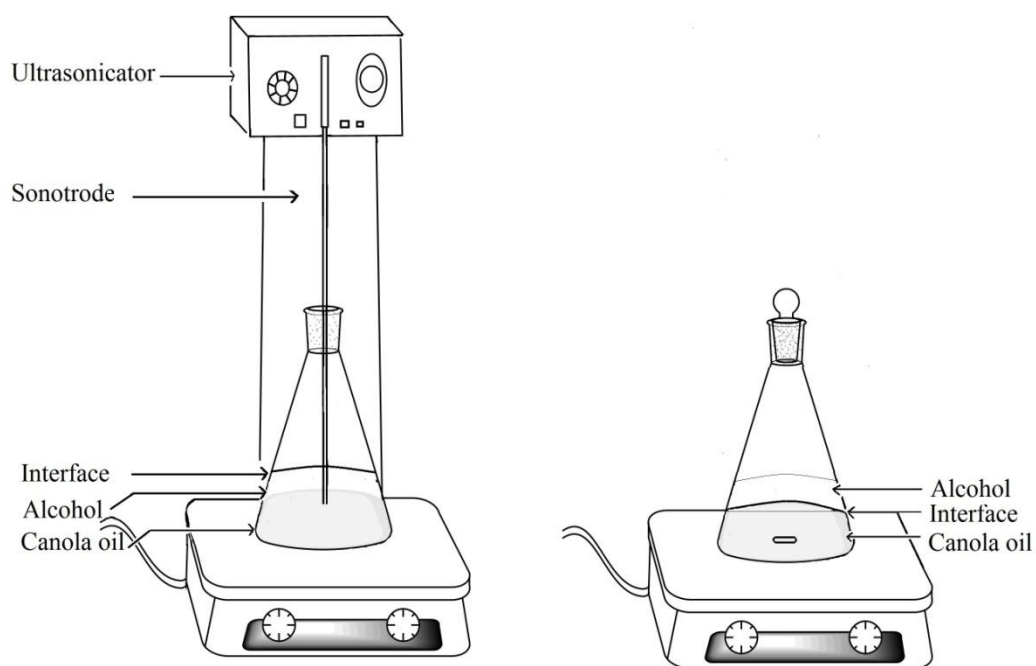
Figure 3.3 Experimental layout for low frequency ultra-sonication and mechanical agitation in 100ml system.

A number of experiments were carried out in one liter jacketed glass reactor equipped with an impeller and four baffles. The inside diameter of the reactor was 100 mm and the height was 154 mm. The reactor was also designed with a sampling port and a drain port for sample collecting and reactor draining and cleaning purposes. Sample collecting port

had a stopper to control the sample quantity. This stopper helped to take samples at regular time interval during the reaction. The reactor temperature was controlled by a water bath connected to the jacket of the reactor. It controlled the temperature of the reaction mixture to $\pm 1^0$C. Three ports were provided on the sealed lid of the reactor. One for the inlet of the impeller rod, the other for oil flow inlet and the third for thermocouple. The reactor was sandwiched between the lid and the reactor base support plate with threaded rods. The impeller had a diameter of 63.5 mm and was placed concentrically at 36 mm from the bottom. Figure 3.4 shows the schematic of set up of the experiment used. The oil was stored separately in the sealed flask to prevent oxidation reaction; it was pumped into the system at a specific flow rate.

1. Reactor Cell
2. Oil outlet Pipe (For G-Fed method)
3. Oil inlet Pipe (For G-Fed method)
4. Baffle
5. Jacketed Wall
6. Temperature indicator
7. Metering Pump
8. Oil Tank
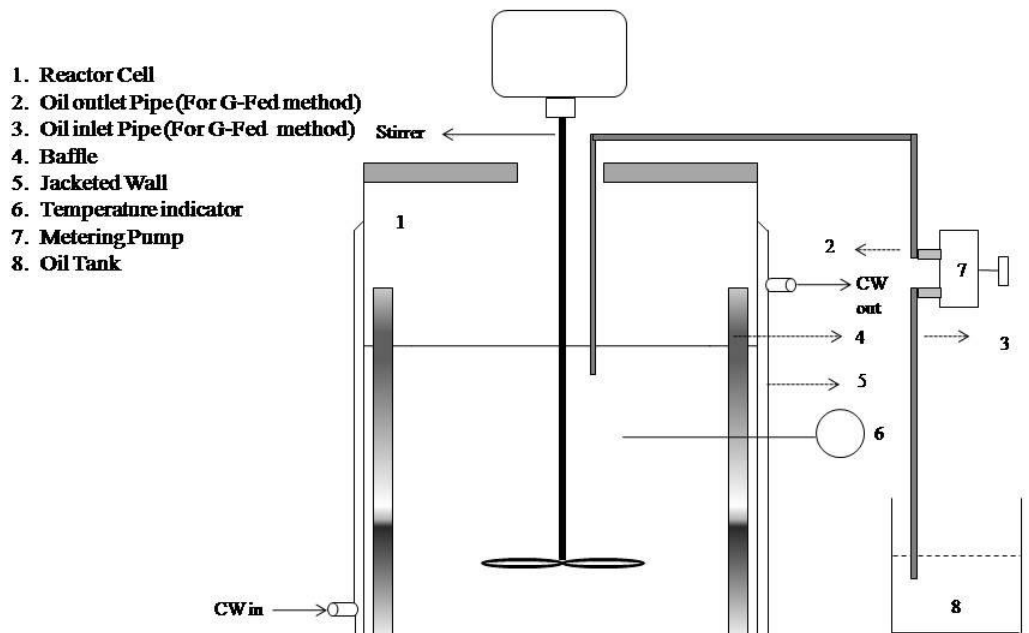
Figure 3.4 Reactor setup for batch mode and gradual feed method

The flow from the oil flask was controlled with the assistance of a metering pump. The metering pump and impeller with motor were purchased from VWR. Other equipment used for the study included Brookfield viscometer for viscosity measurements, Buchi vaporizer (R-114) for drying, centrifuge, and separatory funnels for phase separation.

3.2.1 Preliminary experiments and selection of reaction parameters

The reaction parameters were selected based on the review of literature and some preliminary experiments in the lab. The objective was to achieve high conversions and yield of better quality of biodiesel product. The molar ratio of alcohol to oil was selected as 6:1, this ratio has been demonstrated as the optimum ratio in literature studies [5, 7, 26-28]. Canola oil has been used as the feedstock since canola seed is grown in abundance in Canada. The temperature of the reaction was selected as 28^0C to minimize heating cost. The catalyst used in the transesterification reaction is 1% potassium hydroxide (wt basis of oil). The utilization of potassium hydroxide has some environmental and cost benefits since at the end of reaction the washed mixture can be neutralized with phosphoric acid to synthesize potassium phosphate. Potassium phosphate produced from this neutralization process can be used as fertilizer. The problems of waste water treatment can be overcome using KOH as a catalyst. The mixing speed of 600 rpm was selected for batch method based on review of literature studies and initial testing with rpm in the range 300 to 600. Higher agitation intensity is important to avoid mass transfer limitations during the initial phase of the reaction [7, 29]. For the new method developed in this study, the mixing was carried out at 300 rpm for initial 15 min. As the quantity of the feedstock increases with time, the mixing is carried out at 400 rpm from 15-30 min. Reaction beyond 30 minutes followed batch mode wherein the mixing is

carried out at 600 rpm. The variation in the mixing speeds was selected after performing initial studies for the new method. Samples were collected at a regular interval of time to perform GC analysis. Reaction was continued for preselected duration in the range 30 to 60 minutes. At the end of the reaction agitation was stopped and reaction mixture was transferred to a separatory funnel to separate the biodiesel and glycerol phases. The crude phases were further purified in order to remove excess alcohol and un-reacted catalyst. Crude glycerol being the heavier liquid in the mixture settled at the bottom of the separatory funnel. The glycerol separation from the alkyl esters takes place in about 10 min after stirring is stopped but complete conversion takes as long as 18h [30]. Thus the mixture was allowed to stand overnight to separate glycerol and alkyl ester phase. Both the phases: alkyl ester and glycerol were sent to a rota-vaporizer to remove excess alcohol. The ester phase was further purified by a washing process to remove residual catalyst and glycerol. The first wash was carried out using 1 N HCl solution while the other two washes were carried out using normal distilled water. The washed ester phase was dried by rota-vaporizing at 100^0C for 20 mins to completely remove the water content from the phase. The methyl esters and the glycerol were weighed for the mass balance calculations. After each step of the process, the viscosity and specific gravity measurements were carried out for alkyl ester and glycerol phases. After each wash the pH test was carried out with the help of a pH meter for washed water, the final washed water had a pH ranging between 7 and 8. With washing, the potassium hydroxide and glycerol collected in the aqueous phase. The esters are left as a separate top layer in the separatory funnel. The volume of distilled water used to wash the samples was approximately 20 vol% of the alkyl ester phase. Usually 3-4 times of water washing was

enough for a litre of alkyl esters. The entire reaction steps are explained in a flow diagram shown in Figure 3.5.
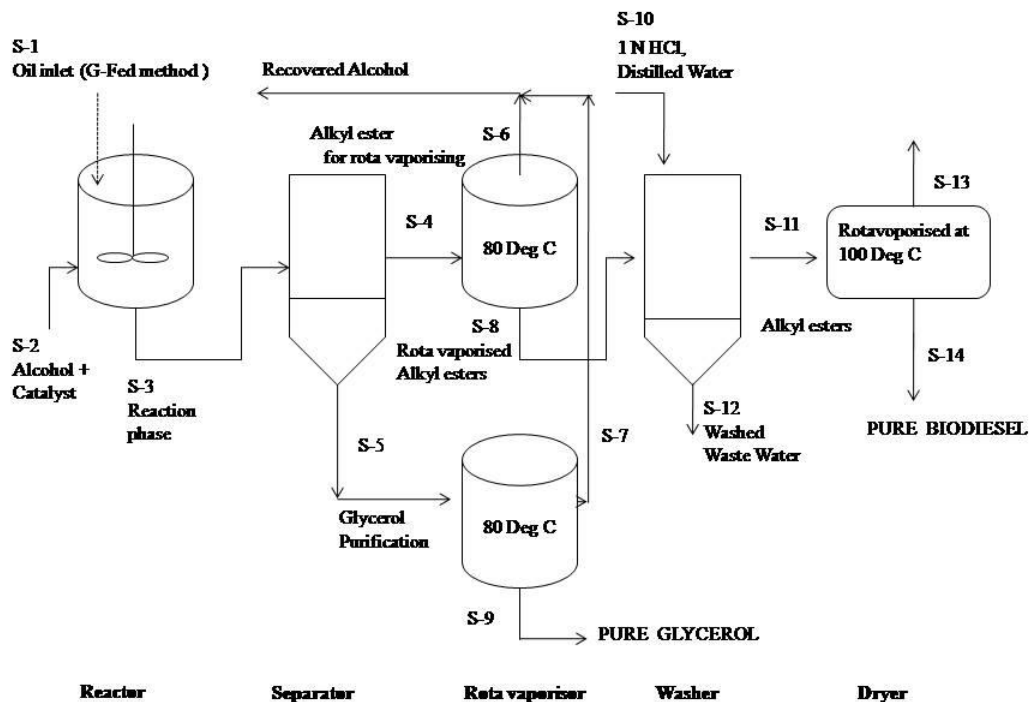
Figure 3.5 Flow diagram for the batch and G-Fed run experiments.

3.2.2 Sample Analysis and Characterization

As the reaction progressed samples were collected at regular interval of five minutes (1.5 ml) and quenched in 1N HCl solution (2ml). The process of quenching was carried out to cease the reaction at that particular time for studies of intermediates. The catalyst from the reaction sample settles down in the HCl solution. The samples were allowed to stand for 2-3 h to remove the catalyst from the alkyl ester phase. The top layer from these samples was centrifuged to help dry the phase. The top layer is pulled out and transferred

to 2 ml centrifuge tube [13]. Anhydrous sodium sulfate was added into the centrifuge vials. Sodium sulfate acts as a drying agent to remove residual water from the samples [31]. The process of centrifuging was carried out for the duration of 15 min and at the speed of 4000 RPM. For GC analysis sample solution was prepared by transferring measured amount of dried sample into 1ml auto sampler vial. Derivatization is carried out with the addition of MSTFA as it improves the chromatographic properties of the hydroxylated materials [32]. The processed sample was allowed to stand for 20 min at room temperature in order to derivatize the glycerides. After 20 min the vial was topped up to 1ml using *n*-Hexane as solvent to dilute the individual sample; this process was repeated for all the samples. The samples were analyzed by GC-FID using DB-5 column of dimension 30X0.25X0.25. Samples (1µl) were injected on-column by an AOC 20s Auto sampler (Mandell instruments) at an oven temperature of 60^0C and injector temperature of 300^0C. The analysis was carried out in split mode. Helium was used as the carrier gas; the linear velocity of the gas was 48.5 cm/sec. The temperature program, 2 min at 60^0C, heating at the rate of 12^0C/min to 300^0C and holding for 15 mins. The detector temperature was fixed at 300^0C with hydrogen gas at 30ml/min.

3.3   Results and Discussion

3.3.1   Sonication vs. Mechanical Agitation

Sonication studies using low frequency wave were carried out in conical flasks of 100 to 400ml size while mechanical mixing was carried out using a magnetic stirrer. The sonication was carried out at 100% amplitude and 100% cycle for all the systems for the duration of 5 mins at 28 ^{0}C. Batch mode runs with mechanical stirring was carried out for the duration of 1hr keeping all the other parameters constant. Figure 3.6 below shows the

yield of ethanolysis for both low frequency ultra-sonication and mechanical stirring. It was observed that sonication with the sonotrode of 25mm tip gave better results for 100ml and 200ml system as compared to mechanical stirring with longer duration of reaction time. However it did not achieve better conversion for 400ml system, higher yield was obtained by conventional mixing for 400ml system. The process of cavitation results in conditions of very high local temperatures and pressures which intensifies the chemical reaction with release of free radicals [14].
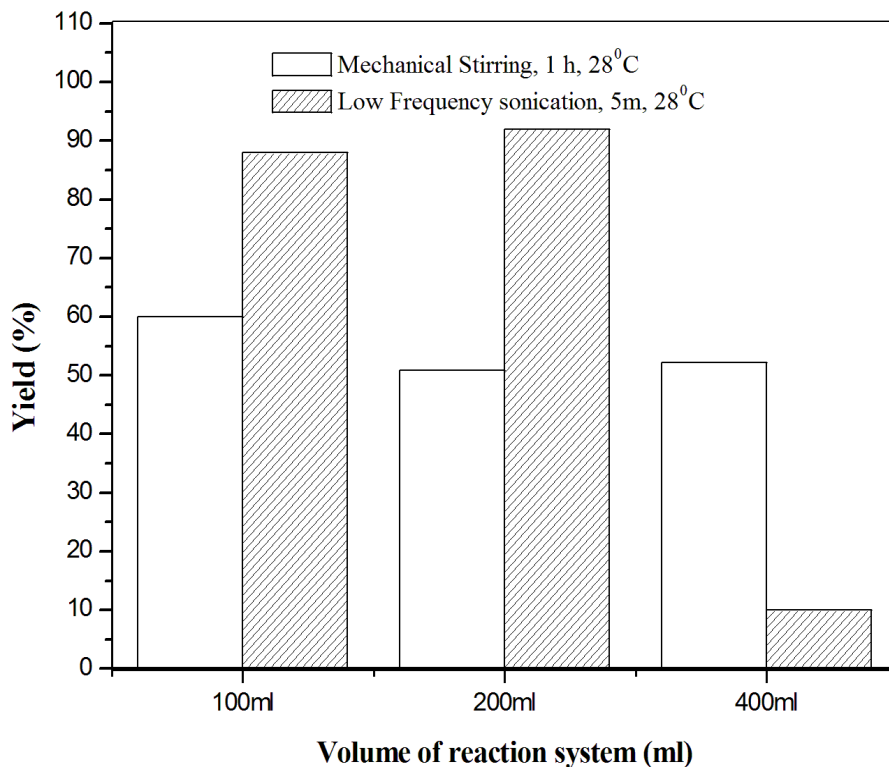
Figure 3.6 Comparison of Yield obtained using mechanical stirring and low frequency sonication.
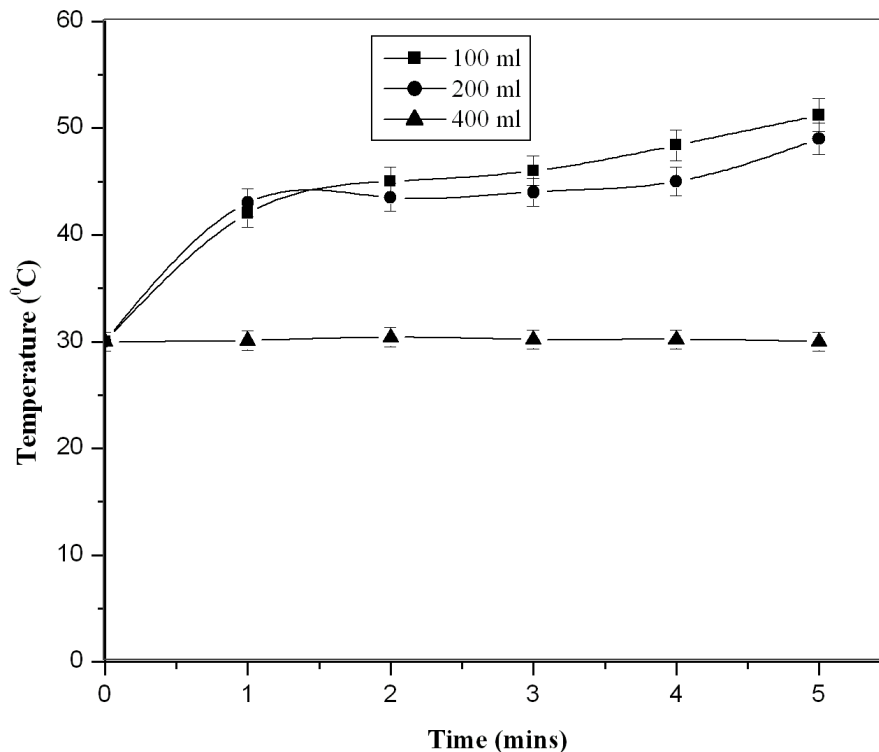
Figure 3.7 Temperature profiles for different volume system using low frequency ultra-sonication (n =2, error bars = 3%).

The increase in the temperature for the systems with cavitation is depicted in Figure 3.7. The temperature remained approximately constant for 400ml system; this can be one of the reasons for low yield as temperature plays an important part in kinetics of transesterification. Low frequency ultra-sonication can reduce the mass transfer limitation but on the other hand increases the cost of equipment for larger systems. In order to achieve high conversion at low reaction temperature and less reaction time, a new method discussed below was incorporated.

3.3.2 New Method Based on Gradual Feed Flow

In order to overcome limitations of different known methods described in literature studies, a new approach based on feeding the oil gradually into the reactor containing all the alcohol feed was tested and developed. This study presents results obtained with

methanol as transesterification agent. This new method dubbed 'G-Fed' was developed based on the following considerations.

1. Solubility of oil (triglycerides) is low in methanol phase requiring good dispersion and large excess of alcohol.

2. Small amounts of oil added to alcohol can be easily dispersed to create small droplet size in the dispersion even with low intensity of agitation.

3. Small amounts of oil added to pool of alcohol created large alcohol to oil ratios to help push the reaction in forward direction for the reversible reaction toward desirable product.

4. Solubility of both triglycerides and methanol is higher in methyl esters leading to better contact and conversion as the reaction progressed.

5. Near complete conversion to product could be achieved, thus would eliminating need to separate and recycle un-reacted oil feed.

The reactor was initially charged with methanol premixed in catalyst. Prior to injecting the oil in the reactor, it was preheated to the reaction temperature conditions. The reactions were carried out at two different temperatures of 28^0C and 45^0C. The molar ratio of oil to alcohol was 1:6 and oil was pumped into the reactor by means of a metering pump. The oil was fed into the reactor at a rate of 18 ml/min for thirty minutes and the reaction was continued for another thirty minutes in batch mode. The mixing intensity was 300 rpm for first 15 minutes and 400 rpm for the remaining period. The progress of the reaction was followed by collecting samples from the reaction mixture at predetermined intervals and analyzing with GC. The reaction was timed as the stream of oil got in contact with the alcohol phase. For comparison, the study was performed with

conventional mixing batch method. The oil and methanol (mixed with catalyst) were added into the reactor and preheated to the reaction conditions. The reaction was carried out at 28^0C and 45^0C using 300 and 600 rpm as mixing speeds. The reaction was timed once the agitation was started; samples were taken at regular time interval to study the transesterification process. Once the reaction was stopped the homogenous phase was transferred to the separatory funnel in order to separate glycerol and methyl esters (biodiesel). The top (methyl ester) and the bottom (glycerol) were purified to calculate the yield and measure properties such as viscosity and specific gravity. The experiments were carried out twice and the sample analysis is carried out in triplicates in order to investigate on the reproducibility of the results.

3.3.3   Comparison of Gradual Feed Method with Conventional Batch Method

A comparison of the triglycerides concentration during the progress of the reaction in batch and G-fed method is presented in Figure 3.8. It is seen that the concentration of triglycerides obtained in the new method is significantly lower up to the end of reaction indicating higher conversion of the feed with application of this method. In the G-fed method, as the quantities of TGs are introduced into the pool of methanol in controlled feeding process it provides large excess of methanol which helps the solubility of the two phases and overcomes diffusional limitations by increasing interfacial area of the dispersed oil phase. The methanol: oil molar ratios is approximately 36:1, 18:1, 12:1, 9:1, 7:1 and 6:1 at 5, 10, 15, 20, 25 and 30 min respectively. Excess alcohol to oil ratios also helps to push the reaction in forward direction for the reversible reaction toward desirable product. Figure 3.9 shows that concentration of methyl esters (desired product) obtained with the G-fed method are significantly higher.
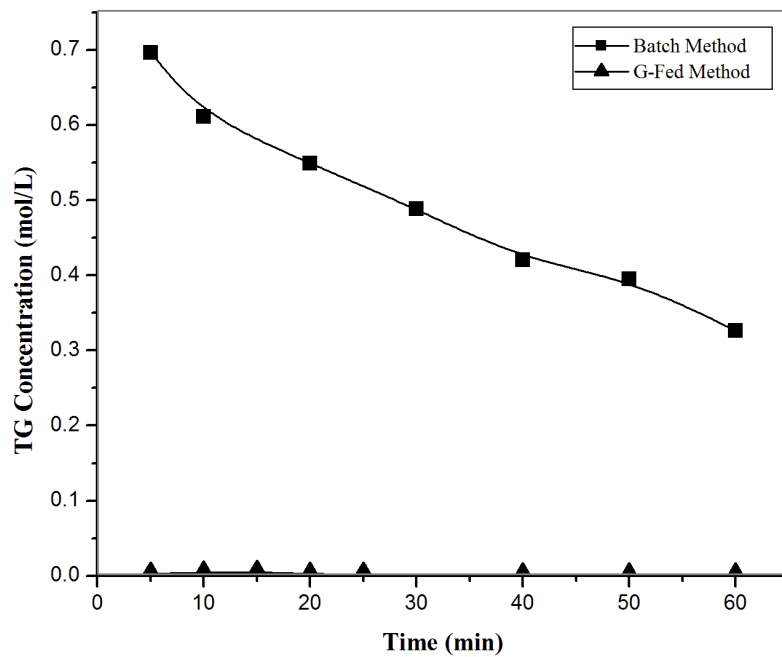
Figure 3.8 Comparison of Triglycerides concentration in the reactor with reaction progress.
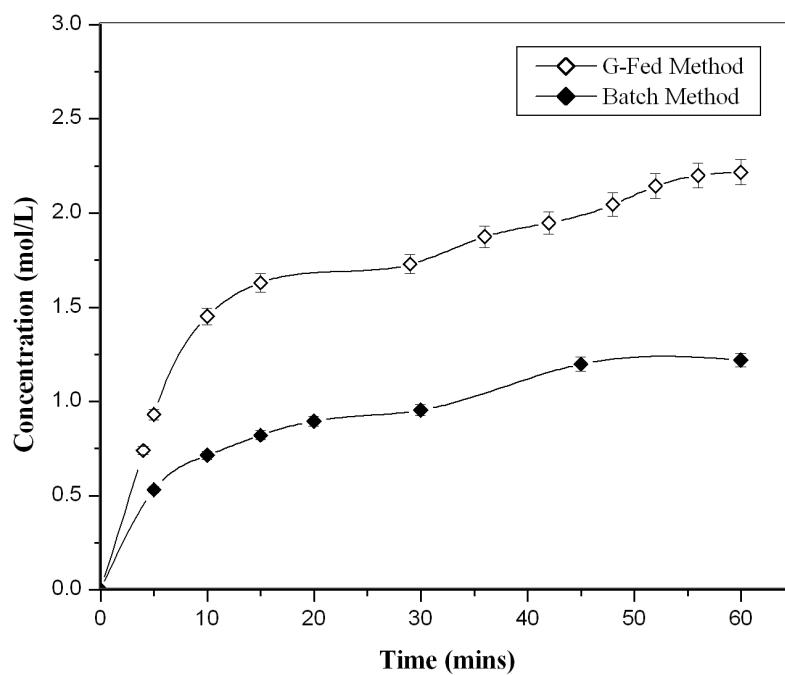
Figure 3.9 Concentration profiles of methyl esters in batch and G-Fed method.

It should also be noted that methyl esters formed also act as co-solvent with methanol to improve mixing the fresh oil being fed to the reactor thus further enhancing the conversion [33]. Systematic error estimation was carried out; therefore the error bars of 3% are shown. The concentrations of reacting and product species were obtained from GC analysis from samples collected during the reaction progress. Two such chromatograms obtained under similar conditions for batch and G-Fed methods are shown in Figures 3.10 and 3.11 respectively. It can be seen that the peak of triglycerides obtained with the G-Fed method is almost negligible as compared to that obtained with the batch method.

3.3.4 Comparison of G-Fed method with co-solvent enabled system

Literature studies have used co-solvents to overcome the diffusion and mass transfer limitations to improve triglycerides conversion and improve product yield [18, 19]. The use of co-solvent increased the conversion of triglycerides indicating beneficial effects of the method [18]. Ataya et al. investigated on methanolysis of canola oil using tetra hydro furan (THF) as a solvent and compared the results with conventional batch method. The system with co-solvent was called single agitated system and the conventional batch process was called two phase agitated system. The team reported that the conversion of TG and the yield of ME was better for single phase agitated mixture (co-solvent enabled system) as compared to two phase conventional batch method [18]. The conversions reported with co-solvent enabled method are compared with G-Fed method in Figure 3.12. It can be seen that TG conversions with G-Fed method are 5 to 10% higher compared to co-solvent enabled technique. The reaction parameters were similar for both the systems.
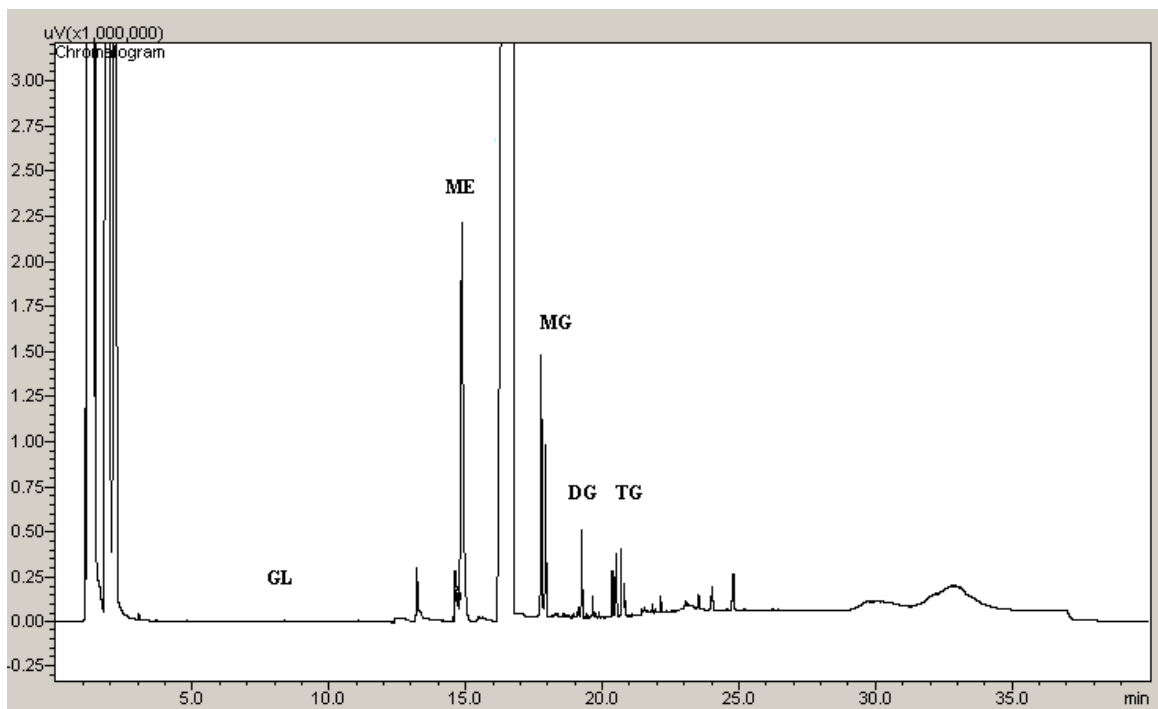
Figure 3.10 Chromatogram obtained with G-Fed run during initial stage of reaction.
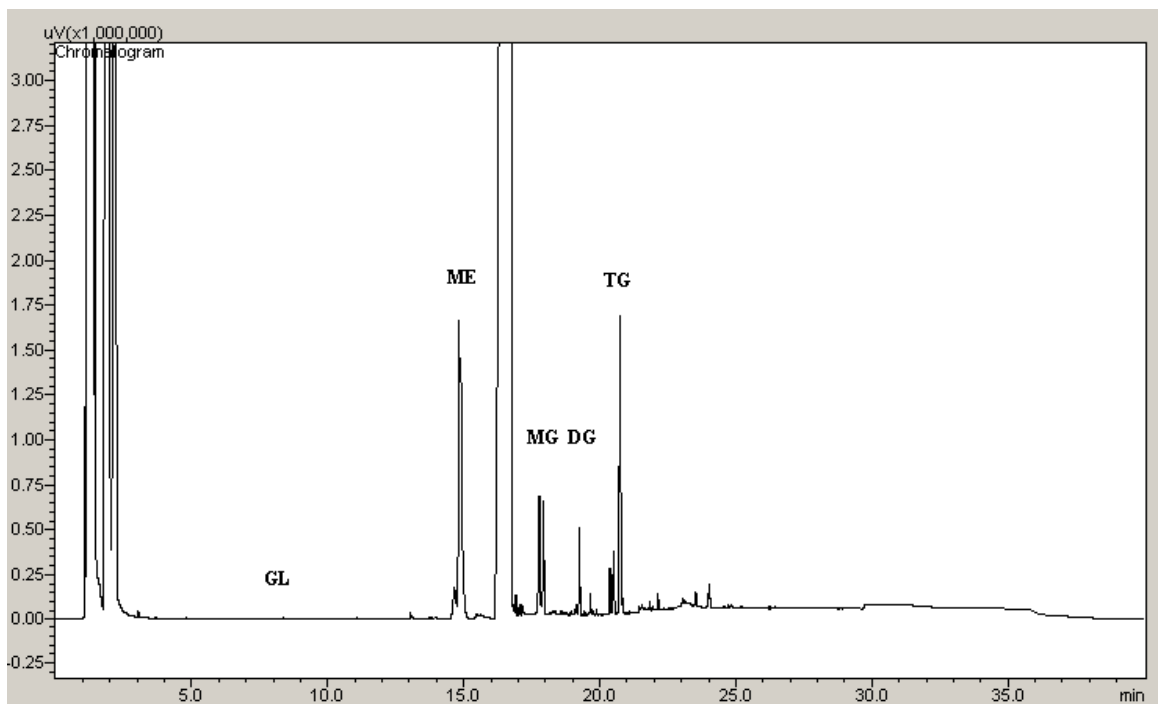
Figure 3.11 Chromatogram obtained for batch run during initial stage of reaction.

