# Impact of Mixing on Biodiesel Production from Canola Oil

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# Abstract

With the globally increasing demand of energy and fast consumption of fossil fuels, research on finding alternative resources for replacing traditional energy has become extremely important. Biodiesel, which could be obtained from vegetable oils and animal fats from transesterification process, is one of these renewable and eco-friendly resources. Mechanical mixing of vegetable oils with alcohols and alkali catalysts is the most commonly used mixing method for industrial production of biodiesel due to its comparatively low cost. Although the mixing parameters are known to influence the overall yield of biodiesel production, the accurate determination of the mixing process has always been a challenge. Again, the measurement of biodiesel yield has always relied on expensive and time-consuming processes. This study was formulated to evaluate the impact of mixing parameters such as time, speed, and impeller height on biodiesel yield by imaging technology and to examine the potential of quantifying the biodiesel conversion in real time using a simplified and cheap technique which employs the refractive index of the biodiesel. Biodiesel yield from the transesterification process of canola oil with methanol and KOH were measured and compared with thermogravimetric analysis (TGA) to ascertain the validity of the refractive index technique. Having established the technique, the impact of mixing on biodiesel production was evaluated using five mixing intensities (200, 250, 275, 300 and 325 rpm) at five different reaction times (1, 5, 10, 15 and 20 min). Two impeller locations were employed in the study at room temperature and atmospheric pressure. The drop sizes and distribution of mixing bubbles were recorded and analyzed using imaging analysis techniques. The results indicated that refractometer is a promising tool for determining the biodiesel yield from transesterification of canola oil with less than 5% variation compared to the TGA technique. Moreover, increasing mixing intensity would accelerate the transesterification reaction, speeds of 200 -325 rpm would all eventually result in high biodiesel yield (up to 80%). It was also established that biodiesel yield increased when the vertical location of the impeller blade was less than 50% of the height of the mixture in the reaction vessel.

# Résumé

Avec la demande mondiale croissante d'énergie et la consommation rapide de combustibles fossiles, la recherche de ressources alternatives pour remplacer l'énergie traditionnelle est devenue extrêmement urgente. Le biodiesel, qui pourrait être obtenu à partir d'huiles végétales et de graisses animales provenant du processus de transestérification, est l'une de ces ressources renouvelables et respectueuses de l'environnement. Le mélange mécanique d'huiles végétales avec des alcools et des catalyseurs alcalins est la méthode de mélange la plus couramment utilisée pour la production industrielle de biodiesel en raison de faible coût. Bien que l'on sache que les paramètres de mélange influent sur le rendement global de la production de biodiesel, cette détermination précise a toujours été un défi. Encore une fois, la mesure du rendement en biodiesel a toujours reposé sur des processus coûteux et longs. Cette étude a été formulée pour évaluer l'impact des paramètres de mélange tels que le temps, la vitesse, la hauteur de la turbine sur le biodiesel et la possibilité de quantifier la conversion du biodiesel en temps réel en utilisant une technique simple et bon marché. Le rendement en biodiesel du procédé de transestérification de l'huile de canola avec du méthanol et du KOH a été mesuré et comparé à l'analyse thermogravimétrique (ATG) pour vérifier la validité de la technique de l'indice de réfraction. Après avoir établi la technique, l'impact du mélange sur la production de biodiesel a été évalué en utilisant cinq intensités de mélange (200, 250, 275, 300 et 325 rpm) à cinq temps de réaction différents (1, 5, 10, 15 et 20 min). Les emplacements ont été utilisés à la température ambiante et à la pression atmosphérique. Les tailles et distributions de

gouttes ont été enregistrées et analysées en utilisant des techniques d'analyse d'imagerie. Les résultats indiquent que le réfractomètre est un outil prometteur pour déterminer le rendement en biodiesel de la transestérification de l'huile de canola avec moins de 5% de variation par rapport à la technique TGA. De plus, l'augmentation de l'intensité de mélange accélérerait la réaction de transestérification, des vitesses de 200 à 325 rpm aboutiraient toutes à un rendement élevé en biodiesel (jusqu'à 80%) bien que les temps de réaction soient différents. Encore une fois, il a été établi que la location de la pale de la turbine inférieure à 50% de la hauteur de la surface du mélange était plus efficace et augmentait le rendement en biodiesel.

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# Nomenclature

| | |
|---|---|
| $CO_x$ | carbon oxides |
| FAME | fatty acid methyl esters |
| Fast green FCF | food green 3, FD&C green No. 3, Green 1724, Solid Green FCF, and C.I. 42053 |
| GC | gas chromatography |
| FFA | free fatty acids |
| $^1H$ NMR | proton nuclear magnetic resonance |
| HPLC | high-performance liquid chromatography |
| KOH | potassium hydroxide |
| NaOH | sodium hydroxide |
| NIRS | near-infrared Spectroscopy |
| $NO_x$ | nitrogen oxides |
| PM2.5 | atmospheric particulate matter (PM) (with diameter < 2.5 micrometers) |
| $R^2$ | coefficient of determination |
| rpm | revolutions per minute |
| $SO_x$ | sulphur oxides |
| TGA | thermogravimetric analysis |

# Chapter 1

# Introduction

## 1.1 Background

Fossil fuels, including coal, petrol oils and natural gases, are still the major source of world energy (Borges and Díaz, 2012). However, some renewable energy sources have been harnessed as alternatives to augment the global energy mix. With the depletion of the fossil fuels and increasing concerns about atmospheric pollution, there is a great need to intensify the search for clean and renewable fuels (Leung et al., 2010). Biodiesel obtained from vegetable oils and animal fats, is one prime alternative for petroleum and energy industries. Biodiesel has drawn much attention from researchers during the last few decades, especially for the countries that largely depend on the importation of petroleum and its refined products (Musa, 2016).

Transesterification is the most efficient method to produce biodiesel from vegetable oils due to its low cost and high feasibility. This chemical process requires the reaction of vegetable oils or animal fats with alcohols in the presence of catalysts. Biodiesel can be produced from several types of vegetable oils (e.g. soybean, peanut, palm oil, canola oil, rapeseed, coconut, sunflower oil, etc.) as well as animal fats. Canola oil is the major vegetable oil from Canada. The oil accounts for 70% of Canada's vegetable oil export trade (Canola Council, 2017). Therefore, Canola oil is the leading feedstock for producing biodiesel in Canada.

Although, several mixing techniques have been exploited for biodiesel production (such as traditional mechanical mixing, microwave mixing, ultrasonic mixing and static mixing), the most widely used industrial method is still the traditional mechanical mixing. Mechanical mixing offers low cost for both reactants and equipment. However, mechanical mixing has been reported not to be as effective as the recent advanced mixing techniques. Beside reaction conditions (pressure and temperature) and the amount and type of reactants, mixing intensity has been found to be a crucial factor for industrial production of biodiesel (Meher et al., 2006a; Stamenković et al., 2007). The degree of mixing depends on the mixing parameters. It also influences the yield of biodiesel. Accurately establishing the mixing parameters is critical in optimizing the process conditions for higher yield. Using imaging techniques to accurately determine the bubble sizes and their distribution could positively impact on the mixing conditions. Studies on the impact of mixing parameters have primarily focused the mixing time and speed (Ma et al. 1999; Stamenković et al., 2007; Alcantara et al., 2010; Lakshmi et al., 2011; Mashkour et al., 2016). Very few studies have considered the impacts of the impeller blade location on biodiesel production.

Another important parameter in biodiesel production is the ease of determining the yield. Some biodiesel characterization methods have been proposed and investigated by many researchers, including thermogravimetric analysis (TGA), gas chromatography (GC), near-infrared spectroscopy (NIRS), high-performance liquid chromatography (HPLC) and proton nuclear magnetic resonance ($^1$H NMR) spectroscopy (Freedman et al., 1984; Mittelbach, 1996; Neto et al., 2004; Chand et al., 2009; Balabin et al., 2011; Shang et al., 2012; Farag et al., 2012;). However, these methods may require the pretreatment of samples and tedious calibrations before data analysis as well as expensive instrument and experienced technicians to analyze data. Since different biodiesel-oil or biodiesel-glycerol mixtures would have varied refractive indexes, a cheaper and simple technique could be employed based on the difference in the refractive index. Measuring biodiesel yield using refractometer has been reported to be convenient, cheap and easy (Xie and Li, 2007). Sufficient information on the evaluation of the application of refractometer for monitoring the extent of oil to biodiesel conversion at any time during the transesterification process is still lacking.

### 1.2 Objectives of this study

The major goal of this research is to investigate the impact of mechanical mixing on producing biodiesel from canola oil and methanol using an alkaline catalyst. This goal is achieved through the following two specific objectives:

(1) To examine the potential of quantifying the biodiesel conversion in real time using a simplified and cheap technique which employs the refractive index of the biodiesel mixture.

(2) To evaluate the impact of mixing parameters such as time, speed, and impeller height on fatty acid methyl ester (FAME) content during the transesterification process in canola oil and methanol using imaging technology.

## 1.3 Scope

The study covers the production of biodiesel with a single feedstock (canola oil) and evaluates the impacts of three mixing parameters: mixing time, mixing speed, and impeller height. The work was done at room temperature and pressure conditions with the assumption that these conditions will not inhibit the rate of the transesterification reaction. Overall, fifty samples including five agitation intensities, two blade locations and five reaction times were tested using two equipment to analyze the efficiency of mixing and yield of biodiesel. It is believed that the result of the experiment will compliment and strengthen the biodiesel industry in Canada.

## 1.4 Thesis outline

This thesis is written in a “manuscript based” style. Chapter 1 presents the background and objectives of the present study. Chapter 2 is a review of literature on the chemical mechanism, major reactants and techniques for biodiesel production and characterization. Chapter 3 addressed the first objective which was to evaluate the performance of refractometer for real time analysis of biodiesel production from canola oil and methanol in comparison to a thermogravimetric approach. Chapter 4 examined the effects of mixing on biodiesel production from canola oil with different agitation intensities, reaction times and agitator locations using refractometer. In Chapter 5, the general summary and conclusion reached from this study is presented. All the references cited in the thesis are listed at the end of the thesis in the bibliography section.

# Chapter 2

# Literature Review

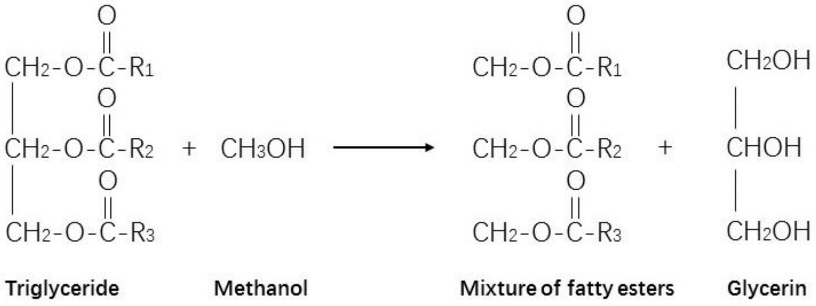
## 2.1 Introduction

With the depletion of fossil fuel resources storage and the exacerbation of environmental pollution, research on alterative clean sources of fuel is increasing. Biodiesel has attracted great attention from researchers and the public as it is a renewable resource that could be produced through the chemical reactions from vegetable oils or animal fat with alcohol (Van, 2005). Since the raw materials for producing biodiesel are natural and renewable, it is considered as biodegradable and nontoxic (Marchetti et al., 2007).

The chemical components for biodiesel are methyl esters with long-chain fatty acids (Leung et al., 2010). The concept of producing biodiesel from transesterification was raised as early as 1940s (Allen et al, 1945; Russell and Colgate-Palmolive, 1945), and continued to be extensively studied by many investigators around the world (Kai et al., 2014; Adewale, 2015; Abbah et al., 2016; Ye et al., 2016; Nomanbhay and Ong, 2017). Researchers have found that the major factors that affect the transesterification process are alcohol to oil molar ratios, the reaction time, pressure and temperature, the type of catalyst, water content as well as the free fatty acids (FFA) levels (Balat, M. and Balat, 2008).

## 2.2 The transesterification process

The main components of biodiesel are the methyl or ethyl esters, which are produced from vegetable oils or animal fats and can be used as alternative of diesel without any modification (Georgogianni et al., 2007). There are four major ways to producing biodiesel: 1) the direct use and blending of raw oils; 2) micro-emulsions; 3) thermal cracking and 4) transesterification (Leung et al., 2010). Among the four techniques, transesterification is the most commonly used chemical reaction for producing biodiesel (Leung et al., 2010), due to its advantages for a wide variety of feedstocks could be produced under mild and eco-friendly reaction condition (Adewale, 2015). This process requires the reaction of the triglycerides and alcohol (methanol or ethanol) to produce esters and glycerin with the presence of a catalyst (Marchetti et al., 2007), which could be explained in the chemical reaction as follows (Van, 2005):



In this reaction, the $R_1$, $R_2$, and $R_3$ are long hydrocarbon chains (fatty acid chains). There are only five chains that are most common in soybean oil and animal fats (others are present in small amounts). The productions of esters are known as biodiesel.

### 2.2.1 Sources of transesterification feedstocks

Vegetable oils are potential alternative fuels for diesel engines which contain 98% triglycerides and lesser amounts of mono- and diglycerides (Motasemi and Ani, 2012). However, they cannot be used directly due to their high fuel viscosity (almost 10-20 times more than diesel) in compression ignition. Direct use of vegetable oils lead to incomplete combustion, high carbon deposits and low volatility due to the presence of large molecules of triglyceride (Demirbaş, 2002; Motasemi and Ani, 2012). Therefore, the production of biodiesel through the transesterification process of the triglycerides with alcohols and catalysts have been extensively studied. In many biodiesel research laboratories, different edible and non-edible oils, animal fats, and other biomass resources have been tested with promising results (Singh and Singh, 2010). A summary of the documented primary feedstocks for the production of biodiesel is presented in Table 2.1.

Canola oil is among the leading feedstock for producing biodiesel because it contains up to 40-45% oil. This is much higher than other vegetable seeds, including soybeans (only 18-20%). Canola seeds produce more oil per unit of crop land area than other crops (Yadava et al., 2012; Yoon et al., 2014). Canola oil biodiesel has been reported as an alternative fuel for a diesel engine without any modifications (Ge et al., 2017). Table 2.2 shows the comparison between pure diesel and canola oil-based biodiesels as reported in the literature.

Table 2.1. Biodiesel feedstock sources

| **Vegetable oils** | **Non-edible oils** | **Animal Fats** | **Other Sources** |
|---|---|---|---|
| Soybeans | Almond | Lard | Bacteria |
| Rapeseed | *Abutilon muticum* | Tallow | Algae |
| Canola | Andiroba | Poultry fat | Fungi |
| Safflower | Babassu | Fish oil | Micro algae |
| Barely | *Brassica carinata* |  | Tarpenes |
| Coconut | *B. napus* |  | Latexes |
| Copra | Camelina |  | Cooking oil (yellow grease) |
| Cotton seed | Cumaru |  | Microalgae (chlorella vulgaris) |
| Groundnut | *Cynara cardunculus* |  |  |
| Oat | *Jatropha Curcus* |  |  |
| Rice | Jatropha nana |  |  |
| Sorghum | Jojoba oil |  |  |
| Wheat | Pongamia glabra |  |  |
| Winter rapeseed oil | Laurel |  |  |
|  | Lesquerella fendleri |  |  |
|  | Mahua |  |  |
|  | Piqui |  |  |
|  | Palm |  |  |
|  | Karang |  |  |
|  | Tobacco seed |  |  |
|  | Rubber plant |  |  |
|  | Rice bran |  |  |
|  | Sesame |  |  |
|  | Salmon oil |  |  |

Table 2.2. Properties of pure diesel, neat biodiesel and biodiesel blends (BD: Canola oil biodiesel blended with diesel fuel)

| **Properties (units)** | **Pure diesel** | **BD 100**[1] | **BD 10**[2] | **BD 20**[3] | **BD 30**[4] | **Test method** |
|---|---|---|---|---|---|---|
| Density (kg/mm$^3$ at 15 °C) | 836.8 | 880 | 842 | 846 | 850 | ASTM D941 |
| Viscosity (mm$^2$/s at 40 °C) | 2.72 | 4.29 | 2.82 | 2.99 | 3.17 | ASTM D445 |
| Calorific value (MJ/kg) | 43.96 | 39.49 | 43.29 | 42.71 | 42.12 | ASTM D4809 |
| Cetane index | 55.8 | 61.5 | - | - | - | ASTM D4737 |
| Flash point (°C) | 55 | 182 | - | - | - | ASTM D93 |
| Pour point (°C) | -21 | -8 | - | - | - | ASTM D97 |
| Oxidation stability (h/110 °C) | 25 | 15 | - | - | - | EN 14112 |
| Ester content (%) | - | 98.9 | - | - | - | EN 14103 |
| Oxygen (%) | 0 | 10.8 | - | - | - | - |

Source: (Yoon et al., 2014).

