# CHAPTER III
# EXPERIMENTAL

The research problem address in this work is the evaluation of the catalytic activity of an organic base and an alkaline earth metal oxide. The performance of these catalysts will be compared against the behavior of a typical industrial catalyst such as sodium methoxide. The catalytic efficiency was examined based on the conversion of canola oil to methyl esters. The quality of the biodiesel produced was also evaluated trough the determination of soap content. The goal is to establish the optimum reaction conditions for the production of high biodiesel yield as a function of catalyst type and concentration, excess reagent, temperature, and biodiesel quality. The heterogeneous catalyst evaluated in this study is Strontium Oxide (SrO) as compare to 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), which is an organic base with potential for heterogenization. The materials, equipment, and procedures used during experimentation are outlined and described in the following sections.

## 3.1 Materials

3.1.1 Reagents
- Raw vegetable oil (Canola oil) was provided by Eastern Greenway Oils (EGO), Waterville, New Brunswick, Canada.
- Sodium methoxide solution 30% in methanol was purchased from Acros Organics.
- 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) ($\geq$ 98.0) was purchased from Sigma-Aldrich.
- Strontium oxide (99.9%) was purchased from Sigma-Aldrich.
- Sodium sulfate powder ($\geq$ 99.0%) A.C.S. reagent anhydrous was purchased from Sigma-Aldrich.
- Hydrochloric acid 0.0100 Normal (N/100) was purchased from Ricca Chemical Company.
- Sodium hydroxide

### 3.1.2 Solvents

- Methanol (99.99%) was obtained by Eastern Greenway Oils (EGO), Waterville, New Brunswick, Canada.
- Acetone ACS, Reagent grade
- Isopropyl alcohol
- Anhydrous Ethyl Alcohol
- Chloroform-D +0.05% v/v TMS (D, 99.8%) was obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA).

### 3.1.3 Indicator

- Bromophenol Blue Solution 0.04% w/v was purchased from Fisher Scientific
- Phenophthalein, Certified A.C.S. grade was purchased from Fisher Scientific

## 3.2 Equipment

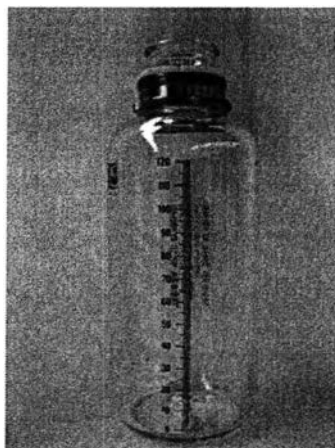### 3.2.1 Lab-Crest® Pressure Reaction Vessels



Figure 3.1 Photograph of the Pressure Reaction Vessel

### 3.2.2 Digi-Sense® Temperature Controllers



**Figure 3.2** Photograph of the Temperature Controller

### 3.2.3 Magnetic Stirrer (Corning PC-410D)



**Figure 3.3** Photograph of the Magnetic Stirrer

### 3.2.4 Thermocouple (Type T), Omega® engineering
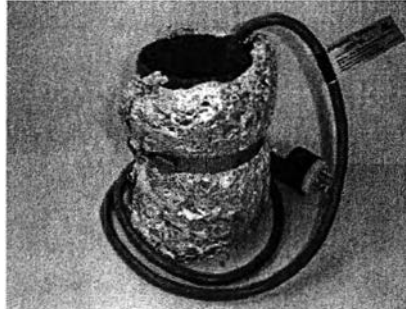
### 3.2.5 Heater Band



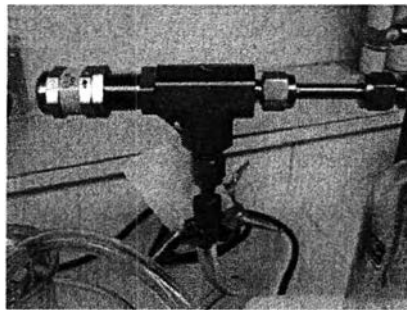**Figure 3.4** Photograph of the Heater Band