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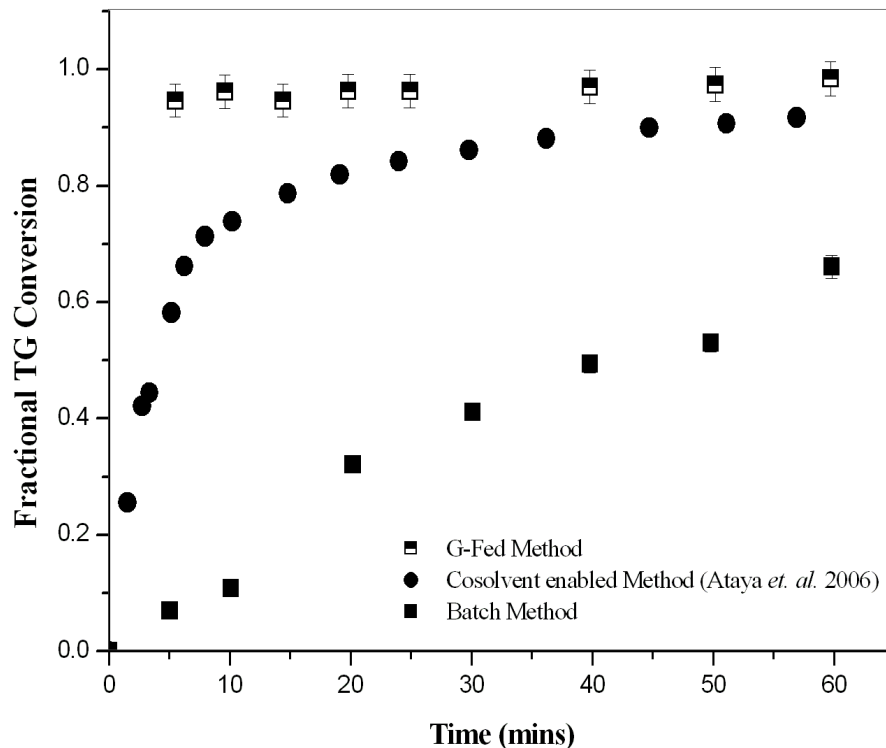
Figure 3.12 Comparison of TG conversion obtained with G-Fed method with literature study using co-solvent (n = 2, error bars = 3%)

Thus G-Fed method is not only better than batch process but also superior to co-solvent enabled technique. In addition, the G-Fed method is easier to implement and more economical. Use of co-solvents increases the problem of hazards in the reaction and complicates purification step and cost of treating the waste water produced is expensive. Moreover, co-solvent method can only be used for lower alcohol oil molar ratios as the presence of co-solvent interferes the separation of glycerol formed. Also the solvent/catalyst is very soluble in glycerol and once the separation occurs the glycerol becomes unusable and becomes a waste rather than a by-product [19]. For the G-Fed method, the purification steps remain the same as in conventional batch method. The alkyl ester produced acts as a co-solvent in the system reducing the solubility issues as the reaction progresses.

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3.3.5   Concentration profiles of intermediate products

The concentrations of intermediates (DGs and MGs) were also monitored during the reaction and are shown in Figure 3.13. The results obtained for the conversion of diglycerides and monoglycerides show similar trend as shown for triglycerides in the methanolysis reaction. The concentrations are remarkably lower with the G-Fed method as compared to the batch method that proposes higher conversion rate to methyl esters in the G-Fed method. The concentration profiles obtained for batch runs supports the results obtained by other literature studies [34].   In batch run, the di- and monoglycerides concentrations increased in the beginning and reduced as the reaction progressed.
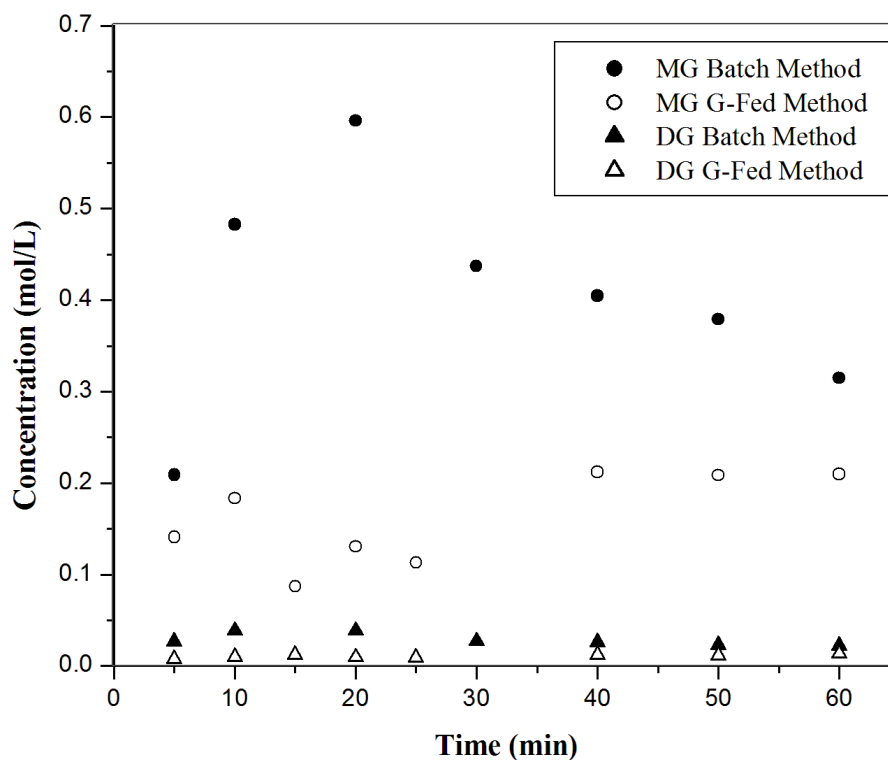
Figure 3.13 Concentration profile for Intermediates using Batch and G-Fed method.

In the G-Fed method canola oil is gradually fed for 30 min and after this time, the system becomes batch mode as the agitation is continued with no oil feed. There is a significant rise in concentration of mono glycerides in the G-Fed as well as the batch method in the initial 10 min but DG concentrations remain low. This indicates a faster conversion from DG to MG and slower from MG to ME. Higher MG concentration in the reaction mixture can enhance solubility of TG in catalyst rich polar phase enhancing conversion of TG and DG. It is also noted from Figure 3.13 that after 30 min MG concentration decreases in the batch mode and increases somewhat in the G-Fed mode. This could be attributed to the backward reaction taking place in presence of glycerol and methyl esters. These concentrations would be higher with G-Fed method.

3.3.6   Further analysis and optimization of G-Fed method

Following set of flow rates and reaction time were investigated to determine optimum combination to achieve high product yield and quality.

i)   Oil flow rate at 18ml.min^{-1} for 30 minutes followed by 30 min of batch operation.

ii) Flow run at faster feed rate of 27ml.min^{-1} for 20 minute run.

iii) Slow feed rate at 10 ml/min for initial 10 minutes followed by fast feed at 22 ml.min^{-1} for 20 minutes.

Figure 3.14 below shows conversion of TG in systems with different oil flow rates. The details of the runs carried out are given in Table 3.1. The comparison is carried out with triglyceride conversion in batch mode at 300 rpm and 600 rpm.

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Table 3.1 Summary of the different flow-rate run conditions investigated.

Run#	1	2	3	4	5	6	7	8
Canola oil (gm)	498	498	498	498	498	498	498	498
Methanol (gm)	109	109	109	109	109	109	109	109
Reaction time (min)	30	30	30	60	30	60	60	60
Flow Rate (ml .min^{-1})	27	10-22	18	18	18	Batch	Batch	Batch
RPM	300-400	300-400	300-400	300-400-600	300-400	300	600	600
Temperature (^{0}C)	28	28	28	28	45	28	28	45
Reaction Solution	598	596	597	573	599	597	591	598
Washed and dried product (gm)	407	423	439	432	458	469	463	451
Glycerol (gm)	47	47	51	51	52	42	49	47

The percent conversion is calculated on the basis of reduction of triglycerides from the amount of oil injected into the reactor as the reaction proceeded. The conversion is more than 90% for the system of constant 18ml.min^{-1} flow and the combination flow rates of 10 ml.min^{-1} for first 10 min and 22 ml.min^{-1} for the remaining 20 min. The conversion rate for the faster flow rate of 27 ml.min^{-1} for 20 min is higher than that of batch run but lower than the other flow runs. The batch run can be viewed as one with very high feed rate since all feed is added in about one minute. Thus increase in flow rate reduces the conversion rate of triglycerides which affects the yield.
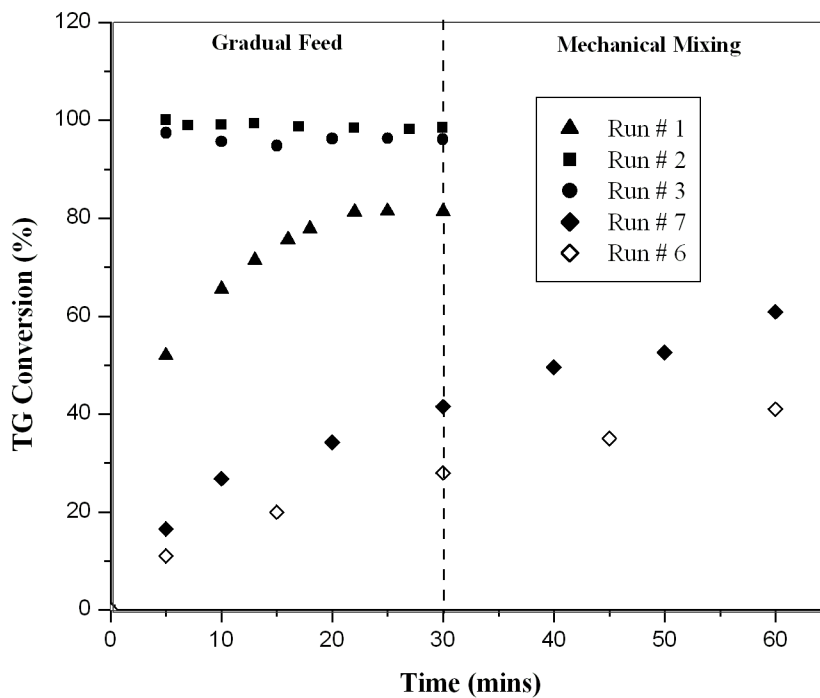
Figure 3.14 Comparison of TG conversion obtained with different flow rates
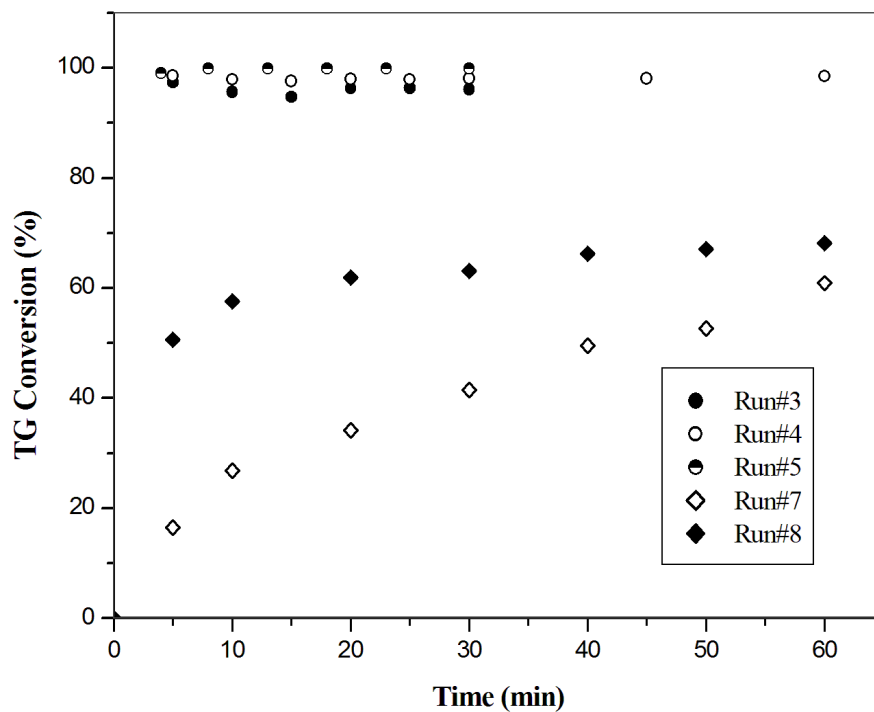
Figure 3.15 TG Conversion with different reaction conditions for oil flow of 18 ml.min^{-1}.

The increase in flow rate of the oil fed would reduce dispersion of oil in the methanol phase affecting mass transfer rate. Effects of temperature ($28^{o}C \rightarrow 45^{o}C$) were investigated for selected flow rate of 18 ml/min and compared with batch run (600 rpm). Figure 3.15 shows that while TG conversion increased significantly with temperature with the batch mode, however temperature effect was less noticeable with G-Fed run. For all the flow runs the reaction rate increased in the initial reaction zone indicating significantly enhanced rate compared to batch runs. The shape of the graph also indicates that mainly two regimes (chemical controlled and equilibrium) are followed as the reaction proceeds. Also values for combined flow and batch run (Run # 4) are close to the lowest values. Figure 3.16 shows the formation of methyl esters with reaction progress for various flow runs.
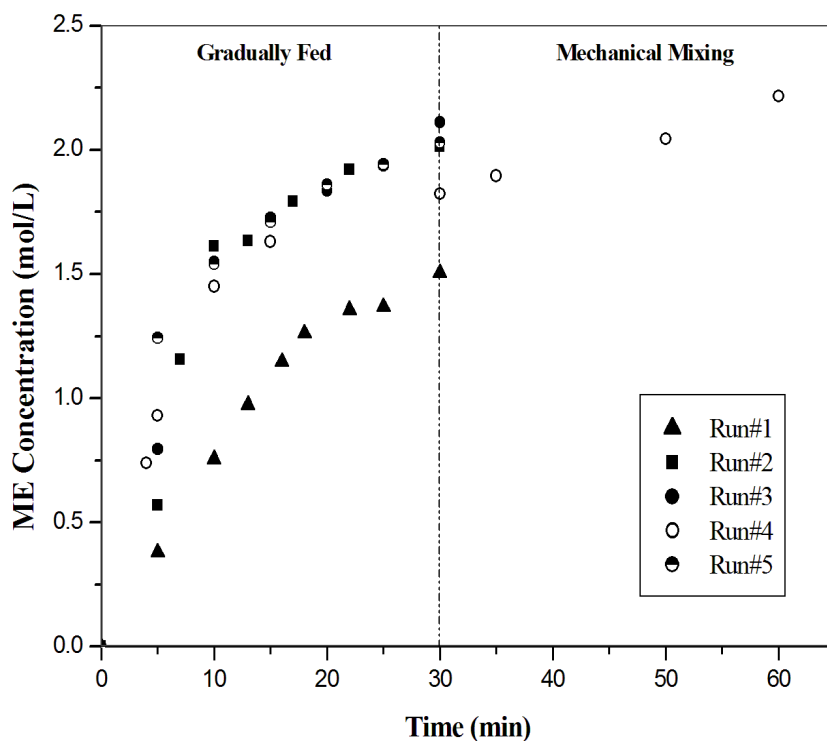
Figure 3.16 Concentration profile for methyl esters obtained with different oil flowrates.

It can be seen that an optimum feed flow rate is reached at about 18 ml.min^{-1} and below which gains become less significant. Different run conditions were assessed further based on detailed product quality assessments.

3.3.7 Product quality and comparison with standards

The biodiesel product obtained with different runs was further tested for viscosity, density, total glycerol, cetane number to assess required fuel properties as per ASTM standard (Table 3.2).

Table 3.2 Specification for Biodiesel (B100) ASTM D 6751

Property	Test Method	Specification Limits
Acid Number	ASTM D 664	0.50 maximum mg KOH/g
Calcium and Magnesium	EN 14538	5 ppm maximum
Carbon Residue	ASTM D 4530	0.05 maximum Wt%
Cetane Number	ASTM D 613	47 min
Cloud Point	ASTM D 2500	Report in ^{0}C
Cold Soak Filterability	ASTM Annex A1	360 max^F seconds
Copper Strip Corrosion	ASTM D 130	No. 3 maximum
Flash Point	ASTM D 93	130 minimum ^{0}C
Glycerin-Free	ASTM D 6584	0.020 maximum Wt%
Glycerin-Total	ASTM D 6584	0.24 maximum Wt%
Kinematic Viscosity-40^{0}C	ASTM D 445	1.9-6.0 mm^2/s
Methanol Content	EN 14110	0.20 maximum Wt%
Oxidation Stability	EN 14112	3 hours minimum
Phosphorus Content	ASTM D 4951	0.001 Wt% or 10 ppm
Sodium and Potassium	EN 14538	5.00 ppm maximum
Sulfated Ash	ASTM D 874	0.020 maximum Wt%
Sulfur (S15)	ASTM D 5453	15.0 ppm maximum
Sulfur (S500)	ASTM D 5453	500 ppm maximum
Water and Sediment	ASTM D 2709	0.050 maximum Vol%

Total Glycerin

Estimation of total glycerol also required concentration of TG, DG and MG in the product. Table 3.3 lists percentages of TG, DG and MG in the product layer which were used to calculate total glycerol TG conversion, as well overall product yield for different runs. As shown in Table 3.3 MG content was highest in Run # 1 and lowest in 5. High MG content in the product layer leads to emulsification during washing stage and their loss in wash water [35]. The concentration profiles for flow runs follows a trend of MG>DG>TG, while the trend is different with conventional batch runs MG>DG<TG. The presence of glycerides in the product increases chemically bound glycerol (CBG) for which there is upper limit of 0.24 wt % as per ASTM standards. The total glycerol in the system is related to the free glycerol (G) and CBG in the following manner:

$$G_{total} = G + [(MG \times 0.25) + (DG \times 0.15) + (TG \times 0.10)]$$

$$= G + CBG$$

The ASTM limit for free glycerol is 0.02 wt % and the total glycerol (free and chemically bound glycerol (CBG)) is limited to 0.240 wt. %. In the above equation, respective concentrations of TG, DG and MG are being multiplied by the respective glycerol moiety, which is collectively referred to as CBG or chemically bound glycerol. Increased levels of free and chemically bound glycerol in biodiesel are associated with carbon deposits in the engine due to incomplete combustion. [37]. It can be seen from Table 3.3 that ASTM limit for CBG is easily met by run # 5 and closely by run 4, while other runs fail to meet this standard. The percentage of MG in the final product obtained by run #4 and 5 is lower as compared to other runs. Low MG concentration is obtained with increase in temperature and it reduces the total glycerol to 0.187%. Mixing also helped to

reduce the MG concentration and pushed the reaction towards completion. Although TG% was little higher than the temperature run, the total glycerol in the product was 0.234 wt %.

Table 3.3 Concentrations of glycerides for different runs

Types of Runs	TG(wt%)	DG(wt%)	MG(wt%)	Total Glycerol (wt%)	Product Yield**	TG conversion (%)
1	1.97	1.8	3.85	1.43	73.92	82
2	1.14	1.98	3.46	1.28	78.18	94.34
3	1.4	0.638	1.461	0.608	84.44	97.29
4	1.05	0.497	0.217	0.234*	84.82	98.61
5	0.044	0.683	0.320	0.187*	90.77	99
6	42.09	2.67	2.95	5.35	45.91	75.49
7	28.5	2.04	1.25	3.48	55.86	84.3
8	21.9	0.807	0.89	2.53	66.64	88.36

* Meet ASTM standards

** Calculated to meet ASTM standard.

Overall yield (Y_{ov}) is calculated by using the definition provided below.

Overall Yield (Y_{ov}) = Desired product obtained/Amount of product which could be obtained if all of feed is converted to produce the desired product. Desired product Obtained can be estimated using the expression shown below:

Desired Product = (Wt of Product obtained − Wt of TGs in final product) − (Wt of DGs in final product + Wt of MGs in final product − 0.0024(Wt of Product obtained − Wt of TGs in final product)).

The amount of product which could be obtained is approximately taken as 503g. The estimated overall product yield is reported in table 3.3. The percent TG conversion shown in table 3.3 is calculated by the expression shown below.

$$\text{TG conversion (\%)} = \frac{\text{(TG moles in total feed } - \text{ TG moles in product sample)}}{\text{TG moles in total feed}}$$

Cetane number

Cetane number is one of the important parameter to determine the fuel quality or to be more specific ignition quality. It is the measure of the readiness of the fuel to auto-ignite after injecting into the engine. It relates to the delay between fuel injection into the cylinder till the ignition starts. The minimum value allowed for petroleum diesel in North America is 40. The lowest value for typical biodiesel is the same as a "premium petroleum diesel" at 47. The structure of the FAME component is used to determine the ignition quality of the biodiesel [38]. In literature, studies have been conducted to calculate cetane number from the fatty acid composition of the alkyl esters [24, 39]. The cetane number varies with feedstock for alkyl esters: from soybean oil, It is in the range of 45 to 60 and for rapeseed oil derived biodiesel is in the range of 48 to 61.2 [22]. The cetane number of the vegetable oil is low due to the presence of triglycerides as the major component. The bulky triglycerides molecules increase the viscosity and lower the volatility of the vegetable oil. Therefore these properties can be a cause of longer ignition delay after the injection in the combustion chamber [40, 41]. No studies have been carried out so far to predict the cetane number with respect to the intermediates present in the biodiesel sample. In this study, approximate CN is calculated with respect to the intermediate content (TGs, DGs and MG in the final methyl ester phase. The GC analysis of the samples helps to determine the approximate molecular weight and the molecular weight of the pure methyl ester content in the reaction mixture. The estimation procedure for cetane number is shown in Appendix. Table 3.4 shows the molecular weight of

methyl ester, approximate molecular weight in terms of intermediates. The cetane number for run # 4 and 5 is better as compared to the other runs. The amount of triglycerides is higher in batch runs at various conditions (run # 6, 7 and 8) and therefore lowers the cetane number of the biodiesel [40, 41]. For G-Fed runs (run # 1, 2, 3, 4, 5), the concentration of MGs are higher as compared to DGs and TGs. The results obtained shows that the MG concentration does not play a significant role to reduce the cetane number.

Table 3.4 Cetane Number Estimation

Run#	1	2	3	4	5	6	7	8
MW from ester content in mixture	271	275.4	286	290.4	292.4	179	223	257.4
Overall MW of reaction mixture	310	306.2	302	300	296.9	489	420.5	362
CN of ester content in mixture	54	55.4	58.6	59.9	60.5	26.28	39.5	50
CN of intermediate content	3.2559	2.652	1.226	0.622	0.3549	15.719	9.765	5.096
Approximate CN of reaction mixture	52.896	54.364	57.989	59.596	60.318	31.672	39.654	48.673

Figure 3.17 shows the cetane number and its comparison with all the other runs conducted in the study. Measured value for run # 3 is also shown, which is close to the estimated value.
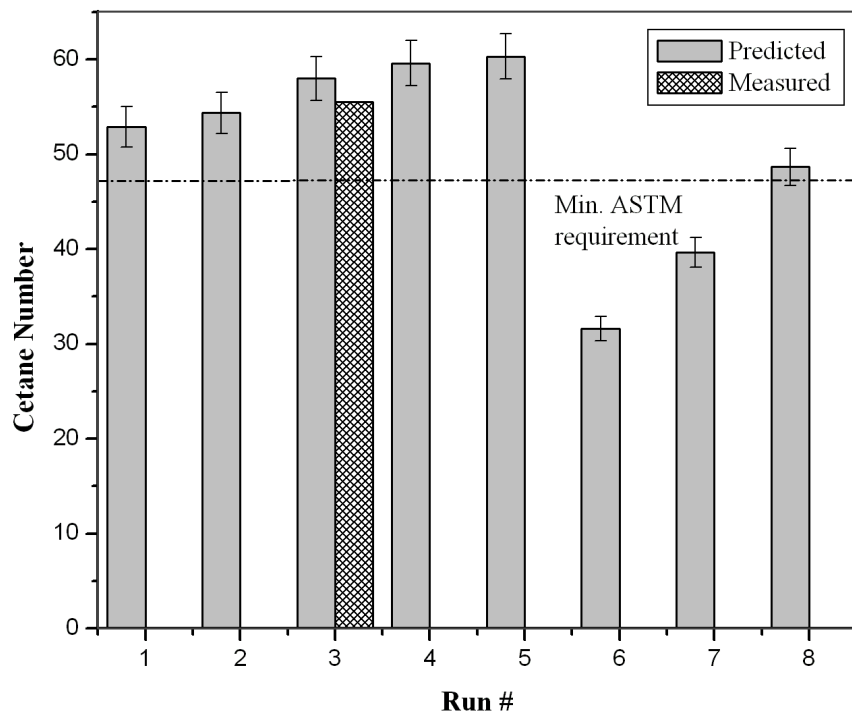
Figure 3.17 Cetane Number for different runs (n = 2, Error-bars = 4%)
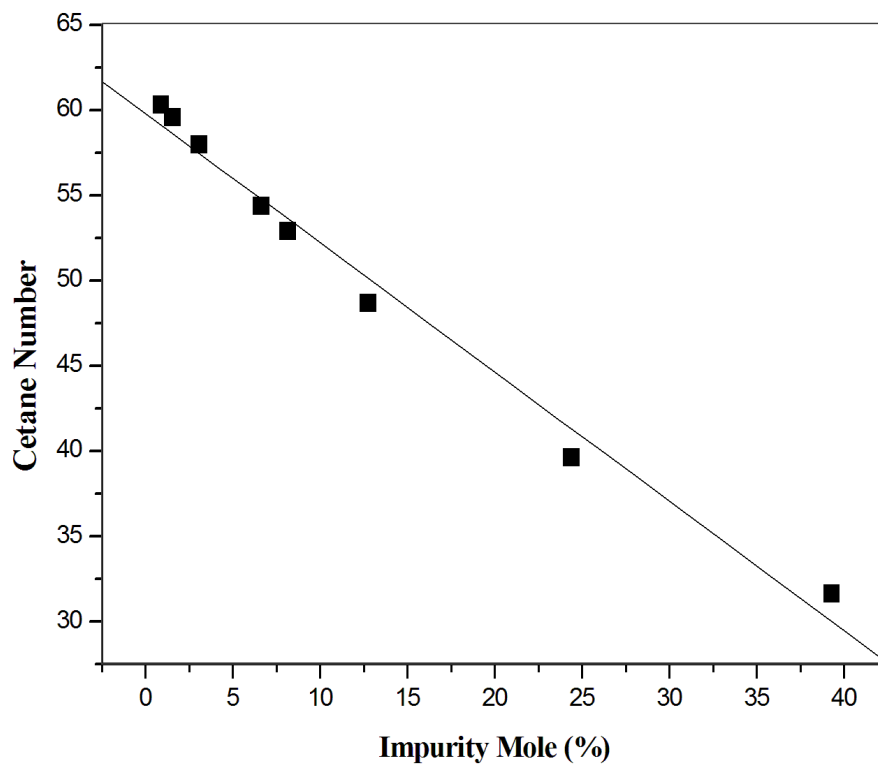
Figure 3.18 Correlation of cetane number and intermediates present in biodiesel.

