CHAPTER III
EXPERIMENTAL

3.1 Materials

Reagents

- Vegetable oil (Canola oil) "Harmonie Canola".
- M1O (99.9%) "Sigma-Aldrich".
- M2O (90.0%) "Sigma-Aldrich".
- M3O (99.9%) "Baker Chemical".
- M4O (99.9%) "Baker Chemical".
- M5O (99.9%) "Sigma-Aldrich".
- Barium Yttrium Tungsten oxide (99.9%) "Sigma-Aldrich".
- Barium Strontium Titanium oxide (99.9%) "Sigma-Aldrich".
- Sodium sulfate powder (≥ 99.0%) A.C.S. reagent "Sigma-Aldrich".
- M1CA (99.9%) "Baker Chemical".
- M3CA (99.9%) "Baker Chemical".
- M6CA (99.9%) "Baker Chemical".

Solvents

- Methanol (anhydrous, 99.8%) "Sigma-Aldrich".
- Acetone ACS, Reagent grade "Sigma-Aldrich".
- Chloroform-D +0.05% v/v TMS (D, 99.8%) was obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA).

Gas

- Nitrogen gas "Air Liquide Canada Inc.".

3.2 Equipment

The equipment used during the transesterification of vegetable oil for the production of biodiesel consisted of the following main items: pressure reaction vessel, temperature controller, heating tapes, magnetic stirrer, thermocuople, pressure relief valve, centrifuge, shaker, and a condenser, among others. The analysis of biodiesel yield was conducted using an NMR 300 machine manufacturated by Varian. Figure 3.1 through Figure 3.9 show pictures of the main components of the experimental apparatus. A photograph and a simplified flow diagram of the experimental set up are shown in Figure 3.9.

Figure 3.1 Lab-Crest® Pressure Reaction Vessel.

Figure 3.2 Digi-Sense® Temperature Controller.

Figure 3.3 Heater Type I.

Figure 3.4 Heater Type II.

The heater type I shown in Figure 3.3 is Barnstead Thermolyne with the maximum power of 180 watt. The heating wire is insulated by silicone rubber. The other one shown in Figure 3.4 is Thermo Scitific BriskHeat with the maximum power of 210 watt. It is made of fibrous glass insulated wire.

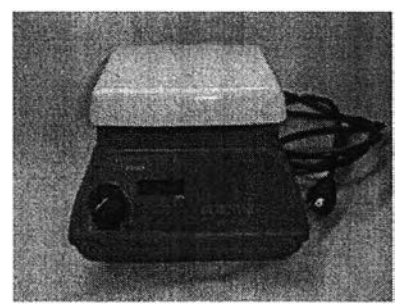

Figure 3.5 Magnetic Stirrer (Corning PC-410D).

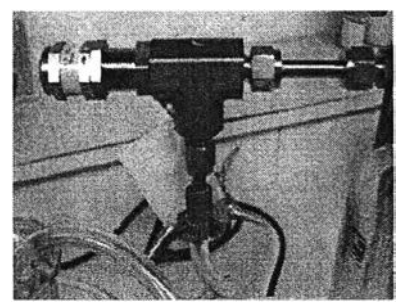

Figure 3.6 Pressure Relief Valve, Swagelok.

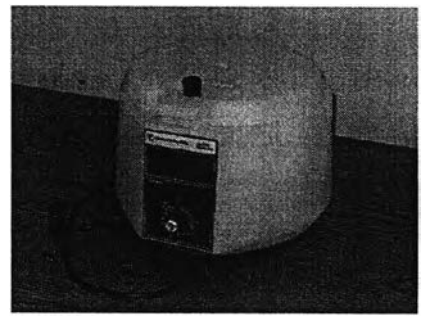

Figure 3.7 Centrifuge, Centrific Model 228, Fisher Scientific.