### 3.2.6 Pressure Relief Valve



**Figure 3.5** Photograph of the Pressure Relief Valve

### 3.2.7 Centrific Model 228, Fisher Scientific



**Figure 3.6** Photograph of the Centrifuge

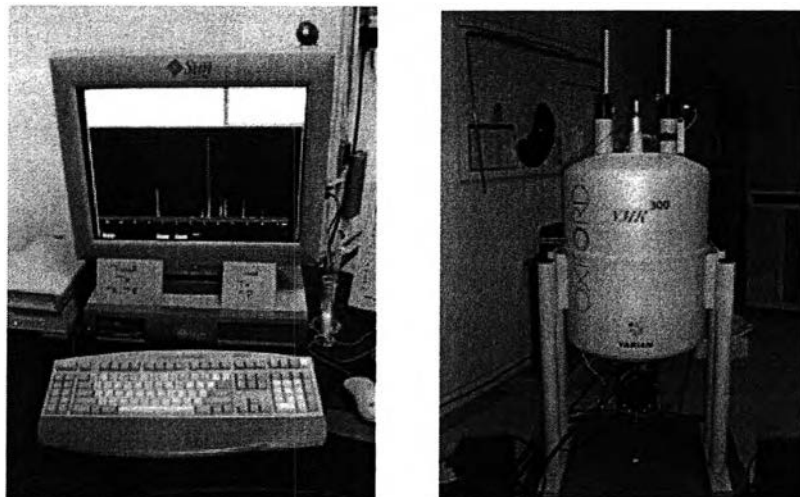### 3.2.8 300 MHz varian NMR Machine



**Figure 3.7** Photograph of the $^1$H NMR Spectroscopy machine

## 3.3 Methodology

Figure 3.10 summarizes the flow diagram of the experimental steps carried out for the evaluation of the transesterification reaction.
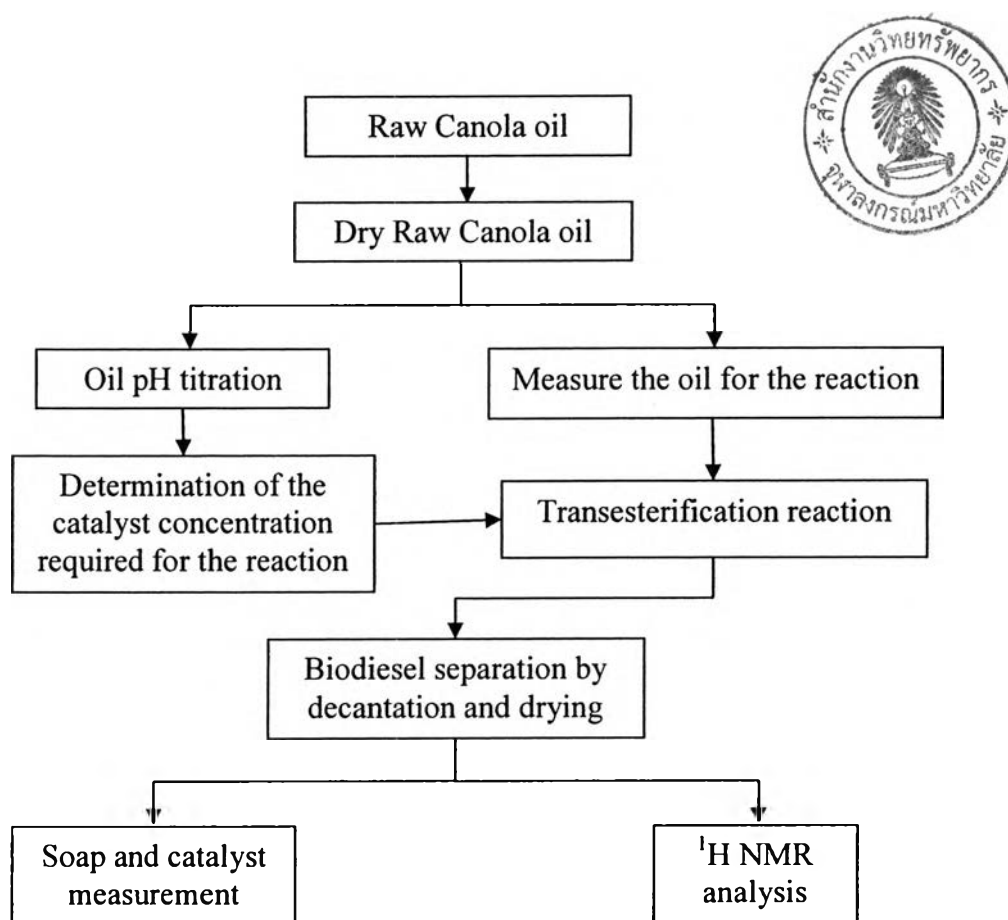
**Figure 3.8** Biodiesel production and analysis procedure flow diagram.

