CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Feedstocks and Chemicals

- Jatropha oil (PTT Public Co,.Ltd.)
- Palm oil (PTT Public Co,.Ltd.)
- Beef fat (PTT Public Co,.Ltd.)
- Pork fat
- Chicken fat
- Dodecane (99.9 % purity, Merck)
- Palladium(II) nitrate hydrate (99.9 % purity, Aldrich)
- Titanium dioxide (TiO_2)
- Distilled water
- Pyridine (C_5H_5N, 98 % purity, Carlo Erba Reagents)
- N,O-bis (trimethylsilyl)-trifluoro acetamide (BSTFA, $C_8H_{18}F_3NOSi_2$, 99 % purity, ACROS)
- Eicosane ($C_{20}H_{42}$, 99 % purity, ACROS)

3.1.2 Gases

- Hydrogen (99 % purity, BIG)
- Nitrogen (99 % purity, TIG)
- Helium (99 % purity, TIG)
- Air zero (99 % purity, TIG)

3.2 Equipment

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

(SIEMENS), ¾ ″ O.D.x16 ″ long stainless steel reactor, and a three-zone tubular furnace with a temperature controller (Cabolite).

- Gas chromatograph (HP GC 7890)
- Hot & stirrer plate (Cole Parmer)

3.3 Experimental Procedures

3.3.1 Catalyst Preparation

1 wt% palladium supported titania catalyst was prepared by using incipient wetness impregnation method. The TiO_2 support was initially dried at 110 °C overnight and calcined at 500 °C for 4 h. The TiO_2 was then impregnated with the aqueous solution of $Pd(NO_3)_2$. Distilled water was used as solvent for preparing the metal precursor solutions. The impregnated catalyst was then dried at 110 °C overnight followed by calcined at 500 °C for 6 h. The prepared catalyst was finally pelletized, mashed and sieved to the particle size of 20/40 mesh.

3.3.2 Catalyst Characterizations

3.3.2.1 Thermo Gravimetry/Differential Thermal Analyzer (TG/DTA)

Thermo gravimetric analysis (TGA) is a type of testing performed on samples that determines changes in weight in relation to change in temperature. A derivative weight loss curve can identify the point where weight loss is most apparent. Thermal gravimetric analysis is the act of heating a mixture to a high enough temperature so that one of the components decomposes into a gas, which dissociates into the air. TGA is commonly employed to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

3.3.2.2 Brunauer-Emmett-Tellet (BET) Surface Area Analysis

The surface area of the fresh and spent catalysts was measured by BET surface area analyzer (Quantachrome/Autosorb 1). The sample

was first outgassed to remove the humidity and volatile adsorbents adsorbed on surface under vacuum at 150 °C for 4 h prior to the analysis. Then, N_2 was purged to adsorb on surface, and the quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressure by static volumetric method was measured. The solid sample was maintained at a constant temperature of the sample cell until the equilibrium was established. This volume-pressure data was used to calculate the BET surface area.

3.3.2.3 Temperature Programmed Oxidation (TPO)

Temperature programmed oxidation (TPO) was carried out to determine the amount and characteristics of coke formed on the spent catalysts. TPO profiles of the spent catalysts were performed in a continuous flow of 2% O_2/He while the temperature was linearly ramped to 1073 K with a heating rate of 12 K/min. The sample (30 mg) was placed in a ¼" quartz fixed bed reactor. The CO_2 produced by the oxidation of coke was further converted to methane over 15% Ni/Al_2O_3 catalyst in the presence of hydrogen at 673 K. The methane obtained was analyzed online by a FID detector. The amount of oxidized coke was calibrated using 100 pulses of pure CO_2.