1: Neat biodiesel; 2: 10% vol. of canola oil biodiesel blend with 90% vol. of pure diesel; 3: 20% vol. of canola oil biodiesel blend with 80% vol. of pure diesel; 4: 30% vol. of canola oil biodiesel blend with 70% vol. of pure diesel

### 2.2.2 Esterification as pretreatment

Although, transesterification has the advantages of being low cost and having a mild reaction condition, some limitations do exist during the reaction process. A major disadvantage is the production of FFAs (Aranda et al., 2008), which leads to the formation of soap, yield loss of biodiesel and more difficulties in separating the products (Kulkarni and Dalai, 2006). Acid-catalyzed transesterification makes it easier to convert high FFA feedstocks, but it requires much longer reaction time and the yield is lower than alkali-catalyzed reaction (Canakci and Van Gerpen, 1999; Kombe et al., 2006).

Acid catalyzed esterification, which directly converts the FFA into esters before alkali transesterification, has been considered as the best route to remove FFA and reduce yield losses (Chai et al., 2014). Therefore, esterification can be applied as a pre-treatment before transesterification to convert the extra FFA into methyl esters and avoid saponification (Aranda et al., 2008).

The esterification reaction can be described by the following chemical reaction:

$$\begin{array}{ccccc} R-COOH & + & R'-OH & \rightarrow & R-COOR'+H_2O \\ (\textit{fatty acid}) & & (\textit{alcohol}) & & (\textit{biodiesel}) \end{array}$$

Observations of faster reaction rate of esterification than transesterification have been reported by Kusdiana and Saka (2001) and Warabi et al. (2004) because the triglyceride transesterification is a three-step reaction while alkyl esterification requires only one step.

### 2.2.3 Catalyst

Although it is possible to obtain biodiesel from oil and methanol without the presence of a catalyst, the conditions for reaction are usually hard to control. For example, to produce biodiesel without any catalyst, the reaction temperatures were reported to be 300 °C–350 °C by Saka and Kusiana (1999), 240 °C by Kreutzer (1984) and 120 °C to 180 °C by Dasari et al. (2003). Though the transesterification process could be started essentially by the mixture of reactants, the presence of catalysts has a significant impact on accelerating the reaction rates (Meher et al., 2006a).

#### *2.2.3.1 Alkali (base) catalyst*

The alkali-catalyzed transesterification is a common way to produce biodiesel (Leung et al., 2009). Freedman et al. (1984) suggested that the transesterification by alkali catalysis was 4000 times faster than by acid catalysis, and others have indicated it is much cheaper than acid-catalyzed transesterification (Aranda et al., 2008)

Quantities of studies have been conducted to optimize the biodiesel production from alkali-catalyzed transesterification using various kinds of oils (Dorado et al. 2004; Meher et al. 2006b; Naik et al. 2008; Georgogianni et al. 2007; Alamu et al. 2008). Meher et al. (2006b) and Naik et al. (2008) conducted the experiment for producing biodiesel using Karanja oil with methanol. The yield of fatty acid methyl esters in the reaction mixture was optimized to 97-98% and 96.6–97% in these two studies, respectively.

Basically, there are two types of alkali catalysts, homogeneous and heterogeneous base catalysts (Ma and Hanna, 1999). Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are the two most widely used homogeneous alkali catalysts due to the lower cost (Leung et al., 2010), and ease of solubilization in methanol. Their rates of reaction are fast (Borges and Díaz, 2012). Dias et al. (2008) investigated the efficiency of three heterogeneous base catalysts in the transesterification process of waste and virgin oils. They concluded that KOH was less effective than the sodium-based catalysts, such as $CH_3ONa$ and NaOH. In contrast, Predojević and Škrbić (2009) compared the biodiesel yields after transesterification of waste oil using KOH and NaOH as catalysts. They reported that the yields from KOH catalyzed reaction (94.86%) were much higher than NaOH (84.28%). They also observed higher yields when the mass: oil ratio was 1.0% compared to when it was 1.5% for both catalysts. However, Colucci et al. (2005) observed no differences of the methyl ester yield (99.7 ± 0.02%) with changing the initial concentration of KOH in methanol for two different catalyst concentrations, while Georgogianni et al. (2007) proposed that the optimum catalyst concentration of NaOH should be 2.0% for the transesterification reaction with methanol using mechanical stirring and ultrasonication.

Apart from the homogeneous catalysts like NaOH, KOH and their alkoxides, researchers have proposed using heterogeneous base catalysts for transesterification because they are noncorrosive, more eco-friendly and easy to be separated from the reactants with higher activity, more selectivity and longer catalyst lifetimes (Liu et al., 2008a). Liu et al. (2008a) conducted the experiment to produce biodiesel from soybean oil and methanol using CaO as a catalyst and obtained up to 95% biodiesel yield. They demonstrated that CaO remained active after being repeatedly used for 20 reaction cycles. Others have reported the application of SrO (Liu et al., 2007), calcined hydrotalcites (Di Serio et al., 2006), calcium methoxide (Liu et al., 2008b), Li–CaO (Watkins et al., 2004) in catalyzing the transesterification to produce biodiesel.

#### *2.2.3.2 Acid catalyst*

Acid catalysts can be classified into homogeneous and heterogeneous ones. Acid catalysts were reported to produce a very high yield of biodiesel if the sample has relatively high free fatty acid (FFA) content. However, the process is usually too slow, taking up to one day to finish (Marchetti et al., 2007). Nevertheless, acid catalysts are insensitive to FFAs when compared with alkaline catalysts (Nomanbhay and Ong, 2017). Homogeneous acid catalysts such as $H_2SO_4$, HF, $H_3PO_4$ and HCl usually show better performance with high FFA feedstocks than heterogeneous catalysts which are solid based. They can simultaneously catalyze esterification and transesterification. However, it should also be noted that these acid liquids are usually hazardous and result in environmental problems (Borges and Díaz, 2012). Nevertheless, the homogeneous catalysts are not favored due to the complexity of product separation (Boey et al., 2013).

Shu et al. (2010) obtained biodiesel from waste vegetable oil and methanol with a carbon-based solid acid catalyst. They showed that the carbon-based solid acid catalyst was recyclable and could simultaneously catalyze both the esterification and transesterification reactions. However, the reaction temperature was 220°C, which required high heating energy. Kiss et al. (2006) compared several different solid acid catalysts for fatty acid esterification under controlled reaction conditions (temperature, pressure and composition). The investigated solid acid catalysts were three types of Zeolite, two Ion-Exchange Organic Resins, and mixed Metal Oxides. They concluded that the sulphated zirconia was the best material with good stabilization and efficiency, while zeolites with small pores were not suitable for biodiesel production because of their diffusion limitation of large fatty acid molecules. They also reported that the Ion-Exchange Resins were good catalysts but required higher temperatures.

### *2.2.3.3 Lipase as catalyst*

Using lipase as a catalyst for transesterification process has several advantages over alkaline and acid catalysts. The steps required are fewer and less waste water is produced during the process (Fan et al. 2012). Lipase catalysis simplifies procedures such as product separation, purification, washing, and neutralization (Nomanbhay and Ong, 2017). In addition, they are applicable to feedstocks with high FFA content. However, they are usually costlier and require long reaction times (Leung et al, 2010).

Studies have been conducted on biodiesel production using lipase as a catalyst.

Liu et al. (2011) used *Burkholderia cenocepacia* for producing biodiesel from soybean oil and methanol mixed at 300 rpm at 40 ºC and got a yield of 98%. Yücel (2011) selected *Thermomyces Lanuginosus* as catalyst and got biodiesel yield of 93% from pomace oil and methanol at a temperature of 25 ºC and agitation intensity of 125 rpm. Park et al. (2008) produced up to 97% biodiesel from waste activated and bleached earth with methanol using Candida *cylindracea* as the catalyst.

#### *2.2.3.4 Use of supercritical alcohol*

None-catalytic processes have been reported in the literatures for transesterification using supercritical alcohol. (Demirbaş, 2002, 2006; Saka et al., 2006). For example, Demirbaş (2002) conducted laboratory production of biodiesel from six different vegetable oils (cottonseed, hazelnut kernel, poppyseed, rapeseed, safflower seed and sunflower seed) using supercritical alcohol without catalyst. These investigators suggested faster reactions and the simpler purification using single homogeneous supercritical alcohols. In addition, the triglycerides transesterification along with the esterification of fatty acids at the same time contribute to higher yields. as the limitation of supercritical alcohols is its high cost due to the high temperatures and pressures requirements (Melero et al. 2009).

### 2.2.4 Alcohol

Methanol, ethanol, butanol, propanol and amyl alcohol, have been used to produce biodiesel by the transesterification process. Methanol and ethanol are among the most commonly used (Leung et al., 2010). The use of methanol is mostly reported in the literature possibly due to its lower cost. Methanol also has the advantage of a fast reaction with triglycerides and is a good solvent for most alkali catalysts (Ma and Hanna, 1999). It should be noted that despite its advantages and adoption in the biodiesel industry, methanol can be easily evaporated as it has low boiling point. Some studies have also indicated that both methanol and the produced methoxide are very hazardous that no one should be exposed to these materials (Leung et al., 2010)

The type of alcohol used was found to have significant impact on total hydrocarbon emission and particulate matter composition, when the diesel emission from trans-esterified waste cooking using methanol and ethanol was compared (Lapuerta et al., 2008). The authors reported that the use of more volatile alcohol resulted in higher hydrocarbon emissions and volatile organic fraction of the particulate matter. Colucci et al. (2005) also showed experimental evidence that the type of alcohol would affect the reaction process because of the difference in the dissociation of the alcohols. They have found that more acidic alcohols reacted faster than secondary and tertiary alcohols.

### 2.2.5 Reaction temperature

Elevating reaction temperature promoted biodiesel yield and reduced the reaction time by decreasing the viscosities of the oils (Leung et al., 2010). However, investigators have pointed out that the yield of biodiesel would decrease when temperature goes beyond the optimal value, due to the enhanced saponification of triglycerides (Leung and Guo, 2006; Evera et al, 2009) and evaporation of methanol (Abbah et al., 2016). Thus, the temperature must be controlled below the boiling temperature of the alcohols to avoid the losses through vaporization (Leung et al., 2010). The most commonly reported optimal reaction temperature range for the transesterification process is 50 to 60°C, depending on the selected oil and type of alcohol (Abbah et al., 2016; Leung and Guo, 2006; Freedman et al., 1984; Radha and Manikandan, 2011).

### 2.2.6 The molar ratio of alcohol to vegetable oil

The molar ratio of alcohol to vegetable oil is also a significant factor that impacts the transesterification process (Chew and Bhatia, 2008). Increased molar ratio of alcohol to vegetable oil promotes the yield and purity of the biodiesel (Balat and Balat, 2008; Chew and Bhatia, 2008). Balat and Balat (2008) overviewed the studies conducted by various investigators and summarized that the universally accepted alcohols to glycerides molar ratios were 6:1–30:1.

The most extensively used molar ratio of methanol to vegetable oils is 6:1 (Stamenković et al., 2007). Freedman et al. (1984) studied the effect of molar ratio of alcohol to vegetable oil on the biodiesel production using soybean, sunflower, peanut and cottonseed oils. The experimental results indicated that the maximum conversion to ester (93-98%) was obtained at the ratio of 6:1, while higher radios did not promote the yields and lower radios resulted in reduced yields for soybean, sunflower, peanut and cottonseed oils. Silva et al. (2011) also suggested that molar ratio of 6:1 was most appropriate for methanol but 9:1 was more suitable for ethanol.

Other studies have been conducted to investigate the impact of ethanol-oil ratio on alkali-catalyzed biodiesel yield. Alamu et al. (2008) found that maximum biodiesel yield (96%) was obtained at the ethanol–palm kernel oil ratio of 0.2 under transesterification conditions of 60 °C temperature, 120 min reaction time and 1.0% KOH catalyst concentration. The yields under other ratios (0.1, 0.125, 0.15, 0.175, 0.225) varied from 29.5% to 93.5%.

## 2.3 Biodiesel production parameters

### 2.3.1 Mechanical mixing (Agitation)

The mixing process of methanol and catalyst enables the production of methoxide which reacts with the oils (Leung et al. 2010). Since the phases of oil and methanol are immiscible, the purpose of intense mixing of oil and methanol is to break the alcohol phase into small drops and subsequently increase the interfacial area for reaction (Frascari, et al., 2008). The agitation is necessary for the reaction since the catalysts in solid form need to be dissolved into the methanol (ICTC, 2006), and the methoxides are added into the oil after the catalysts have completely dissolved (Leung et al. 2010).

The agitation intensity, which also refers to the agitation speed, is another major factor that affects the reaction rate during biodiesel production. Poor mass transfer within the two phases in the initial stage would result in a low reaction rate (Noureddini and Zhu, 1997), since the mixing reaction is heterogeneous with two immiscible phases. The agitation speed controls the mass transfer of triglycerides from oil phase to the methanol-oil interface during the initial stage of the reaction (Stamenković et al., 2007; Lakshmi et al., 2011).

The agitation speed was reported by Ma et al. (1999) to have a significant effect on the transesterification reaction when alkali catalyst was added to beef tallow and methanol. However, once the reaction has started and the two phases are mixed, the agitation speed and time no longer affected the reaction rate and yield. Stamenković et al. (2007) studied the agitation intensity at 90, 120, 150 and 200 rpm used to produce biodiesel from sunflower oil and methanol. They observed that the drop size distributions were narrower and size became smaller with increasing agitation intensity. This was an indication that the higher the intensity of the agitation, to the larger the interfacial area and hence, the higher the reaction rate. Similarly, Alcantara et al. (2010) also showed experimental evidence that the higher agitation rate was necessary to reach faster transesterification. They found that the higher agitation speed of 600 rpm resulted in more complete and faster oil conversion (within 2 hours) than 300 rpm (only 12% in 8 hours) for the transesterification of soybean oil. Lakshmi et al. (2011) investigated the effects of agitation speed on the process for biodiesel production and indicated that the minimum speeds for producing the biodiesel from rice bran and Karanja oils were 700-750 rpm and 550-650 rpm, respectively.

### 2.3.2 Ultrasonic Mixing

Ultrasonic mixing has gained popularity for producing biodiesel due to its commercial advantages which include, faster reaction and smaller equipment than regular mechanical mixing procedure. Ultrasonic mixing enables the formation of small emulsion droplets and increases the contact area between the oil, alcohol and catalyst (Colucci et al., 2005). Ramachandran et al. (2013) reviewed ultrasonic-assisted transesterification with different catalysts and concluded that it is less costly and requires less reaction time, temperature, alcohol to oil ratio, as well as the amount of catalyst.