All the flow runs of this study exceed the ASTM standard for cetane number, however batch runs fall short. Figure 3.18 below shows the correlation of intermediates present in biodiesel and CN for this study. It predicts the correlation given by equation: *y = - 0.7573x + 59.802.*

Kinematic Viscosity and Density

Kinematic Viscosity is another important parameter to analyze the quality of the fuel. It depends on the raw materials used for the production of methyl/ethyl esters. In literature many models have been proposed to predict kinematic viscosity of biodiesel and many of them are focused on the dependency with temperature. Kinematic viscosity for product samples was measured at 28^0C with viscometer and the values at 40^0C were predicted using temperature correction equation (see Appendix). Table 3.5 reports the measured and predicted values obtained with temperature correction.

Table 3.5 Predicted and measured kinematic viscosity

Run#	1	2	3	4	5	6	7	8
η_{Mes} 28^0C	6.62	5.9	5.57	5.48	5.47	7	5.57	5.76
η_{Pre} 40^0C	5.029	4.482	4.231	4.613	4.155	5.318	4.231	4.376

Measured product density are shown in Table 3.6, currently there are no ASTM standards for density of biodiesel.

Table 3.6 Measured density of biodiesel for different runs.

Run#	1	2	3	4	5	6	7	8
Density (g.cm^{-3}) at room temperature (Methyl Ester)	0.84	0.83	0.83	0.84	0.83	0.9	0.88	0.85
Product Loss By Washing and Drying (g)	98	76	61	63	49	52	43	58

3.4 Conclusions

The study clearly demonstrates advantages of the new method based on gradual flow of oil feed over the conventional method in terms of conversion and superior properties of the fuel. In the new method, the alcohol to oil ratio is as high as 36:1 in the initial period of the reaction. This increases the reaction rate of the system which further increases the conversion. Significantly higher conversions obtained with the new method would avoid separation and recycle of un-reacted feed. The quality of the fuel obtained is better with respect to the conventional methods due to lower viscosity, density and chemical bound glycerol. Further studies will be carried out in order to develop a kinetic model for the new method.

3.5 Abbreviations

G-Fed   Gradually Fed

TG   Triglycerides

DG   Diglycerides

MG   Monoglycerides

GL   Glycerol

ME   Methyl esters

G   Free glycerol

CBG   Bound glycerol

KOH   Potassium hydroxide

HCl   Hydrochloric acid

THF   Tetrahydrofuran

MSTFA   N-methy-N(trimethylsilyl) trifluoroacetamide

GC   Gas chromatography

rpm   Revolutions per minute

MW   Molecular weight

m   Mass fraction

wt   weight

Greek Letters

φ Cetane number

ρ Density (g.ml^{-1})

η Kinematic viscosity (mm^2.s^{-1})

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APPENDIX (Chapter 3)

GC Calibration curve using ASTM standards:

Triolein

The plot shows Area under the curve (y-axis, 200000 to 1400000) vs Concentration (ppm) (x-axis, 100 to 500).

$$Y = A + B * X$$

Parameter	Value	Error
A	84696.32	97673.11
B	2419.241	300.533

R	SD	N	P
0.985	91094.117	4	0.015

Diolein

The plot shows Area under the curve (y-axis, 20000 to 140000) vs Concentration (ppm) (x-axis, 100 to 500).

$$Y = A + B * X$$

Parameter	Value	Error
A	1321.687	4656.999
B	267.021	14.329

R	SD	N	P
0.997	4343.316	4	0.003

Monolein

Y = A + B * X

Parameter	Value	Error
A	10287	15734.318
B	178.296	22.981

R	SD	N	P
0.984	12847.017	4	0.016

Methyl Oleate

Y = A + B * X

Parameter	Value	Error
A	58782.965	4082.792
B	1394.583	15.7

R	SD	N	P
1	5902.781	4	1.267E-4

Estimation of Cetane number:

In Chapter 3, approximate CN is calculated with respect to the intermediate content (TGs, DGs and MGs) in the final methyl ester phase. The GC analysis of the samples helps to determine the approximate molecular weight and the molecular weight of the pure methyl ester content in the reaction mixture. The cetane number (CN) of ester content is estimated using equation 1 shown below

$$\varphi_i = -7.8 + 0.302 \cdot M_i - 20 \cdot N \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$

where φ_i is the cetane number of alkyl esters, M_i is the molecular weight of the individual fatty acid composition and N is zero, one and two for C18:0, C18:1 and C18:2 for individual fatty acid composition [1]. For this work: M_i is taken as the molecular weight of the methyl ester content in the biodiesel sample. N is considered as 1 as oleic acid (C18:1) is a major component for canola oil. The individual molecular weight content of the TGs, DGs, MGs and MEs in the final samples are calculated using equation 2.

$$M_{ij} = \text{Mole fraction}_j \cdot MW_j \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2)$$

$$M_i = \sum M_{ij} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(3)$$

In Equation 2, j represents intermediates and product for each calculation (i. e. TG, DG, MG and ME). MW_j is theoretical values of molecular weight for all the intermediates ($MW_{TG} = 877$ g.mol^{-1}, $MW_{DG} = 621$ g.mol^{-1}, $MW_{MG} = 356.96$ g.mol^{-1}, $MW_{ME} = 295$ g.mol^{-1}). The average molecular weight of the samples in terms of the intermediate content is estimated with equation 3. The CN for the intermediates present in the biodiesel sample is approximated as per equation 4. [TG][DG] and [MG] are the mole

fraction of the intermediates and CN_{TG} CN_{DG} and CN_{MG} are the approximate values of cetane number for TGs, DGs and MGs.

$$\Phi_j = [TG].CN_{TG} + [DG].CN_{DG} + [MG].CN_{MG} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(4)$$

The CN_{TG} CN_{DG} and CN_{MG} is considered as 40 as per the cetane value of canola oil. The total approximate CN is obtained by using equation 5.

$$\Phi_{avg} = [ME\%] \; \Phi_i + \Phi_j \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(5)$$

Estimation of Density

In chapter 3, the density of the reaction mixture is calculated using various correlations available in the literature. Equation 6 is used to estimate the density for the methyl ester content in the final biodiesel sample for 20^0C. The individual and average molecular weight is calculated using equation 2 and 3.

$$\rho_i = 0.843 + \frac{4.9}{M_i} + 0.0118 . N \qquad\qquad (6)$$

In equation 5, M_i is the attributed molecular weight of ith FAME [1] in the biodiesel sample. In this study the M_i is taken as the molecular weight of the total FAME present in the reaction mixture excluding the intermediates. The density for the ester content is calculated using the expression provided in equation 5. Density of the intermediate content in the final reaction mixture is calculated using equation 7. ρ_j is the density of methyl ester content in the reaction mixture at 20^0C. [TG][DG] and [MG] are the wt fraction of the intermediates and ρ_{TG}, ρ_{DG} and ρ_{MG} are the approximate values of density for TGs, DGs and MGs. The density for TGs, DGs and MGs are taken as the density

value of canola oil (0.92 gm.ml^{-1}). The approximate density values are calculated as per the expression (Equation 8). From the equation 5, 6 and 7 the prediction of density values was obtained.

$$\rho_j = [TG].\ \rho_{TG}\ + [DG].\ \rho_{DG} + [MG].\ \rho_{MG} \ ....(7)$$

$$\rho_{avg} = \rho_i + \rho_j ....(8)$$

Estimation of Kinematic viscosity:

In Chapter 3, the estimation of kinematic viscosity is carried out as follows:

In literature many models have been proposed to predict kinematic viscosity of biodiesel and many of them are focused on the dependency with temperature. Ramirez Verduzco et al. [1] reported an expression (equation 9) after studying other models.

$$\ln(\eta_i) = -12.503 + 2.496\ .\ \ln(Mi) - 0.178\ .\ N ....(9)$$

η_i is the kinematic viscosity at 40^0C with units of mm$^{2.}$s^{-1} for ith FAME (eg methyl oleate, methyl linolenic). The equation is used here to predict the viscosity of total FAME in the biodiesel content using MW attributed from the ester phase. In order to calculate the approximate viscosity of biodiesel with the presence of intermediates is estimated using mixing equation determined by Grunberg [2] to predict the viscosity of blends.

$$\log \eta_b = m_1 \log \eta_1 + m_2 \log \eta_2$$

Thus the equation was determined for these studies as equation 10:

$$\log \eta_b = m_{TG} \log \eta_{TG} + m_{DG} \log \eta_{DG} + m_{MG} \log \eta_{MG} + m_{ME} \log \eta_{ME} \dots\dots (10)$$

In the above equation $m_{TG} \log \eta_{TG} + m_{DG} \log \eta_{DG} + m_{MG} \log \eta_{MG}$ is replaced by $m_{can} \log \eta_{can}$. Thus the m_{can} is taken as the mass fraction of impurities (intermediates) and η_{Can} is kinematic viscosity of canola oil at 40^0C. The equation 10 is modified as equation 11 for the prediction of kinematic viscosity.

$$\log \eta_b = m_{Can} \log \eta_{Can} + m_{ME} \log \eta_{ME} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(11)$$

Kinematic viscosity is measured at the temperature of 28^0C, the predicted viscosity obtained from equation 11 is for 40^0C. The conversion is carried out using equation 12[1].

$$\log \eta = A + \frac{B}{T} + \frac{C}{T^2} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (12)$$

In Equation 12 the constants: A = 0.7883; B = -1638; C = 582500; T = Temperature in Kelvin.

Chapter 4

4   Ethanolysis versus methanolysis of vegetable oil using a new Gradual feed flow method.

4.1   Introduction

Human existence depends on energy used in different forms for various tasks and activities important for survival. It is used for food and agriculture production, industrial operations, generation of electricity, fuel for transportation and many more. Fossil fuels currently play a major role in world's total energy consumption. But the world is no longer endowed with new sources of fossil fuels and the experts have warned of their depletion in near future. Increased environmental concerns, tougher Clean Air Act standards, and depletion of raw material are driving industry to come up with viable alternative fuels that burn more cleanly. These fuels for diesel engines are becoming significantly important. The concerns about the environmental problems like global warming and air pollution has furthered the need for eco-friendly fuels. Large amount of time and money is being invested in the sources for renewable and eco-friendly fuels. The alternatives to diesel fuel must be technically and environmentally acceptable, economically competitive and readily available [1]. Many governments are considering policies for establishing economies based on renewable fuels. BIODIESEL is one of the possible alternatives to fossil fuels. Exploring new energy resources, such as biodiesel fuel is growing importance in recent years. Biodiesel derived from vegetable oil or animal fat, is recommended for use as a substitute for petroleum based diesel. Vegetable oils have been considered as fuel for diesel engines since the earliest days of the

compression-ignition engine. Biodiesel in general has many advantages which makes it a promising fuel for future. It is made from renewable biological sources such as vegetable oils and animal fats. The non toxic property and biodegradable nature makes it a valuable fuel. Biodiesel in general has low emission profiles, this quality makes it environmentally beneficial: less greenhouse effect, less air, water and soil pollution and less health risk, compared to the use of the fossil fuel [2]. The common method of biodiesel production is transesterification (or alcoholysis), a chemical reaction between triglyceride and alcohol in presence of a catalyst. It consists of a sequence of three reversible reactions wherein triglycerides are converted to diglycerides, diglycerides are converted into monoglycerides and monoglycerides are converted into glycerol. With each reaction step one mole of alkyl ester is produced. Triglycerides are obtained from vegetable oil or fats, various varieties of plant and animal sources can be used. The three step reaction for transesterification of vegetable oil is as shown below in figure 4.1:

Triglyceride	+	Alcohol	⇌	Diglyceride	+	Alkyl Esters
Diglyceride	+	Alcohol	⇌	Monoglyceride	+	Alkyl Esters
Monoglyceride	+	Alcohol	⇌	Glycerol	+	Alkyl Esters
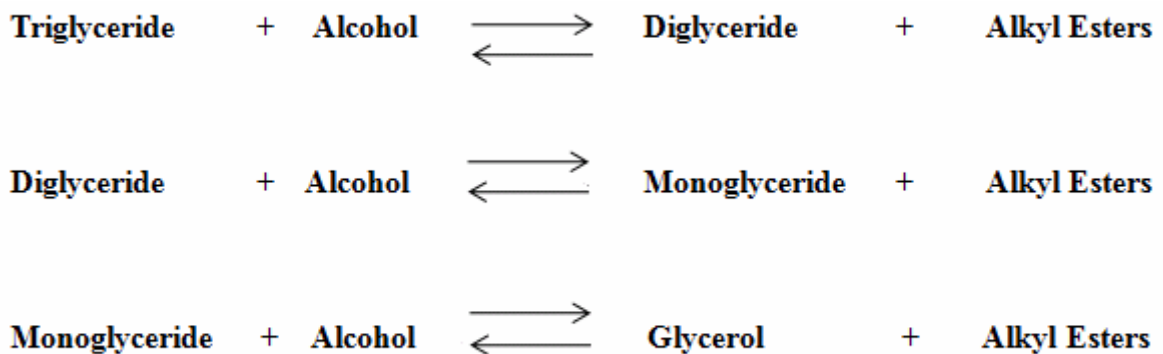
Figure 4.1 Stepwise transesterification reaction

Methanol and Ethanol are the most frequently used alcohols for the transesterification of vegetable oils. Although methanol is preferred more as it has the suitable physical and chemical properties, low cost and easy availability. Methanol has more reactivity for the

process of transesterification as compared to ethanol [3]. The production of methyl esters is commercialized so far, however ethyl esters are of considerable interest due to their high heat content and cetane number as compared to methyl esters. The higher heat of combustion of ethyl esters is due to the extra carbon in the ethanol molecule [5]. Moreover, ethanol is obtained from bio-based materials and is less toxic than methanol. It can be considered green fuel as ethyl esters tends to reduce the emissions of carbon monoxide, particulate matter and nitrogen oxides (NOx). The biodegradable properties of ethyl esters are better as compared to methyl esters [6, 7]. Studies carried out for lubricity and wear properties proved ethyl esters better as compared to methyl esters [10, 11]. Ethyl esters have the better cold temperature properties i.e. cloud point and pour point [9]. Another advantage of using ethanol as transesterification agent is its superior dissolving power with vegetable oils [8, 9]. Some of the limitations include lower reactivity and possible formation of stable emulsions during transesterification. It has been pointed out that the reactivity decreases with increase in the length of the carbon chain [4]. Ethyl esters forms stable emulsions and thus make the separation and washing stages difficult [19].

The alcoholysis reaction is a complex process due to the presence of two phases [12]. Mixing and mass transfer between the phases is of critical importance for the transesterification reaction system. The reaction starts with mass transfer of the triglycerides from the oil phase to the alcohol phase (with catalyst). This region can indirectly decrease the conversion and product yield for biodiesel synthesis [13-16]. Attempts have been made in literature studies to minimize mass transfer limitations by different methods [17-21]. The mass transfer lag observed in methanolysis can be

reduced by using ethanol as the alcohol [8, 23]. This is attributable to better solvent properties and solubility of ethanol with vegetable oils which overcome mass transfer limitation in the initial phase of the reaction [23].

Although initial mass transfer limitations are reduced with ethanol, the lower reactivity and difficult separation of glycerol is of concern [23]. Literature studies have attempted higher alcohol to oil ratios and co-solvent combination to overcome these problems while making a product to meet ASTM standards [23]. In this study a new method earlier introduced by the authors with methanolysis has been tested. The method is based on gradually feeding oil to a pool of alcohol thus allowing significantly higher alcohol to oil ratio to be maintained during major part of reaction. This approach allowed higher conversion rate and better yield as compared to conventional batch method. Systematic comparison has been made between ethanolysis and methanolysis to point out the differences while taking advantage of the new method.

4.2 Experimental Details

Materials: Refined and edible Canola oil was purchased from Metro, Canada. Potassium hydroxide, anhydrous Ethanol (100%) and aqueous HCl (1N) were purchased from VWR (Canada). The reference standards required for the GC analysis were purchased from Sigma Aldrich. The standards were solution of glycerol, 1- mono-olein, 1,3-di-olein (1% 1,2 isomer) and triolein. *n*-Hexane (HPLC grade) was used as a solvent to dilute the samples for GC analysis. N-methyl-N-trimethylsilyl trifloroacetamide (MSTFA) was used as a derivatizing agent.

Method: The experiments were carried out in one liter jacketed glass reactor equipped with an impeller and four baffles. The reactor inside diameter and height was 100 mm and 153 mm respectively. The reactor was sandwiched between the lid and the reactor base support plate with threaded rods. The reactor lid was designed with a four ports: for sampling, inlet of the impeller rod, inlet of thermocouple to monitor the change in temperature during the progress of the reaction and for reflux condenser to avoid methanol and ethanol losses. The reactor was properly sealed with viton in order to obtain a leak proof system. The temperature in the reactor was controlled by a water bath connected to the jacket of the reactor. It controlled the temperature of the reaction mixture to an accuracy of $\pm 1\ ^0$C. The diameter of the impeller was 63.5mm and was placed concentrically at 36 mm from the bottom. Other equipment used for the study included Brookfield viscometer for viscosity measurements, Buchi vaporizer (R-114) for drying, centrifuge, and separatory funnels for phase separation. Figure 4.2 shows the schematic of set up of the experiment used. For batch runs, the oil was preheated to 28^0C in the reactor, the reaction was stirred and timed after the addition of methanol/ethanol premixed in 1% (w/w of oil) KOH.

The agitation was carried out at 600 rpm for the batch runs of methanolysis and ethanolysis. In case of gradually fed (G-Fed) method, the oil was stored separately in the sealed flask to prevent oxidation reaction; it was pumped into the system at a known flow rate. The flow from the oil flask was controlled with the help of a metering pump. In the G-Fed method the mixing was carried out at 300 RPM for initial 15 min. As the quantity of the feedstock increased with time, the mixing was carried out at 400 rpm from 15-30 min. Reaction beyond 30 minutes followed batch mode wherein the mixing was carried

out at 600 rpm. The variation in the mixing speeds was selected after performing initial studies with the new method. This process was carried out using both methanol and ethanol to compare effect of alcohols on the conversion of triglycerides for different systems. Samples were collected at the regular interval of time to study the progress of the reaction with GC analysis.

1. Reactor Cell
2. Oil outlet Pipe (For G-Fed method)
3. Oil inlet Pipe (For G-Fed method)
4. Baffle
5. Jacketed Wall
6. Temperature indicator
7. Metering Pump
8. Oil Tank
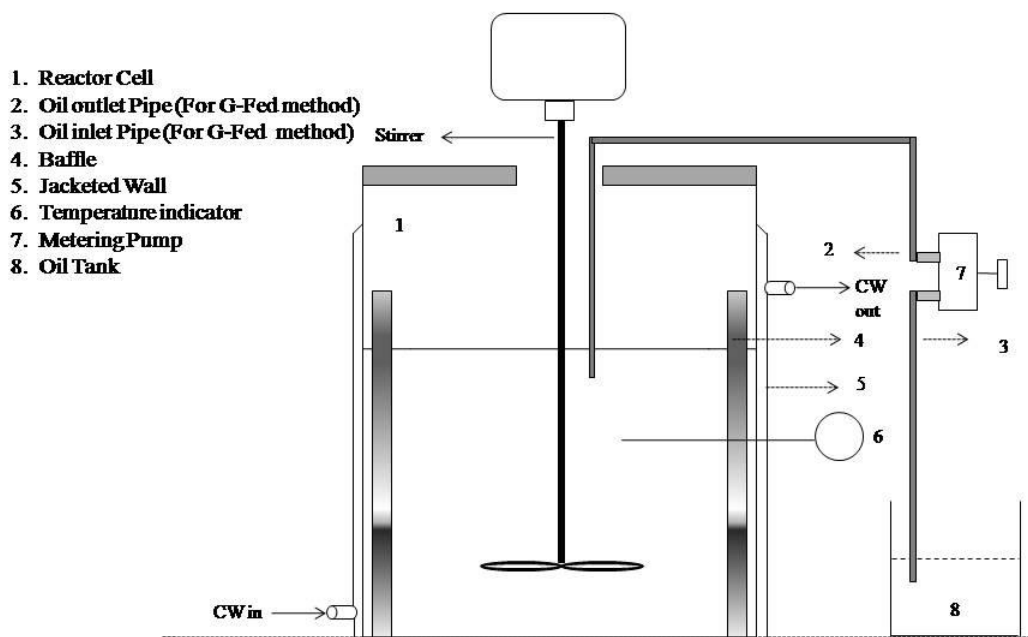
Figure 4.2 Experimental setup for Batch and G-Fed method.

The reaction was stopped after 60 min and the reaction mixture was transferred to a separatory funnel to separate alkyl esters and glycerol phases. The product and the byproducts followed a series of purification steps to obtain excess alcohol and remove un-reacted catalyst. The glycerol separation from the alkyl esters takes place in about 10 min after stirring is stopped but complete separation takes as long as 18h [24]. Thus the

mixture was allowed to stand overnight to separate glycerol and alkyl ester phase. Both the phases: methyl/ethyl ester and glycerol were sent to a rota-vap to separate excess alcohol. The ester phase was purified with washing process to remove catalyst and free glycerol. To neutralize the ester phase, the first wash was carried out with 1 N HCl solution followed by two to three washes with distilled water. The volume of the water to wash the ester phase is approximately 20% of the ester phase. The pH of the washed water was measured after each wash; washing was stopped once the pH reached in between 7 and 8. The washed ester phase was dried by rotavaporising at 100^0C for 20 mins to completely remove the water content from the phase. The methyl/ethyl ester and the glycerol were weighed for the mass balance calculations. After each step of the process, the viscosity and specific gravity measurements were carried out for alkyl ester and glycerol phases. The experiments were conducted twice and the sample analysis were carried out in triplicates in order to investigate on the reproducibility of the results.

4.2.1 Sample analysis and characterization:

As the reaction progressed samples were collected at regular interval of five minutes (1.5 ml) and quenched in 1N HCl solution (2ml). Quenching was carried out to cease the reaction at that particular time for studies of intermediates. The catalyst from the reaction sample settles down in the HCl solution. The samples were allowed to stand for 2-3 h to remove the catalyst from the alkyl ester phase. The top layer from these samples was centrifuged to help dry the phase. The top layer is pulled out and transferred to 2 ml centrifuge tube [13]. Anhydrous sodium sulfate was added into the centrifuge vials. Sodium sulfate acts as a drying agent to remove residual water from the samples [25]. The process of centrifuging was carried out for the duration of 15 min and at the speed of

4000 rpm. For GC analysis sample solution was prepared by transferring measured amount of dried sample into 1ml auto sampler vial. MSTFA was added to derivatize the samples in order to increase the peak resolution. The samples were diluted in the concentration range of 200-600 ppm with respect to the calibration studies. The calibration was carried out for triglycerides, diglycerides, mono glycerides and alkyl esters. The processed sample was allowed to stand for 20 min at room temperature in order to derivatize the glycerides. After 20 min the vial was topped up to 1ml using *n*-Hexane as solvent to dilute the individual sample; this process was repeated for all the samples. The samples were analyzed by GC-FID. Samples (1μl) were injected on-column by an AOC 20s Auto sampler (Mandell instruments) at an oven temperature of 60^0C and injector temperature of 300^0C. The analysis was carried out in split mode. Helium was used as the carrier gas; the linear velocity of the gas was 48.5 cm/sec. The temperature program, 2 min at 60^0C, heating at the rate of 12^0C/min to 300^0C and holding for 15 min. The detector temperature was fixed at 300^0C with a hydrogen make of gas at 30ml.min^{-1}.

4.3 Results and Discussions

4.3.1 Comparison of G-Fed and Batch methods for methanolysis and ethanolysis

Variations of TG concentration with time obtained with two methods are presented in Figure 4.3. It can be seen that TG concentrations with G-Fed method were significantly lower up to the end of the reaction indicating higher conversion with this method. This indicates higher overall reaction rate most likely due to better mixing and mass transfer characteristics of the new method.
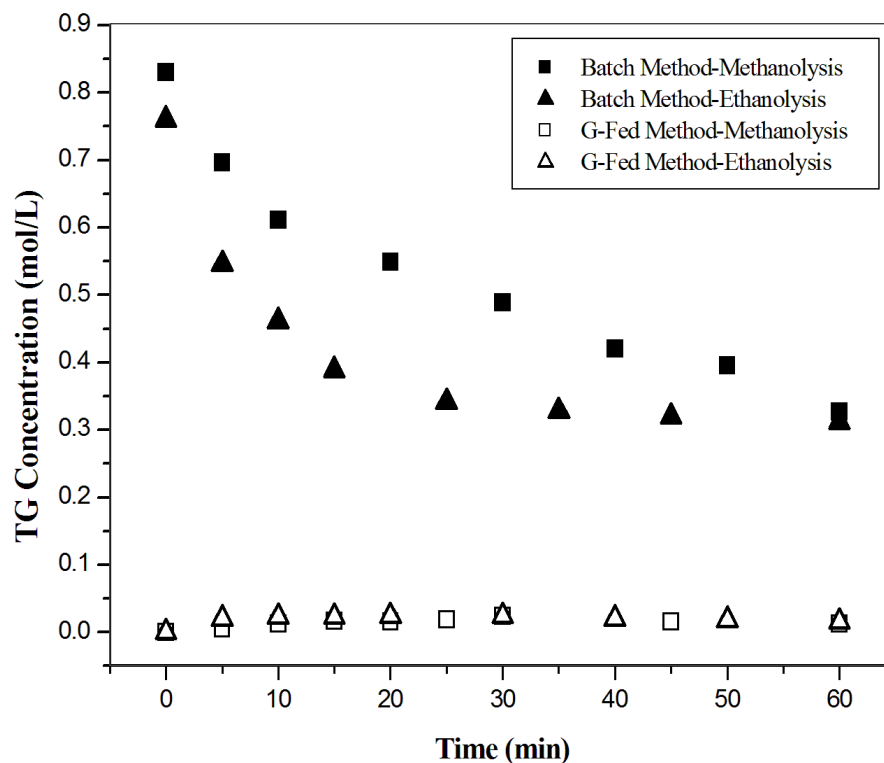
Figure 4.3 Concentration profiles for triglycerides with batch and G-Fed methods

It can also be seen from Figure 4.3 that with the batch method, TG concentrations are higher with methanol compared to ethanol; however any difference between the two alcohols is not clear with the G-Fed method due to significantly lower concentrations. The TG concentrations obtained with G-Fed method are re-plotted in Figure 4.4 using different scale to clarify the difference. It can be seen from Figure 4.4 that TG concentration was higher with ethanolysis at the beginning and approached closer to the methanolysis system as the reaction progressed. Beyond thirty minutes, the reactor operated in batch mode and TG concentration decreased with time but remained slightly higher in the ethanolysis system.
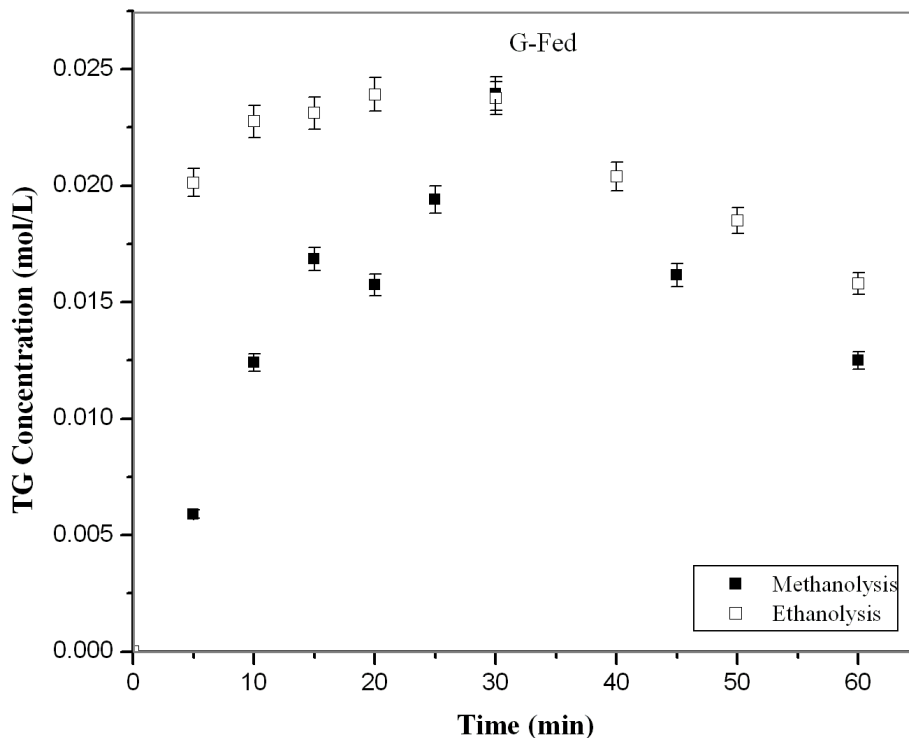
Figure 4.4 Variation of triglyceride concentration with reaction time obtained with two alcohols with G-Fed method (n = 2, error-bars = 3%)

This behavior is reverse of what is observed with the batch method where the TG concentration is observed to be higher with methanol. This could be a result of mass transfer limited conditions in the batch reactor especially during early stage of the reaction. The higher solubility of TG in ethanol works in favor of ethanol under mass transfer limited conditions of the batch method. Visual observations showed that the oil phase was easily dispersed in about 30 seconds with ethanol. In methanolysis in spite of using high agitation, the oil phase took 4 to 5 min to become miscible in the methanol phase. However, with G-Fed method, no distinct difference was observed between reaction mixtures of the two alcohols. With the batch method, the rate of drop in TG concentration is much faster with ethanol at the beginning but slows down significantly beyond about 25 minutes while with methanol; there is gradual decrease up to the end of

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the run. As the reaction progressed, dispersion improved with product formation leading to better solubility characteristics in methanolysis as well. In base catalyzed transesterification, alkoxides anion is formed by the reaction between a base and alcohol [28]. Methoxide anions CH_3O^- are formed in case of methanolysis and ethoxide anions $C_2H_5O^-$ in the ethanolysis systems. Reactivity of methoxide is reported higher than the ethoxide anion since nucleophilicity of the alkoxides anion decreases (leading to a decrease in the reactivity of alkoxides anion) as the length of the carbon chain increases, [28]. Decrease in transesterification reactivity with increase in alcohol carbon chain has been documented in literature [29]. The mass transfer region was essentially eliminated using G-Fed method. Thus, G-Fed method can be described with chemical reaction controlled region most of the time followed by equilibrium dominated region towards the end.