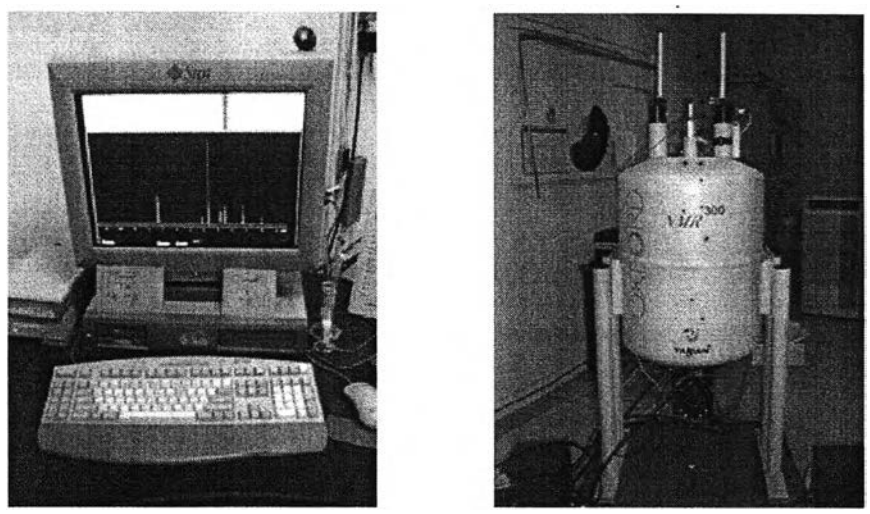

Figure 3.8 NMR 300 Machine with Computer, Varian.

3.3 Methodology

A flow diagram showing the procedure followed for the transesterification of vegetable oil is presented in Figure 3.9.

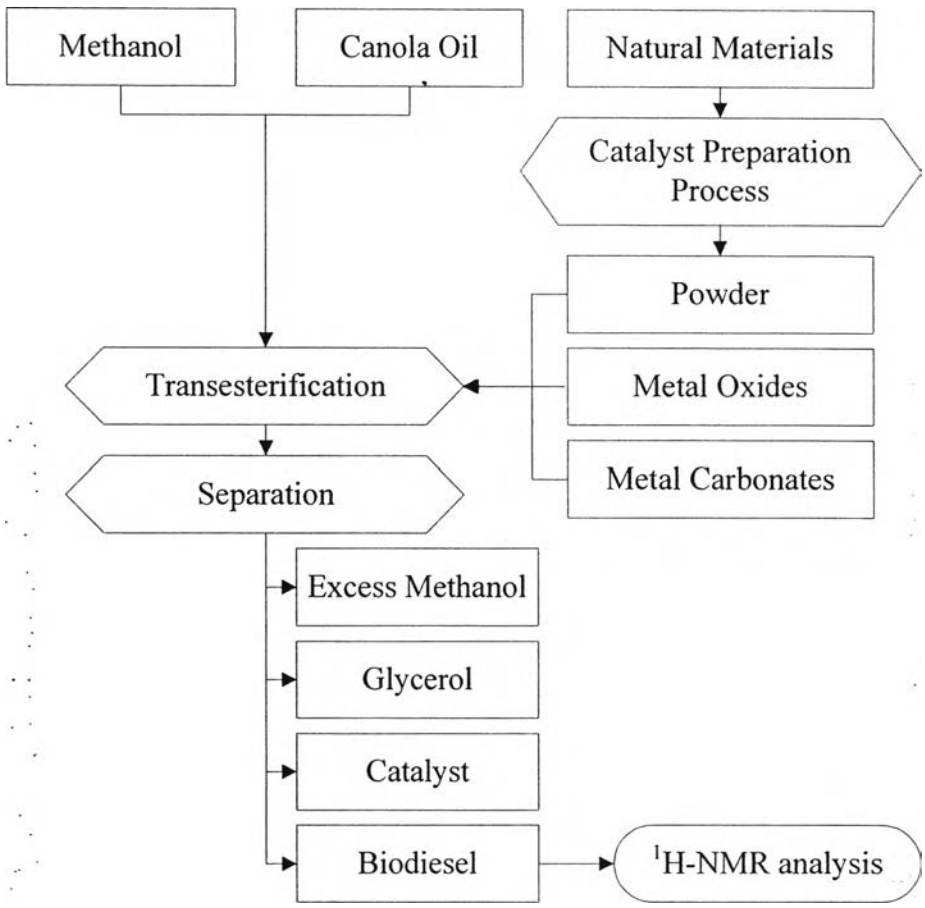

Figure 3.9 Flow diagram of the experimental steps.

The different experimental steps shown in Figure 3.9 are described as follows.