### 3.3.1 Drying Canola Oil

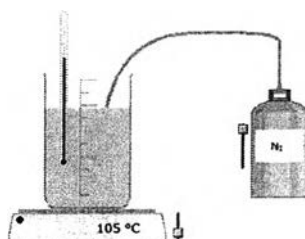Canola oil was heated at 105°C and stirred with nitrogen injection.



**Figure 3.9** Schematic of the apparatus setup for drying Canola oil

### 3.3.2 Oil Titration

The acidity of oil is determined by using a titration method based on a modification of the AOCS Official Method Ca 5a-40 for determination of free fatty acids, which is described below (Rukunudin I.H. et al., 1998).

Raw canola oil of 1 $cm^3$ was mixed with 9 $cm^3$ of isopropyl alcohol in a graduated cylinder until the canola oil was completely dissolved in the alcohol. Then, pour solution into 100 ml beaker. Then, ten drops of the phenolphthalein marker solution was added into the solution. Finally, the solution was titrated with 0.001 wt% NaOH solution until end point was reached (pink color > 10 sec). The procedure was repeated for 3 samples.

### 3.3.3 Sodium Methoxide as Homogeneous Catalyst-Baseline Data

The aim of this experimental section was to identify the best reaction conditions for the transesterification reaction of raw canola oil using sodium methoxide that maximize reaction yield and conversion while minimizing soap formation. The ester phase was analyzed for soap and catalyst content using the modified AOCS method Cc 17-79. The biodiesel conversion was determined by $^1$H-NMR.

The experimental steps that were used in this first series of experiments with sodium methoxide are explained below. Each of these experiments was repeated twice and in some cases three times. The standard deviation was determined.

### 3.3.3.1 Effect of Mixing Time

The mixing rate was the first parameter studied. The effect of mixing rate on the transesterification of the Canola oil was investigated with its mixing rate varying from to 120 rpm to 1000 rpm. The operation conditions during the whole reaction process were fixed at: reaction temperature of 90°C, reaction time of 1 hour, molar ratio of methanol to oil at 4.8:1, and 0.59% of sodium methoxide by weight of the oil. Once the optimal mixing rate for the transesterification reaction was determined, a set of reactions was repeated under identical conditions but in these

case applying a mixing scheme where the reactants were mixed at the optimal mixing rate for the first 10 min of the reaction followed by a decrease in the mixing rate by half of the optimal mixing rate for the rest of the reaction time.

### 3.3.3.2 Effect of Reaction Temperature

To determine the effect of reaction temperature on biodiesel conversion, the transesterification reaction was carried out under the optimal conditions obtained in the previous section. In this part of the study, the effect of reaction temperatures on biodiesel yield were evaluated by using three different reaction temperatures 60°C, 70°C, and 90°C.

### 3.3.3.3 Effect of Methanol to Oil Molar Ratio

In order to study the effect of molar ratio on biodiesel conversion, experiments were conducted with various molar ratios of methanol to oil in the range of 3:1 to 6:1. The optimized mixing time and reaction temperature as obtained in the previous sections were adopted.

### 3.3.3.4 Effects of Catalyst Concentration

The effects of catalyst concentrations on the transesterification of the canola oil were investigated with their concentration varying from 0.10% to 0.75% based on weight of the oil. The optimal conditions achieved in the previous section were adopted.

After the establishment of the best conditions for sodium methoxide, some of these conditions were fixed for the remaining experimental series.

### 3.3.4 Transesterification

Raw canola oil (200 g) was placed in a beaker equipped with a magnetic stirrer and a thermometer. Under agitation, the raw canola oil was heated up to 60°C on a heating plate. Simultaneously, a fixed amount of freshly prepared Catalyst-Methanol solution was added into the reactor and heated up to 40°C under

agitation (the optimal mixing rate achieved in the previous section). When both of them reached a desired temperature, the heated raw canola oil was added into the reactor, taking this moment as the starting time of the reaction. Then, nitrogen gas was added to the reactor to maintain the reaction pressure of 15 psi. Finally, the mixture was heated to a desired reaction temperature under a certain agitation rate (800 rpm) and kept at that condition for the remaining of the reaction.