The reaction characteristics of the two systems were studied further with the analysis and distribution of final and intermediate products. Figure 4.5 shows that significantly higher alkyl ester concentrations (by about 50%) were achieved with G-Fed method compared to conventional batch method as the reaction progressed. Although at the initial stages of the reaction, differences are small especially with ethanolysis compared to methanolysis. As discussed below, higher solubility of TG in ethanol could explain this behavior. Figure 4.5 also shows that with the G-Fed method, methyl ester concentration was higher than ethyl ester concentration while a reverse trend is observed with batch method. The results indicate that dominant reaction mechanisms are different for the two cases.
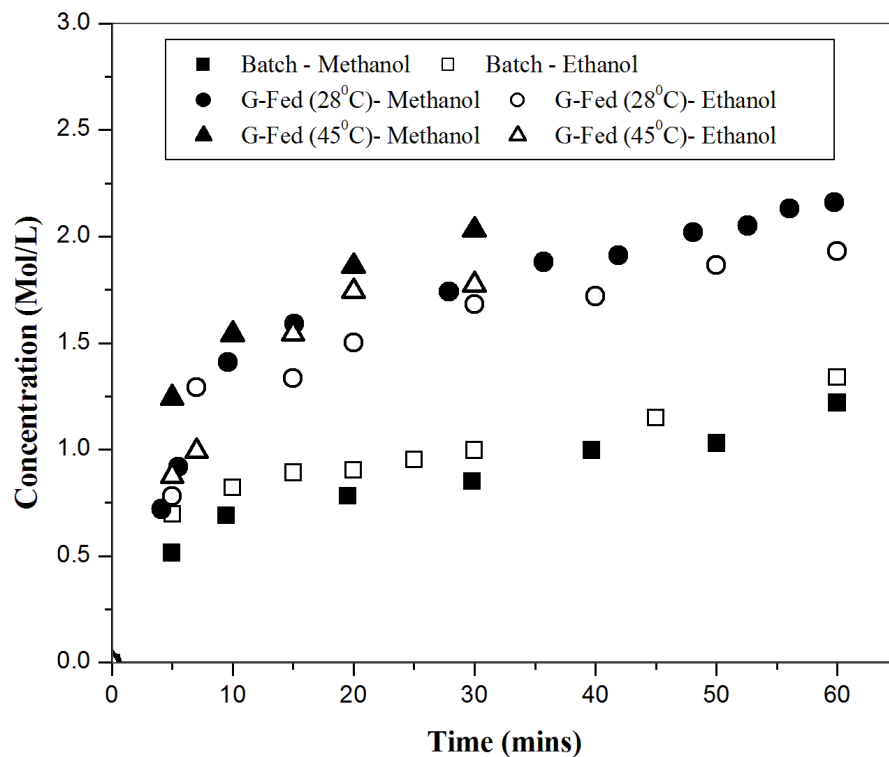
Figure 4.5 Comparison of the synthesis of methyl and ethyl esters using batch and G-Fed method.

In case of G-Fed method, high mass transfer rates are achievable due to gradual addition of oil feed, allowing easy and quick dispersion to small droplet size. Thus reaction kinetics may be a dominant mechanism in G-Fed method. In the batch operation, dispersion of oil is achieved more slowly since all of oil is added at the beginning. Thus mass transfer is expected to be slow and thus controlling mechanism for the reaction system. These aspects are further analyzed in detail in subsequent sections.

4.3.2 Separation behavior of alkyl esters and glycerol phases

The reaction solution is separated into glycerol and alkyl ester phase by gravity decantation in a separatory funnel. The homogeneous reaction mixture breaks down very quickly and easily to produce a top methyl esters rich layer and a bottom glycerol rich layer for the methanolysis process. Around 90% of the glycerol separated in 30 min from

the methyl esters synthesized with both batch as well as G-Fed method. Near complete

settling out of glycerol phase from methyl esters could be achieved after 6-7 hours. While

in case of ethanolysis, formation of emulsions complicates the separation step elongating

the separation of glycerol from the ethyl ester phase. About 80% of glycerol and ethyl

esters phases separated after 5 hours and complete separation took nearly 24 hours. The

separation became even more difficult with G-Fed ethanolysis at 45^0C, no glycerol phase

settling out occurred for 8 hours. The complete phase separation took longer and was

observed after 2-3 days. Glycerol phase collected was small and it was difficult to see the

separation from the ethyl ester phase. Ethyl esters obtained were of a deeper color as

compared to methyl esters for both the method.

4.3.3 Trends of Intermediate products with reaction progress

Figure 4.6 below present variation diglyceride (DG) concentration with time obtained

with the two alcohols (methanol and ethanol). It is seen that DG concentration is much

higher with ethanolysis. The concentration builds rapidly from the beginning and remains

high during feeding stage and drops during the batch stage. The buildup of DG

concentration with ethanol indicates slower conversion rate to monoglyceride compared

to methanolysis. The trend for MG concentration plotted in Figure 4.7 is reversed since

MG concentration is higher with methanol. This is an expected result based on DG

concentration profile in the previous figure 4.6. The slow conversion of DG to MG with

ethanol will give rise to lower concentration of MG. High DG concentration during

ethanolysis process may be a result of emulsification created due to polar hydroxyl

groups as well as non-polar hydrocarbon chains. Emulsification is produced when the

concentration of these intermediates reach a peak point [38].
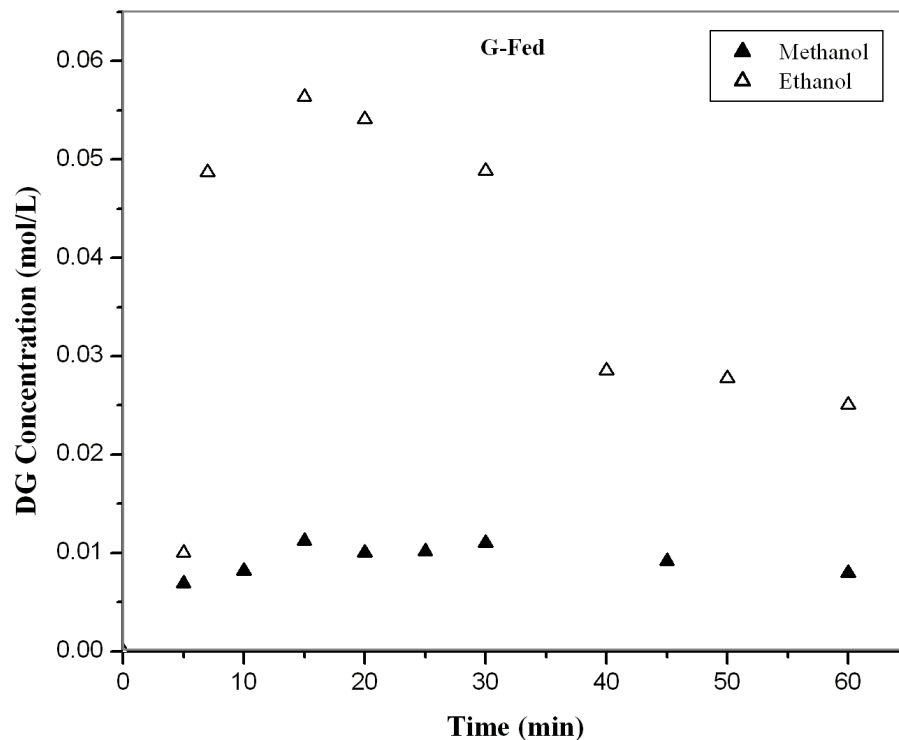
Figure 4.6 Variation of diglyceride concentration obtained with two alcohols with G-Fed method.
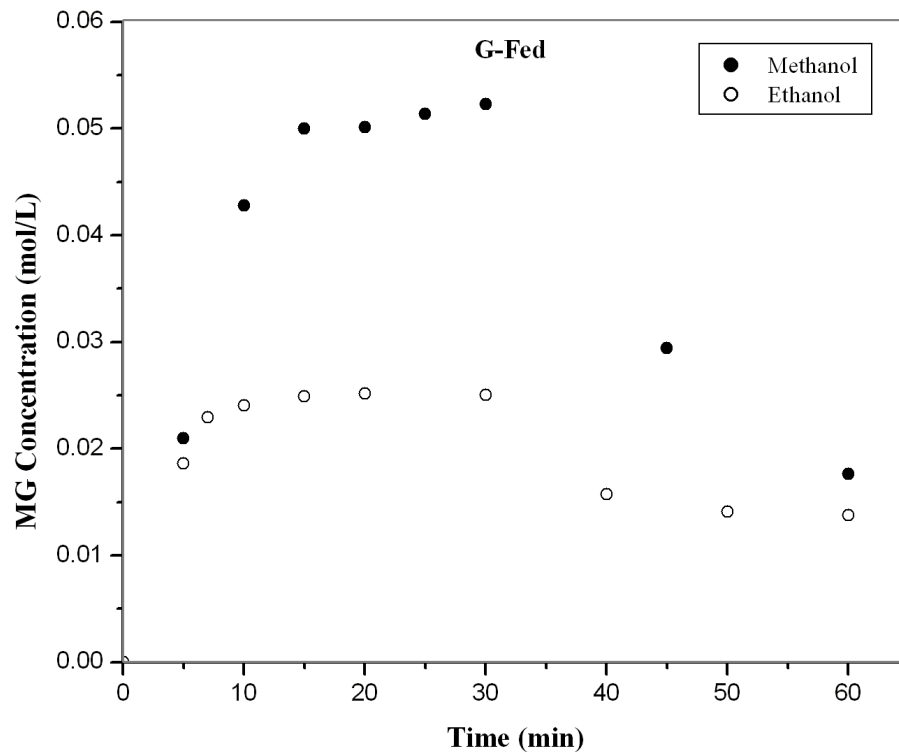
Figure 4.7 Changes in monoglyceride concentration with time with G-Fed method

Emulsions hinder the reactivity of glycerides, as the catalyst from the ethanol phase cannot be easily diffused into glyceride phase [19]. On the other hand ethanol has better solvent properties as compared to methanol as it is less polar. Thus in that context, the conversion reaches the second step forming diglycerides. However; due to the formation of emulsions the reaction rate decreases affecting the concentration of monoglycerides and ethyl esters. Thus the conversion of DGs to MGs becomes slow building up the DG concentration in the ethanolysis reaction solution. The mass transfer limitation foreseen for methanolysis is almost eliminated with the assistance of G-Fed method. Methanol being more reactive improves the reaction rate and pushes the reaction towards formation of MGs (3rd step of reaction). A tabular comparison of methyl and ethyl esters is presented in Table 4.1. The comparison is for the product obtained from different modes in terms of physical properties yields and product losses due to washing and drying. For each wash about 20 vol % of distilled water was used to wash the free glycerol and catalyst from the alkyl ester phase. In case of methanolysis four water washes reduced the pH of the washed water in the range of 7-8. However 6-7 water washes were carried out for ethyl esters to completely remove catalyst and free glycerol from the content. Large amount of water wash is needed to improve the separation process [9]. Due to the soap formation, the loss is more for ethyl esters as compared to methyl esters in both batch as well as G-Fed method. The emulsions formed due to the water wash take very long time to break for the ethyl esters as compared to methyl esters. Washing being very critical and complex in ethyl esters results in washing away of esters while separating the wash water. Ethanol increases the catalyst solubility in the oil–ethyl ester phase, thus accelerates the saponification reaction [19].

Table 4.1 Mass balance and product properties

Run	Batch	G-Fed	Batch	G-Fed
Canola Oil (g)	498	498	498	498
Alcohol type	Methanol	Methanol	Ethanol	Ethanol
(g)	109	109	157	157
Reaction Time (min)	60	30 Fed +30 Batch mode	60	30 Fed + 30 Batch mode
RPM	600	300-400-600	600	300-400-600
Reaction Temperature (^{0}C)	28	28	28	28
Reaction solution (Alkyl Esters and glycerol rich phase)	600	573	581	597
Weight of washed and dried products (g)	448	432	452	463
Weight of Glycerol (g)	51	51	52	54
Kinematic Viscosity at 28^{0}C mm^2.s^{-1}	6.92	5.48	5.9	5.0
Density at room temperature (g.cm^{-3})	0.88	0.84	0.89	0.87
Product loss by washing and drying (g)	53	63	75	78

Eliminating the water washing step or replacing it with dry washing can avoid saponification in ethanolysis increasing the product yield. The amount of methyl esters and ethyl esters obtained by complete conversion as per the theoretical calculations are 501 g and 528 g respectively. The theoretical calculation of glycerol produced in both the

cases is 52.2 g. For the G-Fed method using ethanol as precursor, the glycerol phase is more than the theoretical values. This can be due to the loss of ethyl esters in the glycerol phase. The non polar ethyl esters can form emulsions with the polar glycerol phase with the influence of soap produced due to saponification in presence glycerides [37]. Ethyl esters form more emulsion than methyl esters during washing [11]. The viscosity of the washed and dried phase of the alkyl esters were in the range of ASTM standards[36]. The viscosity of biodiesel obtained with G-Fed method is lower than the viscosity obtained with batch method. However comparing the G-Fed method approach for both alcohols; the viscosity of ethyl esters was much lower than methyl esters. Along with the product, the amount of intermediates and by product is also of importance for the quality of biodiesel. Viscosity of the biodiesel is influenced by the extent of transesterification reaction and experimental parameters [34].

Table 4.2 lists percentage of TG, DG and MG in the product layer which was used to calculate TG conversion, product yield and total glycerol for this study. Overall yield is calculated by dividing the amount of desired product obtained by the theoretical yield.

Overall Yield = Desired product obtained/Amount of product which could be obtained if all of feed is converted to produce the desired product. The presence of glycerides in the product increases chemically bound glycerol (CBG). The total glycerol in the system is related to the free glycerol (G) and CBG in the following manner:

$$G_{total} \quad = G + [(MG \times 0.25) + (DG \times 0.15) + (TG \times 0.10)]$$

$$= G + CBG$$

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The ASTM limit for free glycerol is 0.02 wt % and the total glycerol (free and chemically bound glycerol (CBG)) is limited to 0.240 wt. %. The total glycerol content for the product (methyl esters) obtained through G-Fed method meets the ASTM requirements.

Table 4.2 Percentage of TG, DG, MG and product yield

Types of runs	TG (wt%)	DG (wt%)	MG (wt%)	Total Glycerol (wt%)	Product yield**	TG conversion (%)
G-Fed Methanol	0.478	0.318	0.593	0.238*	83.77	98.61
Batch Methanol	12.9	1.315	1.39	1.84	44.55	84.3
G-Fed Ethanol	0.478	0.565	0.478	0.25	84.86	98.4
Batch Ethanol	12.17	1.65	1.34	1.8	43.64	63.4

* Meet ASTM standards

** Calculated to meet ASTM standard.

The yield of the methyl/ethyl esters is more for G-Fed method as compared to batch method. However considering only G-Fed method, methanol system is proved better than ethanolysis with respect to the total glycerol content at the similar reaction conditions. Although methyl esters and ethyl esters obtained with the assistance of G-Fed method meets the ASTM standards.

4.3.4   Further analysis of reaction system and derivation of overall reaction rate

The overall behavior of TG conversion for batch run and G-fed method using ethanol and methanol as precursors is presented in Figure 4.8. It can be observed that for batch runs,

the TG conversion is higher for the case of ethanolysis during initial stages of the reaction. This difference has been attributed to solubility and mass transfer issues in literature studies [8, 23]. The solubility issues of methanol in vegetable oil makes the reaction mass transfer controlled resulting in lower conversion in batch run. The mass transfer limitations are avoided in ethanolysis since ethanol has better mixing property in vegetable oil than methanol.
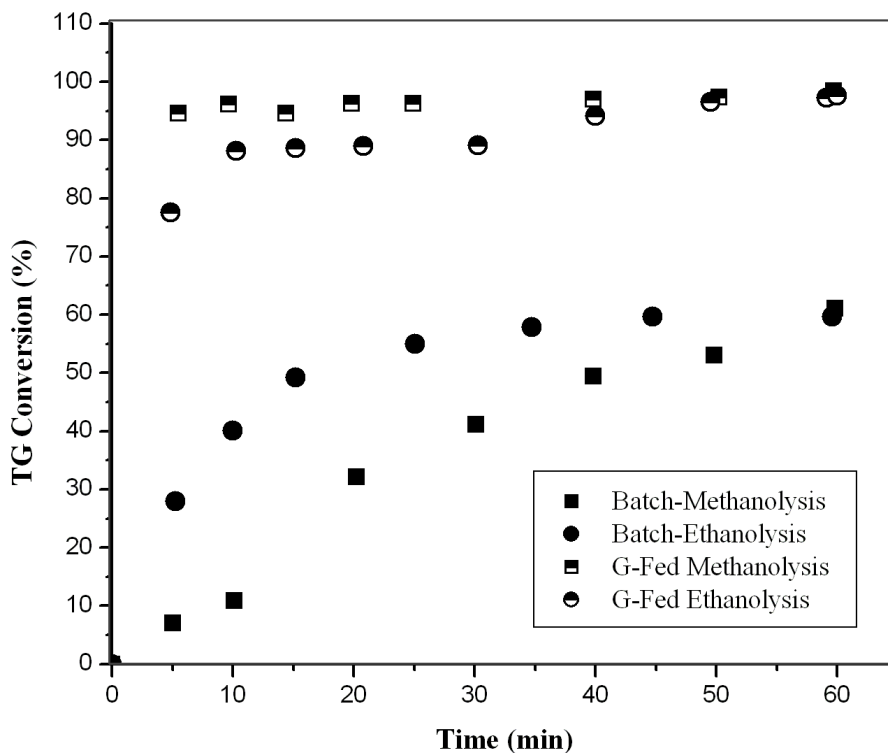
Figure 4.8 Conversion of triglycerides for ethanolysis and methanolysis using Batch and G-Fed method.

It was visually observed that the reaction mixture in methanolysis reaction was not as transparent and clear as in ethanolysis system. However in G-Fed method, the conversion of triglycerides was higher in the case of methanolysis. Finely dispersed oil in the G-Fed method would create high interfacial area for mass transfer making the

reaction more kinetically controlled. This might be the case as the reactivity of methanol in transesterification process is more than ethanol [3]. Although the conversions of TGs were better in the methanol system during initial stages of the reaction, the percent conversion was similar with application of G-Fed method for both the systems (methanolysis and ethanolysis) after 60mins.

Derivation of overall reaction rate

The transesterification reaction of triglycerides involves liquid-liquid extraction with interphase chemical reaction of the reactive species present in two different oil and alcohol phases. The alcohol phase is considered continuous and oil phase is dispersed. The reaction takes place in the alcohol phase where reactive catalyst sites reside. The reactive species TG therefore diffuse to the reaction zone in the alcohol phase. The overall rate of process is controlled by both the kinetics of the reaction and the diffusion or mass transfer characteristics of the systems. However, depending on the conditions, the extraction process may be controlled by kinetics of the reaction or by mass transfer. The overall reaction rate consists of the following processes in series:

1. Mass transfer from the dispersed oil phase to the oil-alcohol interface.

2. Mass transfer of TG from the interface to the bulk-alcohol phase.

3. Reaction in the bulk alcohol phase.

It is reasonable to assume that interface (within individual liquid phase) mass transfer resistances are negligible compared with interface (between two liquid phases) resistance. The rates of mass transfer processes can be expressed as below:

$$r_{TG} = k_{lc}a_c(C^*_{TG,A} - C_{TG,A}) \qquad (4.1)$$

Reaction in the alcohol phase

$$r_{TG} = k_1 \, C_A \, C_{TG,A} \, \varepsilon_{l,A} \qquad\qquad (4.2)$$

where k_1 is reaction rate constant for the second order reaction given by Eq. 4.2.

The various concentrations are shown schematically in Figure 4.9.
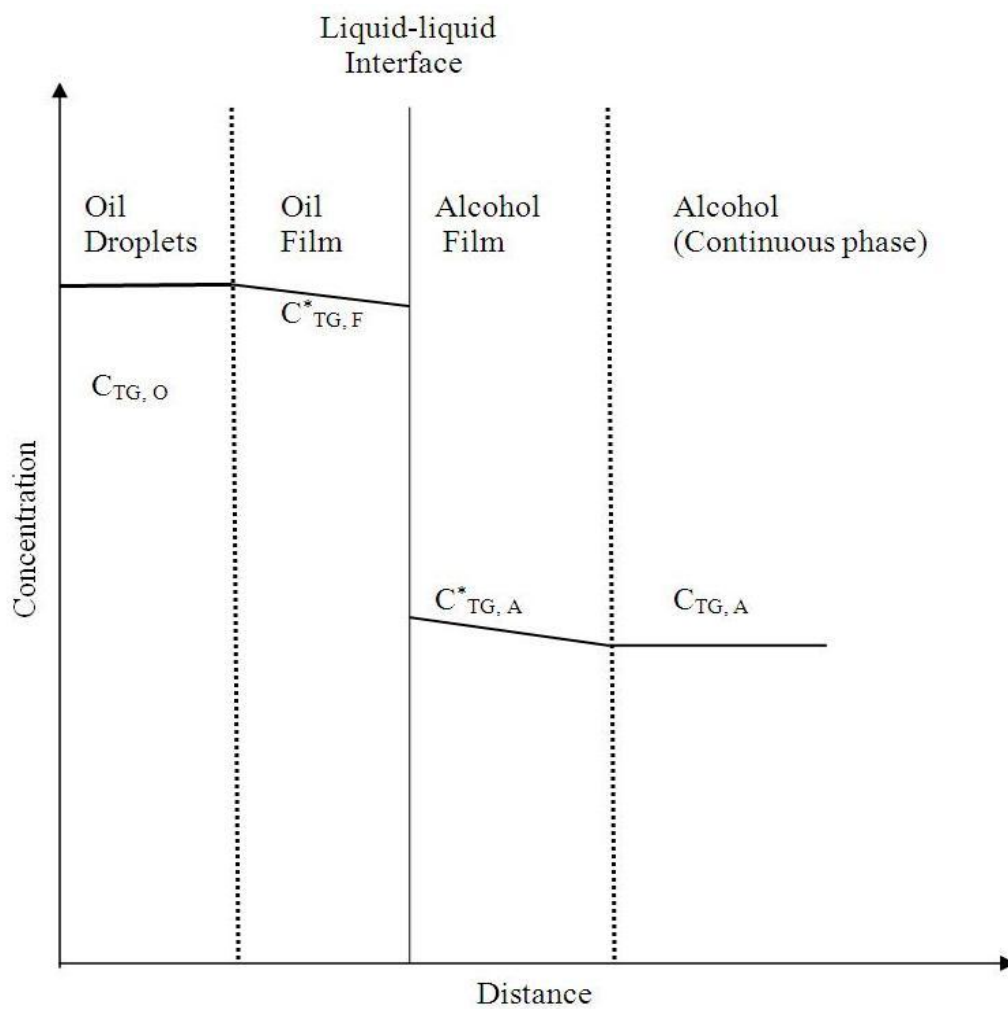
Figure 4.9 Concentration profiles in a liquid-liquid (oil and alcohol) reactor system.

If equilibrium exists at the liquid-liquid interface, $C_{O,TG}$ and C^*_{TG} are related by distribution coefficient (d_{TG}).

$$d_{TG} = C^*_{TG,A}/C_{TG,O} \tag{4.3}$$

The above equations can be combined to eliminate $C_{TG,A}$ $C^*_{TG,A}$. Then the rate can be expressed solely in terms of concentration of reactants in the oil phase:

$$r_{TG} = k_{ov}C_{TG,O} \tag{4.4}$$

here

$$\frac{1}{k_{ov}} = \frac{1}{d_{TG}}\left[\frac{1}{k_{lc}a_c} + \frac{1}{k_1 C_A \varepsilon_{l,A}}\right] \tag{4.5}$$

Equation 4.5 shows that the overall rate constant (k_{ov}) is a function of mass transfer coefficient, interfacial area for mass transfer, specific reaction rate constant (k_1) and bulk alcohol concentration. Equations 4.4 and 4.5 can be used to analyze reaction systems under different conditions. For example when mass transfer rate is slow compared to reaction term, the overall rate would be controlled by mass transfer rate. The ratio of reaction rate with the two alcohols can be expressed as below.

$$\frac{r_{TG,Et}}{r_{TG,Me}} = \frac{(d_{TG,Et})x(k_{lc,Et}a_{c,Et})}{(d_{TG,Me})x(k_{lc,Me}\,a_{c,Me})} \tag{4.6}$$

Calculation of reaction rates ratio in equation 4.6 requires values of distribution coefficients, mass transfer coefficients and interfacial area for mass transfer. These values are difficult to find for this reaction system due to limited number of literature studies in such details. An attempt has been made in this study to estimate these values based on available literature information and presented in Appendix. The estimates are

approximate and mostly on the conservative side. Table 4.3 reports the estimated interfacial area and mass transfer coefficient for different runs. When the values are plugged into equation 4.6, the equation fairly predicts the observed trends with the batch method.

Table 4.3 Properties of reaction mixture

Type of runs	Alcohol/ Temperature (^{0}C)	Interfacial area ($m^2 . m^{-3}$)	Sauter mean diameter d_{32} (mm)	Mass transfer coefficient (m. s^{-1})	Diffusion coefficient (dispersed phase) ($m^2.s^{-1}$)
G-Fed	Methanol 45^{0}C	54770	0.0380	0.0003	5.3443 X10^{-10}
G-Fed	Ethanol 45^{0}C	43617	0.048	0.0001	2.9131 X10^{-10}
G-Fed	Methanol 28^{0}C	54769	0.0383	0.00027	5.058 X10^{-10}
G-Fed	Ethanol 28^{0}C	43616	0.0482	0.0001	2.756 X10^{-10}
Batch	Methanol 28^{0}C	35815	0.1	0.00019	5.0612X10^{-10}
Batch	Ethanol 28^{0}C	31252	0.11	0.00008	2.757 X10^{-10}

If the mass transfer term can be neglected for G-Fed method then instead rate constant term can be used in order to calculate the ratio of reaction rate for both the alcohol reaction as shown by equation (4.7).

$$\frac{r_{TG,Et}}{r_{TG,Me}} = \frac{(d_{TG,Et})(k_{1,Et}C_{Et}\varepsilon_{l,Et})}{(d_{TG,Me})(k_{1,Me}C_{Me}\varepsilon_{l,Me})} \tag{4.7}$$

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Use of equation 4.7 requires kinetic rate constants for both the alcohols. While some data is available for methanolysis, very little work is done with ethanolysis. Available literature data shows higher rate constant for methanolysis compared to ethanolysis [3, 11, 13,15]. The above analysis can be pursued further when more data becomes available. Also, the above analysis is based on first order catalytic reaction assuming complete back-mixing in liquid phase. For higher order reaction rate and multi-reactant systems, numerical methods are required.

4.4 Conclusions

G-Fed method is an effective approach to increase the conversion rate in ethanolysis system. However the method is more promising if methanol is used as an alcohol. The method improves the dispersion resulting into a homogenous system with no mass transfer lag region. The dispersions caused during the reaction increases the emulsions in the ethanolysis reaction making the system more complex. At the temperature of 45^0C the complete phase separation took place after 24 hours. The quality of glycerol was low, less viscous and was not distinguished in the reaction mixture; which resulted in the loss of ethyl ester in the glycerol phase during separation. With application of the G-Fed method monoglyceride concentration were found to be higher in methanolysis while diglyceride concentration were higher in ethanolysis. The methyl esters obtained with implemented this novel technique meets the ASTM standards. In order to apply G-Fed to the ethanol system, optimization studies should be carried out to improve the product quality.

