CHAPTER III

Experimental

3.1 Materials and Equipment

3.1.1 Chemicals:

- Palmitric acid (99 % purity, Merck)
- Oleic acid (88 % purity, Merck)
- Dodecane (99.9 % purity, Merck)
- Hexane (98% purity, Merck)
- Boron Trifluoride Methanol (14% solution, Aldrich)
- Pentadecane (99% purity, Aldrich)
- Hexadecane (99% purity, Aldrich)
- Heptadecane (99% purity, Aldrich)
- Octadecane (99% purity, Aldrich)
- Eicosane (99% purity, ACROS)
- Acetone (99% purity, LabScan)
- Ethanol (99% purity, Merck)
- Sodium Chloride (99% purity, Labscan)
- 10 wt% Ni 30 wt% Mo over gamma alumina (Akzo-Noble)
- 5 wt% Pd over activated carbon (Aldrich)

3.1.2 Gases:

- Hydrogen (99 %purity, TIG)
- Nitrogen (99 %purity, TIG)
- Helium (99 %purity, TIG)
- Air Zero (99 %purity, TIG)
- 5 wt% Hydrogen sulphide/Nitrogen (TIG)

3.1.3 Equipment:

- High pressure packed-bed continuous flow reactor
- Mass flow controller (Brooks instrument 5850E)
- High pressure liquid pump (Water 515 HPLC)

- Gas chromatograph (HP GC 6890)
- Temperature programmed oxidation apparatus (TPO)
- Back pressure regulator (SIEMENS)
- Oven
- Hot & Stirrer plate (Cole Parmer)

3.2 Methodology

3.2.1 Catalyst Pretreatment

The commercial catalysts are crushed and sieved to obtain a particle size (20/40, 40/60, 60/80 mesh) to study the internal mass transfer limitation of the deoxygenation reaction. The catalyst is placed in the reactor and reduced in situ by flowing hydrogen at 500 psig for 3.5 h. The temperature is increased with ramping rate of 5 °C/min until reaching the reduction temperature, 200 °C for Pd/C, and 360 °C for non-sulfided $NiMo/Al_2O_3$.

In the case of sulfided $NiMo/Al_2O_3$, the metal oxide catalyst is sulfided ex-situ. The essence of sulfiding is to decrease the initial high activity of the catalyst and maintain uniform catalyst activity across the catalyst surface. The commercial grade $NiMo/\gamma\text{-}Al_2O_3$ (10 wt% NiO, 30 wt% MoO_3) catalyst is sulfided with a mixture of 5 % H_2S in N_2 (500 ml/min) at 400°C and atmospheric pressure. 5 g of the catalyst is placed in a 1 inch O.D. quartz tubular reactor. The catalyst is heated from room temperature to 360°C at a rate of 5 °C/min and reduced in a flow of H_2 for 3.5 h. After that, catalyst is further heated up to 400°C at a rate of 5 °C/min in flowing H_2 and 5 % H_2S/N_2 and maintained at the temperature for 8 h for sulfidation. The gas flow rate is kept at 500 ml/min. Then the sulfided catalyst is purged by a flow of N_2 for 30 min. Figure 3.1 shows the schematic diagram of the sulfidation unit.

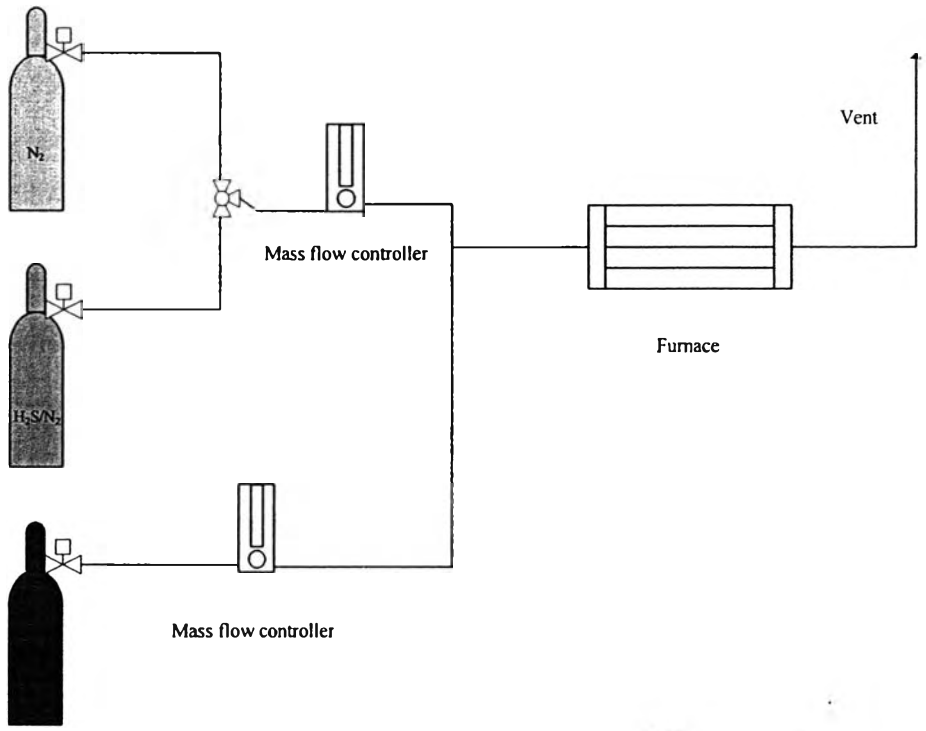

Figure 3.1 Simplified schematic diagram of sulfidation unit.