### 3.3.5 Aliquot Removal

Aliquots of 2.0 ml were removed from the batch reaction using a glass syringe. The aliquots were immediately transferred into a test tube containing 2.5 times the amount of catalyst in the aliquot of 10 M HCl (only NaOCH₃ sample) and placed on ice to stop the transesterification reaction by neutralization of NaOCH₃. The aliquots were allowed to settle producing two distinct liquid phases: crude ester phase at the top and glycerin phase at the bottom for 1 hour. The crude ester phase separated from the bottom glycerol phase by decantation. Then, it was washed using warm saturated aqueous NaCl solution several times until the washed water become clear. Then, it was dried using anhydrous sodium sulfate and submitted to $^1$H-NMR analysis in CDCl₃ using TMS as internal standard to determine the biodiesel conversion. The soap content in final biodiesel product was also determined.

This procedure was used to monitor the progress of the reaction by the extraction of aliquots from a batch reactor at given time intervals (30 s, 60 s, 90 s, 120 s, 150 s, 180 s, 5 min, 10 min, 20 min, 30 min, 40 min and 60 min). The extent of the reaction was determined by $^1$H-NMR analysis. The optimal value of each parameter involved in the process was determined while the rest of the parameters were kept constant. After each optimal was attained, this value was adopted for the optimization of the next parameter.

The catalysts evaluated in this study are Sodium methoxide (NaOCH₃), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), Strontium Oxide (SrO), animal shells and combinations of them. The experimental matrix used in the second experimental phase is presented below in Figure 3.12.

## Experimental Matrix

C = Catalyst concentration
T = Temperature (°C)
R = Methanol/Oil molar ratio
P = 15 psi
Mixing rate = 800 rpm

### FOR ANY CATALYST

| GROUP A | Fixed $T_3$ $R_3$ | Kinetic Data |
| --- | --- | --- |
| C1 | T3,R3,C1 | **Catalyst Concentrations Effect** |
| C2 | T3,R3,C2 | C1,R3,T3  C2,R3,T3  C3,R3,T3 |
| C3 | T3,R3,C3 | |

The optimal catalyst concentration from Group A = C*

| GROUP B | Fixed C*,$T_3$ | (Compare with C*,$T_3$,$R_3$ from Group A) | Methanol to Oil Ratio Effect |
| --- | --- | --- | --- |
| R1 | C*,T3,R1 | | C*,R1,T3  C*,R3,T3  C*,R3,T3 |
| R2 | C*,T3,R2 | | |

The optimal methanol to oil ratio from group B = R*

| GROUP C | Fixed C*,R* | (Compare with C*,R*,$T_3$ from group A or B) | Reaction Temperatures Effect |
| --- | --- | --- | --- |
| T1 | C*,R*,T1 | | C*,R*,T1  C*,R*,T2  C*,R*,T3 |
| T2 | C*,R*,T2 | | |

The optimal temperature from Group C = T*

| Catalyst types | $C_1$ (wt%) | $C_2$ (wt%) | $C_3$ (wt%) | $T_1$ (°C) | $T_2$ (°C) | $T_3$ (°C) | $R_1$ | $R_2$ | $R_3$ |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| NaOCH₃ | 0.59 wt% | 1.00 wt% | 1.50 wt% | 60 | 70 | 90 | 3.5:1 | 4.5:1 | 6:1 |
| TBD | 1.53 wt% | 2.29 wt% | 3.05 wt% | 60 | 70 | 90 | 3.5:1 | 4.5:1 | 6:1 |
| SrO | 1.00 wt% | 3.00 wt% | 5.00 wt% | 60 | 70 | 90 | 4.5:1 | 6:1 | 12:1 |

**Figure 3.10** The experimental matrix

The experimental matrix consists on the evaluation of the effect of three independent variables such as catalyst concentration, methanol to oil molar ratio, and temperature on biodiesel yield. In order to obtain the optimal condition, the reaction was conducted at a fixed mixing rate of 800 rpm, reaction time of 1 hour, and under nitrogen atmosphere at 15 psi using a lab-scale reactor. First, the effect of catalyst concentration on the transesterification of the canola oil was investigated. Catalyst concentrations are shown in Figure 3.12. The resultant optimal catalyst concentration in each case is kept fixed for the next series of the experimental phase. Then, the effect of methanol to oil molar ratio were studied. The experiments were conducted using molar ratios of methanol to oil in the range of 3.5:1 to 6:1 for NaOCH₃ and TBD and 4.5:1 to 12:1 for SrO. After the optimal methanol to oil molar ratio was determined, this condition was adopted as a constant for the next set of experiments. Finally, the effects of reaction temperature were investigated with