3.3.1 Natural Materials Preparation Processes

All of the natural materials were washed with water, broken into a small pieces, dried at 105 °C over night in order to eliminate excess moisture, grinded to produced a fine powder that was sieved to obtained a paticle size of 90 μm. After sieving the powder was further dried at 105 °C over night again, and kept in a desicator until use. This procedure was used for the preparation of all types of natural materials; crustaceans shells: CS1, CS2, animal shells: AS, mollusk shells: MS1, and MS2.

3.3.2 Transesterification Reaction

The effect of the following reaction variables: reaction time and temperature, catalyst concentration, and ratio of catalyst combinations on biodiesel yield was evaluated. The methanol-to-oil molar ratio was held constant at 6:1 as well as the mixing rate (800 rpm) and the reaction pressure (15 psig under N_2 atmosphere).

I. **Using metal oxides as catalysts:** the effects of using synthetic metal oxide catalysts on the transesterification of canola oil with methanol were evaluated at the following experimental conditions.
   a. Reaction time: 60 minutes
   b. Reaction temperature: 65°C at a constant heating rate of 5°C/min
   c. 3% of the catalyst by weight of oil

II. **Using natural materials as catalysts:** the effect of using natural materials as catalysts on the transesterification of canola oil with methanol were evaluated at the following reaction conditions.
   a. Reaction time: 60 minutes
   b. Reaction temperature: 65°C at a constant heating rate of 5°C/min
   c. 10% of the catalyst by weight of canola oil

III. **Effect of the reaction time on the activity of catalyst combinations:** the effect of the reaction time on the activity of the catalyst combinations during the transesterification of canola oil with methanol was evaluated at the following reaction conditions.
   a. Reaction time: 30 and 60 minutes
   b. Reaction temperature: 45°C at a constant heating rate of5°C/min
   c. 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0% of the metal oxides by the weight of canola oil
   d. 1.0% of the cattalyst combinations by the weight of canola oil with the ratio of 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, and 9:1

IV. **Effect of the reaction temperature on the activity of catalyst combinations: synthetic metal oxide and natural materials:** the effect of reaction temperature on the activity of the catalyst combinations during the transesterification of canola oil with methanol were evaluated at the following reaction conditions.

a. Reaction time: 30 minutes
b. Reaction temperature: 45, 55, and 65°C at a constant heating rate of 5°C/min
c. 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0% of the metal oxides by weight of canola oil
d. 1.0% of the cattalyst combinations by weight of canola oil with the ratio of 5:5, 6:4, 7:3, 8:2, and 9:1

V. **Effect of the type of natural materials used for catalysts combinations on the transesterification reaction:** the effect of the type of natural material used for catalyst combinations on the transesterification reaction of canola oil with methanol was evaluated at the following reaction conditions.

a. Reaction time: 30 minutes
b. Reaction temperature: 45°C at a constant heating rate of 5°C/min
c. 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0% of the metal oxides by weight of canola oil
d. 1.0% of the cattalyst combinations by weight of canola oil with the ratio of 5:5, 6:4, 7:3, 8:2, and 9:1

VI. **Effect of the type of metal oxides used for catalysts combinations on the transesterification reaction:** the effect of the type of the metal oxides used for catalysts combinations on the transesterification reaction of canola oil with methanol were studied at the following reaction conditions.

a. Reaction time: 30 minutes
b. Reaction temperature: 45°C at a constant heating rate of 5°C/min

c. 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0% of the metal oxides by the weight of canola oil

d. 1.0% of the cattalyst combinations by the weight of canola oil with the ratio of 5:5, 6:4, 7:3, 8:2, and 9:1

VII. Effect of the type of metal carbonates used for catalysts combinations on the transesterification reaction: the effect of the type of metal carbonates used for catalyst combinations on the transesterification reaciton of canola oil with methanol were determined at the following reaction conditions.

a. Reaction time: 30 minutes

b. Reaction temperature: 45°C at a constant heating rate of 5°C/min

c. 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0% of the metal oxides by the weight of canola oil

d. 1.0% of the cattalyst combinations by the weight of canola oil with the ratio of 5:5, 6:4, 7:3, 8:2, and 9:1

3.3.3 Biodiesel Separation

The biodiesel was separated by decantation, centrifugation, and filtration. After separation, the biodiesel was washed 3 times using lukewarm saturated solution of sodium chloride (NaCl). Finally the biodiesel phase was dried using anhydrous sodium sulfate and analyzed for biodiesel content.