4.5 Abbreviations

G-Fed   Gradually Fed

TG   Triglycerides

DG   Diglycerides

MG   Monoglycerides

GL   Glycerol

ME   Methyl esters

EE   Ethyl esters

KOH   Potassium hydroxide

HCl   Hydrochloric acid

THF   Tetrahydrofuran

O   Oil

A   Alcohol

Me   Methanol

Et   Ethanol

MSTFA   N-methy-N(trimethylsilyl) trifluoroacetamide

GC   Gas Chromatography

RPM   Revolutions per minute

Nomenclature

C   Concentration (mol/L)

r   Reaction Rate (mol. $L^{-1}\ s^{-1}$)

k_1 Reaction Rate Constant (s^{-1})

d   Distribution coefficient

k   Mass Transfer coefficient (m. s^{-1})

a   Interfacial area ($m^2.\ m^{-3}$)

D_a Impeller diameter (m)

D   Diffusion coefficient ($m^2.s^{-1}$)

d_{32} Sauter mean diameter (m)

vol   Volume

Greek Symbols

ε Volume Fraction

Subscripts

Ov   Overall

c   Continuous Phase

d   Dispersed Phase

l   Liquid Phase

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APPENDIX (Chapter 4)

Calculation of Distribution Coefficient

In Chapter 4, the distributions coefficient is described as equation (1), if equilibrium exists at the liquid-liquid interface, $C_{O,TG}$ and C^*_{TG} are related by distribution coefficient (d_{TG}) :

$$d_{TG} = C^*_{TG,A}/C_{TG,O} \tag{1}$$

Where, $C^*_{TG,A}$ = Triglycerides in Alcohol Film

$C_{TG,O}$ = Triglycerides in bulk of Oil.

From the literature data [39], the values of $C^*_{TG,A}$ and $C_{TG,O}$ are estimated as

$C^*_{TG,A}$ = Weight of canola oil in alcohol film / Molecular weight of canola oil

Total weight of mixture / Density of mixture.

$C_{TG,O}$ = Weight of oil in canola oil bulk / Molecular weight of canola oil

Total weight of mixture / Density of mixture.

The distribution coefficient for methanol and ethanol system is 0.00527 and 0.0554 respectively.

Estimation of interfacial area

For Batch Method: Alcohol is in dispersed phase and oil is in continuous phase [32].

For G-Fed Method: Oil is assumed to be in dispersed phase and alcohol is in a continuous phase.

The interfacial area can be calculated by the equation (2)

$$a = \frac{6\varepsilon_d}{d_{32}} \tag{2}$$

Where, ε_d is the fraction of the dispersed phase and d_{32} is the Sauter Mean Diameter.

The sauter mean diameter can be estimated using the correlation from the literature work [40,41] The correlation can be expressed as shown in equation 3:

$$\frac{d_{32}}{D_a} = Af(\varepsilon_d)We^{-0.6} \tag{3}$$

$f(\varepsilon_d)$ is the linear correlation of volume fraction of the dispersed phase. It can also be obtained by using equation (4a). This expression is used when the dispersed phase hold up for **batch runs** ($\varepsilon_d > 0.3$) [42]. $f(\varepsilon_d)$ for **G-Fed runs** is estimated by equation (4b) [43]. ε_d for batch run is assumed to be 0.6 while for G-Fed it was assumed as 0.35. A is obtained from the literature study as 0.081 [41].

For Batch runs ($\varepsilon_d > 0.3$)

$$f(\varepsilon_d) = (\frac{\ln(c_2 + c_3\varepsilon_d)}{\ln c_2})^{-3/5} \tag{4a}$$

Where, $c_2 = 0.011$ is a constant, c_3 is assumed to be 1.

For G − Fed runs

$$f(\varepsilon_d) = 1 + B\varepsilon_d \qquad\qquad (4b)$$

Weber number We is calculated using the equation (5)

$$We = \frac{\rho_c n_a^2 D_a^3}{\sigma} \qquad\qquad (5)$$

Weber number is dependent on the mixing intensity; the weber number estimated using above equation (5) for 300 rpm = 3889.958, 400 rpm = 6915.481 and 600 rpm = 15559.83.

Sautar Mean Diameter can be approximately calculated by using equation (4) and (5) in equation (3). d_{32} obtained can be used in equation (2) to calculated the interfacial area.

Estimation of Diffusion Coefficient:

The diffusion coefficient is carried out by the correlation as obtained from literature [44]:

$$D_{12} = 7.4 X 10^{-12}\ (T|m\mu)(C\ M_2)^{0.5}(V_1)^{(-0.6)}$$

Where:

D_{12}	= Diffusion coefficient of TG	$(m^2.s^{-1})$
T	= Temperature	(K)
$m\mu$	= dynamic Viscosity of Alcohol (Methanol/Ethanol)	$(mPa\ .s)$
M_2	= Molecular Weight of Alcohol (Methanol/Ethanol)	$(gm\ .mol^{-1})$
V_1	= Molar Volume of TG at NBP	$(cm^3\ .mol^{-1})$

C   = Association factor of Methanol/Ethanol

The values and constant for the equations is as follows:

M_2 for methanol is 32 gm mol^{-1}, M_2 for ethanol is 46 gm mol^{-1}

mμ for methanol is 0.56 mPa.s, mμ for ethanol is 1.095 mPa.s

C for methanol = 1.9, C for ethanol = 1.5

Estimation of Mass Transfer Coefficient

The mass transfer coefficient of the dispersed phase can be estimated by Sherwood number:

$$Sh_d = \frac{2\pi^2}{3} = \frac{k_d d_{32}}{D}$$

The sauter mean diameter and diffusion coefficient as calculated as per appendix B and C. The above expressions can be used to calculate mass transfer coefficient. The derived correlation is obtained from literature [45]:

$$k_d = \frac{2\pi^2 D}{3d_{32}}$$

Where:

k_d = Mass Transfer coefficient $(m^2.s^{-1})$

D = Diffusion Coefficient of TG $(m^2.s^{-1})$

d_{32} = Sauter Mean Diameter of droplets   (m)

Chapter 5

5 Kinetics studies for ethanolysis of canola oil using potassium hydroxide as catalyst in a batch reactor.

5.1 Introduction

The consumption of the energy is increasing day by day and the sources like petrochemical, coal and natural gas which supplies energy is finite and will diminish in the nearing future [1]. This issue has raised a need to develop alternative sources to produce fuel similar to petroleum based fuels. The alternative fuel should be biodegradable along with nontoxic and environmentally friendly properties. Recent trends have focused the research on producing biodiesel from vegetable oils and animal fats. Biodiesel is an alternative diesel fuel produced from biological and renewable sources [2]. Biodiesel is considered as one of the alternative fuel to diesel and petro-diesel in the future. Biodiesel in general has many advantages which makes it a promising fuel for future. It is made from renewable biological sources such as vegetable oils and animal fats. The non toxic property and biodegradable nature makes it a valuable fuel. It has many other advantages like low emission profiles: Biodiesel in general has low emission profiles. This quality makes it environmentally beneficial: less greenhouse effect, less pollution of air, water and soil and less health risk, compared to the use of the fossil fuel. Commercially biodiesel is produced by transesterification of vegetable oil with alcohol in presence of catalysts. The parameters that influence the reaction are: the type of feedstock, catalyst type and concentration, feedstock to alcohol molar ratio, the reaction temperature and the mixing intensity [1, 3]. Methanol and Ethanol are mostly

used for this process, if the added alcohol is methanol the process is called methanolysis and in case of ethanol the process is called ethanolysis. For the transesterification process, methanol is preferred more as it has advantages like: suitable physical and chemical properties, easy availability and low cost, more reactivity as compared to ethanol [4]. The energy consumption for the methanolysis is lower as compared to ethanolysis [5]. However the low boiling point of methanol brings in a huge risk of explosion due to the methanol vapors. Methanol and Meth oxide are extremely hazardous chemicals and care must be taken in handling these materials [6]. Some of these disadvantages brought in by methanol systems increase the attention of replacing methanol with ethanol. Ethanol has become a subject of interest in transesterification processes as it is produced from renewable sources [7]. The reactivity decreases as compared to methanol with increase in the length of the carbon chain [8].

However the extra carbon in ethanol enhances the heat content and the cetane number of the fuel [9]. It has the property of superior dissolving power with vegetable oils. [7, 10]. Ethyl esters forms from the ethanolysis process have some advantages which have lured scientist to focus more on ethanol over methanol. It has better biodegradable properties is better than methyl esters [11, 12]. The studies carried out shows that the lubricity and wear properties are better for biodiesel obtained by ethanolysis reaction [13, 14]. The cold properties i.e. cloud point and pour point in low in ethyl esters [10]. Thus this quality helps to improve the storage properties [15]. As ethyl esters are produced from ethanol, the exhaust gas emissions have less negative impact on the environment as compared to methyl esters [11]. The kinetic studies of this process are an important tool to analyze and develop the scale up models. It is very crucial in designing the chemical

reactors for the individual system. So far in literature may kinetic studies have been carried out for methanolysis of various feed stocks like soybean, sunflower oil, cotton seed oil, rapeseed oil, palm oil, jatropha [16-22]. The kinetic studies are carried out with different parameters like mixing intensity, reaction temperature, unanalyzed systems [23].

Table 5.1 below gives the details of kinetic studies carried out so far with respect to three reversible reactions. In literature, except few [24] not many kinetic studies and models have been reported on ethanolysis reaction. In this work, the kinetics of ethanolysis of canola oil using potassium hydroxide as a catalyst has been investigated. The experiments were carried out for the temperature of 25-60^{0}C in a 1 L batch reactor. A mat lab model was developed to obtain the optimized values of the forward and backward rate constants for ethanolysis of canola oil at different reaction temperatures.

5.2 Experimental Section

5.2.1 Materials

Refined and edible Canola oil was purchased from Metro, Canada. Potassium hydroxide (<99% purity), anhydrous Ethanol (100%) and aqueous HCl (10 N) were purchased from VWR (Canada). The reference standards required for the GC analysis were purchased from Sigma Aldrich. The standards were solution of glycerol, 1-mono-olein, 1,3-di-olein (1% 1,2 isomer) and triolein. *n*-Hexane (HPLC grade) was used as a solvent to dilute the samples for GC analysis. N-methyl-N-trimethylsilyl trifloroacetamide (MSTFA) was used as a derivatizing agent.

Table 5.1 Details of the kinetic studies in literature

Oil	Alcohol	Catalyst/Catalyst Concentration(%)	Molar ratio of alcohol:oil	T^0C	Reaction Mechanism	Kinetic Model	Reference
Soya bean	Methanol	NaOH/0.2	6:1	30-70	Three consecutive reversible reaction	Second Order	Noureddini and Zhu [17]
Palm	Methanol	KOH/1	6:1	55-65	Three consecutive reversible reaction[a]	Second Order	Darnoko and Cheryan [22]
Rapeseed	Methanol	KOH/0.29-1.59	1:1-6:1	22.7	Three consecutive reversible reaction+saponification reaction	Second Order	Komer et al. [41]
Sunflower	Methanol	KOH/0.5-1.5	6:1	25-65	Three consecutive reversible reactions	Second Order	Vicente et al. [29]
Brassica carinata oil	Methanol	KOH/0.5-1.5	6:1	25-65	Three consecutive reversible reactions	Second Order	Vicente et al. [34]
Sunflower Oil	Methanol	KOH/1	6:1	10-30	Irreversible reaction, Reversible overall reaction in the final period	Second Order	Stamenkovic et al. [19]
Vegetable Oil	Methanol	NaOH	6:1	55	Three consecutive reversible reactions[b]	Second Order	Slinn and Kendall [32]
Rapeseed Oil Waste Sunflower oil	Methanol	KOH/1	6:1	40 and 50	Three consecutive reversible reaction with shunt reactions	Second Order	Klofutar et al. [20]
Palm Oil	Trimethylolpropane	Sodium Methoxide	10:1	70-110	Irreversible reaction	Second Order	Hamid et al. [33]
Sunflower Oil	Ethanol	NaOH/0.75, 1. 1.25	6:1,9:1,12:1	25 - 75	Irreversible reaction, Reversible overall reaction in the final period.	Second Order	Marjanovic et al. [24]
Canola Oil	Ethanol	KOH/1	6:1	28-60	Three consecutive reversible reactions	Second Order	This work

a Only forward reactions were considered. b Kinetics for Mass transfer regime included.

5.2.2 Method

Canola oil (500g) was introduced into the reactor and heated at the desired temperature with the help of water bath. The catalyst, KOH (1% w/w canola oil) was dissolved in the anhydrous ethanol (160g). The ethanol and catalyst solution was added into the feedstock and agitation was started, this was considered as the start of the reaction. The impeller was set at 600 rpm for the entire duration of the reaction. The ethanolysis reaction was carried out for 60m and at the temperature of 28^0C, 40^0C, 50^0C and 60^0C respectively for four sets of experiments. The temperature in the reactor was controlled by a water bath connected to the jacket of the reactor with an accuracy of ± 1 ^{0}C. A reflux condenser was connected to the system in order to recover the vaporized ethanol into the system. The samples were collected at a regular interval of time to study the reaction kinetics by gas chromatography analysis. After 60min, the reaction was stopped and homogenous mixture was transferred to separatory funnel in order to separate glycerol from the reaction solution. The reaction mixture was allowed to stand overnight for complete separation of two phases. Glycerol being the heavy phase will settle down as the bottom phase. The crude phases separated were rotavaporised at 80^0C to remove excess ethanol. The ethyl ester phase was further washed to remove catalyst and glycerol content. The washing was carried out till the pH of the washed water reaches approximately 7. The final washed ethyl esters were dried at 100^0C by means of rotavaporisor. Buchi vaporizer (R-114) for drying, centrifuge, and separatory funnels for phase separation. The experiments were carried out twice and the samples were collected in triplicates in order to study the reproducibility of results. Figure 5.1 shows the experimental set up for the ethanolysis of canola oil.
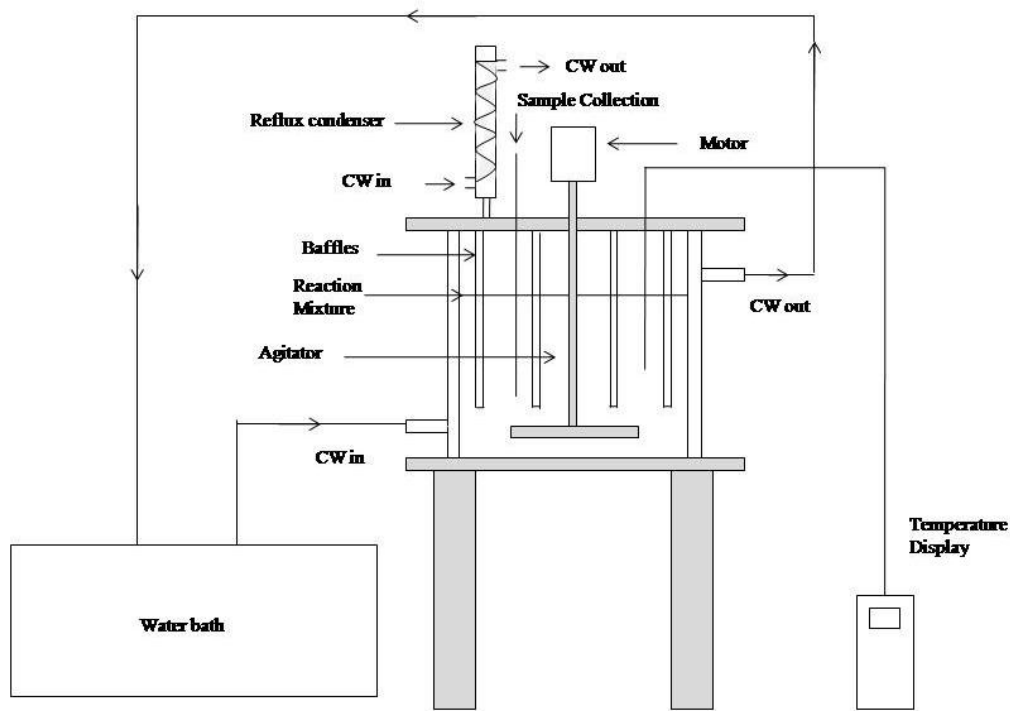
Figure 5.1 Experimental setup for batch runs of ethanolysis of canola oil.

5.2.3 Sample Analysis

The samples (1.5 ml) were taken at a regular time interval of 5, 10, 15, 20, 25, 30, 45 and 60 min and quenched in 2 ml of 1 N HCl solution. The quenching ceases the reaction at that particular interval by removing the catalyst and glycerol in the water phase (bottom phase). After allowing the samples to stand overnight, the top phase is pipette out into a 4 ml centrifugal Sodium sulphate is added into the vial before centrifuging process. The mixture is centrifuged for 15 min at 4000 rpm to remove moisture from the samples. 15 ul of the top phase is added into the 2 ml GC vials. 50 ul of tricaprin following 50ul of derivatizing agent MSTFA is added to the vial and the vials are left for 20 min at the room temperature. After this time, the vials are topped up to 1500 ul using *n-Hexane* as a

solvent. The samples are now ready for GC assays. Samples (1µl) were injected on-column by an AOC 20s Auto sampler (Mandell instruments) at an oven temperature of 60^0C and injector temperature of 300^0C. DB-5 gas chromatography column of dimension 30X0.25X0.25 was used for the analysis of the samples. The analysis was carried out in split mode. Helium was used as the carrier gas; the linear velocity of the gas was 48.5 cm/sec. The temperature program, 2 min at 60^0C, heating at the rate of 12^0C.min^{-1} to 325^0C and holding for 15 min. The detector temperature was fixed at 325^0C with a hydrogen make of gas at 30ml.min^{-1}.

5.3 Kinetic Model

The ethanolysis of canola oil can be described as three step reversible reaction as shown below in Figure 5.2 The triglycerides present in canola oil react with ethanol in presence of KOH as catalyst to produce di-glycerides and a mole of ester. Later the di-glycerides formed reacts with ethanol to produce mono-glycerides, similarly mono-glycerides reacts with ethanol to form glycerol. In each step a mole of ethyl ester is produced. Thus the stoichiometry of the reaction is 1:3 for oil to ethanol ratio. Mostly excess ethanol (i.e. molar ratio of 1:6 for oil to ethanol) is preferred to push the reaction to product side (Le-Chatelier's principle).

$$\text{Triglyceride} + CH_3CH_2OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{Diglyceride} + R_1COOCH_2CH_3$$

$$\text{Diglyceride} + CH_3CH_2OH \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \text{Monoglyceride} + R_2COOCH_2CH_3$$

$$\text{Monoglyceride} + CH_3CH_2OH \underset{k_6}{\overset{k_5}{\rightleftharpoons}} \text{Glycerol} + R_3COOCH_2CH_3$$

Overall reaction :

$$\text{Triglyceride} + 6\,CH_3OH \rightleftharpoons 3\,RCOO\overset{\overset{\displaystyle CH_2}{|}}{C}H_2 + \text{Glycerol}$$
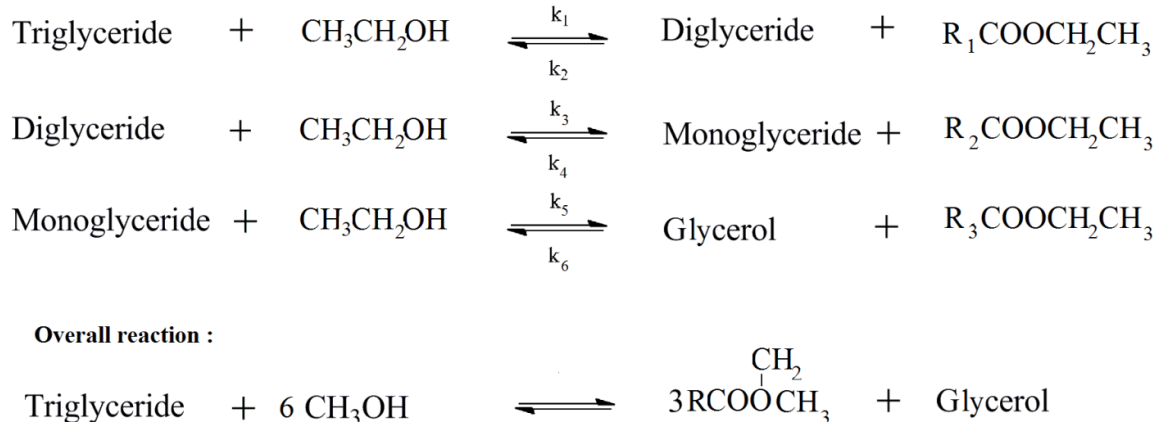
Figure 5.2 Three step transesterification reaction [16, 25, 26].

In Figure 5.2, k_1, k_3 and k_5 are rate constants for forward reactions; k_2, k_4 and k_6 are rate constants for reverse reactions. The reactants canola oil and ethanol are immiscible and therefore the reaction system in the initial stage contains two layers. In order to develop a kinetic model for ethanolysis of canola oil various assumptions were introduced.

5.3.1 Assumptions to develop the mathematical model

1. The process of ethanolysis follows two reaction regimes: It starts with the initial chemical controlled regime, the phase being pseudo homogenous due to the better mixing ability of ethanol in canola oil. Further the equilibrium state is reached in the reaction. These two possibility of regimes were explained by few studies and research work carried out in this field [7, 10].

2. Unlike Methanolysis, initial mass transfer limitations are not present for the system of ethanolysis. The mixing intensity can decrease the mass transfer controlled regime [28]. Proper mixing of two phases makes the entire phase; homogenous and perfectly mixed into each other. Thus uniform composition can

be assumed for both alcohol and oil. The mixing intensity of 600 rpm is selected in order to neglect the mass transfer regime [18, 28].

3. The reverse reactions were considered to be neglected as the alcohol concentration is in excess in the beginning and the product concentration is low. The reaction of TG is considered to be irreversible pseudo second order in the initial period of the chemically controlled regime. The reversible reactions are considered after reaching the equilibrium state [24, 22].

4. The forward and reverse reactions both follow a trend of second order for the overall reaction near the equilibrium state. These investigations were made by Vicente and his team for the methanolysis of sunflower oil [29, 34].

5. The impurities like free fatty acids, MGs and DGs in the canola oil feedstock can be neglected especially when refined oil is used for the study.

6. It was proved that the loss of alkyl esters due to saponification reactions were not more than 3mole% when the methanolysis of sunflower oil was carried out at 65^0C [29]. Thus it can be stated that the loss will be less at lower temperatures. The saponification reaction is higher if the catalyst concentration is more than 1.5%(w/w) in the methanolysis reaction [35]. Thus the saponification reactions were neglected to develop a simple kinetic model for the ethanolysis reaction.

7. The catalyst concentration can be assumed almost constant if the saponification reactions are not considered. The loss of catalyst due to the soap formation will be an eliminated step.

8. The initial 5 min of the ethanolysis reaction is not taken into consideration for the simulation in order to simplify the model.

Transesterification reaction progress for methanolysis is shown by three regimes. These regimes are: (a) mass transfer controlled regime in the initial period of the reaction (slow). (b) chemical controlled regime for almost the entire period of reaction (fast) and (c) equilibrium regime during the completion of the reaction (slow) [16, 17]. Many studies confirmed that the mass transfer controlled regime can be decreased by changing the other variables of the reaction [27-29]. However in literature it is reported that the mass transfer controlled regime is not present in the ethanolysis reaction [7, 10]. Ethanol is a better solvent than methanol to form homogenous mixture with canola oil [7]. The visual observations in this study state that the two phase heterogeneous system of canola oil and ethanol became one phase homogenous system in less than 5 sec after the reaction mixture was stirred. The transesterification reaction can be described as differential equations wherein kinetic rate constant is shown as the function of reaction time [17, 18, 22]. Similarly the rate equations for ethanolysis can be written as shown in figure 5.3. In figure 5.3, [TG], [DG], [MG], [EE], [GL], [ROH] is used to described as mole concentrations of triglycerides, di-glycerides, mono-glycerides, ethyl esters, glycerol and ethanol respectively. In order to solve the differential equation, a nonlinear matrix with six unknowns was generated as shown in figure 5.4. The matrix is formed of the experimental mole concentrations of the reactants and intermediates. The variables b_1-b_6 is the differential mole concentrations with respect to the reaction times. These values are obtained from the experiments carried out for four different reaction temperatures (28^0C-60^0C). The dependent variables (b_1-b_6) are calculated by estimating the point slope method at any interval of time. The interval of 10 min is selected for the current study and therefore six sets of values are available for reaction time of 60 min. The available

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experimental data was divided into six interval of time. The matrix generated with non linear equations was resolved using build in F-solve function in Matlab computer software, (R2007b) Version 7.5.0.342. The Mathswork Inc. The m.file was generated for the input values and simulation. The concentration (in mol/L) and differential of concentration with respect to time for the reactants (TGs and ROHs), intermediates (DGs and MGs), by-products (GL) and products (EE) from the experiments were fed in the input file. The simulation was carried out for each interval of time to obtain six set of reaction rate constants (k_1-k_6) and the results were generated in a form of output file. An optimized set of k values (k_1-k_6) is obtained from the six set of reaction rate constants by minimizing the objective function as stated in equation 1. [30].

$$E^2 = \sum_{i=1}^{n} [b_i - a_{i1} k_1 + a_{i2} k_2 + \ldots + a_{n6} k_6]^2 \qquad (5.1)$$

$$\frac{d[TG]}{dt} = -k_1[TG][ROH] + k_2[DG][EE]$$

$$\frac{d[DG]}{dt} = k_1[TG][ROH] - k_2[DG][EE] - k_3[DG][ROH] + k_4[MG][EE]$$

$$\frac{d[MG]}{dt} = k_3[DG][ROH] - k_4[MG][EE] - k_5[MG][ROH] + k_6[GL][EE]$$

$$\frac{d[GL]}{dt} = k_5[MG][ROH] - k_6[GL][EE]$$

$$\frac{d[EE]}{dt} = k_1[TG][ROH] - k_2[DG][EE] + k_3[DG][ROH] - k_4[MG][EE] + k_5[MG][ROH] - k_6[GL][EE]$$

$$\frac{d[ROH]}{dt} = - \frac{d[EE]}{dt}$$

Figure 5.3 Differential equations for second order reaction (Rate Constants as a function of time)

$$\begin{bmatrix} -[TG][ROH] & [DG][EE] & 0 & 0 & 0 & 0 \\ [TG][ROH] & -[DG][EE] & -[DG][ROH] & [MG][EE] & 0 & 0 \\ 0 & 0 & [DG][ROH] & -[MG][EE] & -[MG][ROH] & [GL][EE] \\ 0 & 0 & 0 & 0 & [MG][ROH] & -[GL][EE] \\ [TG][ROH] & -[DG][EE] & [DG][ROH] & -[MG][EE] & [MG][ROH] & -[GL][EE] \\ -[TG][ROH] & [DG][EE] & -[DG][ROH] & [MG][EE] & -[MG][ROH] & [GL][EE] \end{bmatrix} \begin{bmatrix} k_1 \\ k_2 \\ k_3 \\ k_4 \\ k_5 \\ k_6 \end{bmatrix} = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \\ b_6 \end{bmatrix}$$

Figure 5.4 Generation of Nonlinear Matrix [30]

The flow chart in figure 5.5 shows the steps to obtain the optimized k value. The optimized set of k values are used as input variables in m.file using ode45 (build in Matlab function) to obtain the analytical concentration for the reactant (TG), products (EE), intermediates (DG and MG) and byproducts (GL). Curve fitting is carried out in order to compare the experimental concentration data (obtained with experiments) and analytical concentration data (obtained with Matlab simulation) [31]. The simultaneous fitting of the analytical data and the experimental data was carried out using the optimum k values. The model was verified with the literature values obtained from the work of Noureddini and Zhu [17].
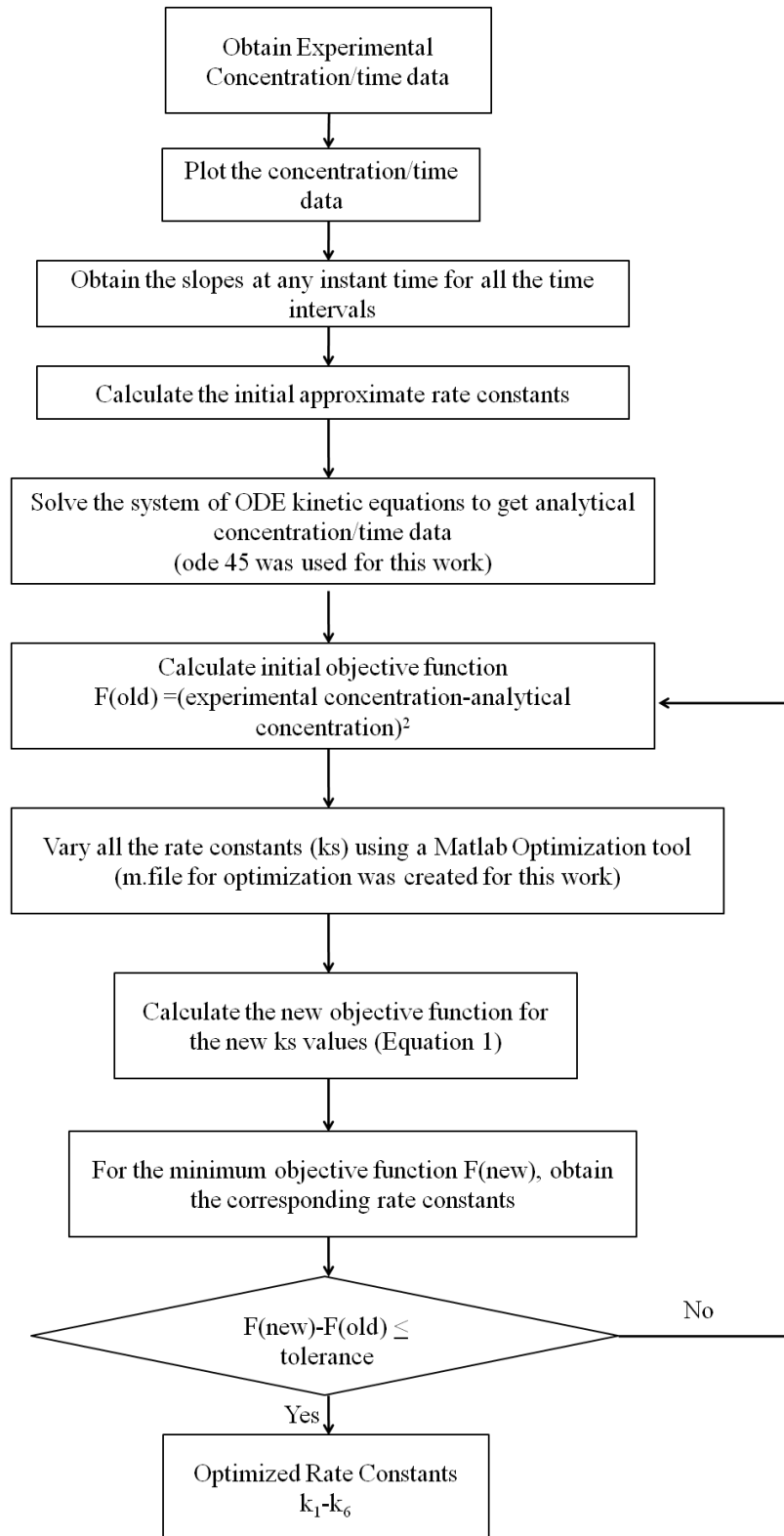
Figure 5.5 Flow chart to predict the optimum rate constants [31].