reaction temperature varying from 60°C to 90°C for all type of catalysts. Finally, the optimal conditions for all type of catalyst were evaluated. Figure 3.13 (a) and Figure 3.13 (b) show the experimental set up and a flow diagram of the experimental procedure.
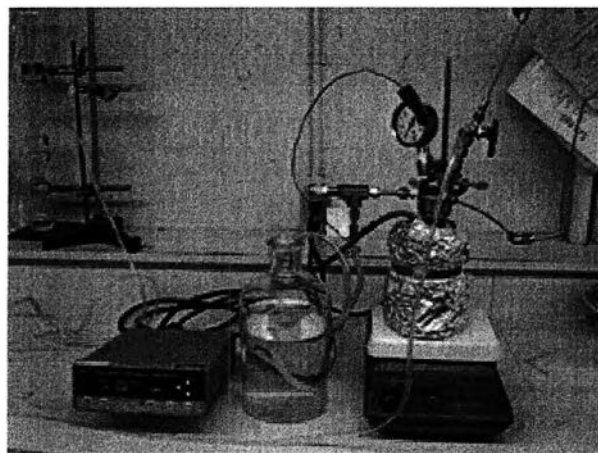


(a) Picture showing the current experimental set up for biodiesel production
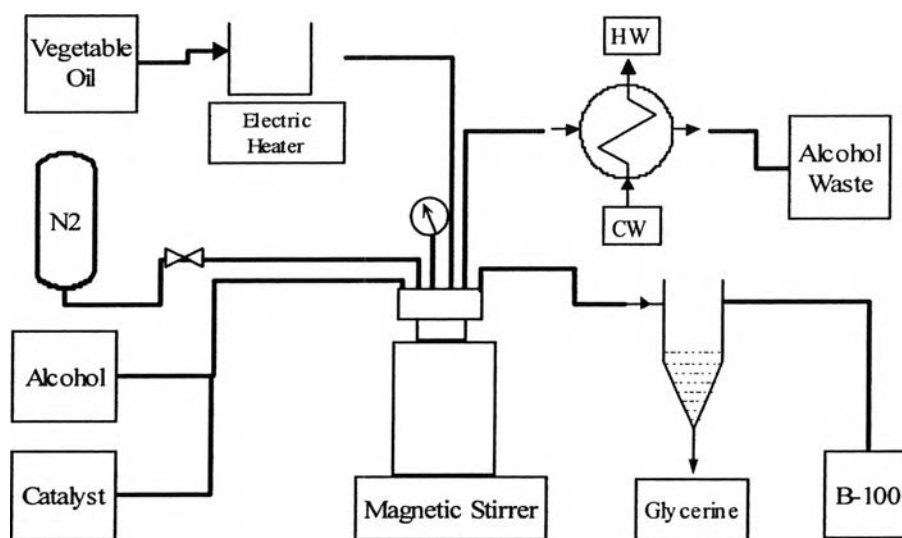


(b) Flow diagram showing the experimental set-up for the transesterification reaction

**Figure 3.11** shows (a) the experimental setup and (b) a flow diagram explaining the experimental set-up.

### 3.3.6 The Synergistic Effect of Catalyst Combinations

The synergistic effect of catalyst combinations were studied by using the optimum condition obtained from the previous results. TBD and SrO were mixed in a proportion of 30:70, 50:50 and 70:30. These combination sets were used for the transesterification reaction. In addition, both TBD and SrO was also mixed with egg shell and lobster shell in a proportion of 70:30 to determine biodiesel conversion. Finally, biodiesel product was also determined for soap content and biodiesel conversion.

### 3.3.7 Soap and Catalyst Measurements

A simple titration procedure can be used to measure the amount of soap and catalyst. The following procedure is a modified version of the AOCS method Cc 17-79 for the determination of soap in oil (Van Gerpen, J., 2005).

The unwashed biodiesel of 5 g was dissolved in 100 ml of acetone containing 2% distilled water. Then, 2ml of 1% phenolphthalein indicator (in isopropyl alcohol) was added to the solution. Then, the solution was titrated with 0.01 N HCl until the phenolphthalein color changed from red to clear. This indicated that the free catalyst in the sample was neutralized. After that 1 ml of bromophenol blue indicator (0.4% in water) was added into the solution. Then, the titration was continued until the bromophenol blue changed from blue to yellow. This procedure is repeated for 3 samples.