3.3.4 Analysis of Biodiesel

A quantitative ^{1}H-NMR analysis was used to monitor the yield from the transesterification reaction. The yield of this reaction is the percentage by weight of the biodiesel contain in the reaction mixture. This was accomplished by first determining the relaxation times for the methoxy groups (-CH_2- groups). The relaxation delay (d1) was set to 60 (d1=60) and the block size (bs) was set to 4. A very clear spectrum was obtained at bs=4 (4 times of scaning). 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 sodium chloride (NaCl) solution, dried with anhydrous sodium sulfate in order to remove the water from the reaction mixture and submitted to NMR analysis using chloroform-D ($CDCl_3$) as a solvent. Therefore, the conversion of the canola oil to a mixture of fatty acid methyl esters is determined by the ratio of the signals at 3.70 ppm (methoxy groups of methyl esters) and 2.30 ppm (carbon in CH_2 groups of all fatty acid derivatives) as shown in Figure 3.10.

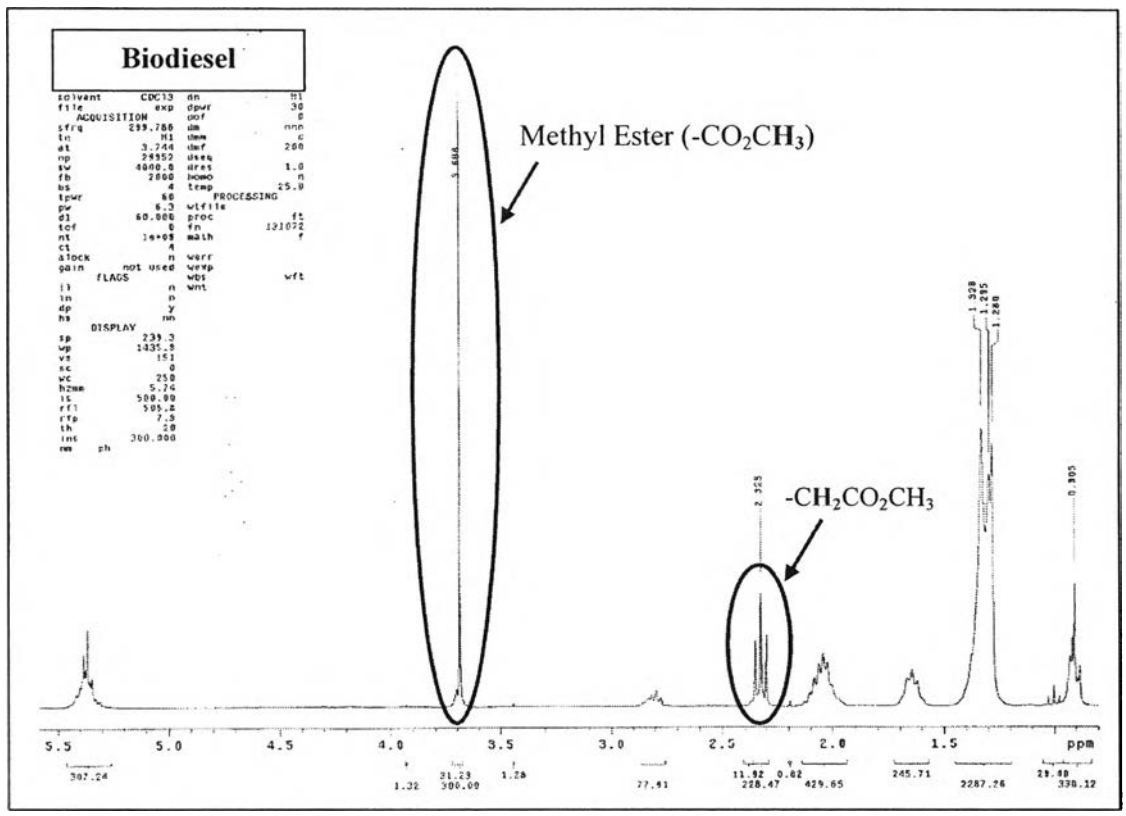

Figure 3.10 ^{1}H-NMR spectrum for biodiesel.