Ultrasonic mixing was reported to produce high yield (up to 99%) with less catalyst (up to half the amount) as well as less methanol than conventional mixing because of the enhanced chemical activities when cavitation is present (Ramachandran et al., 2013). Colucci et al. (2005) also highlighted that ultrasonic mixing was effective in the production of biodiesel, and reduced the reaction and separation time to less than 30 s and 60 min, respectively. Stavarache et al. (2003) hypothesized that the high yield (up to 98%) and much shorter reaction time for the transesterification of vegetable oils is possible with low ultrasonic mixing (28-48 kHz).

### 2.3.3 Microwave assisted heating

Microwave provides a safe, clean, and easier way for transesterification with mild temperature and atmospheric pressure. It also reduces the time for separation of the less important by-products (Hsiao, et al, 2010). Some studies have shown promising results with microwave-assisted transesterification from different oils, such as, coconut oil (Suryanto et al. 2015), waste frying oil (Azcan and Yilmaz, 2013; Patil et al., 2012), Chinese tallow tree (Barekati-Goudarzi et al, 2015), soybean oil (Encinar et al., 2011; Li et al. 2013), microalgae oil (Wahidin et al., 2014), canola oil (Jin et al., 2013) and palm oil (Wahidin et al., 2015; Indarti, 2016; Ye et al., 2016). The biodiesel yields from microwave transesterification varied from 86% to 98% with the reaction temperature around 60 °C. Whatever oil is used, methanol is the most commonly used alcohol for microwave assissted biodiesel production since it has a good capability of absorbing microwaves and has a high polarity (Nomanbhay and Ong, 2017).

Duz et al. (2011) demonstrated that using microwave energy for biodiesel production reduced the reaction time from 2 hours to 6 minutes and produced 4% more yield than conventional mixing. El Sherbiny et al. (2010) applied the microwave technique to produce biodiesel from Jatropha oil using methanol as alcohol and KOH as catalyst. They found that the transesterification process using microwave technique reduced the reaction time from 150 min to 2 min. In addition, Patil et al (2012) reported that the heating energy could be saved by 90% with microwave heating than with conventional heating to produce biodiesel. However, it should be noted that the reaction time should be well controlled to prevent yield loss due to overreaction.

### 2.3.4 Static Mixer

Static mixers were found to be applicable for biodiesel production (Thompson and He, 2007). They effectively mix two immiscible liquids when flowing through the mixers, which were designed with static geometric components in tubular pipes (Qiu et al., 2010). They have been applied in the mixing process in acid-catalyzed esterification reaction to reduce the FFA content. Static mixers advantages over conventional agitation, include lower costs, shorter reaction time, and smaller equipment (Albright, 2008).

A few studies have investigated the transesterification process for biodiesel reaction using static mixers (Frascari, et al., 2008; Thompson and He, 2007; Alamsyah et al., 2010; Sungwornpatansakul et al., 2013). These studies indicated the static mixers were effective in the stirring of the reactants. For example, Alamsyah et al. (2010)

showed experimental evidence that the static mixer significantly reduced the reaction time than mechanical mixing within the temperature range of 50 to 70 ºC. Sungwornpatansakul et al (2013) also indicated a higher reaction rate of the transesterification reaction by static mixers due to larger interfacial area between the reactants.

## 2.4 Techniques for biodiesel characterization

A number of biodiesel characterization methods have been developed to analyze the contents of fatty acid esters, mono-, di-, and tri-glycerides and determine biodiesel yield from the transesterification process.

### 2.4.1 Chromatographic Methods

Gas chromatography (GC) and high-performance liquid chromatography (HPLC) are two widely accepted techniques for biodiesel characterization. Pinto et al (2005) summarized 134 publications on biodiesel production from 2000 to 2004 and found GC (57%) and HPLC (25%) were two of the most frequently used method for biodiesel characterization.

Freedman et al. (1986) gave the first description on using GC technique to quantify the esters, including mono- di and tri-acylycerols. It has been regarded as one of the most accurate methods to analyze glycerol and glycerides contamination in biodiesel (Restek, 2018). HPLC was proposed as a method to monitor biodiesel production in transesterification by Trathnigg and Mittelbach (1990). Their experiment determined the triglycerides and methyl esters of different fatty acids and the di- and monoglyceride of palmitic acid. The authors demonstrated that HPLC is a reliable and simple method for biodiesel characterization.

HPLC is a technique that provides good accuracy with lower temperature during analysis, but the cost of equipment is higher than the GC. Nevertheless, it takes a longer time for sample preparation and experiment operation by HPLC than GC. Others have also reported the combination of GC with liquid chromatography (LC) to reduce the complexity of GC and obtain more reasonable peak assignments (Lechner et al., 2002).

### 2.4.2 Spectroscopy methods

The two most frequently used spectroscopy methods are: near-infrared spectroscopy (NIRS) and proton nuclear magnetic resonance ($^1$H NMR) spectroscopy. NIR spectroscopy was first adapted to monitor the transesterification reaction in late 1990s (Knothe, 1999). The author demonstrated that although NIRS is less sensitive for the quantification of minor component, it has better feasibility and works faster than the GC method. $^1$H NMR spectroscopy was first described by Gelbard et al. (1995), and it is widely accepted as the standard characterization method (Neto et al., 2004; Reddy et al., 2006; Chand et al., 2009).

### 2.4.5 Thermogravimetric analysis (TGA)

TGA is a quick and inexpensive technique to characterize the thermal stability of materials and assess the conversion of biodiesel yield when compared with the mentioned techniques without pretreatment (Andrade et al., 2012). It measures the changes in physicochemical properties of different materials as weight changes under increasing temperature and can be applied to determine the boiling point of esters and thereby monitor the transesterification process (Siraj et al., 2017).

### 2.4.6 Comparison of different methods

Chand et al. (2009) quantified the biodiesel production from alkali-catalyzed transesterification of soybean oil using TGA method by comparing the estimated biodiesel percentages with the values from $^1$H NMR spectroscopy. They demonstrated that TGA method had comparable performance with $^1$H NMR spectroscopy in determining the biodiesel yield with good agreement (within 1.5%) and TGA was a simpler, faster, and more economical technique to monitor biodiesel production. Farag et al. (2012) examined the biodiesel conversion under different reaction temperature, time and alcohol to oil ratio, catalyst concentration and variety using TGA and GC method. The results of biodiesel conversion measured from two analytical methods were found to be similar and fit each other linearly with the $R^2$ of 0.998.

Table 2.3 gives a general comparison between these methods by presenting their advantages and disadvantages.

Table 2.3. Comparison of TGA with other methods known for the quantitation of biodiesel

| **Quantification method** | **Advantages** | **Disadvantages** |
|---|---|---|
| TGA | No reagent or solvent required | Does not differentiate among different fatty acid methyl esters in biodiesel |
| 1H NMR | Differentiates easily between biodiesel and plant oil Relatively inexpensive<br>Simple, accurate and precise in determining the biodiesel content | Deuterated solvents required ($CDCl_3$ in the present case) |
| GC | Can differentiate among glycerides, methyl esters and glycerol | Instrumentation relatively more expensive<br>Standard solutions are required |
| NIR | Can differentiate among soybean oil, biodiesel and glycerol<br>No solvent required | Cumbersome to calculate direct conversion<br>Cannot quantify low levels of contaminants |
| HPLC | Differentiates among mono-, di- and triglycerides, methyl esters and glycerol | External solvents and standards are required to determine particular components of the mixture<br>Cumbersome to calculate direct conversion |

Source: (Chand et al., 2009)

## 2.4 Conclusions

Regarded as the clean and renewable source of fuel, biodiesel which could be obtained from vegetables oils and animal fats through the transesterification reaction by the mixing of alcohols and catalysts can serve as alternative energy source. Among all the techniques and methods for the production biodiesel, the alkali-catalyzed transesterification of vegetable oils is the most traditional and commonly accepted one. Although microwave assisted and ultrasonic mixing are promising tools to accelerate the reaction, the cost of the microwave equipment in industrial production are still higher than traditional chemical reaction, and the reaction temperature is hard to control during the ultrasonic mixing. There are many factors that have crucial impacts on the production of biodiesel during the transesterification process, such as the catalyst, alcohol, reaction time and temperature, and molar ratio of alcohol to oil. Very few studies have been conducted to investigate the effect of mixing locations on the reactions from mechanical mixing using vegetable oils and alcohols using alkaline catalysts.

In producing biodiesel from transesterification process, it is crucial to determine the biodiesel quality from the reactions. Lots of quantification methods have been developed, while many of them have some drawbacks. For example, they may require the pre-treatment of samples, which is time consuming. Again, tedious calibrations are usually needed before data analysis. In addition, very expensive instrument has to be purchased and skilled and experienced technicians are needed to collect and analyze the data (Xie and Li, 2007). Few studies have emphasized the real-time monitoring of biodiesel production. This study aimed to evaluate the efficiency of refractometer as a potential tool to monitor biodiesel yield with lower cost and lesser time. Subsequently, the impact of mixing intensity and duration as well as the location of the agitator for the transesterification of canola oil and methanol was investigated using the refractometer.

# Chapter 3

# Comparative evaluation of thermogravimetric and refractive index techniques in determining biodiesel yield

## Abstract

Biodiesel is a clean and renewable resource that consists of mono-alkyl esters of long chain fatty acid, which could be obtained from the transesterification reaction of vegetable oils and animal fats with alcohols and catalysts. Biodiesel yield has typically been determined using expensive and laborious techniques. The attempt of this study was to examine the potential of quantifying the biodiesel conversion in real time using refractive index in transesterification process of canola oil with methanol and KOH. Biodiesel yield at five different mixing intensities and reaction times were measured using a refractometer. The measured results were then compared with analytical data obtained from thermogravimetric analysis (TGA) technique over a temperature range of 25-600 °C. Experimental results indicated that the FAME conversions at different mixing intensity and reaction time measured from refractometer correlated well to the relative weight losses from TGA method with $R^2=0.93$, however, the refractometer may over-estimate the biodiesel yield when the reaction rate was too low. Overall, the refractometer technique is cheaper and easier to manage and could provide a reliable prediction of biodiesel yield in real time.

**Key words:** FAME; thermogravimetric analysis; refractive index; mixing; real-time monitor

### 3.1 Introduction

Fossil fuels, including oil, coal, natural gas, are still the leading energy for human activities. However, these resources, which were formed over hundreds of millions of years, are non-renewable and will run out in the near future (Conceicao et al, 2011). Nevertheless, the burning of traditional fossil fuels results in high emissions of air pollutants, such as $CO_x$, $SO_x$, $NO_x$ and ambient PM2.5, leading to the greenhouse gas effects and affecting human health. Therefore, it is urgent to find clean and renewable resources. Biodiesel is one of these alternatives, which could be obtained from vegetable oils and animal fats by the reaction with alcohols with the presence of catalysts through transesterification process in mild condition.

A number of biodiesel characterization methods have been proposed and investigated by many researchers, including thermogravimetric analysis (TGA), gas chromatography (GC), near-infrared Spectroscopy (NIRS), and high-performance liquid chromatography (HPLC) and Proton nuclear magnetic resonance ($^1$H NMR) spectroscopy (Freedman et al., 1984; Mittelbach, 1996; Neto et al., 2004; Chand et al., 2009; Balabin et al., 2011; Shang et al., 2012; Farag et al., 2012;). Among all these methods, $^1$H NMR spectroscopy is widely accepted as the standard characterization method (Neto et al., 2004; Reddy et al., 2006; Chand et al., 2009). However, these methods have some drawbacks. For example, they may require a pretreatment for samples, which is time consuming; meanwhile, tedious calibrations are usually needed before data analysis; nevertheless, very expensive instrument has to be equipped and experienced technicians are needed to collect and analyze data (Xie and Li, 2007).

TGA is a less expensive technique to characterize the thermal stability of materials and assess the conversion of biodiesel yield when compared with the mentioned techniques without requirement of pretreatment (Andrade et al., 2012). It measures the changes of physicochemical properties in different materials as weight changes under increasing temperature (Siraj et al., 2017). Chand et al. (2009) quantified the biodiesel production from alkali-catalyzed transesterification of soybean oil using TGA method by comparing the estimated biodiesel percentages with the values from $^1$H NMR spectroscopy. They have demonstrated that TGA method had comparable performance with $^1$H NMR spectroscopy in determining the biodiesel yield with good agreement (within 1.5%) and TGA was a simpler, faster, and more economical technique to monitor biodiesel production. Farag et al. (2012) examined the biodiesel conversion under different reaction temperature, time and alcohol to oil ratio, catalyst concentration and variety using TGA and GC method. The results of biodiesel conversion measured from two analytical methods were found to be similar and fit each other linearly with a $R^2$ of 0.998.

Although TGA does not require pretreatment of samples, it cannot provide real time monitoring of biodiesel conversion because it requires heating of samples, which may take a few hours. Comparatively, the characterization of biodiesel using refractometer is much cheaper than TGA and has a higher time resolution. The method of using refractive index for biodiesel synthesis monitoring was first examined by Xie and Li (2006). They found that the yields of methyl ester from soybean oil with ethanol estimated by refractive index were within 4% error when compared with the results from $^1$H NMR. Other investigators have also reported using refractometers for biodiesel characterization from soybean oil (Furuta et al., 2006; Tubino et al., 2014), canola oil (Dubé et al., 2007), microalgae (Du et al., 2011), linseed oil (Ullah et al., 2013), *Pongamia pinnata* (Meher et al., 2006b), rapeseed oil (Qiu et al., 2011) and etc. However, these studies did not sufficiently evaluate the application of refractometer as a method for monitoring the extent of oil to biodiesel conversion at any time during the transesterification process.

Therefore, the objective of the present work is to test the agreement of TGA and refractometer for determining FAME content from the transesterification process in canola oil and methanol with KOH, and thereby to evaluate the performance of refractometer for analyzing real time biodiesel production in research and industrial settings.

## 3.2 Methods and materials

### 3.2.1 Materials

Canola oil (Selection, Canada) was obtained from the Montreal local market. HPLC grades of methanol (99.8%) was purchased from Fisher Scientific. Potassium hydroxide (86.4%) was purchased from Fisher Scientific as the chemical catalyst. Biodiesel standard for the calibration was purchased from LGC Standards (U.S.A.)

### 3.2.2 Experimental setup

The biodiesel production set up consisted of a 1-L glass reactor, an overhead agitator was equipped with a digital display unit and a two flat-blade paddle agitator. The impeller diameter and the blade width were 60 mm and 20 mm, respectively. The speed range of the agitator varied from 80 rpm to 1000 rpm. A Thermo Scientific Sorvall Legend XT centrifugation was used for separating the materials in each sample.

The methanol: oil volume corresponding to a molar ratio of 6 was estimated at 1:3.96. All the experiments were conducted at room temperature (25±1.5 °C) and atmospheric pressure. The impeller speeds were 200, 250, 275, 300 and 325 rpm to cover the whole range of mixing from immiscible phase to uniform dispersion. The blade was set at 1/2 H (47.5mm from the bottom). The total height (H) of the emulsion was 95 mm.

### 3.2.3 Experimental procedures

The biodiesel was produced with canola oil and methanol with KOH as the catalyst. 2.74 g of potassium hydroxide was dissolved in a 100 ml of methanol in a conical flask. The mixture was continuously stirred until all the KOH were dissolved into the methanol. Afterwards, 595 ml of canola oil was poured into the reacting vessel, followed by 50 ml of pure methanol. After the two solutions were separate and stable, the remaining 100 ml of the methanol was added gently with KOH. The agitator is then started at the preset speed to attain a specific rpm.

To investigate the processes of transesterification reaction, a 5 ml sample was withdrawn from the mixing reactor by a 2-ml pipette during the agitating process at different times. To ensure a sample was taken randomly, each sample set was drawn from bottom, middle and top of a stirred vessel for a proper representation of the entire sample. The reaction was stopped at the set time with the immediate addition of few drops of pH 6.2 phosphate buffer and allowed to stay for 5min. The sample was then centrifugated at 3500 rpm for 5 min after which it was separated into upper phase (biodiesel and residual canola oil) and lower phase (methanol, glycerine and buffer). The lower phase was decanted and the upper phase was kept in the refrigerator for further analysis.