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5.3.2 Verification of kinetic model using literature values

In literature, concentration profiles for ethanolysis are not available so far. Therefore; kinetic model verification was carried out using literature values for methanolysis from the work of Noureddini and Zhu [17]. The concentration of reactant (TGs and AL), intermediates (DGs and MGs), by-products (GL) and products (ME) was extracted using computer software GetData Graph Digitalizer 2.24. The forward and back ward reaction rate constants were obtained with the simulation and the Matlab codes generated for the ethanolysis reaction. Table 5.2 reported below shows the rate constants obtained from this work and are compared with the literature values. The simulation is designed to simultaneously generate the analytical values of concentration and fit with the experimental concentration values. Figure 5.6 shows the kinetic curve fit of the generated concentrated profiles with the measured experimental work of Noureddini. The model developed has a limitation of not considering the initial region for 5 min. The mass transfer regime is not considered in developing the model for this work as ethanolysis reaction is not mass transfer controlled reaction.

Table 5.2 Comparison of the rate constants

	Obtained by this model for literature data [17]	Noureddini and Zhu 1997
k_1 (L s .mol^{-1})	0.044	0.05
k_2 (L s .mol^{-1})	0.103	0.110
k_3 (L s .mol^{-1})	0.197	0.215
k_4 (L s .mol^{-1})	1.278	1.228
k_5 (L s .mol^{-1})	0.238	0.242
k_6 (L s .mol^{-1})	0.008	0.007
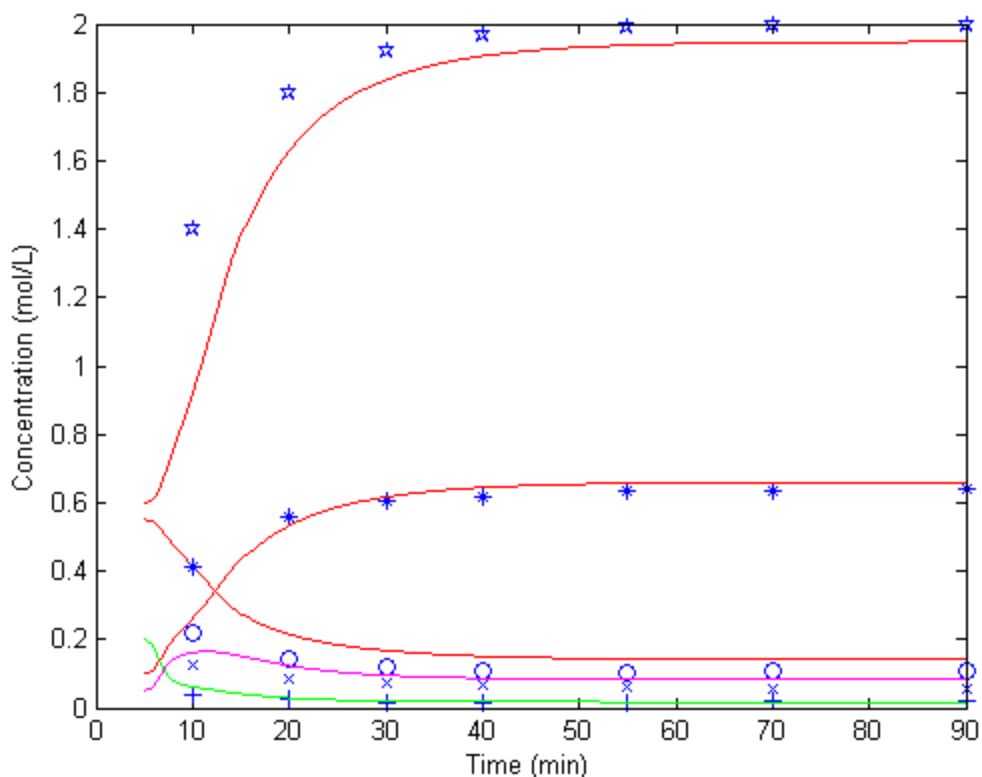
Figure 5.6 Kinetic Curve fitting for Noureddini and Zhu [17] using the optimization program

The concentration values for the initial mass transfer region in methanolysis are not considered in this model. The values of rate constant obtained with the simulation are approximately similar to the literature values. The comparison provides the proof of the verification of developed mat lab codes to extract and optimize the rate constants from the concentration profiles obtained from the experimental analysis.

5.3.3 Ethanolysis analysis

The ethanolysis of canola oil was carried out using KOH as the catalyst with a temperature range of 28^0- 60^0C. The molar ratio of ethanol to canola oil, the catalyst concentration and mixing intensity was kept constant as 6:1, 1(%w/w) and 600 rpm respectively. An effort has been made in this study to understand the kinetics of

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ethanolysis and calculate the reaction rate constants. The conversion of TGs for ethanolysis at various temperatures is shown in Figure 5.7. Ethanol solubility is higher as compared to methanol and thus the mass transfer region is eliminated [10, 24]. The mixing intensity of 600 rpm was selected as a precaution to avoid the mass transfer controlled region.
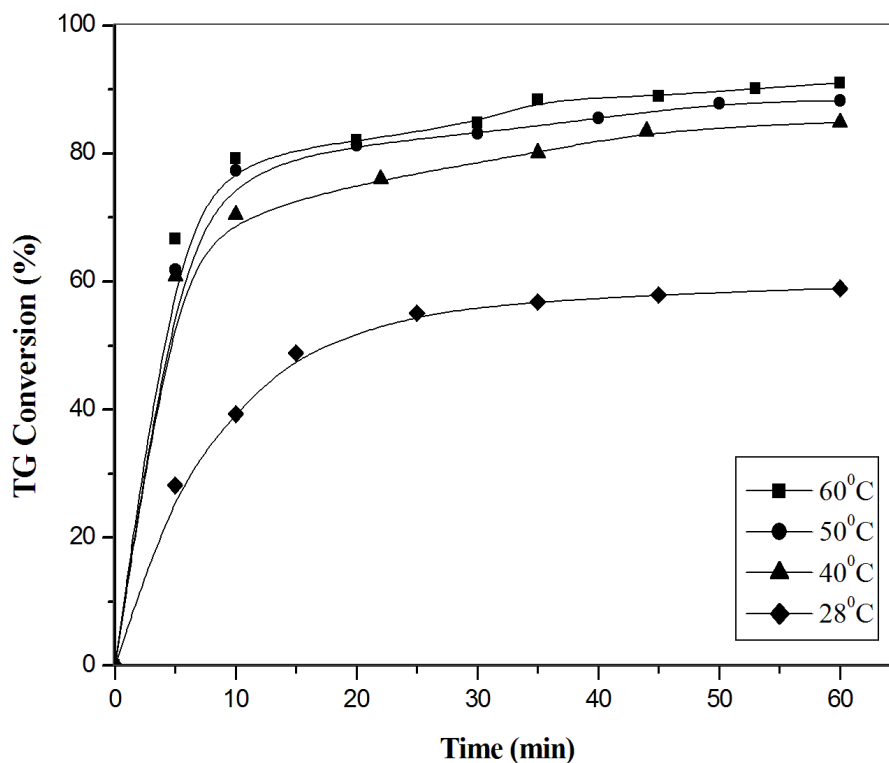
Figure 5.7 TG conversion in ethanolysis of canola oil at different reaction temperatures.

Examination of figure 5.7 reveals that the reaction is not mass transfer controlled even at the low reaction temperature of 28^0C. The TG conversion is enhanced with the increase in reaction temperature; however the conversion rate is almost similar for 50 and 60 of reaction temperatures. The concentration profile for the production rate of ethyl esters is depicted in figure 5.8. The reaction rate is higher for temperature higher than 28^0C however the studies are not made to obtain the optimized reaction conditions in terms of

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temperature. Ethanolysis follows only two reaction regimes: initial chemically controlled regime and final slow region as the equilibrium is reached. Although few studies are carried out for the transesterification of vegetable oil using ethanol as precursors, similar observations are reported in literature [10, 24].
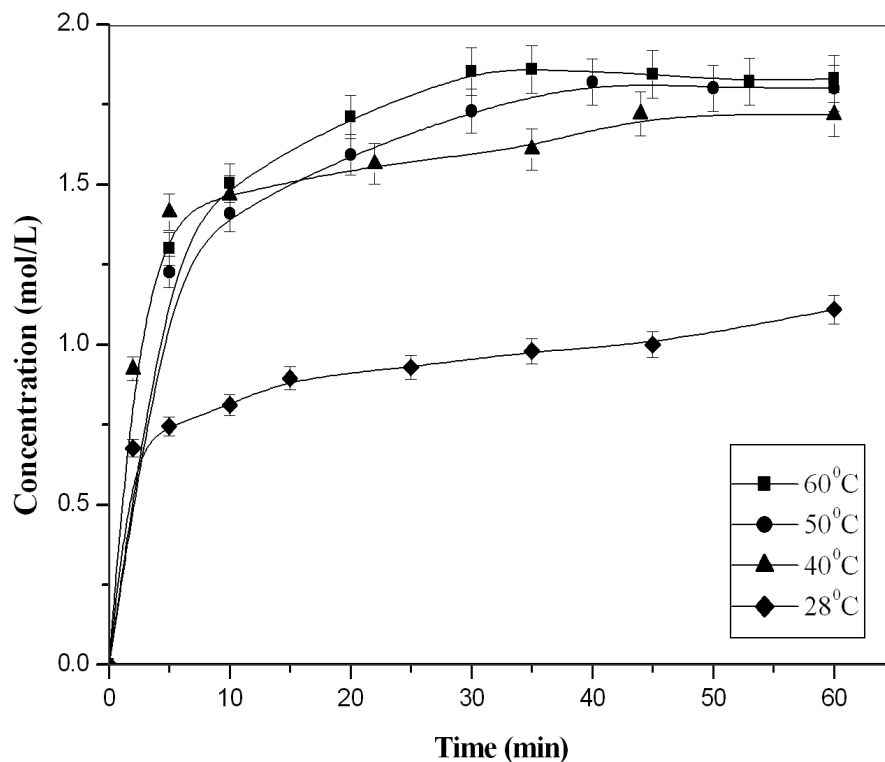
Figure 5.8 Concentration Profile for Ethyl Esters (n =2, error-bars = 4%)

However increase in temperature enhances the production rate of ethyl esters. The production is almost similar for 50^0C and 60^0C. The increase in reaction temperature after 40^0C does not have a significant effect on the production rate. Many literature studies states that the parameters which affect the ethanolysis reactions is catalyst concentration and molar ratios. Most studies have reported that the increase in temperature do not have an obvious impact on the reaction [36-39]. However the optimization studies are not carried out for the different reaction temperatures.

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5.3.4 Calculation of the reaction rate constants

The simulation procedure is designated to obtain 6 sets of rate constants for each time interval. Table 5.3, 5.4, 5.5 and 5.6 shows the rate constants evaluated for the four different temperature runs for regular interval of time. There are no literature studies for ethanolysis wherein kinetic modeling is carried out to calculate the reaction rate constants for each reaction step. Thus the initial guess vector for k values were taken from the kinetic studies carried out for methanolysis system [17]. From the sets of k values generated from the simulation an optimized set of k values are estimated by minimizing the objective function as stated in equation 5.1.

Table 5.3 Six set of rate constants at 28^0C

Time interval range (min)	k_1 (L s .mol^{-1})	k_2 (L s .mol^{-1})	k_3 (L s .mol^{-1})	k_4 (L s .mol^{-1})	k_5 (L s .mol^{-1})	k_6 (L s .mol^{-1})
5-10	0.009	0.106	0.222	1.279	0.036	0.088
10-20	0.013	0.107	0.244	1.274	0.062	0.107
20-30	0.019	0.107	0.217	1.280	0.074	0.114
30-40	0.020	0.107	0.188	1.284	0.117	0.123
40-50	0.019	0.107	0.208	1.281	0.123	0.123
50-60	0.018	0.107	0.297	1.261	0.141	0.120

Table 5.4 Six set of rate constants at 40^{0}C

Time interval range (min)	k_1 (L s .mol^{-1})	k_2 (L s .mol^{-1})	k_3 (L s .mol^{-1})	k_4 (L s .mol^{-1})	k_5 (L s .mol^{-1})	k_6 (L s .mol^{-1})
5-10	0.032	0.107	0.380	1.230	0.211	0.081
10-20	0.042	0.104	0.377	1.231	0.223	0.063
20-30	0.049	0.101	0.409	1.215	0.225	0.059
30-40	0.061	0.094	0.436	1.200	0.229	0.050
40-50	0.062	0.093	0.417	1.211	0.230	0.049
50-60	0.064	0.091	0.402	1.219	0.231	0.046

Table 5.5 Six set of rate constants at 50^{0}C

Time interval range (min)	k_1 (L s .mol^{-1})	k_2 (L s .mol^{-1})	k_3 (L s .mol^{-1})	k_4 (L s .mol^{-1})	k_5 (L s .mol^{-1})	k_6 (L s .mol^{-1})
5-10	0.045	0.103	0.556	1.110	0.156	0.117
10-20	0.057	0.096	0.685	0.937	0.166	0.113
20-30	0.065	0.089	0.501	1.157	0.221	0.065
30-40	0.071	0.082	0.489	1.165	0.229	0.051
40-50	0.074	0.077	0.474	1.176	0.231	0.046
50-60	0.075	0.075	0.375	1.232	0.234	0.036

Table 5.6 Six set of rate constants at 60^{0}C

Time interval range (min)	k_1 (L s .mol^{-1})	k_2 (L s .mol^{-1})	k_3 (L s .mol^{-1})	k_4 (L s .mol^{-1})	k_5 (L s .mol^{-1})	k_6 (L s .mol^{-1})
5-10	0.041	0.105	0.378	1.231	0.224	0.062
10-20	0.059	0.096	0.609	1.054	0.212	0.079
20-30	0.071	0.084	0.616	1.046	0.222	0.065
30-40	0.078	0.070	0.571	1.097	0.227	0.055
40-50	0.079	0.068	0.530	1.134	0.229	0.052
50-60	0.081	0.059	0.434	1.202	0.233	0.040

The optimum values are listed below in table 5.7 for different temperature systems. The m.file for estimation and optimization of the forward and backward reaction rate constant is provided in Appendix of this chapter. At low temperature (28^{0}C), the value of k_1 was lowest as compared to the k_1 values obtained for higher temperature of 40^{0}C, 50^{0}C and 60^{0}C. Thus at low temperature the rate of conversion of TG to DG was slowest. These values are lower than the k_1 values evaluated for the system of methanolysis at similar experimental conditions in literature studies. Ethanol being less reactive than methanol is a cause of slower reaction kinetics. The forward reaction rate constant is lowest with the corresponding values of k_2, k_3, k_4, k_5 and k_6 for all the temperature runs. It can be stated that the step 1: TG → DG being the slowest controls the transesterification process [18, 19].

Table 5.7 Optimized Forward and Backward Reaction Rate Constant

Reaction Temperature ^{0}C	k_1 (L s .mol^{-1})	k_2 (L s .mol^{-1})	k_3 (L s .mol^{-1})	k_4 (L s .mol^{-1})	k_5 (L s .mol^{-1})	k_6 (L s .mol^{-1})
28	0.018	0.107	0.187	1.279	0.142	0.108
40	0.061	0.091	0.381	1.216	0.210	0.081
50	0.071	0.075	0.490	0.938	0.167	0.036
60	0.070	0.105	0.378	1.134	0.233	0.080

Considering the forward reaction rate constants (i.e. k_1, k_3 and k_5) for different reaction temperatures 28^0C, 40^0C, 50^0C and 60^0C it was observed that the value of k_3 (DG $\rightarrow$ MG) is observed to be the highest corresponding to k_1 (TG $\rightarrow$ DG) and k_5 (MG $\rightarrow$ GL). Thus with the production of DGs in the reaction, the reaction was pushed towards the formation of MGs. The step 2: DG $\rightarrow$ MG is the fastest in the three step ethanolysis reaction. The rate constants increased with the increase in the reaction temperature. However the reaction rate constants were almost similar for the reaction temperature of 50^0C and 60^0C. The value of k_6 decreased with the increase in the reaction temperatures, it can be explained that the backward reaction rate is reduced with the increase in the reaction temperature. Ethanolysis reaction has a tendency to form emulsions, these emulsions are more stable at 25^0C, and the emulsions tend to reduce with increase in the temperature [40]. This might be one of the reasons for the decrease in the reversible rate of the reaction step: GL $\rightarrow$ MG with the increase in the reaction temperature of the ethanolysis system. The immiscibility of glycerol and ethyl esters introduces a great mass transfer resistance in the backward direction [18].

The overall reaction for ethanolysis can be predicted as chemically controlled process [24]. The reaction rate constants obtained with the ethanolysis studies are lower as compared to that of literature values in methanolysis studies. The mass transfer rate in terms of TG conversion is higher; however the reaction rate is lower. This can be explained: the increase in carbon length decreases the reactivity for ethanolysis reaction [4, 8]. The reversible second order kinetic model fitted adequately for ethanolysis of canola oil. The analytical values obtained from the models were almost similar to the experimental results. Marjanovic et al. [24] reported second order for the ethanolysis reaction of sunflower oil. Figure 5.9, 5.10, 5.11 and 5.12 shows the curve fitting of analytical and experimental points for the ethanolysis of canola oil at 28^0C, 40^0C, 50^0C and 60^0C.
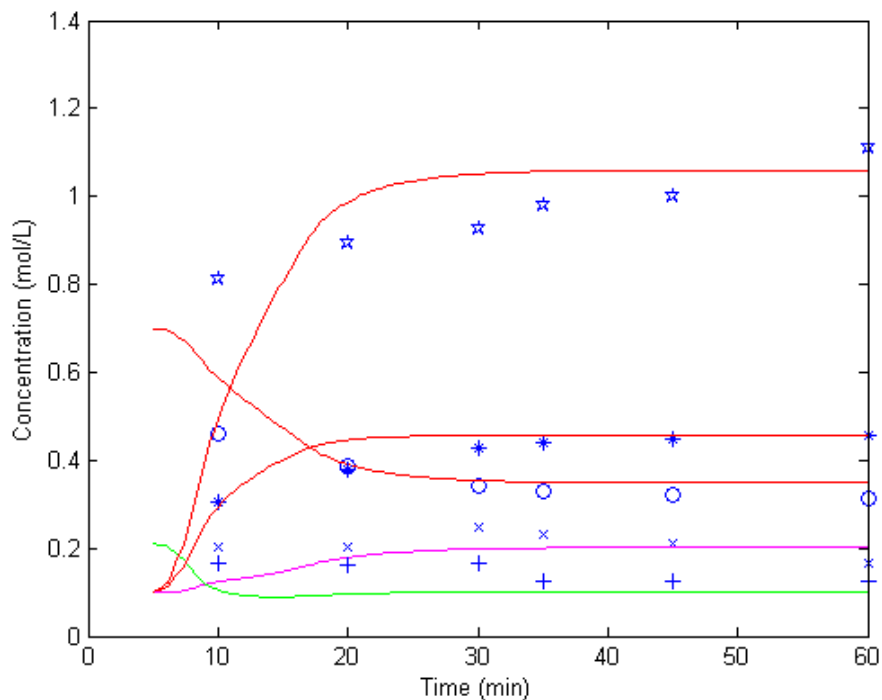
Figure 5.9 Kinetic modeling curve fit (28^0C)
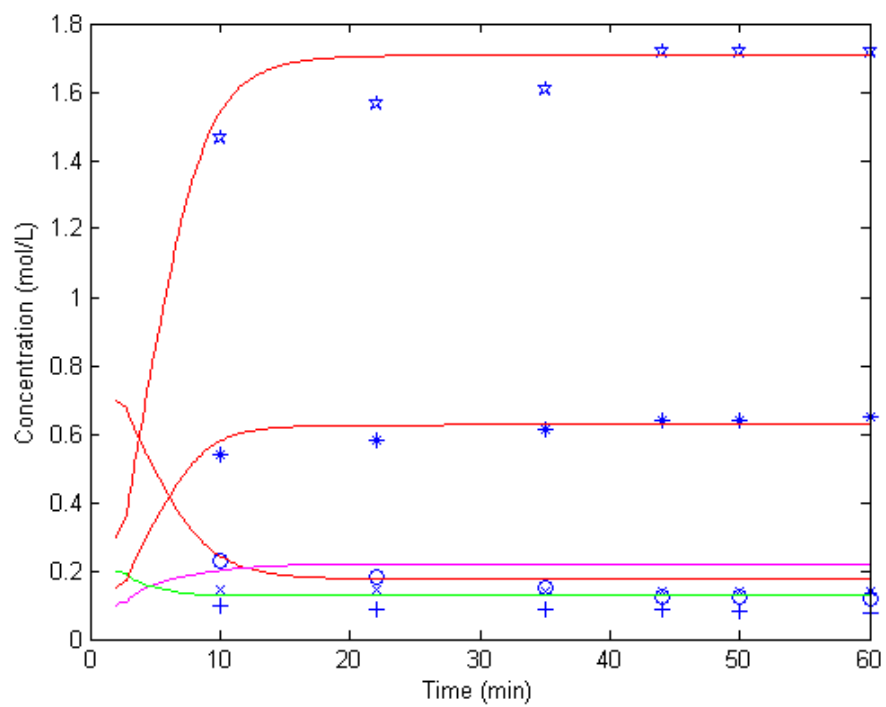
Figure 5.10 Kinetic modeling curve fit (40^0C)
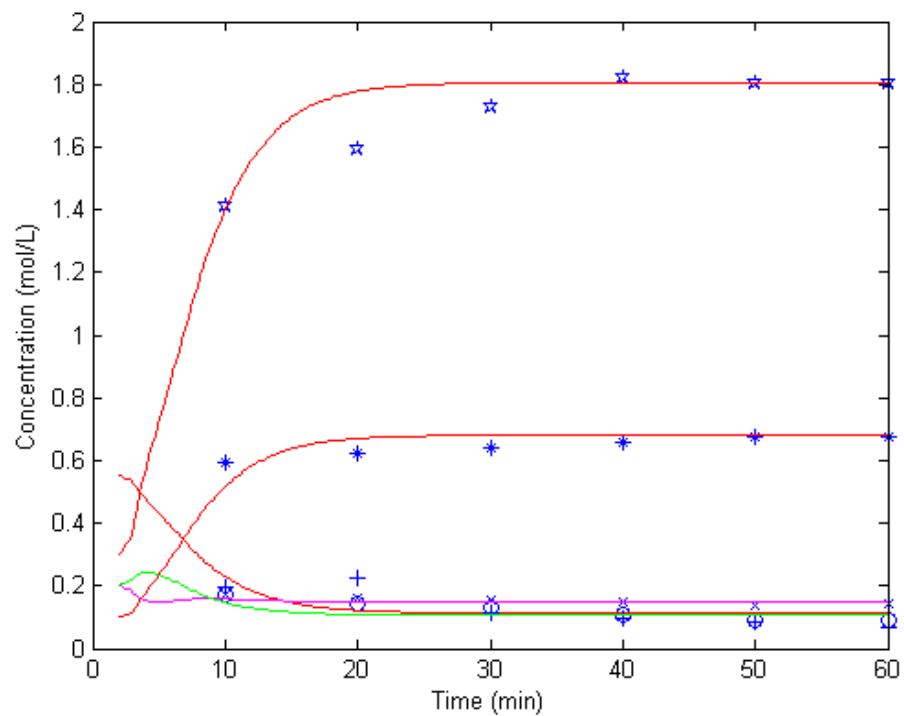
Figure 5.11 Kinetic modeling curve fit (50^0C)
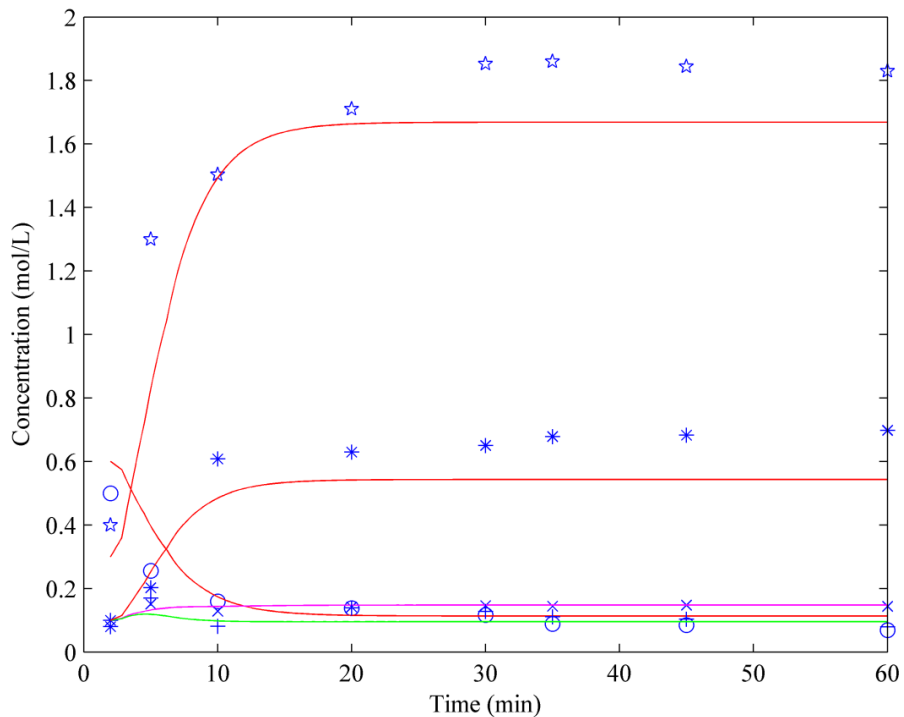
Figure 5.12 Kinetic modeling curve fit (60^{0}C)

5.4 Conclusions

The production of biodiesel using ethanol has become a focus of investigation as ethanol is produced using bio-renewable sources. The kinetics studies of ethanolysis investigated in this work reports do not have a mass transfer controlled regime unlike methanolysis. Ethanolysis follows a second order rate for forward and backward reaction. The kinetic model is developed using the Mat lab simulation technique. The second order kinetic model can predict the optimized set of forward and backward reaction rate constants for alcoholysis reaction with second order of the reaction. The results obtained by the study over the range of investigations carried out reports that Arrhenius kinetics for the forward reaction dominates the reaction. The analytical values of concentration of reactants and products fit significantly with the experimental values.

