CHAPTER III
Experimental

3.1 Materials

Methyl Butyrate ($C_3H_7COOCH_3$, 99%), 4-Heptanone ($C_3H_7COC_3H_7$, ≥98%), Dibutyl ether ($C_4H_9OC_4H_9$, 99%), and Butyl butyrate ($C_4H_9COOC_4H_9$, ≥98%) were purchased from Aldrich Co., Ltd., Butyric acid (C_3H_7COOH, 99%) was purchased from Fluka Co.,Ltd., Butanal (C_3H_7CHO, 99%), and n-Butanol (C_4H_9OH, >99.4%) were purchased from Sigma-Aldrich Co.,Ltd., n-Heptane (C_7H_{16}, 99.5%) was purchased from Carlo Erba Co., Ltd., n-Octane (C_8H_{18}, 99%) was purchased from Labscan Asia Co., Ltd. The commercial $NiMo/Al_2O_3$ (KF-840, containing 12-16 wt% molybdenum and 3-5 wt% nickel) was supported by PTT Research and Technology Institute, PTT Public Company Limited, Thailand. The commercial 5wt% Pd/C was purchased from Sigma-Aldrich Co., Ltd.

3.2 Equipment

- High pressure packed-bed continuous flow reactor
- Mass flow controller (Brooks instrument 5850E)
- High pressure liquid pump (Waters 515 HPLC)
- Gas chromatograph (HP GC 5890)
- Gas chromatograph (HP GC 6890)
- Back pressure regulator (SIEMENS)
- Oven

3.3 Methodology

3.3.1 Catalyst Pretreatment

The commercial catalyst with particle size 40/20 mesh is placed in the reactor and reduced in a flowing hydrogen at 400 psig for 3.5 h. The temperature is increased with a heating rate of 10 °C/min until reaching the reduction temperature, typically, 200 °C for Pd/C, and 360 °C for $NiMo/Al_2O_3$.

3.3.2 Hydrogenation Experiments

The hydrogenations of oxygen-containing C4 compounds are carried out in a 3/4 inch O.D., continuous flow fixed-bed reactor under high pressure conditions. The catalytic activity measurements are conducted by feeding stream of oxygen-containing C4 compound to reactor by using a high pressure pump. The reaction pressure is controlled by a mass flow controller and a back pressure regulator. The liquid product was trapped and collected in a condenser while the gas product was sent directly to sample loop of 10-port valve. Both gas product and liquid product were collected and analyzed hourly. The gas product was injected automatically to a gas chromatograph, Hewlett Packard 5890 equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID). The liquid product was analyzed by a gas chromatograph, Hewlett Packard 6890 equipped with a flame ionization detector (FID).

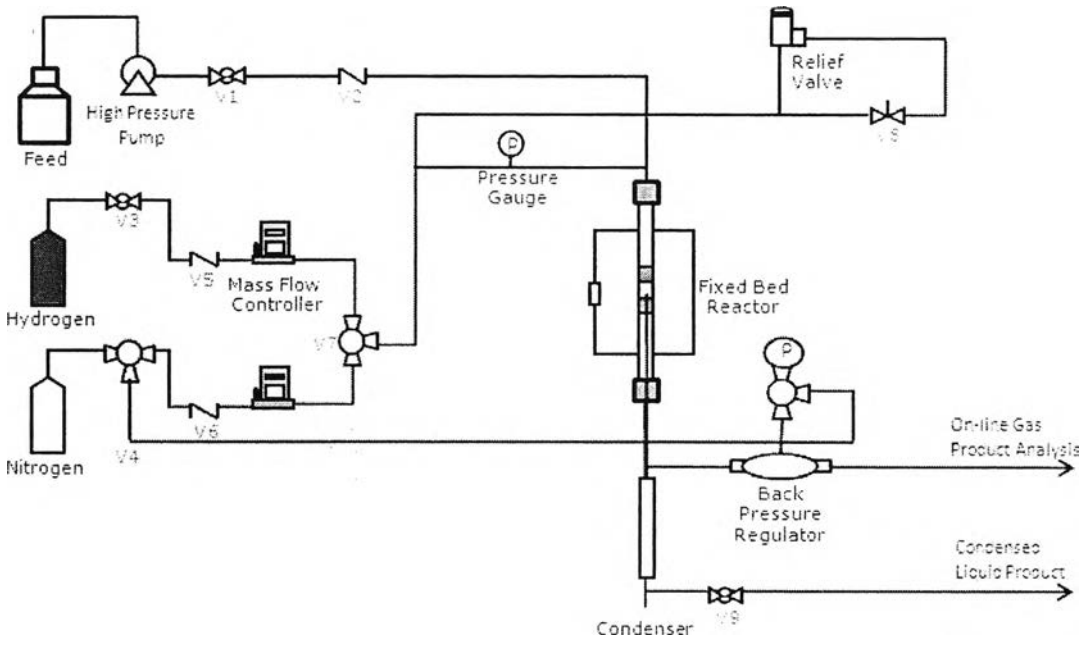

Figure 3.1 A schematic flow diagram of high pressure experiment set.

3.3.3 Products Analysis

In experiment for oxygen-containing C4 compounds, the composition of gas and liquid products was analyzed qualitatively on-line in interval of 1 h, GC/FID and GC/TCD (HP 5890) is used for gas phase products. While the liquid phase products is analyzed by using GC/FID (HP 6890), The GC operating condition is summarized as follows:

For on-line gas phase product:

Injection temperature :	200°C
Detector temperature :	300°C
Carrier gas :	He
Column type :	Packed column

(Hyasep D: diameter 1/8 inch, length 10 m)

Injection temperature : 200°C

Detector temperature : 300°C

Carrier gas : He

Column type : Capillary column

(HP-PLOT U: diameter 0.53mm length 30 m)

For liquid phase product:

Injection temperature : 200°C

Detector temperature : 270°C

Carrier gas : He

Column type : Capillary column

(Stabilwax: diameter 0.32mm length 30 m)

The following chromatographic temperature program is used for product analysis:

Table 3.1 The chromatographic temperature program for gas phase product analysis

Step	Temperature (°C)	Rate (°C/min)	Hold time (min)
1	40	-	5
2	180	10	10

Table 3.2 The chromatographic temperature program for liquid phase product analysis

Step	Temperature (°C)	Rate (°C/min)	Hold time (min)
1	40	-	5
2	180	8	5

For the quantitative calculations of liquid products, n-octane (C_8H_{18}) was used as the standard. The response factors of each product are calculated based on the following formula, as shown in Equation 1:

$$R_x = \left(\frac{m_{is}}{A_{is}}\right)\left(\frac{A_x}{m_x}\right) \quad (1)$$

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 conversion and product selectivity percentage are calculated by Equations 2 and 3, respectively. Conversion of feed is defined as the moles ratio of C atom in product to moles of C atom in feed, as shown in Equation 2. Selectivity is defined as the moles ratio of C atom of product i to moles of C atom of overall product, as shown in Equation 3.

$$\text{Conversion (\%)} = \frac{\text{moles of C atom in producted (wt\%)}}{\text{moles of C atom in feed (wt\%)}} \times 100 \quad (2)$$

$$\text{Selectivity of product i (\%)} = \frac{\text{moles of C atom in product i (wt\%)}}{\text{moles of C atom in overall product (wt\%)}} \times 100 \quad (3)$$