### 3.2.4 Analytical methods

Thermogravimetric analysis (TGA) of the unwashed biodiesel was conducted by 10 μL samples of biodiesel/ oil mixture heated at a constant heating rate of 10°C/min in the nitrogen atmosphere in a titanium pan (Fig. 3.1). The temperature ranged from 25°C to 600°C. Based on previous TGA study, the heating rate of 10°C/min has been reported to be a reliable heating rate and it minimizes experimental error compared with other heating rates (Chand et al. 2009).

Refractometer analysis was considered as a simplified alternative method to several analytical methods including the thermogravimetric analysis used in the study (Frascari, D. et al., 2008). A handheld grand index refractometer model (RND025/ATC) with refractive index range of 1.435-1.520 and 0.001 graduation was used in determining the biodiesel yield. A calibration curve was developed with pure biodiesel and canola oil mixtures at different ratios. All measurements were taken in triplicates.

Fig. 3.1. Thermogravimetric analyzer (TGA)

### 3.2.5 Statistics for the comparison between methods

The performance of the refractometer in determining the biodiesel yield was estimated using the calibration curve. The computed biodiesel yields from refractive indexes were compared with the TGA results using two statistical indices, including the percent bias (PBIAS) and coefficient of determination ($R^2$). Percent bias (PBIAS) determines the difference of mean values between refractometer and TGA measured values (Eq. 3.1). Coefficient of determination（$R^2$）is defined as the proportion of variation of y data that was explainable by variation in x data (Eq. 3.2).

$$PBIAS = \frac{(x_i - y_i)}{x_i} \times 100\% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3.1$$

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(y_i - x_i)^2}{\sum_{i=1}^{n}(x_i - x_a)^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3.2$$

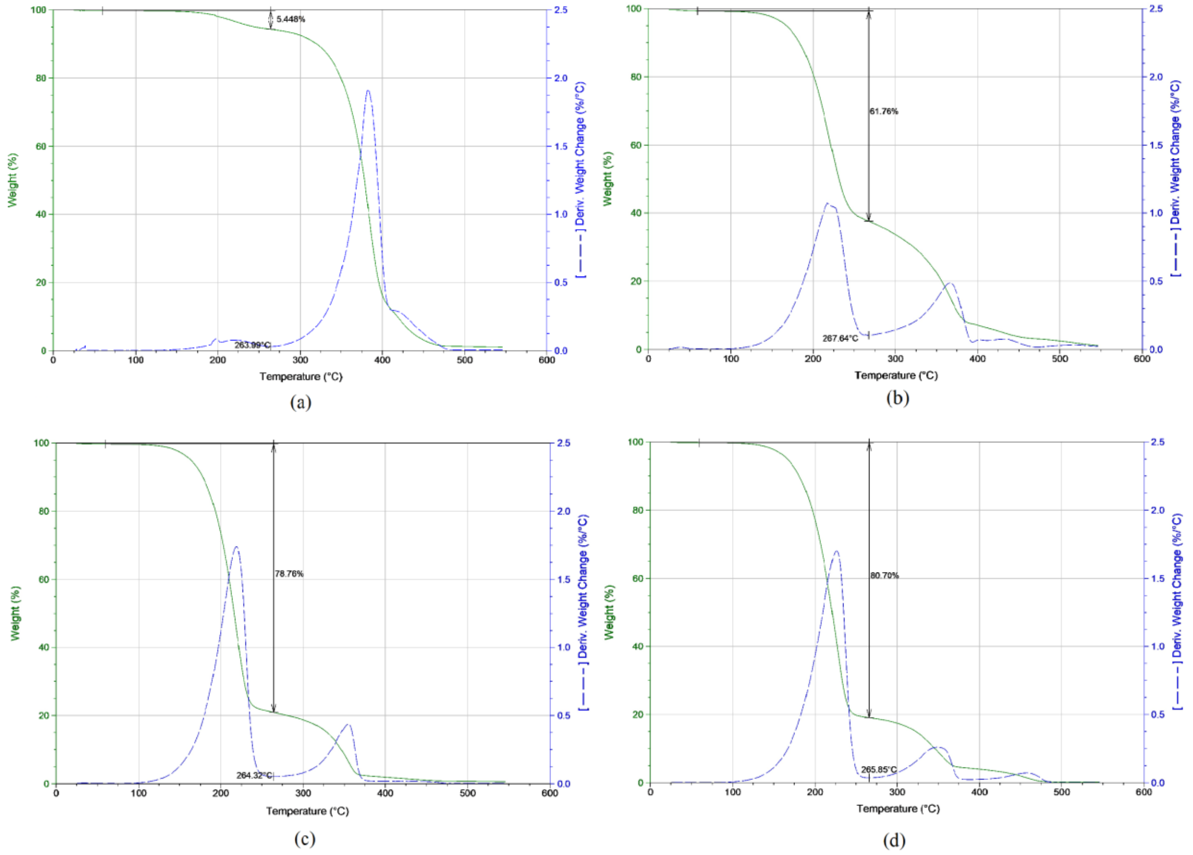
Where $x_i$ is the biodiesel yield from TGA, $y_i$ is the computed yields by refractive index, n is the total number of measurements, $x_a$ is the average value of TGA measured yields.

## 3.3 Results and discussion

### 3.3.1 Analytical evaluation using Thermogravimetric (TGA)

#### *3.3.1.1 Impact of agitation speed on biodiesel yield*

Typical TGA thermographs for biodiesel production over the mixing time are shown in Fig 3.2. The impacts of the mixing speed are also shown in Fig 3.3. The results showed a general exponential rise in biodiesel production as the mixing progresses. As anticipated, the biodiesel yield at the beginning of the process were minimal for all rpm selected. This low initial yield can be attributed to the very low reaction rate at the start of the process due to the mass transfer limitations between methanol and oil phase (Hou et al., 2007). As mixing continued the transesterification between the canola oil and methanol began and biodiesel yield increased. This was because the mixing process enabled the dissolution of alcohol and oil, thereby increasing reaction rates (Hosseini et al, 2012). Lesser yield was observed at lower agitation intensity and shorter reaction time, which was supported by Hosseini et al (2012), who demonstrated that increasing agitation speed led to an increasing contact between oil and alcohol molecules and faster mass transfer, which is a key step in the transesterification process.



(a) (b)

(c) (d)

Fig 3.2. Typical TGA thermographs for biodiesel production over the mixing time (a) 1 min (b) 5 min (c) 10 min (d) 20 min

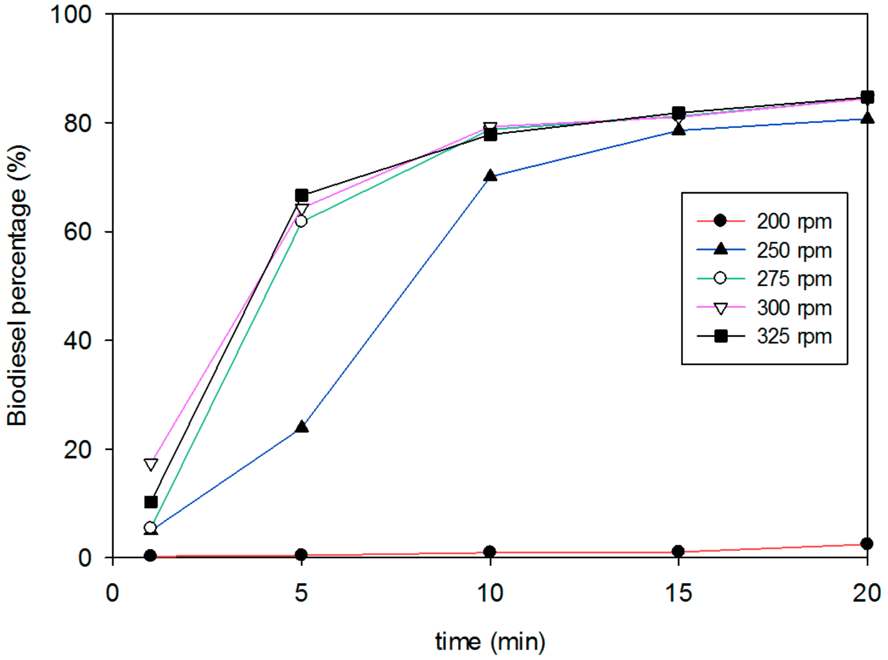


Fig 3.3. Biodiesel yields measured by TGA under different agitation intensities

After 5 min's agitation, weight losses as indicated by TGA shows only 0.47% biodiesel was produced at 200 rpm, while up to 66.63% biodiesel was obtained when mixing intensity reached to 325 rpm for the same time duration. Experimental evidence showed that with an increase of mixing intensity, biodiesel yield increased accordingly after 5 min's agitation. As mixing continued for 10 min marginal increase in biodiesel yield was observed for lower rpm. For instance, 0.98% yield was observed when agitation speed was at 200 rpm, but significantly higher yield of 70.06% and 78.75% were obtained at 250 and 275 rpm, respectively. A comparison of the mean biodiesel yield using Tukey-Kramer HSD shows that there is no significant difference ($p > 0.05$) in yield beyond 275 rpm. This is evident in the less than 1.5% variation in the biodiesel yield at 300 and 325 rpm. Similar minimum variation was observed at higher mixing time.

### 3.3.2 Analytical evaluation using refractive index

#### *3.3.2.1 Calibration of refractometer*

The refractometer was calibrated using the standard pure biodiesel (B100) and canola oil from 0 to 100% with an interval of 20%. The linear relationship between the biodiesel conversion percentage and refractive index is shown in Fig 3.4. The linear regression equation for determining the biodiesel yield used in the experiment is shown in Eq. 3.3. The estimated coefficient of determination shows that 97.99% of the variation in the refractive indexes could be explained by the variation in biodiesel yield thus indicating the statistical reliability of the linear model.

$y = -0.0211x + 1.4725 \qquad R^2 = 0.9799$ ……………………………………………... 3.3

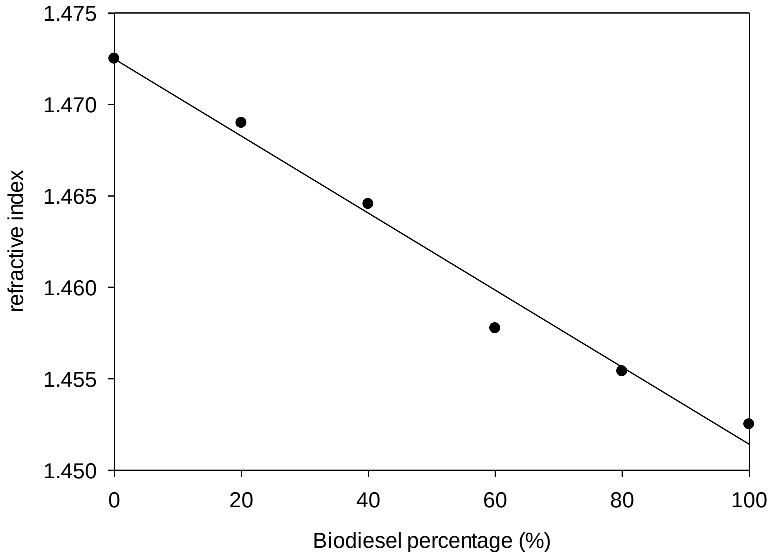


Fig 3.4. Refractive index calibration using standard biodiesel

*3.3.2.2 Biodiesel yield estimation and analysis*

The computed biodiesel yields from measured refractive indexes at five agitation intensities as a function of agitation time is shown in Fig 3.5. The result shows that both mixing time and mixer impeller speed increases biodiesel yield. Although, relatively low amount of biodiesel was observed at lower mixing speed, the recorded yield was up to 5 times higher than that value by the thermogravimetric approach. Up to 88% biodiesel yield could be achieved when the rpm higher than 250. Like the thermogravimetric analysis, a comparison of the mean biodiesel yield using Tukey-Kramer HSD shows that there is no significant difference ($p > 0.05$) in yield beyond 275 rpm with less than 5% variation at all mixing times.

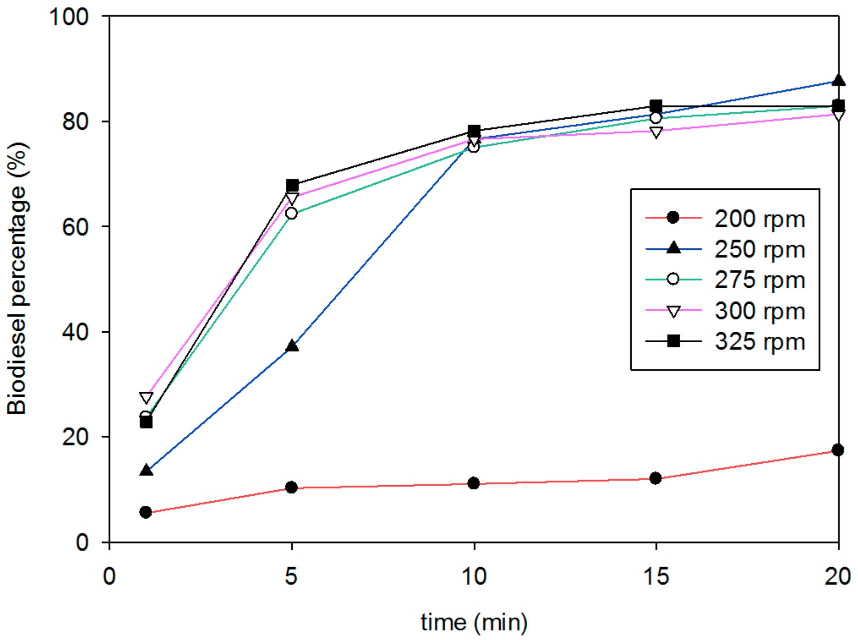


Fig 3.5. Biodiesel yields computed from measured refractive indexes under different agitation intensities and reaction times

### 3.3.4 Comparative evaluation of the two analytical methods

#### *3.3.4.1 Resources*

Thermogravimetric techniques for biodiesel yield assessment has been a validated method for assessment reported by several authors (Chand et al., 2009). It is comparatively simple, requiring no sample preparation compared to the mainstream analytical methods- Spectroscopy techniques. However, the cost of a thermal analyzer is more than $50,000. For laboratories and many developing countries thermal analyzer may not exist. However, a simple refractometer costs less than $100 and could be an alternative for the much complex and expensive analytical equipment.

The average processing time for analysis using the TGA approach was 50 ±5 min including preparing the equipment. The refractometer, in addition to requiring no sample preparation requires less than a minute to determine the refractive index from which the yield is determined. The refractometer has the potential of providing a real time determination of the biodiesel yield.

#### *3.3.4.2 Biodiesel yield*

Table 3.1 represents the statistical comparison between thermogravimetric analysis (TGA) and refractometer (RM) techniques. There was a generally good agreement between the yield determined by TGA and refractometer techniques. Overall, the variation in the mean yield for all agitation intensities and times were within 9%. The relationships between the conversions as determined TGA and refractive indexes of the products at each agitation speed were investigated. The biodiesel yields computed from measured refractive indexes were plotted as a function of the TGA yields as seen in Fig. 3.6 and refractometer measured biodiesel yields were found to be very close to TGA measured values. The linear fit between the two data series results in an average $R^2$ value of 0.93 for all agitation intensities and reaction times, which support this finding.

Although both methods reported the lowest yields at an agitation intensity of 200 rpm, TGA measured yields were only 0.3~2.5% (1.1% on average), while values from refractive indexes were 5.5~17.3% (11.2% on average). It should be noted that the PBIAS of biodiesel yields between two methods were extremely high (-953%) and $R^2$ was -185 (Table 3.1), indicating weak match and significant difference of the two measurements at 200 rpm when reaction time was within 20 min.