### 3.3.8 Analysis of Biodiesel Yield

A quantitative $H^1NMR$ analysis was used to monitor the progress of the reaction. This was accomplished by first determining the relaxation times for the methoxy and carbon $CH_2$ groups. The relaxation delay (d1) was set at 60 (d1=60). The block size (bs) was set at 4. A very clear spectrum was obtained at bs=4. The accuracy of this technique in terms of biodiesel yield is in the range of ±2% (Gelbard, G. et al, 1995).

The oil phase was separated by decantation, washed with warm saturated aqueous NaCl solution, dried with anhydrous sodium sulfate and submitted to NMR analysis in $CDCl_3$. Therefore, the conversion of the canola oil to a mixture

of methyl esters is determined by the ratio of the signals at 3.70 ppm (methoxy groups of methyl esters) and 2.30 ppm (carbon $CH_2$ groups of all fatty acid derivatives) as shown in Figure 3.14. A simple equation (Eq. 1) is used to calculate biodiesel conversion as follows.

$$C = 100 \times \left( \frac{2A_{ME}}{3A_{\alpha-CH_2}} \right) \ldots \ldots (Eq.1)$$
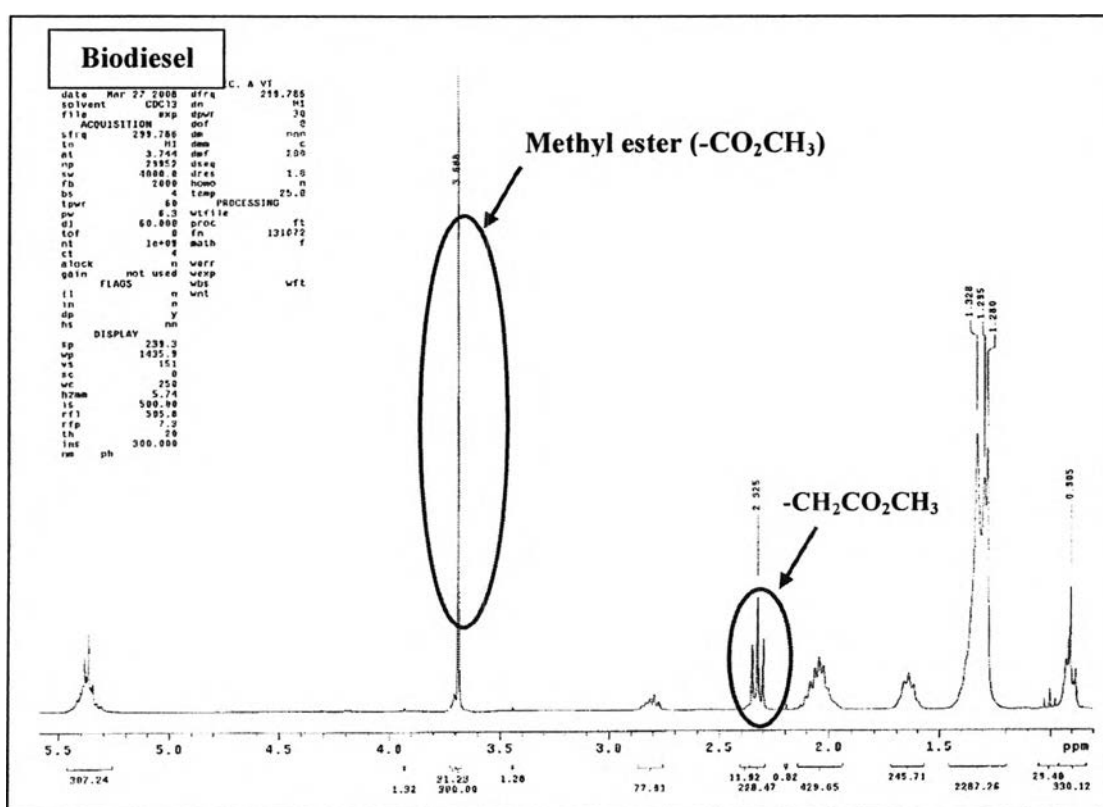


**Figure 3.12** $^1$H-NMR spectrum for biodiesel