3.2.2 Catalyst Characterization

Temperature programmed oxidation (TPO): This technique is employed to analyze the amount and characteristics of coke formation on the spent catalysts. TPO of the spent catalysts was performed in a continuous flow of 2%O_2 in He and the temperature is linearly increased with a heating rate of 12°C/min. The oxidation reaction was conducted in a ¼" quartz fixed-bed reactor. The spent catalyst are placed in between the layers of quartz wool. The sample is flushed by flowing 2%O_2 in He for 30 min before the TPO was performed. CO_2 produced by the oxidation of coke species was further converted to methane using a methanizer filled with 15% Ni/Al_2O_3 and operated at 400°C. The methane is analyzed as a function of temperature using an FID detector.

3.2.3 Deoxygenation Experiments

The experiments are carried out in a high pressure fixed bed reactor as shown in Figure 3.2 and Figure 3.3. The stream of fatty acid in solvent, dodecane, is fed in the reactor using a high pressure pump. The flow of carrier gas and the reaction pressure are controlled by a mass flow controller and a back pressure regulator, respectively. The liquid product is collected in a condenser immersed in an ice bath, at the bottom of reactor. The catalytic activity is conducted at various temperatures, pressures, WHSV (Weigh Hourly Space Velocity), and H_2/Feed ratio as shown in Table 3.1.

Table 3.1 The reaction conditions for studying the optimum conditions for deoxygenation of palmitic acid and oleic acid

Parameters	Range
Reaction temperature	300-450°C
Reaction pressure	300-650 psig
WHSV	0.5-10 hr^{-1}
H_2/feed ratio	3-50 mole ratio
Feed concentration	5-100 wt%

The liquid product is analyzed by a gas chromatograph equipped with a FID detector. Gas phase sample is also collected and analyzed by a gas chromatograph equipped with a TCD detector.

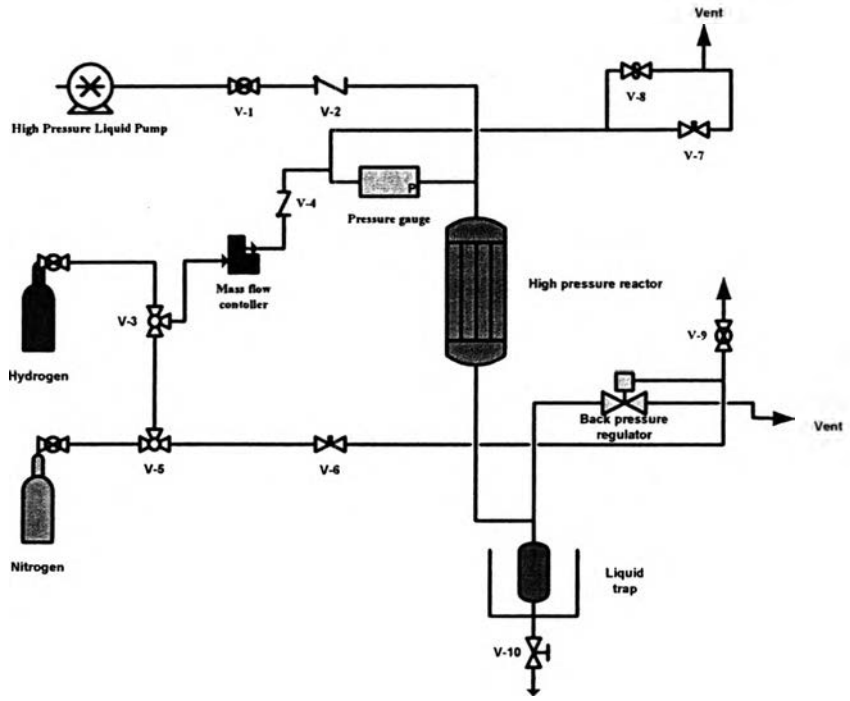

Figure 3.2 Schematic flow diagram of high pressure experiment unit.