Table 3.1 Statistical comparison of thermogravimetric analysis (TGA) and refractometer (RM) techniques

| RPM | Mean % biodiesel | | PBIAS | $R^2$ |
|---|---|---|---|---|
| | TGA | RM | | |
| 200 | 1.1 | 11.2 | -953% | -185 |
| 250 | 51.3 | 58.7 | -14% | 0.95 |
| 275 | 62.3 | 64.9 | -4% | 0.92 |
| 300 | 65.3 | 65.9 | -1% | 0.96 |
| 325 | 64.2 | 67.0 | -4% | 0.96 |

When agitation intensity was increased to 250 rpm, average biodiesel yields measured by TGA and refractometer increased to 51.3% and 58.7%, respectively. The difference between the two measurements were within 15% and $R^2$ was 0.95. Lower PBIAS were found when agitation speed continued to increase to 275~325 rpm, with percent difference between 1~4% and $R^2$ from 0.92~0.96.

In general, the biodiesel yields computed from measured refractive indexes were comparable to TGA measure values, and both methods provided a similar trend of increasing yields with elevating agitation intensities. As illustrated in Fig. 3.6 and Table 3.1, there was a linear correlation between the biodiesel conversion measured from TGA and refractometer. Such linear correlation of the two methods demonstrated the reliability of refractometer compared to TGA. Nevertheless, each sample takes at least one hour to be analyzed from TGA, while the refractometer gives results within a few seconds. Therefore, despite the high sensitivity of TGA technique, it is hard to monitor the reactions in real time, while refractometer could provide reliable and comparable results with low cost and less time.

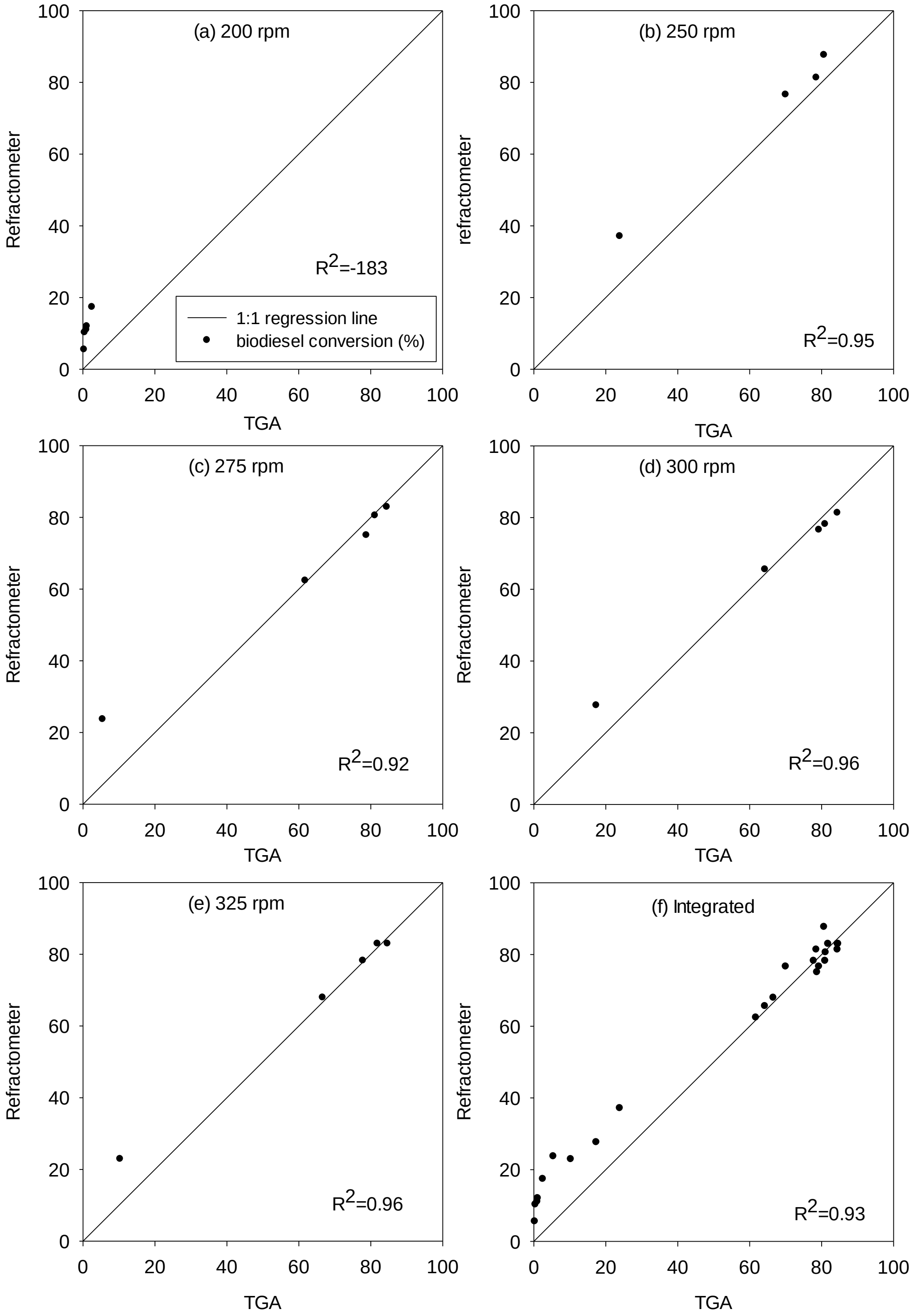


Fig 3.6. Comparison between TGA and refractometer measured biodiesel conversion (%) from transesterification in canola oil and methanol under agitations of (a) 200 rpm, (b) 250 rpm, (c) 275 rpm, (d) 300 rpm, (e) 325 rpm and (f) all treatments.

### 3.3.4.3 Modeling the biodiesel yield

The biodiesel yield data was fitted to an exponential rise model shown in Equation 3.4 to predict the biodiesel yield as a function of the mixing time.

$$Y = a(1 - e^{-bt}) \quad \text{.........................................................} \quad 3.4$$

Where Y represents the biodiesel yield and a represents a mixing constant reflecting agitator resistance and b represents the rate of biodiesel yield.

The result shows that the model was a good fit for predicting biodiesel yield using mixing time. The model parameters shown in Table 3.2 indicates a general rise in the rate of biodiesel production as the agitation speed increased in both evaluation methods. This increase in the rates may be attributed to the mass transfer limitations between methanol and oil phase. As expected, a general decline in the agitation resistance ‘b’ was observed as speed increased. It is important to note that there was a wide variation in the two methods at lower speed, thus it supports the earlier assertion that the refractometer over predicts at lower speed. The changes in model parameter ‘a’ and ‘b’ were not significantly different ($p<0.05$) at higher speeds (rpm > 275). Overall, the rate of biodiesel yield was relatively higher with the refractometer technique compared to the TGA. The rate of biodiesel yield ranged from 0.000068~0.2528 and 0.0254~0.3850 per minute for thermogravimetric and refractometer techniques, respectively. Some investigators had also observed the higher rates and decreased agitation resistance which have been described as shorter delay in FAME appearance with increasing agitation speed (Noureddini and Zhu, 1997; von Blottnitz et al., 2004; Vicente et al., 2005; Stamenković et al., 2007).

Table 3.2 Biodiesel prediction rate constants

| | TGA | | | RM | | |
|---|---|---|---|---|---|---|
| RPM | a | b | $R^2$ | a | b | $R^2$ |
| 200 | 1539 | 6.82E-05 | 0.85 | 14.23 | 0.0254 | 0.67 |
| 250 | 107.10 | 0.0807 | 0.94 | 98.67 | 0.1194 | 0.97 |
| 275 | 86.59 | 0.2152 | 0.96 | 81.24 | 0.3014 | 0.99 |
| 300 | 84.17 | 0.2728 | 0.99 | 79.08 | 0.3850 | 0.99 |
| 325 | 85.20 | 0.2528 | 0.97 | 82.79 | 0.3319 | 0.99 |

## 3.4 Summary and conclusion

This paper examined the potential of using a refractometer to measure the biodiesel yield in real time from the transesterification reaction in canola oil and methanol with the presence of KOH as the catalyst. The computed biodiesel yields under five different agitation intensities and five reaction times were compared with the measured values by TGA. Our results indicated that the values measured from two methods were comparable within 9% difference on average for all agitation intensities and reaction times. The linear fit between the two data series results in an average $R^2$ value of 0.93. The linear regression between TGA biodiesel yields and refractometer measured yields suggests that the refractometer can accurately quantifies the amount of biodiesel present.

In conclusion, compared with TGA method, using the refractometer for monitoring the transesterification of vegetable oils with methanol has comparable accuracy and it is faster, more convenient and cheaper than TGA method with portable devices, which make it a more appropriate method for real-time process monitor purposes.

# Connecting text to Chapter 4

Chapter 3 investigated the potential of using refractive indexes for biodiesel characterization and made a comparison of biodiesel measurements between TGA and refractometer techniques. The results indicated that refractometer provided reasonable estimation and has comparable performance in determining biodiesel conversion with TGA. Therefore, Chapter 4 aims to study the impact of mixing intensity, time and agitator location on biodiesel production from transesterification process using refractometer.

# Chapter 4

# Impact of mixing intensity and time on biodiesel production using canola oil

## Abstract

Biodiesel is an alternative source of fossil fuels, which is recyclable, non-toxic and eco-friendly. It is the result of the transesterification reaction between lipids (vegetable oils and animal fats) and alcohols in the presence of catalysts. The most widely accepted method of obtaining biodiesel is the mechanical mixing technique, due to its low cost of reactants and equipment. This paper investigated the impact of agitation speed and reaction time on canola oil methanolysis at two different agitator locations in both non-reacting and reacting systems. The drop sizes and distributions in non-reacting system were recorded by image capture techniques. The images were analyzed using MATLAB and Photoshop. The conversion rates of the fatty acid methyl esters (FAME) during different treatments were measured by means of a refractometer. The results indicated that the stirring location at 3/4H was more effective in FAME conversion than 1/2H. Moreover, increasing mixing intensity would result in higher distribution of small drop sizes in non-reacting system and faster transesterification reaction in reacting system. The results further showed that when the agitator was located at 3/4H and the speed range was 250 – 325 rpm, the reactions were completed (80% biodiesel conversion) within 5-10 min, while it took 15 min to complete the reaction at agitation speed of 200 rpm. When agitator was located at 1/2H, longer reaction time (15-20 min) was required to obtain equivalent biodiesel yield at agitation speed over 250 rpm, and no reaction was found at 200 rpm.

**Key words:** alkali-catalyzed; canola oil; methanolysis; transesterification; agitation; refractometer

### 4.1 Introduction

The global demand for the energy required for economic development has continued to increase due to rising population. The high consumption of fossil fuel to meet this demand has resulted in an energy crisis along with global warming. These negative outcomes are of great concern to the public (Ajala et al., 2017; Peiter et al., 2018). It is becoming increasingly urgent to find new resources to meet the ever-rising demand for energy. Biodiesel has great potential as the alternative to the traditional diesel. It is renewable, non-toxic and biodegradable. In addition, using biodiesel as alternative fuel could help reduce the air pollution (Ge et al., 2017). Biodiesel is a mixture of alkyl esters with long-chain fatty acids. It is obtained from the reaction of lipids (vegetable oils or animal fats) with alcohols and catalysts by the transesterification or esterification processes (Marchetti et al., 2007; Leung et al., 2010).

However, since the phases of oil and alcohol are immiscible, it is crucial to manually mix them and increase the contact of these reactants. Mechanical agitation is the most widely used technique to break up the reactants into droplets, thereby increasing the interfacial area and accelerating the chemical reaction. In addition, mixing is also necessary to dissolve the solid catalysts into the alcohol (ICTC, 2006). Mechanical mixing has the advantages of low cost and high feasibility (Frascari, et al., 2008).

The transesterification reaction takes place in a heterogenous mixture of two immiscible phases. Agitation is used to enhance the mass transfer of triglycerides from the oil phase to the methanol-oil interface during the initial stage of the reaction (Stamenković et al., 2007; Lakshmi et al., 2011; Lakshmi et al. 2011). The agitation intensity, which refers to the agitation speed, is the major factor that affects the reaction rate of biodiesel production. Insufficient agitation will lead to poor mass transfer within the two phases at the initial stage and would result in low reaction rate (Noureddini and Zhu, 1997).

Several studies have been initiated to investigate the impact of mixing intensity on biodiesel production from different feedstocks, such as sunflower oil (Stamenković et al., 2007), beef tallow (Ma et al., 1999), soybean oil (Alcantara et al., 2010), rice bran and Karanja oils (Lakshmi et al. 2011). The influence of agitation speeds and times on different feedstocks vary. Agitation speed was reported by Ma et al. (1999) to have significant effects on the transesterification when alkali catalyst was added to beef tallow and methanol. However, once the reaction has started and if two phases remain mixed, the agitation speed and time no longer affected the reaction rate and yield. Stamenković et al. (2007) studied the agitation intensity at 90, 120, 150 and 200 rpm to produce biodiesel from sunflower oil and methanol. They observed that the drop size distributions were narrower and sizes became smaller with increasing agitation intensity, which indicated that the higher intensity led to larger interfacial area and correspondingly higher reaction rate. Similarly, Alcantara et al. (2010) demonstrated that higher agitation rate resulted in faster transesterification. They found that higher agitation speed of 600 rpm resulted in more complete and faster oil conversion (≤ 2 hours) than 300 rpm which gave only 12% yield in 8 hours after the transesterification of soybean oil. Lakshmi et al. (2011) investigated the effects of agitation speed on the process for biodiesel production and reported that the minimum speeds for producing biodiesel from rice bran and Karanja oils were 700-750 rpm and 550-650 rpm.

Among all these mentioned vegetable oils, canola oil is the leading feedstock for producing biodiesel. Canola seed contains up to 40-45% oil. This is similar to the oil content of sunflower seed, but much higher than soybeans (18-20%). In addition, canola seeds produce more oil per unit of crop land area than many oil crops (Yadava et al., 2012; Yoon et al., 2014). Experiments on canola oil based biodiesel and its blends with diesel, their performances and emissions in diesel engines, have been studied by some research groups (Ozsezen et al., 2009; Sayin et al., 2012; Roy et al., 2013). Carbon monoxide (CO) emission was reported to be reduced by up to 73% using canola biodiesel than pure diesel (Ozsezen et al., 2009). Canola oil biodiesel has been reported as an alternative fuel in diesel engine without any modifications (Ge et al., 2017). About 70% of the world's canola oil export trade comes from Canada. The interest in the maximum utilization of canola oil as a feedstock for biodiesel production has continued to increase. Some studies have investigated the effects of different agitator locations on biodiesel production. The impact of mixing intensity and duration on biodiesel production from canola oil has not been fully investigated. Therefore, the objective of this study was to find the optimal mixing intensity and duration for producing biodiesel from canola oil and thereby to provide references for the industrial production of biodiesel in Canada.

## 4.2 Materials and Methods

### 4.2.1 Materials

Food grade Canola oil (Selection, Canada) was obtained from a local supermarket in Montreal. The Chemical Catalyst Potassium hydroxide (86.4% KOH) was purchased from Fisher Scientific company. HPLC grades of methanol of 99.8% was purchased from Fisher Scientific (Fair Lawn, NJ, USA). Fast green FCF which was used as the stain in the non-reacting system was purchased from J.T. BAKER Chemical Co (Center Valley, PA, USA). Saturated biodiesel for calibration curves of refractometer was purchased from VHG Labs (Manchester, NH, USA). To quench the transesterification reaction, the phosphate buffer PH 6.2-6.5 was purchased from LabChem Company (Zelienople, PA, USA).

### 4.2.2 Experimental setup

The reactor used was 1 L glass vessel (108 mm (inner diameter) x 200 mm (height)). The overhead agitator was a two flat-blade paddle agitator with a digital display screen. The impeller diameter and the blade width are 60 mm and 20 mm, respectively. The speed range of the agitator was varied from 80 rpm to 1000 rpm. A Sorvall Legend XT centrifuge (Thermo Fisher Scientific, Waltham, MA, USA) was used for separating the biodiesel and canola oil mixture in each sample at 3500 rpm for 5 min after the treatments.

