CHAPTER III
Experimental

3.1 Materials and Equipment

3.1.1 Chemicals

- Crude Palm oil
- Dodecane (99.9 % purity, Merck)
- Pyridine (99.9% purity, CARLO ERBA)
- N, O-bis(trimethyl)trifloroacetamide (98% purity, ACROS)
- 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)
- 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, Prax Air)
- Nitrogen (99 %purity, Prax Air)
- Helium (99 %purity, Prax Air)
- Air Zero (99 %purity, Prax Air)

3.1.3 Equipment

- High pressure packed-bed continuous flow reactor system consisting of mass flow controller (Brooks instrument 5850E), high pressure liquid pump (Water 515 HPLC), back pressure regulator (SIEMENS),

¾ " O.D.X16" long stainless steel reactor, and tubular furnace with temperature controller.

- Gas chromatograph (HP GC 7890)
- Temperature programmed oxidation apparatus (TPO)
- Hot & Stirrer plate (Cole Parmer)

3.2 Methodology

3.2.1 Catalytic Activity Testing

The catalytic deoxygenation of vegetable oil is carried out in a fixed-bed continuous flow reactor. A schematic of reactor system is shown in Fig. 3.1. In the experiment, the catalyst is first reduced for 3.5 h under flowing H_2 at the reduction temperature of each catalyst, typically, 200°C for Pd/C and 360°C for NiMo/γ-Al_2O_3. After the reduction, the temperature and pressure of the reactor are set to the desired value in flowing H_2. Then, the vegetable oil stream is introduced into the reactor using a high-pressure liquid pump. The liquid product is collected in an ice bath.

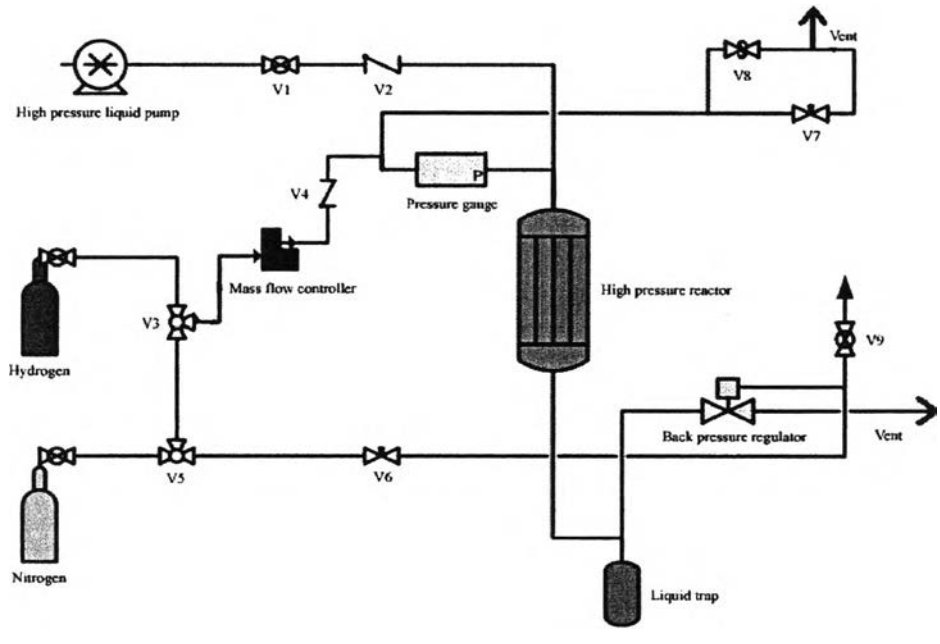

Figure 3.1 A schematic of high pressure catalytic testing unit.

Table 3.1 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

The catalytic activity is conducted at various temperatures, pressures, LHSV, and H_2/feed molar ratios as shown in Table 3.2.

Table 3.2 The reaction conditions for studying the optimum conditions for deoxygenation of palm oil

Parameters	Range
Reaction temperature	300–375°C
Reaction pressure	400–700 psig
LHSV	0.05–5 h^{-1}
H_2/feed molar ratio	15–30

3.2.2 Product Analysis

3.2.2.1 Liquid products

Typically, liquid samples are dissolved in pyridine and silylated with N,O-bis(trimethyl)-trifloroacetamide, BSTFA (Acros Organics, 98+%) in order to analyze by GC. Generally, 30 wt% pyridine and 100 wt% excess of BSTFA are added to the sample. After addition of silylation agent, the samples are heated at 120°C for 2 hours. The internal standard eicosane, $C_{20}H_{42}$ (Acros Organics, 99% of purity), is added for quantitative calculations.

In this research, the liquid reaction products were analyzed by an Agilent 7890 gas chromatograph equipped with a capillary column (DB5-HT) and a flame ionization detector. The GC operating condition is summarized as follows:

Injector temperature:	50°C
Detector temperature:	380°C
Carrier gas:	He
Column type:	Capillary column
	(DB-5HT: diameter 0.32mm length 30 m)

The following chromatographic temperature program is used for product analysis:

Table 3.3 The chromatographic temperature program for liquid product analysis

Step	Temperature (°C)	Rate (°C/min)	Holding time (min)
1	50	-	5
2	169	10	10
3	380	20	10

For the quantitative calculations of liquid 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

A_x is peak area of reference substance x

A_{is} is peak area of internal standard

The composition of each product is calculated following formula:

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

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 products selectivity of each product is calculated following equation:

$$\text{Selectivity to product i (\%)} = \frac{\text{wt\% of product i}}{\text{wt\% total liquid products}} \times 100$$

2.3.2.2 Gas products

In selected experiments, the gaseous products were collected using gas bag and analyzed by a gas chromatograph equipped with packed column (hayesep D100/120, PERKIN ELMER Autosystem GC, ARNEL) and a thermal conductivity detector to understand the reaction pathway.

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)

3.2.3 Catalyst Characterization

Temperature Programmed Oxidation (TPO)

This technique is employed to analyze the amount and characteristics of the coke deposited on the catalysts during reaction. TPO of the spent catalysts were 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 is conducted in a ¼" quartz fixed-bed reactor. The spent catalysts 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.