3.3.3 Feedstock Characterizations

3.3.3.1 Gas Chromatography with Flame Ionization Detector (GC/FID) - Modified AOAC 996.06 Method

All feedstocks were sent to Central Laboratory (Thailand).Co.,Ltd. to determine fatty acid compositions by gas chromatography with flame ionization detector (GC/FID) in accordance with a modified AOAC 996.06 method. In this analysis method, fat and fatty acids were extracted from feedstocks by hydrolytic methods. Pyrogallic acid was added to minimize oxidative degradation of fatty acid during analysis. Triglyceride, triundecanoin ($C_{11:0}$), was added as internal standard. Fat was extracted into ether, and then methylated to fatty acid methyl esters (FAMEs). Total fat was calculated as sum of individual fatty acids expressed as triglyceride equivalents. Saturated and monosaturated fats were calculated as sum of respective fatty acids. Monosaturated fat includes only *cis* form.

3.3.3.2 Inductively Coupled Plasma Optical Emission Spectrometry
(ICP-OES)

Inductively coupled plasma optical emission spectrometry (ICP-OES) is an analytical system used for the detection of trace metals. The sample was prepared follow the flow chart as shown in Figure 3.1. This analysis is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample. The ICP-OES is composed of two parts: the ICP and the optical spectrometer. The ICP torch consists of 3 concentric quartz glass tube and a coil of the radio frequency (RF) generator which surrounds part of this torch. Argon gas is typically used to create the plasma.
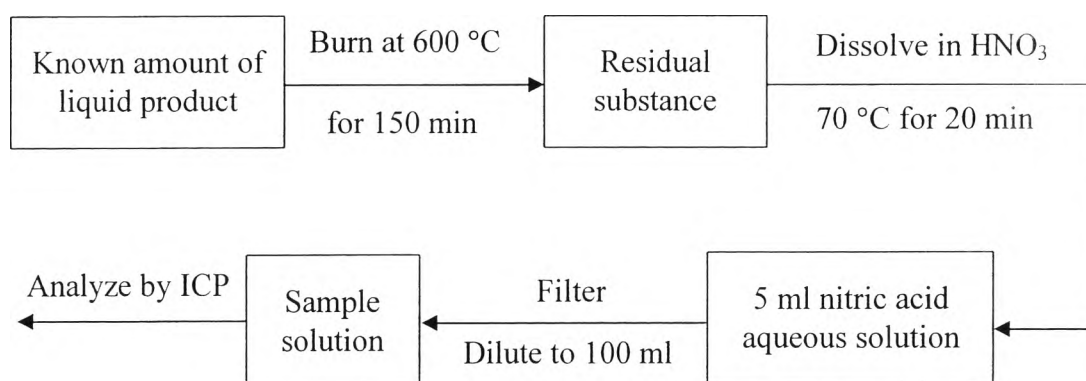
Known amount of liquid product	Burn at 600 °C for 150 min	Residual substance	Dissolve in HNO$_3$ 70 °C for 20 min

Analyze by ICP	Sample solution	Filter Dilute to 100 ml	5 ml nitric acid aqueous solution

Figure 3.1 Flow chart to prepare the sample for ICP Analysis

3.3.4 Hydrodeoxygenation Experiments

The experiments were carried out in a high pressure fixed bed reactor, as shown in Figure 3.2. First, the prepared catalysts were placed in the reactor and reduced by flowing hydrogen at 500 psig for 3.5 h. The temperature was increased with a rate of 5 °C/min until reaching the reduction temperature, typically 200 °C for the Pd metal catalysts. Then, the stream of feedstock was fed to the reactor using a high pressure pump. The flow of carrier gas and the reaction pressure was controlled by a mass flow controller and a back pressure regulator, respectively. The liquid product was collected in a condenser immersed in an ice bath at the