The molar ratio of methanol to canola oil was 6:1 and the volume ratio of methanol to oil was 1:3.96 as suggested by Freedman et al. (1984), Frascari et al. (2008) and Stamenković et al. (2007). All the experiments were operated at room temperature (23.5 °C) and atmospheric pressure (1 atm). The stirring speeds tested were 200, 250, 275, 300 and 325 rpm to cover the entire range of mixing from immiscible phase to uniform dispersion. The total height (H) of the emulsion in the reactor vessel was 95 mm. The paddle agitator was set at 3/4H and ½ H for the different sets of the experiment, the distance of the 3/4H and 1/2H locations from the bottom of the reactor were 71.25 mm and 47.5 mm, respectively.

### 4.2.3 Experimental design

The statistical analyses were performed using JMP statistical version 12 (Statistical Analysis System, Cary, NC, USA). The optimum conditions for maximizing the biodiesel yield were evaluated. The main parameters investigated were: agitation speed (rpm), agitator location (height) and agitation time.

### 4.2.4 Non-reacting system description

#### *4.2.4.1 Property measurement*

The density and the viscosity were measured using an electronic scale and a rotational viscometer at room temperature.

#### *4.2.4.2 System description*

A small amount of dye (Fast green FCF) was dissolved completely in 150 mL methanol. This turned the colorless methanol into dark green. About 595 mL of canola oil was poured into the reactor vessel and the dyed methanol was added. The agitator blade was accurately located at the chosen height (3/4H or 1/2H). The agitator was powered on and the blades rotated at the set predetermined revolution speed. To determine the drop size and drop size distribution corresponding to the different agitation speeds, pictures were taken every minute until emulsions are well mixed.

#### *4.2.4.3 Image capture and drop size measurements*

In the non-reacting system, pictures were taken to capture the drop size and distribution, and thereby study the effects of rotating speed, agitator height and rotating time on the mixing process. During each agitation speed, pictures were taken every minute until the emulsions are well mixed. The imaging system included a DSLR Camera NIKON D-610, an AF-S NIKKOR 50 MM F 1.4G lens, a 300 W light source and a tripod. The pictures were taken five times with light from five directions (right, left, up, front, back) for each sample. The camera was fixed on the tripod and located in front of the agitator at 35 cm’s distance from the reactor. The lens was focused on the middle of the vessel. Pictures were taken by the cable release to reduce the effect of manual operation, subsequently were processed by image software photoshop and MATLAB to analyze and determine the drop size and drop size distribution.

### 4.2.5 Reacting system description

The alkali catalyst was first prepared by dissolving 2.74 g potassium hydroxide (KOH) in100 mL methanol in a conical flask. The flask was shaken until all the KOH were dissolved in the methanol. Then 595 mL of canola oil was poured into the vessel, and 50 mL pure methanol was added. After the two solutions were stable and separated, the methanolic KOH (100 mL) was added slowly. Then the agitator was operated to rotate at different predesigned speeds and heights.

### 4.2.6 Sample withdrawal and treatment

In the reacting system, to investigate the completion of the transesterification reaction, 5 mL samples were drawn at 1 min, 5 min, 10 min, 15 min and 20 min, respectively from the mixing reactor using a pipette during the agitation is processing. The sampling was randomly done three times, from the bottom, middle and top of the stirred vessel. The drawn samples were poured into 15 mL Falcon centrifuge tubes and appropriately labelled. In each tube, the reaction was quenched by immediately adding a few drops of pH 6.2 phosphate buffer and store in the refrigerator at 4°C for 5 min. The tubes containing the samples were then centrifuged at 3500 rpm for 5 min. Following centrifugation, the samples separated into an upper phase (biodiesel and residual canola oil) and a lower phase (methanol, glycerine and residual buffer). The upper phase was carefully recovered using disposable glass micro-pipettes into sample vials for the analyses that followed. The lower phase was appropriately discarded.

### 4.2.7 Analytical methods and biodiesel yield detection

The method described by Frascari et al., (2008) was used to characterize the mass fraction of the biodiesel in the upper phase. A handheld grand index refractometer model (RND025/ATC) with refractive index range of 1.435-1.520 and 0.001 graduation was used by measuring the refractive index of the canola oil and the biodiesel mixture. Measurements were taken in triplicates and the average values reported. A calibration curve was prepared using the refractive indexes of different weight ratio mixtures of standard biodiesel and canola oil. The linear relationship between the biodiesel standard curve and its regression equation was the basis of the calculating the biodiesel yield in the samples. The calibration curve showing the regression equation and coefficient of determination $R^2$ is shown in Fig. 4.1 and Eq. 4.1

$y = -0.0211x + 1.4725 \quad R^2 = 0.9799$ ………………………………………... 4.1

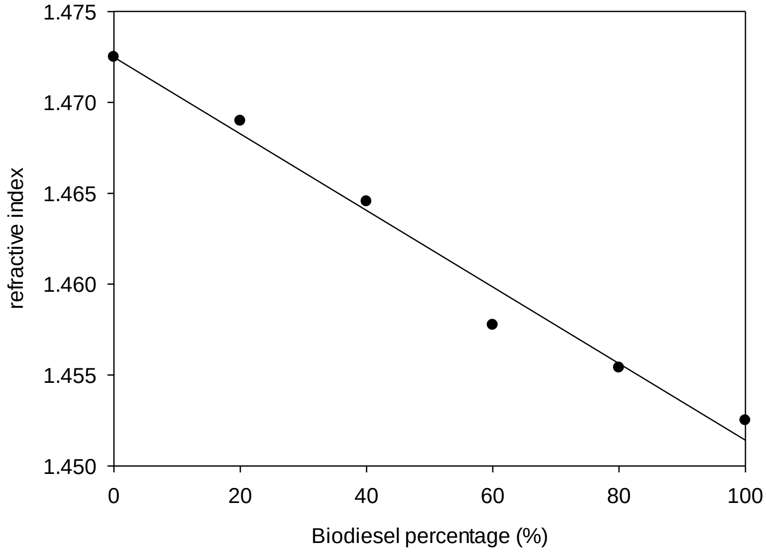


Fig. 4.1. Refractive index calibration using standard biodiesel

4.2.8 Statistical Analysis

All the figures were created using Sigmaplot 12.5 (IBM Corparation, Chicago, IL, USA). Data are expressed as the means ± standard deviation (SD). Statistical analyses were performed using SPSS 21.0 (IBM Corparation, Chicago, IL, USA). Significant differences were based on either one-way, or two-way analysis of variance (ANOVA), followed by means separation using Duncan's means test. $\alpha = 0.05$ were considered as statistically significant differences.

## 4.3 Results and discussion

### 4.3.1 Non-reacting system

#### *4.3.1.1 Flow regime*

The mixing intensity is expressed by the impeller Reynolds number $R_{ei}$, which could be defined in Eq. 4.2 as

$$R_{ei} = \frac{\rho N D_i^2}{\mu} \quad \text{……………………………………………………………….4.2}$$

Where N is the agitation speed, $\rho$ and $\mu$ are the density and viscosity of the emulsion, and $D_i$ is the diameter of the impeller.

The result of the measured viscosity and density as well as the $R_{ei}$ of the aqueous mixture of canola oil and methanol at the agitation speed of 200-400 rpm is shown in Table 4.1. The range of the computed Reynolds numbers was 24464 to 38576. These $R_{ei}$ values indicated that the flow of agitated methanol into canola oil was turbulent within the selected speed ranges.

Table 4.1. The viscosity, density and Reynolds number of aqueous canola oil-methanol mix at different agitation speeds

| Speed(rpm) | viscosity μ (Pa·s) | density ρ (kg $m^{-3}$) | Reynolds number |
|---|---|---|---|
| 200 | 0.02632 | 894.3 | 24464 |
| 300 | 0.03116 | 897.54 | 31108 |
| 400 | 0.03353 | 898.24 | 38576 |

#### *4.3.1.2 Drop sizes and drop size distributions*

The photographs of the emulsions in the reaction vessel during the process of methanolysis at the different agitation speeds for the 1/2H and 3/4H are shown in Fig. 4.2 and 4.3, respectively. The results indicate that as the speed of the agitation increased, breakage of more drops was observed and the drop sizes became smaller. The largest bubble sizes were observed at the lowest agitation speed of 200 rpm for both height as shown in Fig. 4.2a and 4.3a. Although, the 3/4H showed relatively bigger bubble sizes. Another important observation was the minimum variation in color of the mixture at lower speed. Thus, the color of the mixture was the same as the original color of the oil. At the speed of 250 rpm, more visible large drops were found and the color of the aqueous medium became darker (Figure 4.2b). With the increasing agitation speeds, the rate of methanolysis became higher, and significantly higher numbers of small drops were observed. The intensity of the color of the media slowly changed to green, however, after the oil and methanol are completely mixed, the color in the interface changed from dark green to light green because of the dilution of the canola oil. (Figure 4.2 d, e). Similar trend of increasing small drops with higher agitation speeds was observed when agitator was located at 3/4H (Figure 4.3). However, smaller sized drops distribution was found at 3/4H than at 1/2H for the same agitation intensity.

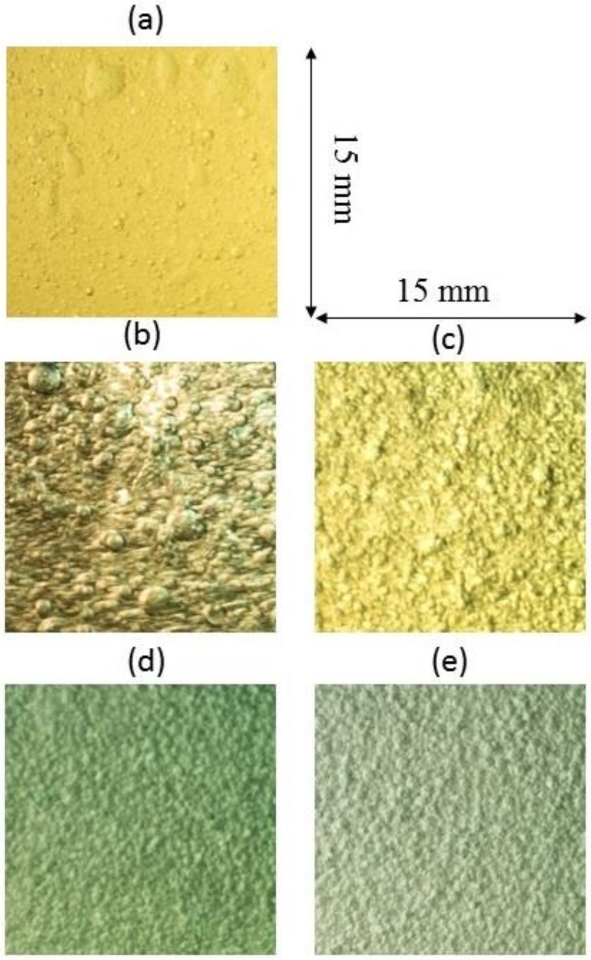


Fig 4.2. Photographs showing drop sizes and distributions in the emulsions at 1/2H location during the methanolysis process: (a) 200 rpm, (b) 250 rpm, (c) 275 rpm, (d) 300 rpm and (e) 325 rpm.

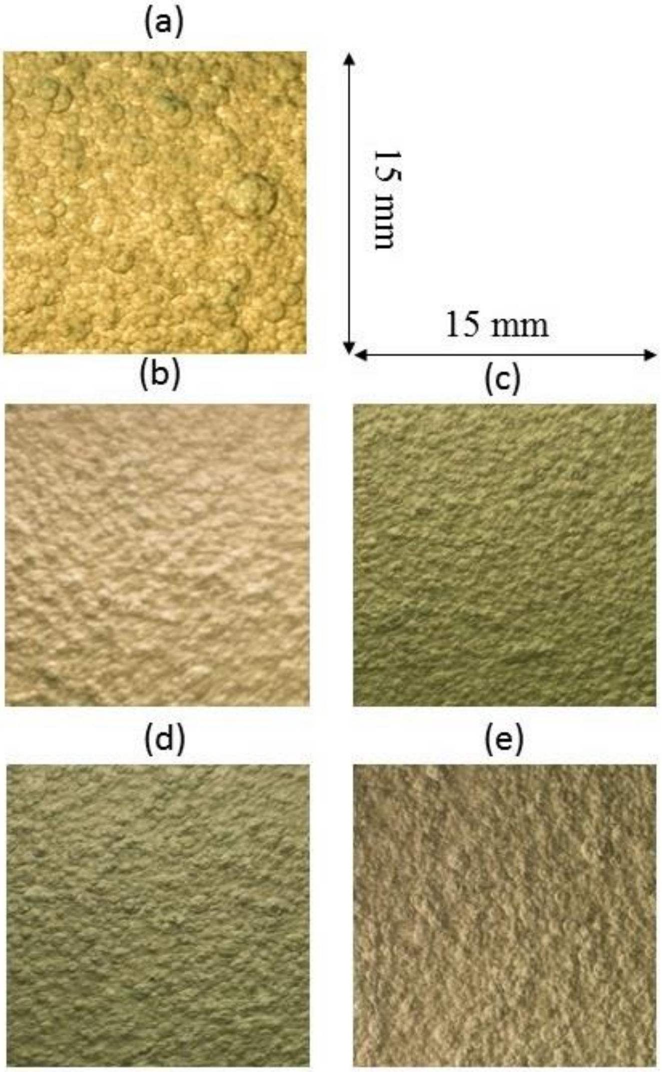


Fig. 4.3. Photographs showing drop sizes and distributions in the emulsions at 3/4H location during the methanolysis process: (a) 200 rpm, (b) 250 rpm, (c) 275 rpm, (d) 300 rpm and (e) 325 rpm

The plots of drop size distributions at five different agitation intensities and the two impeller locations are presented in Fig. 4.4. Higher agitation speeds led to more drop breakages and thereby resulted in greater distribution of smaller drops. It was found that least proportion (less than 25%) of small drops (diameter < 0.2 mm) were distributed at the agitation speed of 200 rpm. The frequency of the low diameter (< 0.2 mm) drops increased with the elevation of agitation speeds. The frequency peak value (about 33%) was recorded at the agitation speed of 325 rpm. Fig 4.4 also show that at the five agitation speeds, there were more small drops at the agitator location 3/4H than 1/2H. At least about 12% increase in the 0.2 drop sizes was found for the 3/4H height compared to the 1/2H. This variation can be attributed to the closer distance of the agitator to the interfaces between the reactants at the 3/4H location than the 1/2H location. Smaller drop sizes depict better mixing hence the potential for higher biodiesel yield. The results therefore suggest that the 3/4H could lead to increase yield.