5.5 Abbreviations

TG	Triglycerides
DG	Diglycerides
MG	Monoglycerides
GL	Glycerol
EE	Ethyl esters
KOH	Potassium hydroxide
HCl	Hydrochloric acid
MSTFA	N-methy-N(trimethylsilyl) trifluoroacetamide
GC	Gas chromatography
RPM	Revolutions per minute

Nomenclature

k	Reaction Rate Constant ($L s .mol^{-1}$)
a	Concentration of species
b	differential of concentration
t	time (s, min)

Subscripts

1	Triglyceride to Diglyceride
2	Diglyceride to Triglyceride
3	Diglyceride to Monoglyceride
4	Monoglyceride to Diglyceride
5	Monoglyceride to Glycerol
6	Glycerol to Monoglyceride

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APPENDIX (Chapter 5)

Mat lab Code

Estimation of Kinetic Reaction Rate Constants

```matlab
% program to solve set of non-linear equation

clear all;clc;close all; format long e;

% this is the best possible algorithm available

fn = fopen('K_values_output_file.txt','wt'); % creating a text file to
store output

fprintf(fn,'six set of k values \n');

fn1 = fopen('Optimzed _output_file.txt','wt');



fprintf(fn1,'six set of optimized  values \n');

[TG,DG,MG,GL,ME,OH,DTG,DDG,DMG,DGL,DME,DOH] = input_data();

guess = [0.049 0.102 0.218 1.28 0.239 0.007]; % initial guess vector ,,
ur result relies heavily on this data choose accordingly

for i = 1:6

    tg = TG(i);dg = DG(i); mg = MG(i);gl = GL(i); me = ME(i); oh =
OH(i); ddg = DDG(i);dtg = DTG(i);dmg=DMG(i);dgl =DGL(i);dme =
DME(i);doh = DOH(i);

    c = [tg;dg;mg;gl;me;oh;dtg;ddg;dmg;dgl;dme;doh];



    options = optimset('Largescale', 'off', 'maxfunevals', 100000000);

    options.MaxIter = 10000000;
```

```matlab
    options.TolFun = 1.000000e-008;

    [result,fval,exitflag,output] = fsolve(@(x)f1(x,c),guess,options); % 
using MATLAB inbuilt function

    output_k(i,:) = result;

     %guess = result;

end




for i = 1:6

    dat = fi(:,i);

    fprintf(fn1,'Set number set = %3.0f \n',i);

    for j = 1:6

        fprintf(fn1,'%10.10f \t',dat(j));

    end

    fprintf(fn1,'\n');

     fprintf(fn1,'-------------------------------------');

     fprintf(fn1,'\n');


end

for i = 1:6

    dat12 = fi(i,:);

    [f1,in(i)] = min(dat12);

end
```

```matlab
 x0 = [0.6 0.1 0.1 0.1 0.3 4.6];

[T,X] = ode45('diffequationvalues',[2,60],x0);

%plotting

tg_expt =
[0.5;0.25550481;0.159217342;0.137772094;0.116708658;0.088622003;0.08454
5806;0.069001722];

time1 = [2;5;10;20;30;35;45;60];

dg_expt =
[0.1;0.150595909;0.128283201;0.141940823;0.146242475;0.144346352;0.1475
00334;0.143872472];

mg_expt =
[0.1;0.16926385;0.08132382;0.139066124;0.128085546;0.111100555;0.103540
902;0.078855423];

gl_expt =
[0.08;0.202359038;0.608082658;0.629527906;0.650591342;0.678677997;0.682
754194;0.698298278];

me_expt =
[0.4;1.299761401;1.50392811;1.710693514;1.853069443;1.860331991;1.84442
54;1.830336252];

TG_analyt= X(:,1);

d = length(TG_analyt);

DG_analyt = X(:,2);

MG_analyt = X(:,3);

GL_analyt = X(:,4);

ME_analyt = X(:,5);

time2 = linspace(2,60,d);

figure(1);
```

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```matlab
plot(time1,tg_expt,'o'); hold on;

plot(time2,TG_analyt,'color','red'); hold on;

plot(time1,dg_expt,'x'); hold on;

plot(time2,DG_analyt,'color','m'); hold on;

plot(time1,mg_expt,'+'); hold on;

plot(time2,MG_analyt ,'color','g'); hold on;

% figure(2);

plot(time1,gl_expt,'*'); hold on;

plot(time2,GL_analyt ,'color','red'); hold on;

plot(time1,me_expt,'p'); hold on;

plot(time2,ME_analyt ,'color','red'); hold on;

xlabel('Time (min)')

ylabel(' Concentration (mol/L) ');

function dXdt=diffequationvalues(t,X)

k1=0.0706989806;k2=0.1050005047 ;k3=0.3779608273  ;k4=1.1338515782
;k5=0.2333303972 ;k6=0.0793325168  ;

%[k] = optimk(in,fi);

%k1 = k(1);k2 = k(2);k3 = k(3);k4 = k(4);k5 = k(5);k6 = k(6);

%S=0.1; %S is the catalyst concentration; assumed negligible

%X(1)=triglyceride;T

%X(2)=diglyceride;D

%X(3)=monoglyceride;M

%X(4)=glycerol;G
```

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```
%X(5)=ester;E

%X(6)=alcohol;A

% global k1 k2 k3 k4 k5 k6

d1= - k1*X(1)*X(6) + k2*X(5)*X(2);

d2= k1*X(1)*X(6) - k2*X(5)*X(2) - k3*X(2)*X(6) + k4*X(5)*X(3);

d3= k3*X(2)*X(6) - k4*X(5)*X(3) - k5*X(3)*X(6) + k6*X(5)*X(4);

d4= k5*X(3)*X(6) - k6*X(5)*X(4);

d5= k1*X(1)*X(6) - k2*X(5)*X(2) + k3*X(2)*X(6) - k4*X(5)*X(3) +
k5*X(3)*X(6) - k6*X(5)*X(4);

d6= - k1*X(1)*X(6) + k2*X(5)*X(2) - k3*X(2)*X(6) + k4*X(5)*X(3) -
k5*X(3)*X(6) + k6*X(5)*X(4);

dXdt=[d1;d2;d3;d4;d5;d6];
```

Chapter 6

6 Detailed analysis and modeling of the Gradually Fed method for conversion of vegetable oil to biodiesel

6.1 Introduction

The decrease in the fossil fuel feedstock sources, reduction of world oil supplies, increasing environmental pollution has lead the scientists to investigate on alternate resources. Biodiesel is an alternative renewable source of fuel produced by transesterification of vegetable oil and alcohol. Vegetable oils can be directly used as fuel; however the viscosity of oils is high as compared to diesel fuels. The purpose of using transesterification is to reduce the viscosity of oil to the range of diesel fuel. Transesterification can be accelerated in presence of base and acid catalyst. However; alcohol and vegetable oil phases are nearly immiscible in the transesterification and the reaction mixture is heterogeneous especially in the initial stages of the reaction. The mass transfer of the triglycerides from the oil phase to the alcohol oil interface is of critical importance. In spite of mixing the two phases, the initial mass transfer controlled region results in a slow reaction rate which affects the conversion of triglyceride [1-4]. In literature; many methods are applied to reduce the mass transfer region like low frequency ultra-sonication and cavitation [5], application of ultrasound [6].

G-Fed Method for methanolysis and ethanolysis is incorporated to resolve the issue of mass transfer. This novel approach is developed in order to increase mixing rate and efficiency, eliminating the mass transfer controlled regime by increasing the diffusion of

the triglyceride into alcohol phase at low reaction temperature. The characteristics of the reactants, final product and intermediates are investigated and reported in previous studies [7, 8]. Better results have been obtained by applying this technique to methanolysis over ethanolysis. The objective of this work is to develop appropriate reaction rate equations to design a kinetic model for G-Fed method.

6.2   Experimental Section

Refined and edible Canola oil was purchased from Metro, Canada. Potassium hydroxide, 100% Ethanol, 100% Methanol and aqueous HCl (1N) was purchased from VWR (Canada). The reference standards required for the GC analysis were purchased from Sigma Aldrich. The standards were solution of glycerol, 1- mono-olein, 1,3-di-olein (1% 1,2 isomer) and triolein. *n*-Hexane (HPLC grade) was used as a solvent to dilute the samples for GC analysis. MSTFA was used as a derivatizing agent.

The reactions were carried out in 1 L jacketed glass reactor equipped with an impeller and four baffles. This stopper helps to take samples at regular time interval during the reaction. The water bath is connected to the jacket of the reactor, which controls the temperature of the reaction mixture to $\pm 1^0$C. The water bath is manually operated to maintain a specific temperature inside the reactor. Three ports were provided on the sealed lid; the ports provide the inlet of the impeller rod, oil flow inlet pipe. The impeller has a diameter of 63.5mm and is placed concentrically at 36 mm from the bottom. A thermocouple is used to monitor the temperature of the reaction mixture. The flow from the oil flask is controlled with the help of metering pump. The metering pump helps to maintain a fixed flow rate of the oil in the glassware cell. Figure 6.1 shows the set up of

the experiment for the batch reaction method and drip method. Metering pump and impeller with motor was purchased from VWR, Buchi Vaporizer R-114, Centrifuge, Thermocouple, Water bath, Separatory funnels and flask were also used for the study.

1. Reactor Cell
2. Oil outlet Pipe (For G-Fed method)
3. Oil inlet Pipe (For G-Fed method)
4. Baffle
5. Jacketed Wall
6. Temperature indicator
7. Metering Pump
8. Oil Tank
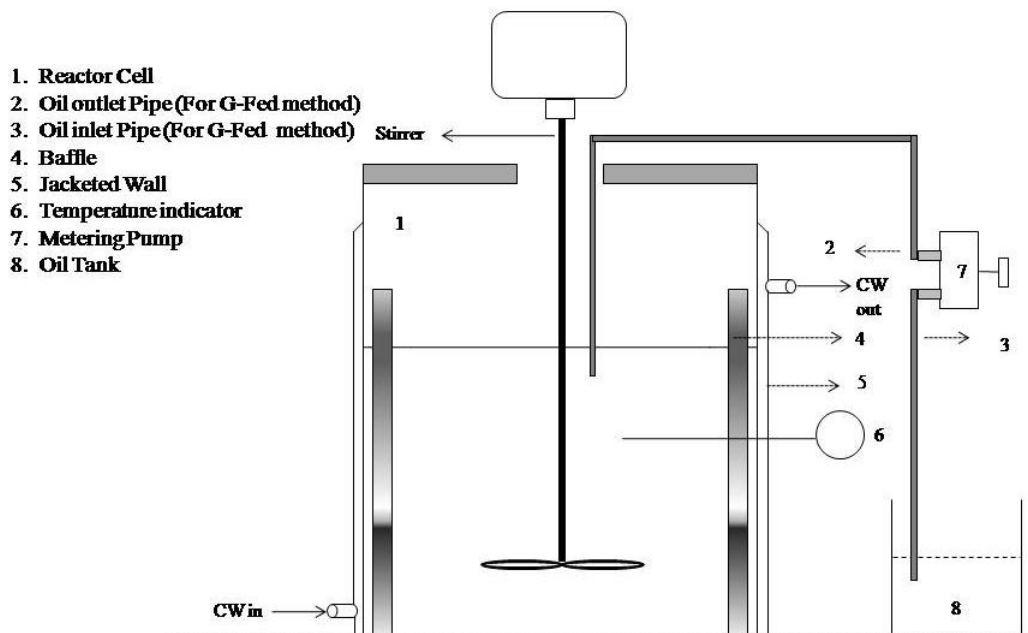
Figure 6.1 Reactor setup for G-Fed method

Selection of Reaction Parameters:

The reaction parameters were selected based on review of literature studies and some initial experiments in the lab. The higher end of molar ratio at the initial phase is more than 30:1. The lower end of molar ratio of alcohol to oil when the feed is completely introduced into the reactor was selected as 6:1 as this has been demonstrated an the optimum ratio [9]. Canola oil is used as the feedstock which is grown in abundance in Canada. The temperature of the reaction was selected at 28^0C to minimize heating cost. The catalyst used in the transesterification reaction is 1% potassium hydroxide (wt basis

of oil). The utilization of potassium hydroxide has some environmental and cost benefits since at the end of reaction the washed mixture can be neutralized with phosphoric acid to afford potassium phosphate. Potassium phosphate produced can be used as fertilizer. The problems of waste water treatment can be overcome using KOH as a catalyst. Methanolysis and Ethanolysis are carried out with the application of G-Fed method wherein the flow rate was maintained at 18ml/min. The flow rate is varied for methanolysis to study the effect of flow rate on the efficiency of the system. This process was carried out using both methanol and ethanol to compare effect of alcohols on the conversion of triglycerides. This transesterification reaction employing methanol and ethanol as precursors subsequently led to the production of their corresponding esters. Samples were collected at a regular interval of time to perform GC analysis. After the fixed reaction time, the reaction was stopped and homogeneous mixture was transferred to separatory funnel. The crude phases were further purified in order to get rid of excess alcohol and un-reacted catalyst. Crude glycerol being the heavier liquid in the mixture will settle at the bottom of the separatory funnel. The glycerol separation from the alkyl esters takes place in 10 min after the stirring is stop but complete conversion takes as long as 18h [10]. Thus the mixture was allowed to stand overnight to separate glycerol and alkyl ester phase. Both the phases: methyl/ethyl ester and glycerol were rota-vaporised to separate excess alcohol. The ester phase was washed with distilled water till the washed water obtained was clear.

Characterization and Sample Analysis

As the reaction progressed the samples of 1.5 ml were collected at regular time interval of five minutes (1.5 ml) and quenched in 1N HCl solution (2ml). Quenching was carried out
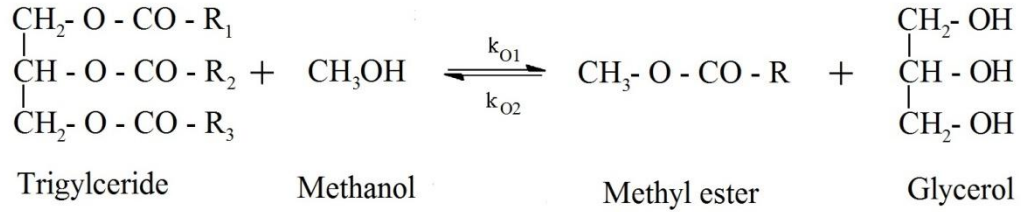
to cease the reaction at the particular time for kinetic studies of intermediates. The catalyst from the reaction sample settles down in the HCl solution. The samples were allowed to stand for 2-3 h to get rid of the catalyst from the alkyl ester phase. The top layer from these samples is further centrifuged; centrifuging helps to dry the phase. The top layer is pulled out and transferred to 2 ml centrifuge tube [13]. Anhydrous sodium sulfate was added into the centrifuge vials. Sodium sulfate acts as a drying agent to remove residual water from the samples [11]. The process of centrifuging was carried out for the duration of 15 min and at the speed of 4000 rpm. The analysis sample solution was prepared by transferring the measured amount of dried sample into 1ml auto sampler vial. The samples were derivatized with the addition of MSTFA in the sampling vial, the processed sample is allowed to stand for 20 min at room temperature in order to completely derivatize the glycerides.

After 20 min the vial is topped up to 1ml using *n*-Hexane as solvent to dilute the individual sample; this process was repeated for all the samples. The samples were analyzed by GC-FID. Samples (1µl) were injected on-column by an AOC 20s Auto sampler (Mandell instruments) at an oven temperature of 60^0C and injector temperature of 300^0C. The analysis was carried out in split mode. Helium was used as the carrier gas; the linear velocity of the gas was 48.5 cm.s^{-1}. The temperature program, 2 min at 60^0C, heating at the rate of 12^0C.min^{-1} to 300^0C and holding for 15 min. The detector temperature was fixed at 300^0C with a hydrogen make of gas at 30ml.min^{-1}. Individual experiments were carried out two times to justify the reproducibility of the results. The sample analyses were carried out in triplicates for each collected sample at a regular interval of time.

6.3 Kinetic Model

The chemical reaction equations showing forward and backward reactions are presented

below for methanolysis.

Overall Reaction

$$
\begin{array}{c}
CH_2\text{-}O\text{-}CO\text{-}R_1 \\
| \\
CH\text{-}O\text{-}CO\text{-}R_2 \\
| \\
CH_2\text{-}O\text{-}CO\text{-}R_3
\end{array}
+ \; CH_3OH \;
\underset{k_{O2}}{\overset{k_{O1}}{\rightleftharpoons}}
\; CH_3\text{-}O\text{-}CO\text{-}R \; + \;
\begin{array}{c}
CH_2\text{-}OH \\
| \\
CH\text{-}OH \\
| \\
CH_2\text{-}OH
\end{array}
$$

Trigylceride   Methanol   Methyl ester   Glycerol

Stepwise Equation

$$
\begin{array}{c}
CH_2\text{-}O\text{-}CO\text{-}R_1 \\
| \\
CH\text{-}O\text{-}CO\text{-}R_2 \\
| \\
CH_2\text{-}O\text{-}CO\text{-}R_3
\end{array}
+ \; CH_3OH \;
\underset{k_2}{\overset{k_1}{\rightleftharpoons}}
\; CH_3\text{-}O\text{-}CO\text{-}R_3 \; + \;
\begin{array}{c}
CH_2\text{-}O\text{-}CO\text{-}R_1 \\
| \\
CH\text{-}O\text{-}CO\text{-}R_2 \\
| \\
CH_2\text{-}O\text{-}OH
\end{array}
$$

   Trigylceride   Methanol   Methyl ester   Digylceride

$$
\begin{array}{c}
CH_2\text{-}O\text{-}CO\text{-}R_1 \\
| \\
CH\text{-}O\text{-}CO\text{-}R_2 \\
| \\
CH_2\text{-}O\text{-}OH
\end{array}
+ \; CH_3OH \;
\underset{k_4}{\overset{k_3}{\rightleftharpoons}}
\; CH_3\text{-}O\text{-}CO\text{-}R_1 \; + \;
\begin{array}{c}
CH_2\text{-}O\text{-}OH \\
| \\
CH\text{-}O\text{-}CO\text{-}R_2 \\
| \\
CH_2\text{-}O\text{-}OH
\end{array}
$$

   Digylceride   Methanol   Methyl ester   Monogylceride

$$
\begin{array}{c}
CH_2\text{-}O\text{-}OH \\
| \\
CH\text{-}O\text{-}CO\text{-}R_2 \\
| \\
CH_2\text{-}O\text{-}OH
\end{array}
+ \; CH_3OH \;
\underset{k_6}{\overset{k_5}{\rightleftharpoons}}
\; CH_3\text{-}O\text{-}CO\text{-}R_2 \; + \;
\begin{array}{c}
CH_2\text{-}OH \\
| \\
CH\text{-}OH \\
| \\
CH_2\text{-}OH
\end{array}
$$

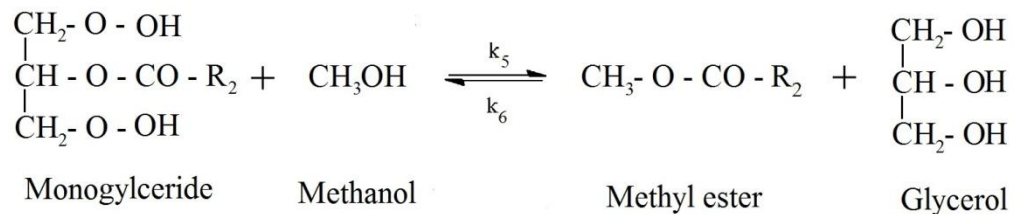   Monogylceride   Methanol   Methyl ester   Glycerol
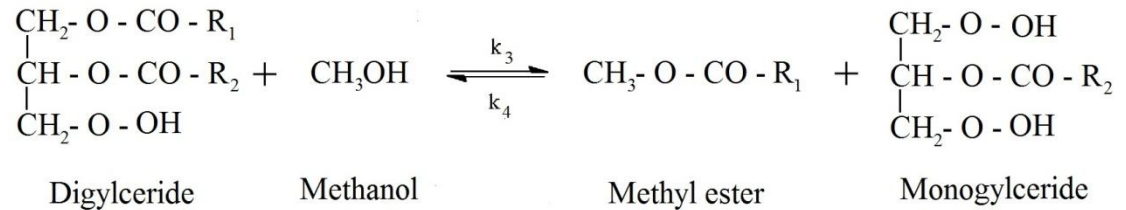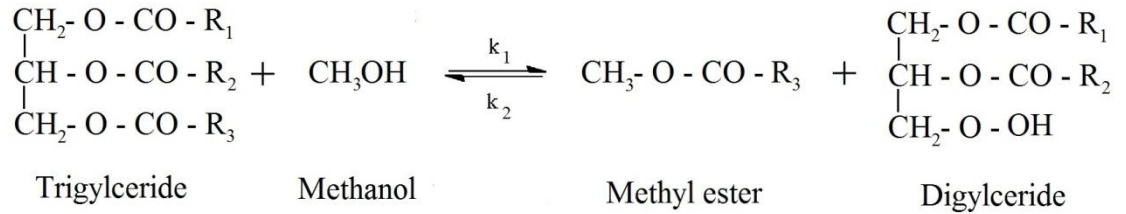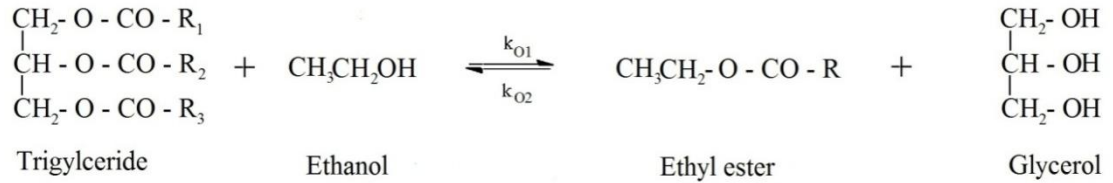
Figure 6.2 Transesterification reaction for methanolysis of vegetable oil

Similar chemical equations can be written for ethanolysis reaction and is shown is figure 6.3

Overall Reaction
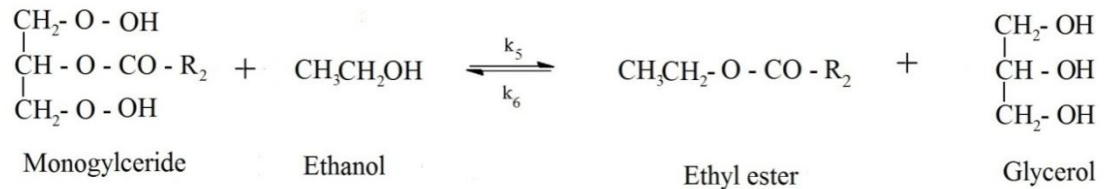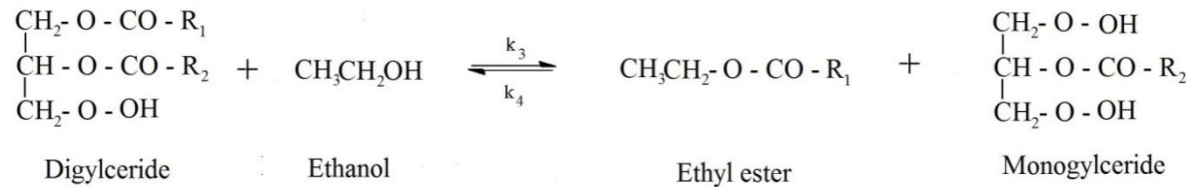

Stepwise Equation

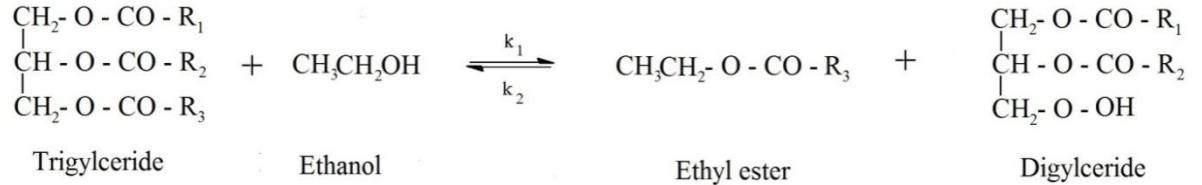**Figure 6.3 Transesterification reaction for ethanolysis of vegetable oil**

In batch method experimented so far in many studies: alcohol and feedstock (oil) is introduced into the reactor prior to mechanical mixing. In G-Fed method the oil feed is introduced into the reactor at various flow-rates to obtain highest conversion of biodiesel at ambient reaction conditions. The flow rate of the oil into the reactor is a variable and

can be optimized further to obtain better results. In order to obtain kinetic rate constants for the G-Fed method, appropriate reaction rate equations are formulated. The oil feed rate $Q_f(t)$ could vary with time. The reactor was initially filled with the required amount of alcohol and catalyst (Figure 6.4), the agitation was started slowly as soon as the oil stream was pumped into the system.
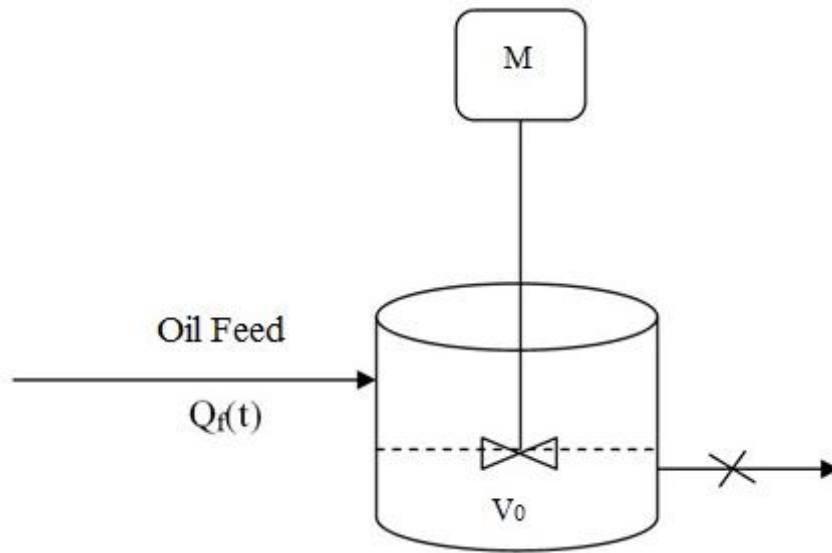
Figure 6.4 Schematic of G-Fed method

The kinetic model is based on a constant flow rate (18ml min^{-1}) which can be further modified for different flow rate as the variable of the system. The mass conservation principle applicable to the mass of species i for the reactor can be stated as:

$$\{Input\ rate\ of\ i\ into\ reactor\} - \{Output\ of\ i\ from\ reactor\}$$

$$+ \{Rate\ of\ production\ of\ i\ within\ the\ reactor\}$$

$$= \{Rate\ of\ accumulation\ of\ i\ in\ the\ reactor\}$$

The above equation can be expressed as below, based on the molar concentration C_i, volumetric flow rate Q, and reactor volume V:

$$(QC_i)_f - 0 + r_i V = \frac{d[V(C_i)_e]}{dt} \tag{6.1}$$

6.3.1 Mass balance equations for individual species

It is more convenient to use moles of species instead of concentration in equation 6.1. Thus for the mass balance equation for individual species can be presented as shown below:

For Triglycerides:

$$F_{TG} - 0 + r_{TG}V = \frac{d(n_{TG})_e}{dt} \tag{6.2}$$

For Diglycerides:

$$r_{DG}V = \frac{d(n_{DG})_e}{dt} \tag{6.3}$$

For Monoglycerides:

$$r_{MG}V = \frac{d(n_{MG})_e}{dt} \tag{6.4}$$

For Alkyl Esters:

$$r_{AE}V = \frac{d(n_{AE})_e}{dt} \tag{6.5}$$

For Alcohol:

$$r_{AL}V = \frac{d(n_{AL})_e}{dt} \tag{6.6}$$

For Glycerol:

$$r_{GL}V = \frac{d(n_{GL})_e}{dt} \tag{6.7}$$

Active reactor volume (V) will vary with time, it can be expressed as function of initial volume (V_o) and feed rate.

$$V = V_0 + Q_f(t)t \tag{6.8}$$

Species concentrations in the reactor (C_i) at any given time are given as:

$$C_i = \frac{n_i}{V} = \frac{n_i}{V_0 + Q_f(t)t} \tag{6.9}$$

Following simplifying assumptions were used to describe the gradually fed reaction system to estimate reaction parameters for the overall reaction giving TG conversion. The major parameters for G-Fed method are:

1. Gradual feeding of oil to the bulk of alcohol.

2. Higher alcohol to oil ratios (more than 30:1 in the initial region).

3. Continuous Mixing of the phases with the assistance of mechanical agitation.

On the basis of the parameters described above the following assumptions can be considered to develop a kinetic model for G-Fed Method

a) The reaction mixture is considered as pseudo-homogeneous system with no mass transfer limitations. This is justifiable due to gradual addition of feed along with agitation intensity.

Based on the assumption (a) as a basic assumption and with other assumptions, the reaction rate of TG, DG and MG can be estimated by developing an appropriate kinetic

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model using different order of the reaction. Derivation of reaction rate constant is carried out for three different cases:

1. Pseudo First Order
2. Irreversible Second Order
3. Reversible Second Order

6.3.2 Derivation of reaction rate equations

6.3.2.1 Case 1: Pseudo first order reaction

b) The order of the reaction can be assumed as pseudo first order as alcohol concentration.

The reaction rate equations of TGs DGs and MGs are taken into consideration to begin the kinetic rate. With the assistance of assumption (a) and (b), equations are generated in terms of concentration and volume as a variable function of time.

For Triglycerides:

$$r_{TG} = -k_1 C_{TG} \qquad\qquad (6.10)$$

For Diglycerides:

$$r_{DG} = -k_3 C_{DG} + k_1 C_{TG} \qquad\qquad (6.11)$$

For Monoglycerides

$$r_{MG} = -k_5 C_{MG} + k_3 C_{DG} \qquad\qquad (6.12)$$

The reaction rate equations (6.10, 6.11 and 6.12) and the mass balance equations (6.2, 6.3 and 6.4) are used to generate appropriate reaction rate in terms of concentration of intermediate species. The equations for TGs, DGs and MGs are shown below.

$$\frac{dC_{TG}}{dt} = -k_1 C_{TG} + \frac{Q}{(V_0 + Q\,t)}\left((C_i)_f - C_{TG}\right) \tag{6.1a}$$

$$\frac{dC_{DG}}{dt} = -k_3 C_{DG} + k_1 C_{TG} - \frac{Q\,C_{DG}}{(V_0 + Q\,t)} \tag{6.2a}$$

$$\frac{dC_{MG}}{dt} = -k_5 C_{MG} + k_3 C_{DG} - \frac{Q\,C_{MG}}{(V_0 + Q\,t)} \tag{6.3a}$$

6.3.2.2 Case 2: Irreversible second order reaction

c) Since large excess of alcohol present in the reaction mixture, alcoholysis of TG can be considered as irreversible second order reaction [2].