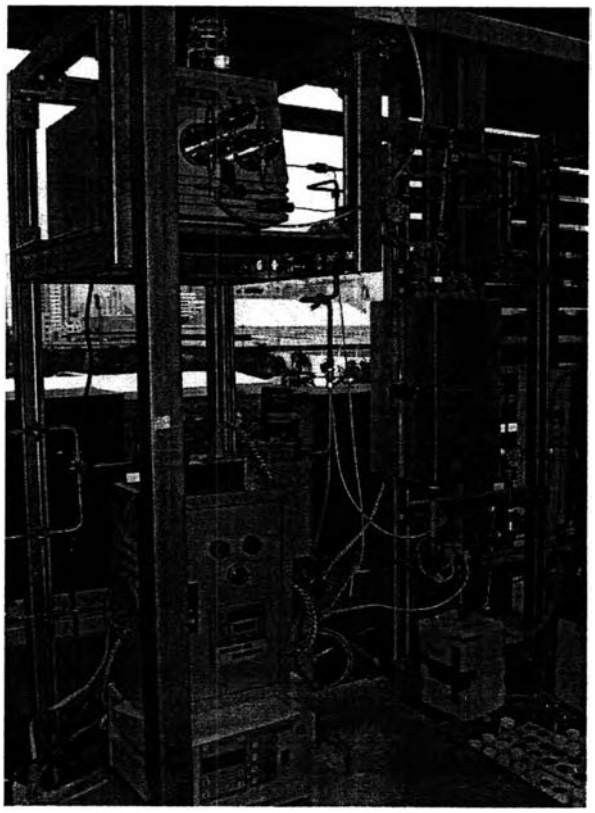

Figure 3.3 High pressure reactor for deoxygenation of fatty acids.

Table 3.2 Description of flow diagram

No.	Items	Functions
1	V1	On-off valve for liquid from high pressure liquid pump
2	V2	Checking valve for avoiding the backward flow of liquid from high pressure pump
3	V3	Three ways valve for switching nitrogen gas to hydrogen gas
4	V4	Checking valve for avoiding the backward flow of hydrogen or nitrogen gas
5	V5	Three valve for switching direction of nitrogen flow
6	V6	Needle valve for controlling pressure in back pressure regulator
7	V7	Needle valve for releasing gas from the system
8	V8	Relief valve to release to pressure overload in the system
9	V9	On-off valve for releasing the pressure from back pressure regulator
10	V10	Metering valve for releasing the product from condenser

3.2.4 Product Analysis

The liquid-phase samples are withdrawn from the bottom of reactor via a liquid trap valve. The liquid products from the deoxygenation contain non-polar and polar hydrocarbon. The non-polar hydrocarbon can be determined by using DB-5 column (non-polar column), whereas, the reactants, palmitic acid and oleic acid, are polar substance and have high boiling point (350-360 °C respectively). As a result, they cannot be analyzed by using the HP-5 column. Therefore, to improve the chromatographic behavior, these substances have to be esterified with BF_3-CH_3OH before injection into GC. The esterification of oleic acid is carried out in a hot oil bath at 64°C for 90 min, while that of palmitic acid is done at 100°C for 60 min.

In this research, GC/FID (HP 6890) is used as liquid product analyzer. The GC operating condition is summarized as follows:

Injection Temperature:	265°C
Detector Temperature:	300°C
Carrier gas:	He
Column Type:	Capillary column (HP-5:diameter 0.32mm length 30 m)

The following temperature program is used for product analysis:

Step	Temperature (°C)	Rate (°C/min)	Hold time (min)
1	130	-	5
2	169	1	5
3	300	5	48

Gas-phase analysis is conducted ex-situ for selected experiments to accomplish necessary data for the reaction pathways. The compositions of gas phase products are determined by GC/TCD.

The gas phase products are collected ex-situ for selected experiments to accomplish necessary data for the reaction pathways. The compositions of gas phase products are determined by GC/TCD (Perkin Elmer Autosystem, ARNEL). The GC operating condition is summarized as follows:

Injection Temperature:	60°C
Detector Temperature:	150°C
Oven Temperature:	35°C
Carrier gas:	He
Column Type:	Packed column (Carboxene1000)

To determine the quantity of the products, eicosane ($C_{20}H_{42}$) was used as the internal standard. The response factors of each product are calculated based on the following formula (Bruschweiler and Hautfenne, 1990):

$$R_x = (m_{is}/m_x) \times (A_x/A_{is})$$

Where R_x is response factor of reference substance x

m_{is} is mass in g of internal standard

m_x is mass in g of reference substance x

Ax is peak area of reference substance x

Ais is peak area of internal standard

The composition of each product is calculated following formula:

$$m'_x = (1/Rx) \times (m'_{is}/ m'_s) \times (A'_x/A'_{is})$$

Where: m'_x is percentage of mass of component x in sample

R_x is response factor of component x in sample

m'_{is} is mass in g of internal standard in sample

m'_x is mass in g of sample

$A'x$ is peak area of component x in sample

$A'is$ is peak area of internal standard in sample

The calculations of conversion and products selectivity are defined as shown in equation 1 and 2, respectively. Conversion of feed is defined as the mole ratio of glycerol consumed to the glycerol input as shown in Equation 1. Selectivity is defined as the ratio of the number of moles of the products formation to that of the feed consumed in the reaction as shown in Equation 2.

$$\text{Conversion (\%)} = \frac{\text{moles of feed converted}}{\text{moles of feed input}} \times 100 \quad (1)$$

$$\text{Selectivity to product i (\%)} = \frac{\text{moles of product i obtained}}{\text{moles of feed converted}} \times 100 \quad (2)$$