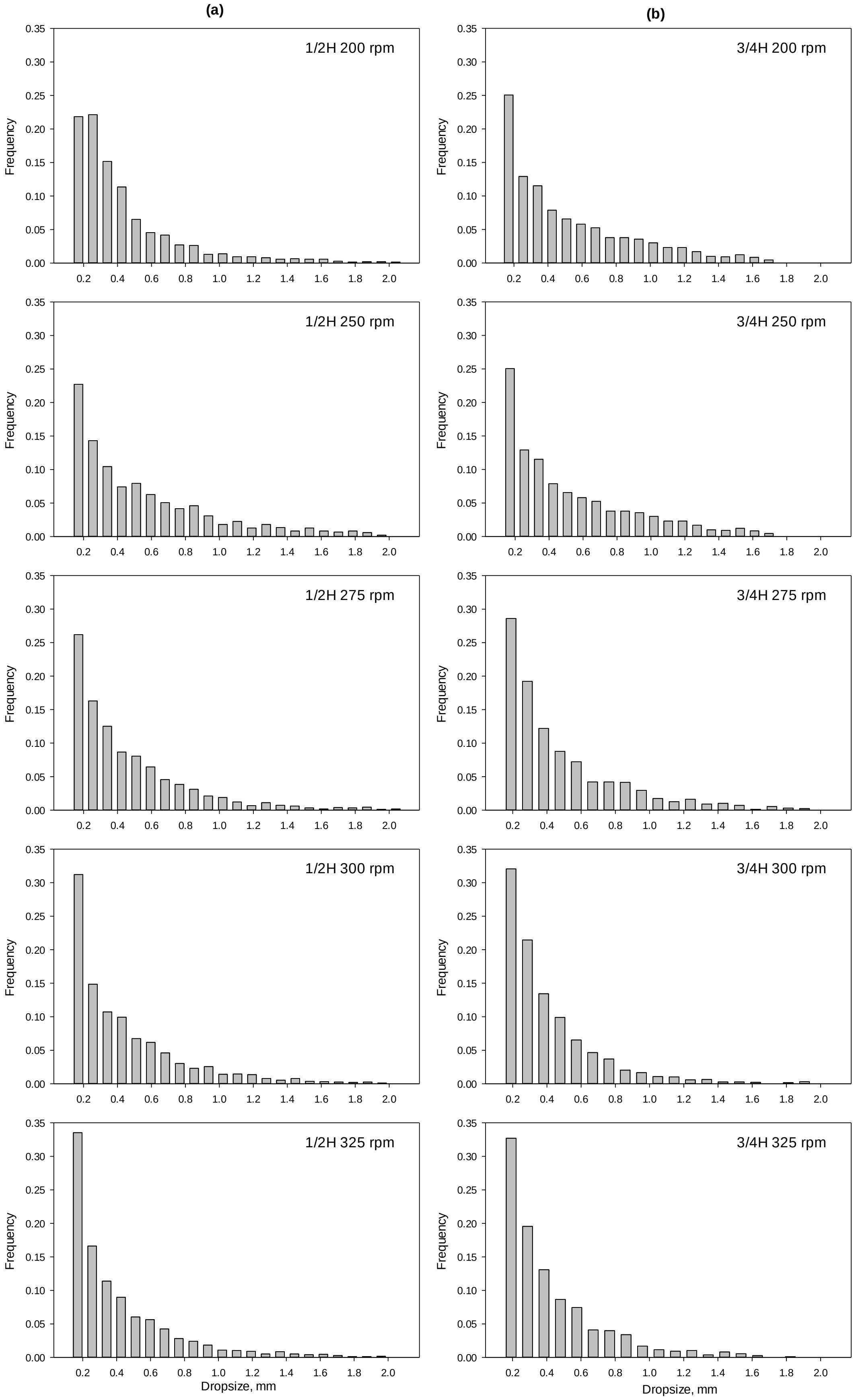


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Fig. 4.4. Drop sizes and distributions under five different agitation intensities at location (a) 1/2H and (b) 3/4H

### 4.3.2 Reacting system

#### *4.3.2.1 Effect of agitation speed on biodiesel yield*

The plots showing the impact of agitation intensity on refractive index and biodiesel yield at different reaction times for 1/2H and 3/4H locations are presented in Fig. 4.5 and 4.6, respectively. At the beginning of the reactions (1 min) for 1/2H location, significantly lower ($P < 0.05$) refractive indexes were obtained when agitation speed reached to 275 rpm. On the other hand, the highest refractive index value was obtained at the agitation speed of 200 rpm (Fig. 4.5A). This indicated very low reaction rate and biodiesel yield at agitation speeds of 200 and 250 rpm. However, at Location 3/4H, there were no significant differences ($P > 0.05$) of the refractive index values obtained at the five agitation intensities (Fig. 4.6A). Both Fig. 4.5A and 4.6A indicated very low biodiesel yield (less than 30%) for all the speeds at 1 min due to incomplete reaction.

When the reaction time increased to 5 min at the 1/2H location, a decreasing trend of refractive index was observed with increasing stirring speed and significant differences ($P < 0.05$) were found between all the speeds (Fig. 4.5B)., This was an indication of elevated biodiesel conversion or yield at higher agitation speeds. However, when the reaction time was 10, 15, and 20 min at 1/2H, significantly higher refractive index was only found at the agitation speed of 200 rpm than the other four speeds (Fig. 4.5 C, D and E). This implied that no significant difference occurred in the biodiesel yield when the agitation speed was higher than 250 rpm. This led to the conclusion that when the reaction time is higher than 10 min, the critical agitation speed should be 250 rpm when the stirring blade is at location 1/2H.

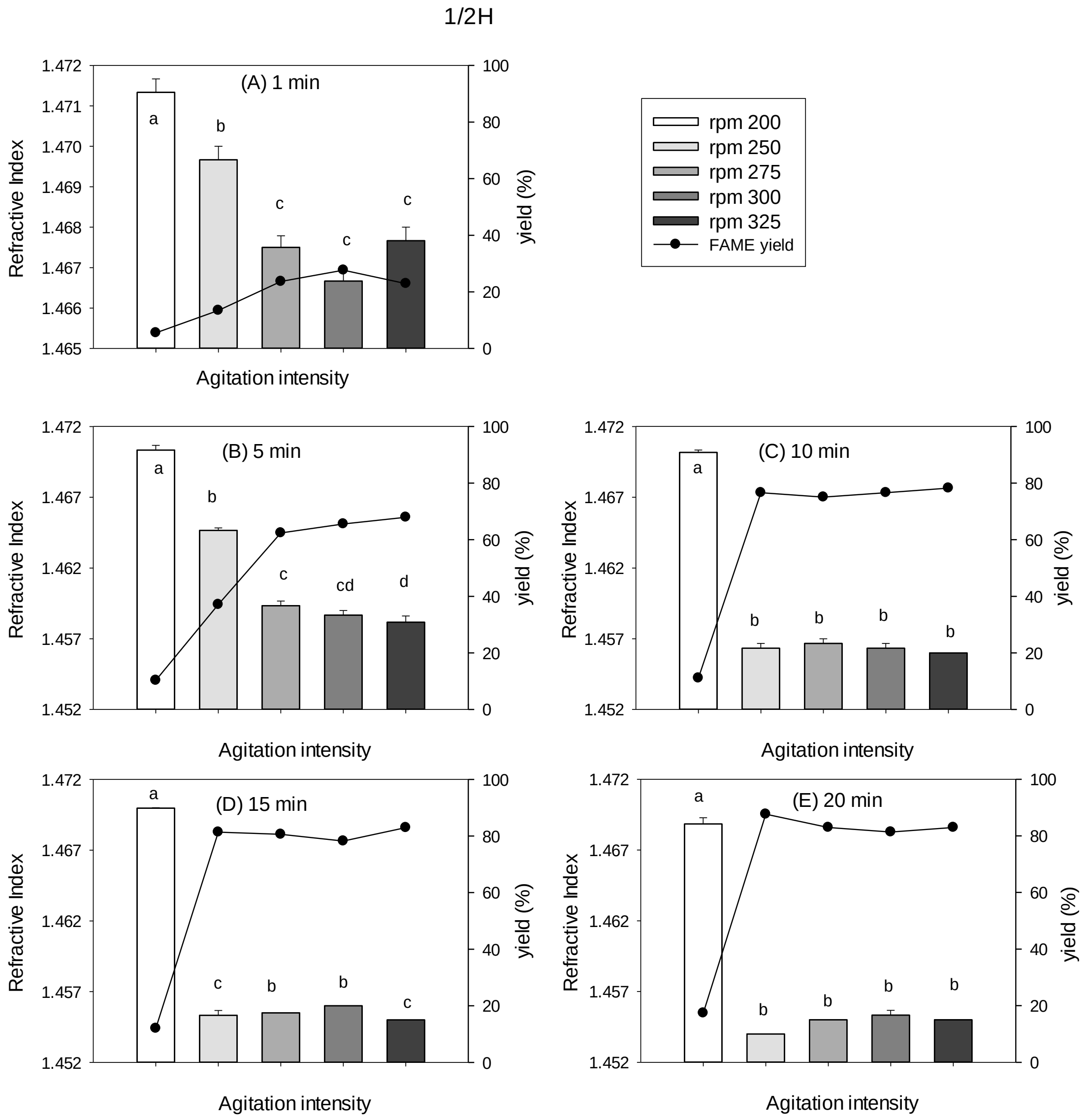


Fig. 4.5. Impact of agitation intensity on refractive index and biodiesel yield at 1/2H with different reaction times (1min, 5min, 10 min, 15 min and 20 min)

Comparable results were also found in stirring location 3/4H for both 5 min and 10 min reaction time (Fig. 4.6 B, C). However, when the reaction time was raised to 15 min, no significant differences in the refractive indexes were observed at the five agitation speeds. The biodiesel yields at all the speeds were close to 80% (Fig. 4.6D, E). This demonstrated high biodiesel conversion and complete reaction at all agitation intensities in these two samples. The results also indicated that when reaction time was higher than 15 min, the stirring speed of 200 rpm would be needed to obtain equivalent yield comparable to other agitation speeds at the 3/4H stirring location.

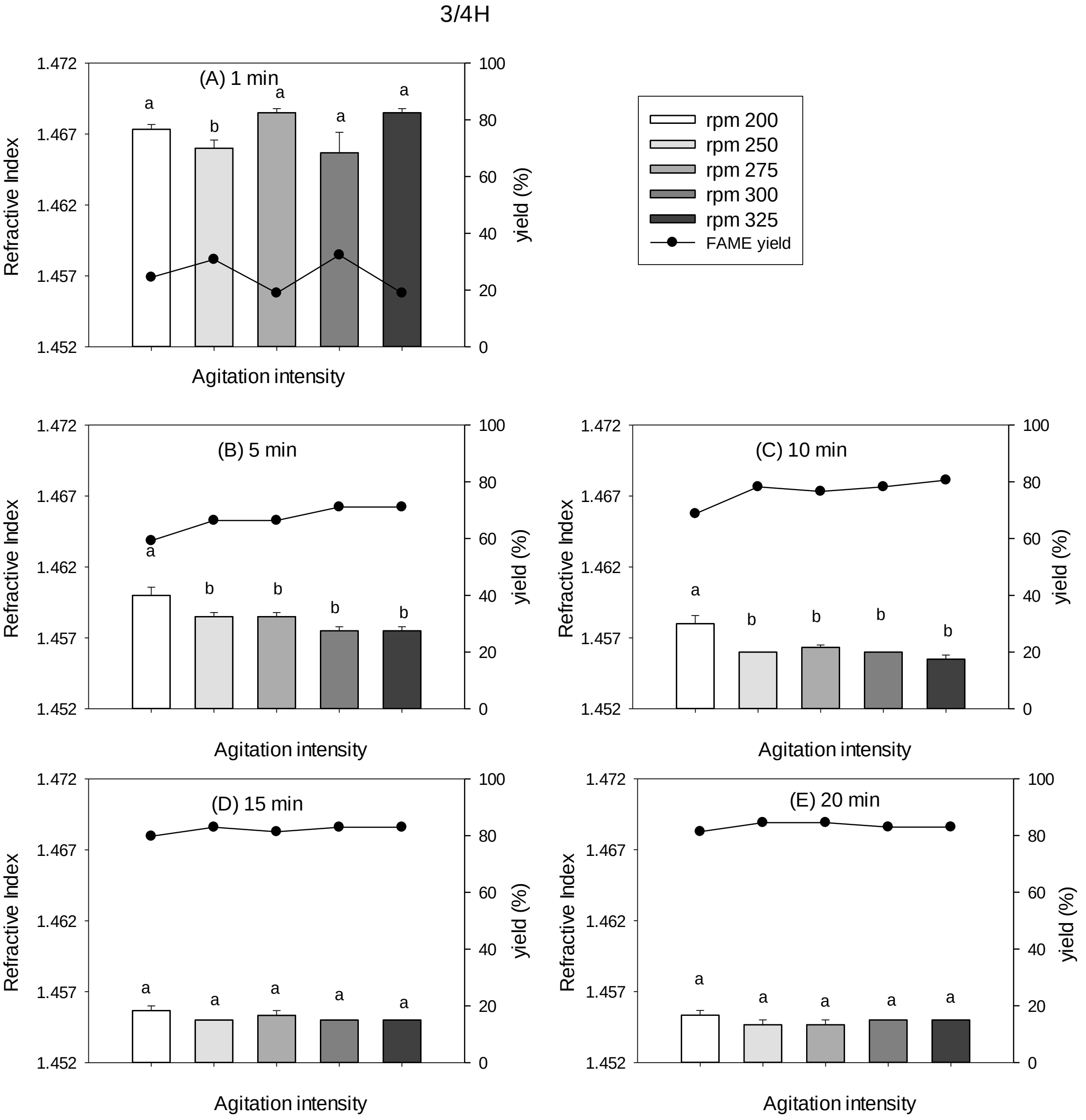


Fig. 4.6. Impact of agitation intensity on refractive index and biodiesel yield at 1/2H with different reaction times (1min, 5min, 10 min, 15 min and 20 min)

### *4.3.2.2 Effect of agitation time on biodiesel conversion and yield*

The impact of different agitation time on refractive indexes and biodiesel yields at five agitation speeds are presented in Fig. 4.7 and Fig. 4.8 for the 1/2H and 3/4H locations, respectively. Both figures show significantly lower ($P < 0.05$) refractive index and higher yield with increasing agitation time. Reaction rate was lowest at the beginning of the experiments under all agitation intensities due to low solubility of the oil in methanol. The transesterification reaction between canola oil and methanol in the presence of KOH is usually stimulated only after agitation has started and contacts of all the reactants are increased.

Significantly high refractive indexes were found at 1 min reaction time than the other agitation speeds ($P < 0.05$). When agitator was located at 1/2H, the biodiesel yield was extremely sensitive to the agitation time. For all the agitation intensities, highest biodiesel yield was found after 15-20 min agitation. Thus, the biodiesel yield was positively correlated with the duration of agitation.

As the stirring speed and reaction time increased, the biodiesel yield increased correspondingly. When the mixing speed became high enough and considerable time has elapsed, an equilibrium state predominates due to the depletion of the reactants. At the agitator location 3/4H, no significant changes ($P > 0.05$) was found in the refractive indexes of the samples from different reaction times after the equilibrium state has been reached. For example, at agitation speed of 200 rpm, stirring duration over 15 min resulted in higher than 80% of biodiesel conversion (Fig. 4.8A). Similarly, 10 min of agitation was long enough to give equivalent yield of biodiesel as 20 min for agitation speeds of 250 and 325 rpm (Fig. 4.8 C, E). When agitation speed was around 300 rpm, the biodiesel conversion rate became slower just after 5 min of reaction. Thus, the equilibrium state was reached faster (Figure 4.8D).

