# CHAPTER III
# EXPERIMENTAL

## 3.1 Materials

### 3.1.1 Feedstocks and Chemicals

- *Jatropha oil*
- *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)*

### 3.1.2 Gases

- *Nitrogen (99 %purity, TIG)*
- *Helium (99 %purity, TIG)*
- *Air Zero (99 %purity, TIG)*
- *Hydrogen (99.95%purity, BIG)*

## 3.2 Equipment

- High pressure packed-bed continuous flow reactor consisting of Brooks 5850E mass flow controllers, a Water 515 high pressure liquid pump, a Glassroom furnace, a Siemens back pressure regulator, and an Agilent 6890 Gas chromatograph

## 3.3 Software

### 3.3.1 ICAS Software

ICAS was developed by CAPEC- Technical University of Denmark. (CAPEC software is closely related to the CAPEC research projects and it is not a commercial software). ICAS is an Integrated Computer Aided System consisting of a number of toolboxes that helps to solve a wide range of problems in an efficient manner. ICAS combines computer-aided tools for modeling, simulation (including property prediction), synthesis/design, control and analysis into a single integrated system. These tools are present in ICAS as toolboxes. (http://www.capec.kt.dtu.dk/ Software/ICAS-and-its-Tools/)

### 3.3.2 PRO/II® Software

PRO/II® process simulation software is a steady-state process simulator for process design, revamp, and operational analysis that performs rigorous mass and energy balances for a wide range of chemical processes. From oil & gas separation to reactive distillation, PRO/II® offers the most comprehensive simulation solution available.

## 3.4 Methodology

### 3.4.1 Catalyst Pretreatment

The commercial catalysts are crushed and sieved to obtain a particle size of 20/40 mesh. The catalyst is placed in the reactor and reduced in flowing hydrogen at 500 psig for 3.5 h. The temperature is increased with a rate of 5 °C/min until reaching the reduction temperature, typically, 200 °C for Pd/C, and 360 °C for $NiMo/Al_2O_3$.

### 3.4.2 Hydrodeoxygenation of Jatropha Oil

The experiments will be carried out in a high pressure fixed bed reactor as shown in Figure 3.1 and the description of flow diagram is shown in Table 3.1. The stream of vegetable oil is fed into the reactor using a high pressure pump. The flowrate of hydrogen 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 and analyzed by a gas chromatograph equipped with a FID detector. Also, gas phase sample is collected and analyzed by a gas chromatograph equipped with a TCD detector.

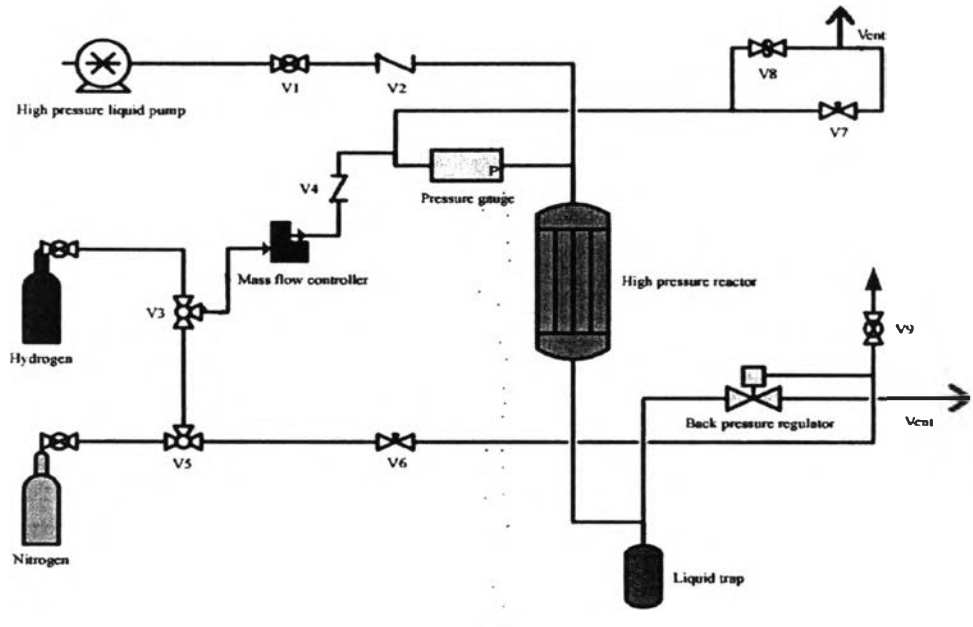


**Figure 3.1** A schematic flow diagram of high pressure experiment set.

Production of the hydrogenated biodiesel by the hydrodeoxygenation of vegetable oils for engine test is conducted at temperatures, pressures, and $H_2$/Feed ratio as shown in Table 3.2.