bottom of reactor and analyzed by a gas chromatograph equipped with a FID detector. Also, gas phase sample was collected and analyzed by a gas chromatograph equipped with a TCD detector.
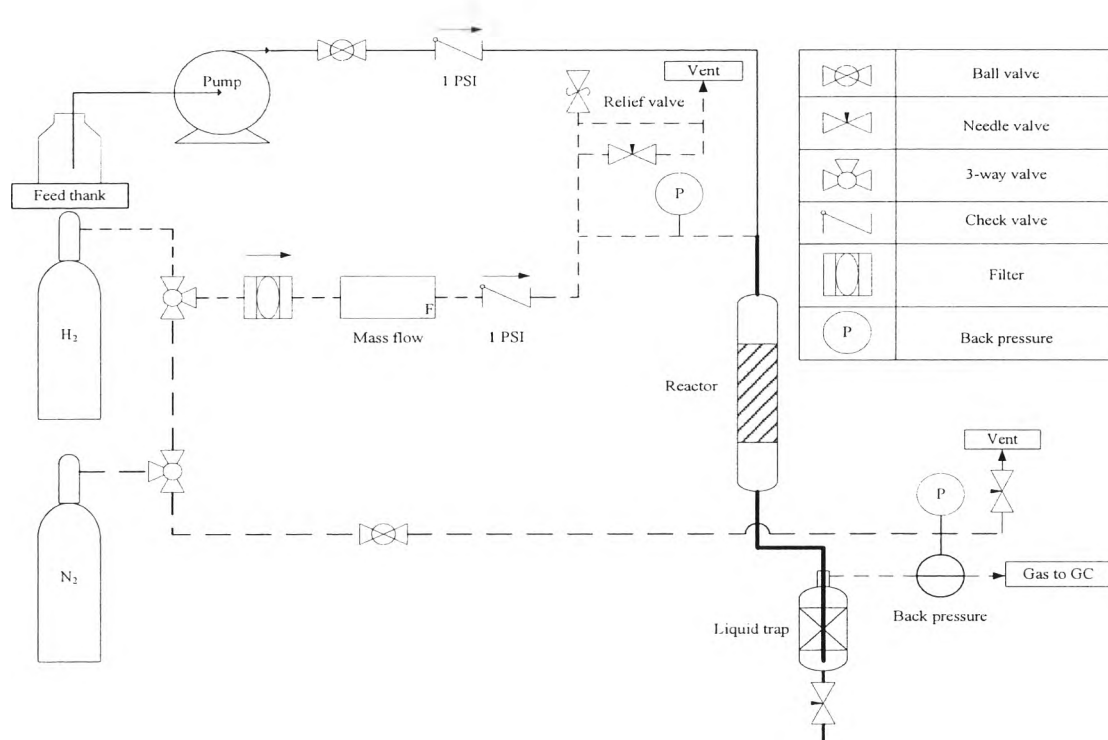

Figure 3.2 A schematic flow diagram of high pressure experiment set.

Production of the hydrogenated biodiesel by the deoxygenation of biomass feedstocks conducted at temperature, pressure, and H_2/feed molar ratio, as shown in Table 3.1.

Table 3.1 The reaction conditions for the production of hydrogenated biodiesel

Parameters	Condition
Reaction temperature	325 °C
Reaction pressure	500 psig
H_2/feed molar ratio	30

3.3.5 Product Analysis

The liquid products were analyzed by a gas chromatograph equipped with a FID detector. The liquid products from the hydrodeoxygenation contain both non polar and polar hydrocarbons. The non-polar hydrocarbons can be determined by using DB-5 column (non-polar column), whereas the polar hydrocarbons cannot be analyzed by using the HP-5 column. Therefore, the liquid products were dissolved in pyridine and silylated with N,O-bis (trimethylsilyl)-trifluoro acetamide (BSTFA) to improve the chromatographic behavior and then were analyzed by an Agilent Technology 7890A gas chromatograph equipped with a FID detector. Eicosane ($C_{20}H_{42}$) was added as internal standard for quantitative calculations.

The GC operating conditions are as follows:

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

In addition, the compositions of gas phase products will be determined by GC/TCD (Perkin Elmer Autosystem, ARNEL).

The GC operating conditions are as follows:

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

The calculations of conversion and products selectivity are defined as shown in Equations 1 and 2, respectively. Conversion of feed is defined as the mole ratio of feed consumed to the feed input, as shown in Equation 1. Selectivity is

defined as the ratio of the number of moles of the products formed to that of the feed consumed in the reaction, as shown in Equation 2.

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

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