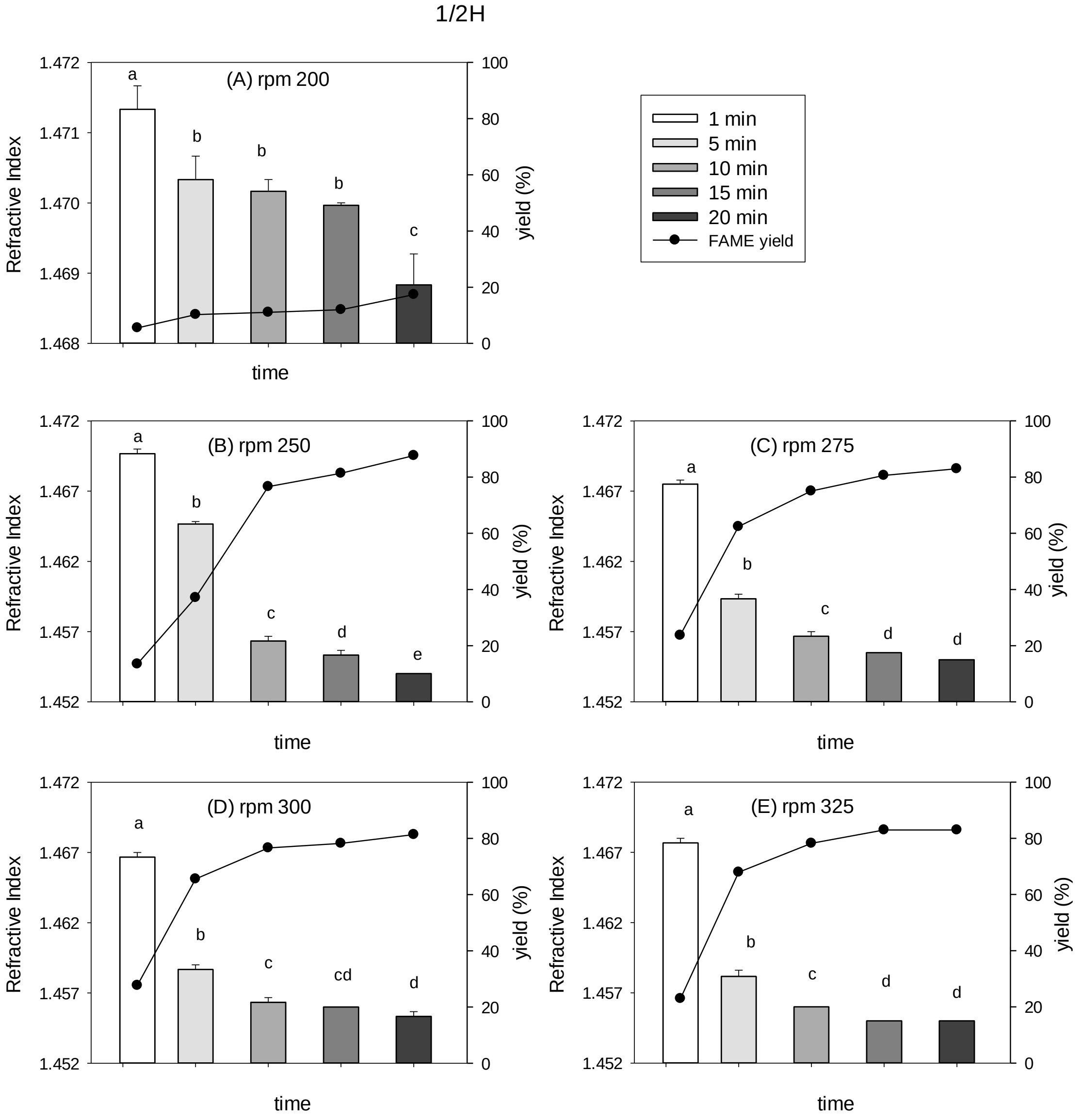


Fig. 4.7. Impact of reaction time on refractive index and biodiesel yield at 1/2H with different agitation intensities

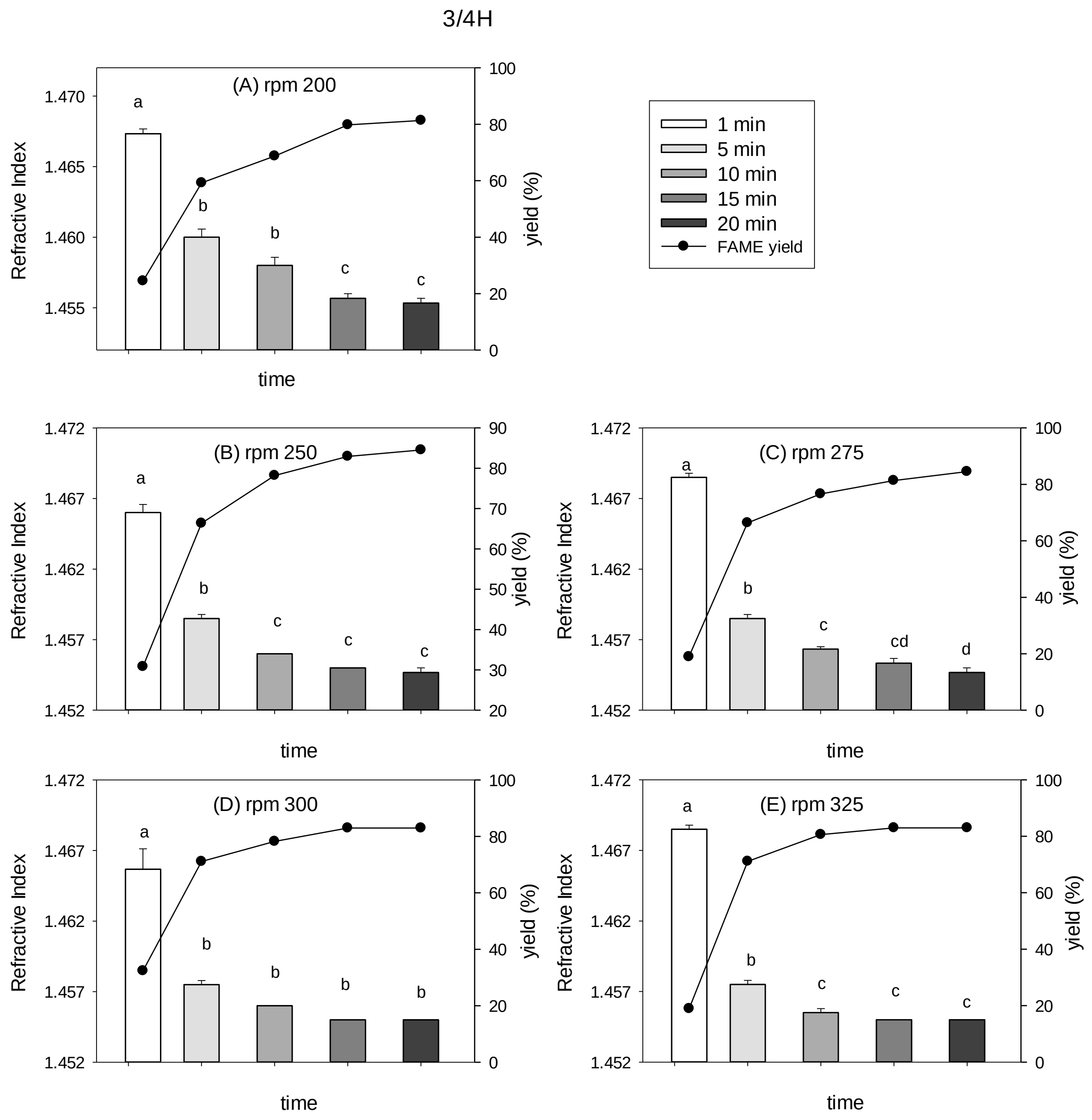


Fig. 4.8. Impact of reaction time on refractive index and biodiesel yield at 3/4H with different agitation intensities

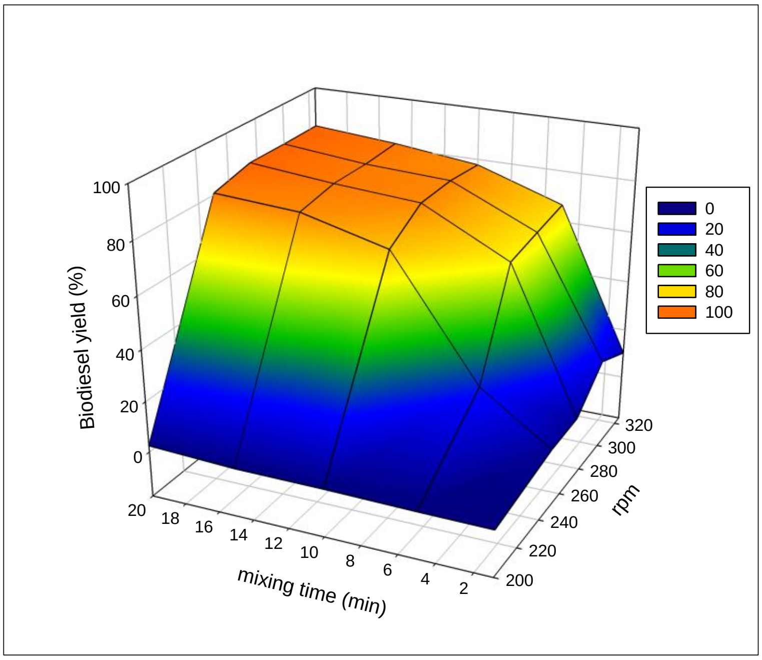
### *4.3.2.3 Effect of agitator location on biodiesel conversion and yield*

As has discussed in 4.321 and 4.322, the responses of biodiesel yield to agitation speed and time were very different at two agitator locations. The agitator 3/4H was closer to the interface between the oil and alcohol than 1/2H; therefore, the reaction was also faster for the former condition than the latter one. When the agitation speed was 200 rpm, the FAME yield was less than 20% for reaction time within 1 to 20 min at 1/2H (Fig. 4.7A), while the FAME yield increased from 20% to 80% when agitation duration rose from 1 to 20 min at 3/4H for the agitation intensity (Fig. 4.8A). Similar phenomena were observed between the two agitator locations at other mixing intensities. Highest FAME yields were obtained around 15 to 20 mins' mixing when agitation speed was between 250 to 325 rpm for 1/2H (Fig. 4.7), but it only took 5 to 15 min to obtain equivalent FAME yields under the same conditions when agitator was located at 3/4H (Fig. 4.8).

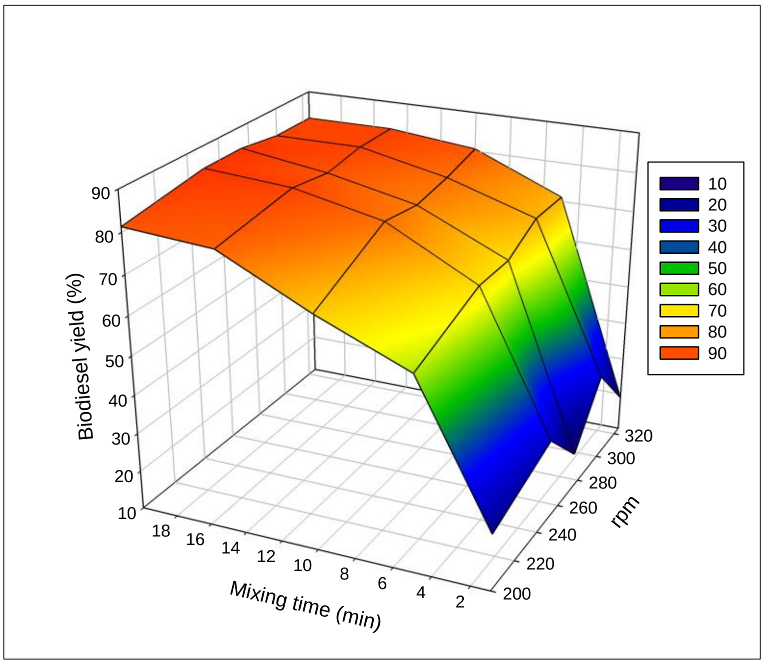
#### *4.3.2.4 Integrated effects*

Taking all the factors into consideration, the integrated comparison of biodiesel conversion for all samples are presented in the plots shown in Fig. 4.9. When agitator was located at 1/2H, the minimum agitation speed should be 250 rpm and it would take at least 15 min to obtain 81% FAME yield (Fig. 4.9a). The transesterification rate was highest within the first 5 min after the start of agitation and became slower with the reduction in the concentration of the reactants.

When agitator was located at 3/4H, all the mixing intensities were effective and gave a minimum yield of 80% FAME. Although the reaction times for each speed varied, it took up to 20 min to get 81% FAME at 200 rpm, while not less than 15 min reaction time was necessary for agitation speeds between 250 to 300 rpm. However, at 325 rpm only 10 min agitation was needed to achieve the target biodiesel yield (≥ 80%). Thus, the closer the agitator is to the interfaces of the reactants and the higher the mixing intensity, the reaction will be accelerated, and equilibrium yield will be attained in a shorter time.



(a)



(b)

Fig. 4.9. Biodiesel yield (%) under different stirring speed for location (a) 1/2H and (b) 3/4H at different reaction times

### 4.4 Summary and conclusion

The transesterification reaction using canola oil and methanol in the presence of KOH was carried out in a glass reactor at different agitation speeds, reaction times and stirring locations. The effects of these parameters on the biodiesel conversion and yield from canola oil were determined and calculated by applying image analysis and refractometer techniques.

Higher agitation speeds improved the stirring and mixing which enhanced contact between the reactants. This together with longer reaction times helped to promote the transesterification reaction and biodiesel yield. However, the reaction is regarded as complete when critical time and speed was reached, and the stirring location seemed to also affect the critical time and speed for the reaction.

Based on the results obtained from this study, the following conclusions were made:

1) Increasing the agitation intensity led to increased breakup of the diameter of the oil drops due to intensive mixing. Increased proportion of lower diameter range droplets are dispersed in the aqueous medium.
2) The closer the distance of the agitator to the interfacial area between the reactants the higher the reaction rate and yield of biodiesel.
3) When agitator was located at 1/2H, the transesterification reaction was highly sensitive to the agitation time and highest biodiesel yield was obtained after 15-20 min agitation. Whereas, at 3/4H location, biodiesel conversion rate became slower and reached equilibrium states faster due to the depletion of the reactants. For the

agitation speeds of 250 and 325 rpm, 10 min reaction time was long enough to obtain ≥ 80% biodiesel yield, while 5 min was enough for 300 rpm speed.

4) Higher agitation speed resulted in more biodiesel conversion and yield. However, when the agitation time is longer than 10 min, the critical agitation speed should not exceed 250 rpm when agitator was located at 1/2H. At the 3/4H location, stirring speed of 200 rpm 15 min reaction time gave biodiesel yield equivalent to the yield at 325 rpm and 5 min.

# Chapter 5

# General Summary and Conclusions

## 5.1 General summary

Biodiesel is a renewable energy resource produced from the transesterification of vegetable oils or animal fat with alcohol. This process requires mixing of the oil, methanol and a catalyst. Mechanical mixing has been the most commonly used method to obtain biodiesel from the transesterification processes. The overall goal of the research was to investigate the impact of mechanical mixing on the yield of biodiesel from canola oil and methanol with alkaline catalyst and to establish a simpler real time and inexpensive method of determining the yield of biodiesel from feedstocks devoid of complexities.

The efficient determination of oil conversion to biodiesel is one of the concerns of the biodiesel industry. While most biodiesel characterization techniques are laborious and costly, this study examined the performance of imaging and refractometer techniques for quantifying the biodiesel conversion in real time. These results obtained from these techniques were compared with the results from Thermogravimetric analysis (TGA).

## 5.2 Conclusions

***Objective 1: To evaluate the performance of refractometer for analyzing real time biodiesel production in research and industrial settings from canola oil.***

The FAME conversions at different mixing intensities and reaction times measured using the refractometer correlated well to the relative weight losses from TGA method with $R^2$= 0.93 except at mixing intensity of 200 rpm. Overall, the refractometer technique is a promising technique that provides reliable prediction of biodiesel yield in real time.

***Objective 2: To find the optimal mixing intensity and duration for producing biodiesel from canola oil that could serve as reference for the industrial production of biodiesel in Canada.***

Higher speed and longer reaction time showed great potentials for improving mixing and stirring, and enhancing contact between the reactants. These promoted the transesterification reaction and biodiesel yield. However, the reaction is regarded as complete when critical time and speed was reached, and the stirring location had impact on the critical time and speed of the reaction.

### 5.3 Future recommendations

1. The experiment was carried out at five mixing intensities, five reaction times and two agitator locations. It is suggested to add a few more treatments of agitation intensity, location and extension of the reaction time.
2. This proposal of using refractometer for determining biodiesel conversion was based on transesterification of canola oil. Further calibration and evaluation should be conducted for quantifying biodiesel yield from other lipid feedstocks.

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