**Table 3.1** Description of flow diagram of high pressure experiment set

| 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 |

| No. | Items | Functions |
|---|---|---|
| 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 |

**Table 3.2** The reaction conditions for producing hydrogenated biodiesel for engine test

| Parameters | Condition |
|---|---|
| Reaction temperature | 325 °C |
| Reaction pressure | 500 psig |
| $H_2$/feed ratio | 30 (mole ratio) |

3.4.3 Product Analysis

The liquid products will be analyzed by a gas chromatograph equipped with a FID detector. The liquid products from the hydrodeoxygenation contain non-polar and polar hydrocarbon. The non-polar hydrocarbon can be determined by using DB-5 column (non-polar column), whereas, the polar hydrocarbon 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. For the reactant, triglyceride has to be transesterified with $CHCl_3/CH_3OH$ before injection into GC.

The GC operating condition:

Injection temperature: 265 °C

Detector temperature: 300 °C

Carrier gas: He

Column type: Capillary column

(HP-5:diameter = 0.32mm, length = 30 m)

In addition, the compositions of gas phase products will be determined by GC/TCD.

The GC operating condition:

| | |
|---|---|
| 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 equation 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 formation to that of the feed consumed in the reaction as shown in Equation 2.

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

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

3.4.4 Process Simulation Procedure

The methodology is divided into three parts, as listed in the Figure 3.2.

*3.4.4.1 Process Design*

In this step, various data for hydrogenated biodiesel and biodiesel production, such as raw materials, products, reaction, process flowsheets and other information, are collected from various sources. In addition, the lab-scale experimental data are collected for hydrogenated biodiesel production.

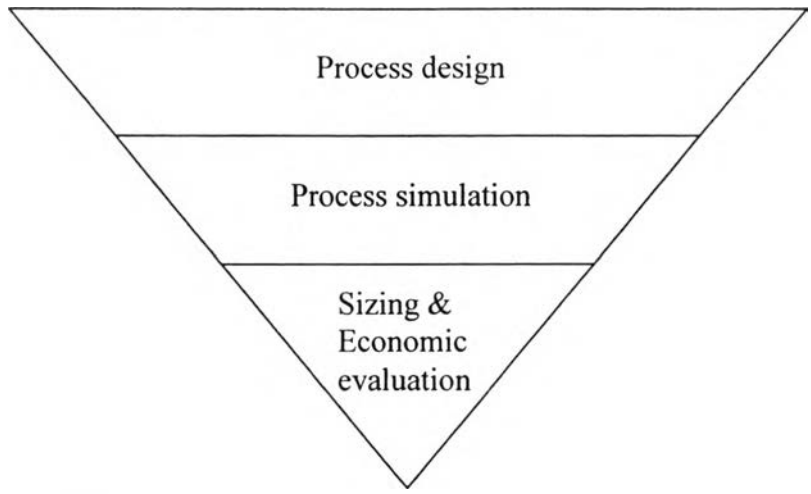


**Figure 3.2** Methodology for process simulation.

*3.4.4.2 Process Simulation*

The collected data are analyzed by ICAS or PRO/II® to discover sensitive points. This is the most important step of the project. It includes three main steps:

1) *Build the structures of components not in the database of PRO/II® in ICAS to obtain the property predictions of those components.*
2) *Build the biodiesel and hydrogenated biodiesel plants in PRO/II® and set-up mass balance for process using data collected from the literature and the lab-scale experiment.*
3) *Build the energy balance for each process.*

*3.4.4.3 Sizing and Economic Evaluation*

The mass and energy balance results from process simulation step will be used as input data to analysis. The purpose of this step is to evaluate the economics and sensitivity of the two processes.