In this case, only reactants (TGs, DGs and MGs) are considered to derive the kinetic reaction rate equations accordingly. Based on assumption a) and c), the possible reaction rate equations are presented below

For Triglycerides:

$$r_{TG} = -k_1 C_{TG}^2 \tag{6.13}$$

For Diglycerides:

$$r_{DG} = -k_3 C_{DG}{}^2 + k_1 C_{TG}^2 \tag{6.14}$$

For Monoglycerides:

$$r_{MG} = -k_5 C_{MG}{}^2 + k_3 C_{DG}{}^2 \tag{6.15}$$

Irreversible second order rate equations are formed by using equation (6.13, (6.14) and (6.15) in mass balance equations (6.2), (6.3) and (6.4).

$$\frac{dC_{TG}}{dt} = -k_1 C_{TG}{}^2 + \frac{Q}{(V_0 + Q\,t)}((C_i)_f - C_{TG}) \tag{6.1b}$$

$$\frac{dC_{DG}}{dt} = -k_3 C_{DG}{}^2 + k_1 C_{TG}{}^2 - \frac{Q\,C_{DG}}{(V_0 + Q\,t)} \tag{6.2b}$$

$$\frac{dC_{MG}}{dt} = -k_5 C_{MG}{}^2 + k_3 C_{DG}{}^2 - \frac{Q\,C_{MG}}{(V_0 + Q\,t)} \tag{6.3b}$$

6.3.2.3 Case 3: Reversible second order reaction

The oil is continuously fed into the reactor which leads to the increase in volume of the oil the system leads to the decrease in the oil to alcohol molar ratio. Thus as per the literature studies [1, 3, 13] and the studies carried out previously [14] for conventional method (Batch) reversible second order was assumed to derive the possible reaction rate equations and verify for G-Fed method. Based on above chemical equations 6.3 and 6.4 kinetic rate equations for individual species of the reaction can be expressed as second order rate for reactants, intermediates and products as follows:

For Triglycerides

$$r_{TG} = -k_1 C_{TG} C_{AL} + k_2 C_{AE} C_{DG} \tag{6.16}$$

For Diglycerides

$$r_{DG} = k_1 C_{TG} C_{AL} - k_2 C_{AE} C_{DG} - k_3 C_{DG} C_{AL} + k_4 C_{AE} C_{MG} \tag{6.17}$$

For Monoglycerides

$$r_{MG} = k_3 C_{DG} C_{AL} - k_4 C_{AE} C_{MG} - k_5 C_{MG} C_{AL} + k_6 C_{AE} C_{GL} \tag{6.18}$$

For Glycerol

$$r_{GL} = k_5 C_{MG} C_{AL} - k_6 C_{AE} C_{GL} \tag{6.19}$$

For Alkyl Esters

$$r_{AE} = k_1 C_{TG} C_{AL} - k_2 C_{AE} C_{DG} + k_3 C_{DG} C_{AL} - k_4 C_{AE} C_{MG} + k_5 C_{MG} C_{AL} - k_6 C_{AE} C_{GL}$$

(6.20)

For Alcohol

$$r_{AL} = -k_1 C_{TG} C_{AL} + k_2 C_{AE} C_{DG} - k_3 C_{DG} C_{AL} + k_4 C_{AE} C_{MG} - k_5 C_{MG} C_{AL} + k_6 C_{AE} C_{GL}$$

(6.21)

The reaction rate equations (6.16-6.21) and the mass balance equations (6.2-6.7) are used to generate appropriate reversible second order rate equations with corresponding mass transfer terms as shown below:

$$\frac{dC_{TG}}{dt} = -k_1 C_{TG} C_{AL} + k_2 C_{AE} C_{DG} + \frac{Q}{(V_0 + Q t)}((C_i)_f - C_{TG}) \qquad (6.1c)$$

$$\frac{dC_{DG}}{dt} = k_1 C_{TG} C_{AL} - k_2 C_{AE} C_{DG} - k_3 C_{DG} C_{AL} + k_4 C_{AE} C_{MG} - \frac{Q C_{DG}}{(V_0 + Q t)} \qquad (6.2c)$$

$$\frac{dC_{MG}}{dt} = k_3 C_{DG} C_{AL} - k_4 C_{AE} C_{MG} - k_5 C_{MG} C_{AL} + k_6 C_{AE} C_{GL} - \frac{Q C_{MG}}{(V_0 + Q t)} \qquad (6.3c)$$

$$\frac{dC_{GL}}{dt} = k_5 C_{MG} C_{AL} - k_6 C_{AE} C_{GL} - \frac{Q C_{GL}}{(V_0 + Q t)} \qquad (6.4c)$$

$$\frac{dC_{AE}}{dt} = k_1 C_{TG} C_{AL} - k_2 C_{AE} C_{DG} + k_3 C_{DG} C_{AL} - k_4 C_{AE} C_{MG} + k_5 C_{MG} C_{AL} - k_6 C_{AE} C_{GL} -$$

$$\frac{Q C_{AE}}{(V_0 + Q t)} \qquad (6.5c)$$

$$\frac{dC_{AL}}{dt} = -k_1 C_{TG} C_{AL} + k_2 C_{AE} C_{DG} - k_3 C_{DG} C_{AL} + k_4 C_{AE} C_{MG} - k_5 C_{MG} C_{AL} k_6 C_{AE} C_{GL} -$$

$$\frac{Q C_{AL}}{(V_0 + Q t)} \qquad (6.6c)$$

The equations obtained with case 1, 2 and 3 are evaluated using the kinetic model developed to predict the forward reaction rate constants for case 1 and 2 and forward and backward reaction rate constants for case 3. However the reaction rate constants obtained from the kinetic model for irreversible second order and reversible second order model fails to fit with the experimental results. The kinetic model for case 1 fits adequately for analytical concentration values obtained from model and experimental values.

6.3.3   Simulation for G-Fed Method

Differential equations are formed in terms of concentration as a function of time for three cases as described for this work. These differential equations are presented in form of non linear matrix in figure 6.5 where in rate constants (k_1-k_6) are the only 'unknowns' to be

evaluated. The concentration of reactants, intermediates and products (a_{11}-a_{ii}) are obtained experimentally by GC analysis of samples collected at the regular interval of time. The differential term for concentration (b_1-b_n) is calculated by the point slope method from the experimental values. The approach is discussed clearly in our previous study [14]. The mat lab code provided in the previous study was modified to develop kinetic model for G-Fed method

$$
\begin{bmatrix}
-a_{11} & a_{12} & 0 & 0 & 0 & 0 \\
-a_{21} & -a_{22} & -a_{23} & a_{24} & 0 & 0 \\
0 & 0 & a_{33} & -a_{34} & -a_{35} & a_{36} \\
0 & 0 & 0 & 0 & a_{45} & -a_{46} \\
a_{51} & -a_{52} & a_{53} & -a_{54} & a_{55} & -a_{56} \\
-a_{61} & a_{62} & -a_{63} & a_{64} & -a_{65} & a_{66}
\end{bmatrix}
\begin{bmatrix}
k_1 \\ k_2 \\ k_3 \\ k_4 \\ k_5 \\ k_6
\end{bmatrix}
=
\begin{bmatrix}
b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \\ b_6
\end{bmatrix}
$$

Figure 6.5 Reaction rate equation in the form of nonlinear matrix [15].

Rate constants of the equation are estimated using the f-solve function build in function of matlab software, (R2007b) Version 7.5.0.342. The code generates rate constants for each interval of time giving six sets of values. The m.file is created to calculate the optimum value of k_1-k_6 out of the set of k values. The optimization code is designed to minimize the objective function shown below in equation 6.A. The algorithm in figure 6.7 represents the steps followed to estimate the rate constants for the system. Unlike batch runs, the differential equations formed for G-Fed method are implicit differential equations. Therefore *ode23tb* (build in mat lab function) is used to solve the differential equations and obtain analytical concentration.

$$E^2 = \sum_{i=1}^{n}[b_i - a_{i1}k_1 + a_{i2}k_2 + \ldots + a_{n6}k_6]^2 \qquad\qquad (6.A)$$
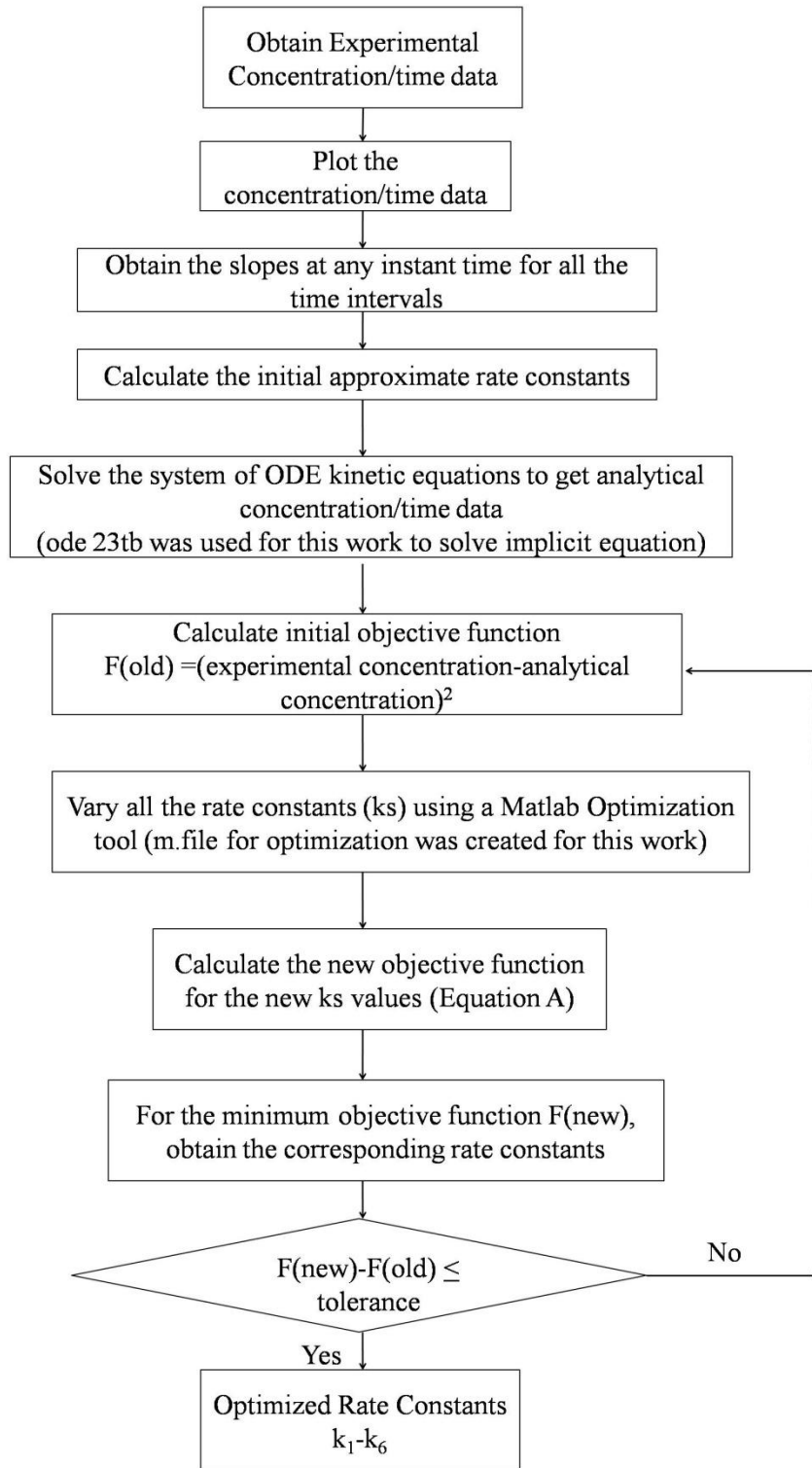
Figure 6.6 Flow chart to evaluate and optimize reaction rate constants [16]

The objective function presented in equation 6.A can be modified according the order of the reaction:

1. **Pseudo first order:** Objective function is modified using equation 6.1a, 6.2a and 6.3a.

2. **Irreversible second order:** Objective function is modified using equation 6.1b, 6.2b and 6.3b.

3. **Reversible Second Order:** Objective function is modified using equation 6.1c, 6.2c, 6.3c, 6.4c, 6.5c and 6.6c.

The curve fitting is carried out between analytical values and experimental values. The analytical values are obtained by using optimum k values using ODE function.

6.4 Results and Discussions

The conversion of triglycerides using different methods (Batch and G-Fed) is demonstrated in figure 6.7. These experiments with different flow-rates are carried out in our previous studies [7]. It can be seen that based on gradually feeding the oil show higher conversions compared to conventional batch method. It is also observed that there is need to determine an appropriate feed rate to achieve very high level of conversions. The simulation is carried out for the flow rate of $18ml.min^{-1}$ for methanolysis and ethanolysis for 30 min. Pseudo first order gives good fit of analytical concentration and experimental concentration.
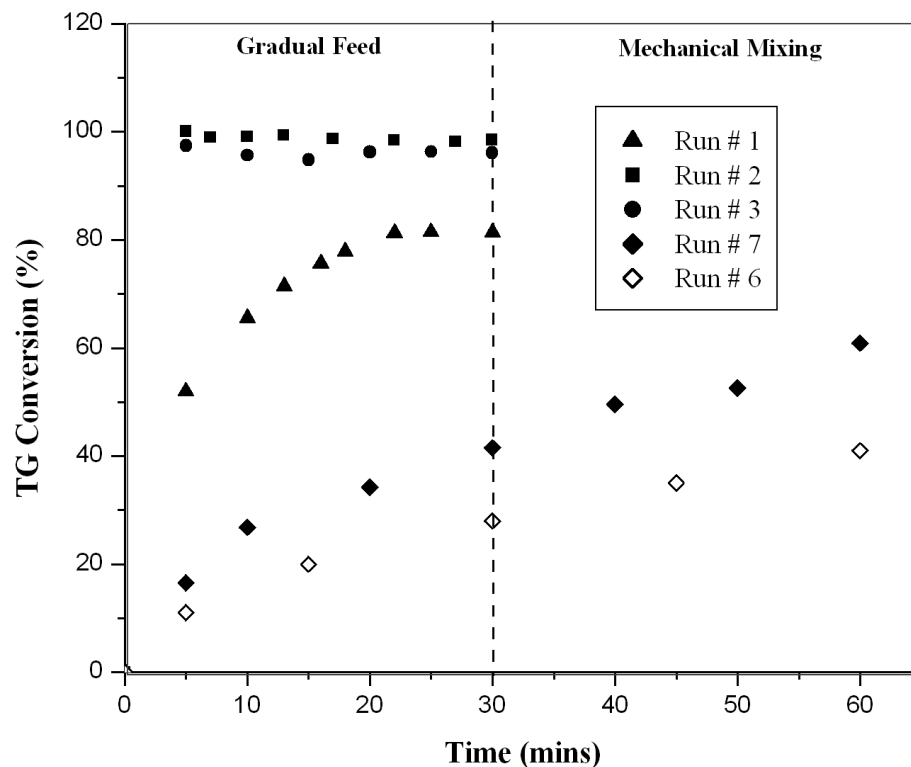
Figure 6.7 TG conversion for methanolysis of canola oil using various flow rates (run 1= 27ml.min^{-1}, run 2= 10-22 ml.min^{-1}, run 3= 18 ml.min^{-1}, run 6= batch run 300 rpm, , run 7= batch run at 600 rpm)

Figure 6.8 and 6.9 shows pseudo first order fitting for methanolysis and ethanolysis for their corresponding reactants. The range of rate constants for each interval is also estimated for both cases. The model was run for pseudo first order for G-Fed methanolysis and the evaluated forward reaction rate constants for each time interval are presented in table 6.1. Similar the reaction rate constants for ethanolysis are depicted in table 6.2. The curve fitting for TG, DG and MG in ethanolysis is shown in figure 6.9. Methanolysis follows the pseudo first order as the analytical fitting over experimental values are good. However ethanolysis follows this trend initially, G-Fed Ethanolysis system might have a mixed reaction order with pseudo first order and second order. Ethanolysis is predicted to follow both first and second order.
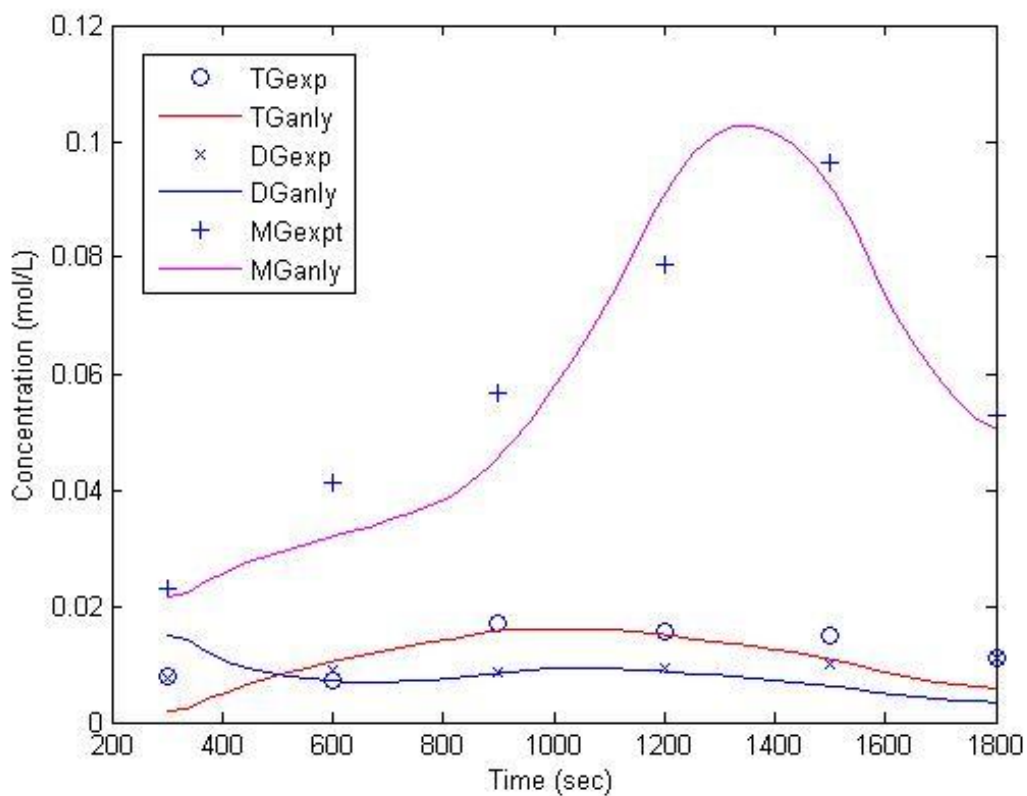
Figure 6.8 Pseudo first order fit for G-Fed methanolysis (18ml.min^{-1})

Table 6.1 Reaction rate constants for G-Fed methanolysis (Pseudo first order)

Time Interval	k_1 s^{-1}	k_3 s^{-1}	k_5 s^{-1}
0-5	0.230	0.176	0.052
5-10	0.077	0.105	0.020
10-15	0.044	0.068	0.011
15-20	0.039	0.054	0.011
20-25	0.031	0.047	0.009
25-30	0.028	0.040	0.011

Table 6.2 Reaction rate constants for G-Fed ethanolysis (Pseudo first order)

Time Interval	k_1 s^{-1}	k_3 s^{-1}	k_5 s^{-1}
0-5	0.052	0.091	0.045
5-10	0.035	0.0153	0.029
10-15	0.028	0.011	0.024
15-20	0.023	0.009	0.020
20-25	0.019	0.009	0.017
25-30	0.016	0.007	0.014

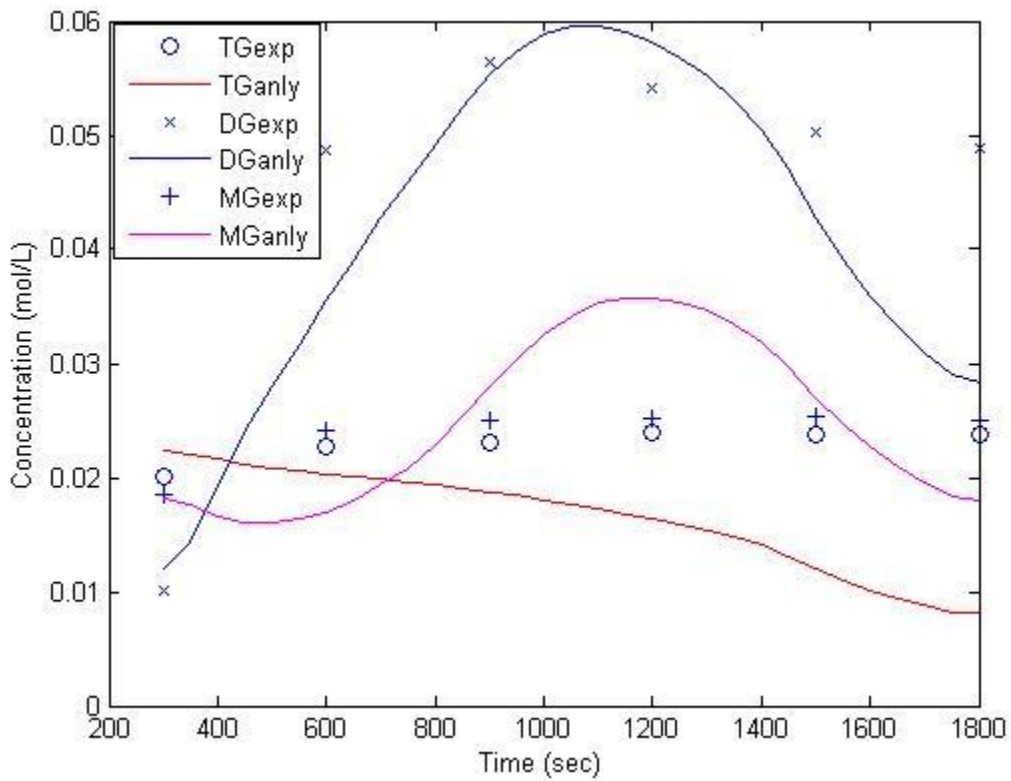**Figure 6.9 Pseudo first order fit for G Fed ethanolysis (18ml.min^{-1})**

Georgogianni et al.[17] investigated on the kinetics of ethanolysis of sunflower oil using base catalyst and reported first and second order reaction with respect to triglycerides. The optimized reaction rate constants obtained from the kinetic model for pseudo first order (Case 1) for methanolysis and ethanolysis is reported in table 6.3. The reaction rate for methanolysis is higher than ethanolysis; G-Fed method is more efficient for methanolysis reaction.

Table 6.3 Overall reaction rate constant (Pseudo first order)

	$k_1 s^{-1}$	$k_3 s^{-1}$	$k_5 s^{-1}$
G-Fed methanolysis (18ml .min^{-1})	0.0794	0.1368	0.00926
G-Fed ethanolysis (18ml .min^{-1})	0.0528	0.0154	0.0295

The model can predict reaction rate constants for G-Fed systems with different flow rates. However at present the mat lab program developed to simulate the kinetic rate constants cannot simulate for G-Fed systems with variations in flow rate. The program can be modified further for such systems.

6.5　Conclusions

These studies are incorporated to initiate the development of kinetic model for G-Fed method. The experimental values selected for the simulation are obtained from G-Fed methanolysis and G-Fed ethanolysis for the flow rate of 18ml.min^{-1}. In drip method, the alcohol oil ratio is as high as 1:36 in the initial period of the reaction and thus pseudo first order of reaction assumed for the kinetic study. The results indicate that a better fit was obtained for the pseudo first order reaction kinetics for both methanolysis and ethanolysis of canola oil. The reaction rate is higher for methanolysis as compared to ethanolysis at the similar experimental conditions. The kinetic model program has a limitation to work for G-Fed systems with constant flow rate of feedstock. Further studies will be carried out to modify the kinetic model program to demonstrate the kinetics of G-Fed method with changing flow rate of feedstock.

6.6 Abbreviations

TG   Triglycerides

DG   Diglycerides

MG   Monoglycerides

AE   Alkyl Esters

AL   Alcohol (Methanol/Ethanol)

GL   Glycerol

HCl   Hydrochloric Acid

MSTFA   N-methy-N(trimethylsilyl) trifluoroacetamide

GC   Gas Chromatography

Nomenclature

C   Concentration $(mol .L^{-1})$

Q   Flow rate

V_0 Initial Volume of Reactor (L)

V   Total Volume of Reactor (L)

r   Reaction rate $(mol\ L^{-1}\ s^{-1})$

n   number of moles

t   time (s)

k   Reaction Rate Constant (s^{-1})

a   Product of concentration

b   differential term for corresponding concentration

Subscripts

i	Species (TG, DG, MG, AE, GL, AL)
f	Feed
1	Triglyceride to diglyceride and alkyl esters
2	Diglyceride to triglyceride and alcohol
3	Diglyceride to monoglyceride and alkyl esters
4	Monoglyceride to diglyceride and alcohol
5	Monoglyceride to glycerol and alkyl esters
6	Glycerol to monoglyceride and alcohol

6.7 References

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Chapter 7

7 Conclusions and Recommendations

7.1 Summary and conclusions for G-Fed method

A novel G-Fed method is developed to overcome the mass transfer issues in conventional method (batch method), to improve the conversion and fuel properties of biodiesel produced by transesterification. Series of experiments are carried out with both batch and G-Fed method using both methanol and ethanol as alcohols. The study clearly reports the advantage of G-Fed method over batch method; the oil is introduced continuously as small stream and is simultaneously mixed by impeller in the reactor filled with excess of alcohol. The high molar ratio along with mechanical mixing overcomes the limitation of mass transfer in the initial phase of reaction. The experiments are carried out for different flow rates of feedstock into the reactor using both methanol and ethanol. Application of G-Fed method using methanol and ethanol, showed that methanolysis is better in terms of conversion and yield as compared to ethanolysis reaction of canola oil.

Out of all the experiments carried out, methanolysis of canola oil for flow rate of 18ml.min^{-1} at temperature of 45^{0}C for the reaction time of 30 min and flow rate of 18ml.min^{-1} at temperature of 28^{0}C for reaction time wherein batch was followed for 30 min gives better conversion with total glycerol content of fuel in ASTM limits (less than 0.24%). Further kinetic studies were carried out to predict reaction rate constants for the

transesterification reaction. The kinetic model developed was applied to study ethanolysis in batch mode and methanolysis and ethanolysis in G-fed method. Second order reaction was followed by ethanolysis in batch method (conventional method) while pseudo first order fits sufficiently for both: methanolysis and ethanolysis in G-Fed method.

7.2   Recommendations and Future Work

1. In G-Fed method developed, optimization studies can be extended to obtain appropriate flow-rate of oil feedstock to achieve maximum conversion and yield of biodiesel at or near ambient reaction conditions to further improve energy efficiency.

2. Pilot scale testing of the G-Fed method is recommended to prove its effectiveness on large scale. These studies should include parameter optimization downstream processing and purification.

3. G-Fed method gives higher conversion as compared to conventional batch runs. Further study can be carried out on effect of droplet size and dispersion of oil in alcohol with application of G-Fed method in methanolysis and ethanolysis of vegetable oils.

4. In these studies the monoglycerides content of the fuel was high therefore optimization studies should look into this further to lower their content in the final product from G-Fed method.

5. Future study can be carried out on the investigation of adsorbents capable to remove MG content which will lead to reduction in total glycerol content of the fuel.

6. In ethanolysis reaction, washing stage results in the loss of fuel due to emulsion formation. Future study can be carried out on investigation on developing alternative methods to purify ethyl esters.

7. The kinetic model developed for G-Fed method can be further modified for the G-Fed system with fluctuating flow rate of feedstock considering mass transfer effects.

Curriculum Vitae

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Post-Secondary Education

2007-2011	Doctor of Philosophy in Chemical Engineering
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Publications

Referred Proceedings

1. Pal, K. D, Prakash, A . Kinetics of ethanolysis of canola oil in batch reactor of 1 L, CSChE, London, Canada, October 2011 (Oral Presentation).

2. Pal, K. D, Prakash, A ., Investigations of mass transfer and kinetic effects during transesterification of canola oil, CSChE Saskatoon, Canada 26th October, 2010 (Oral Presentation)

Submitted/ On desk papers

1. Pal, K. D, Prakash, A. Kinetics studies for ethanolysis of canola oil using potassium hydroxide as catalyst in a batch reactor.
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Papers under review (Withheld due to pending patent application)

1. Pal, K. D, Prakash, A. New cost effective method for conversion of vegetable oil to biodiesel.
   (To be submitted to Fuel Processing Technology Journal)

2. Pal, K. D, Prakash, A. Ethanolysis versus methanolysis of vegetable oil using a new Gradual feed flow method.
   (To be submitted to Journal of Energy and Fuels)

3. Pal, K. D, Prakash, A. Detailed analysis and modeling of the Gradually Fed method for conversion of vegetable oil to biodiesel
   (To be submitted in Fuel Processing Technology Journal)