



## CHAPTER IV

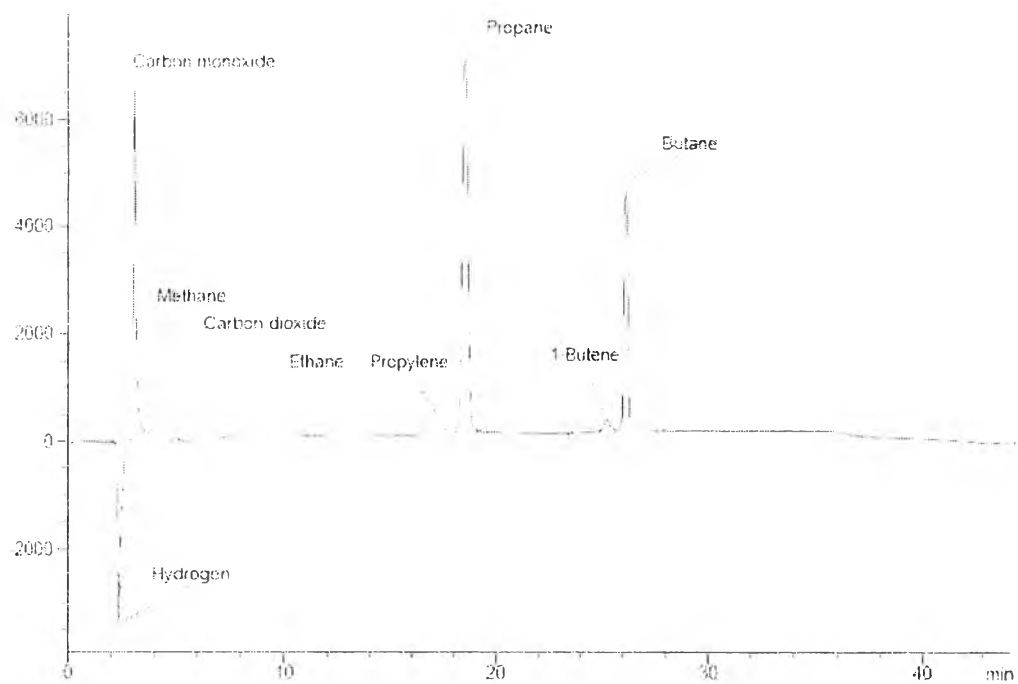
### RESULTS AND DISCUSSION

#### 4.1 Standard Analysis Chromatogram

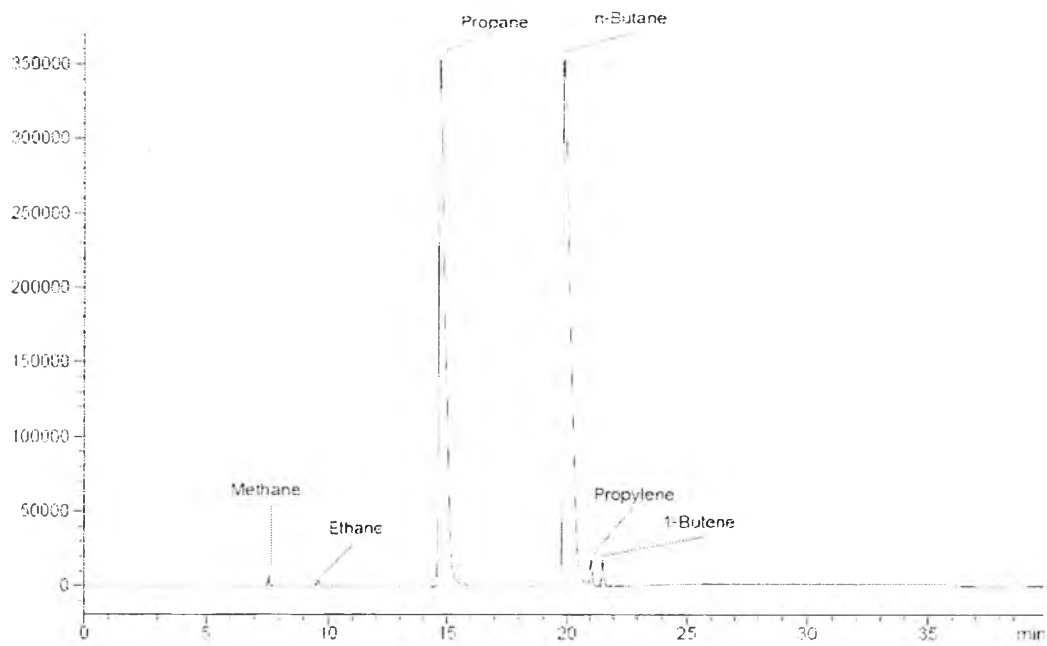
The reference standard for gas product was analyzed by a HP-5890 equipped with both thermal conductivity detector (TCD) with Hyasep-D column (10 m. x 1/8 inch), and flame ionized detector (FID) with HP-Plot U column (30 m. x 0.53 m. x 1.0  $\mu\text{m}$ .). Following the method for product analysis as described in Chapter 3. On TCD signal, it was found that the retention time of hydrogen, carbon monoxide, methane, carbon dioxide, propylene, propane, 1-butene, and butane are 2.2, 2.8, 3.9, 5.0, 17.8, 18.2, 25.6 and 26.1, respectively (see Fig. 4.1). On FID signal, it was found that the retention time of methane, propane, butane, propylene, and 1-butene are 7.6, 14.5, 20.0, 20.7, and 21.5, respectively (see Fig. 4.2).

The reference standard for liquid product was analyzed by a HP-6890 equipped with flame ionized detector (FID) with StabilWax column (30 m. x 0.32 m. x 1.0  $\mu\text{m}$ .). Following the method for product analysis as described in Chapter 3, it was found that the retention time of n-heptane, butanal, dibutyl ether, methyl butyrate, 4-heptanone, n-butanol, butyl butyrate and butyric acid are 1.5, 3.3, 5.5, 6.3, 9.7, 10.3, 12.0, and 18.6, respectively. The chromatogram of standard oxygen-containing C4 compounds is shown in Fig. 4.3.

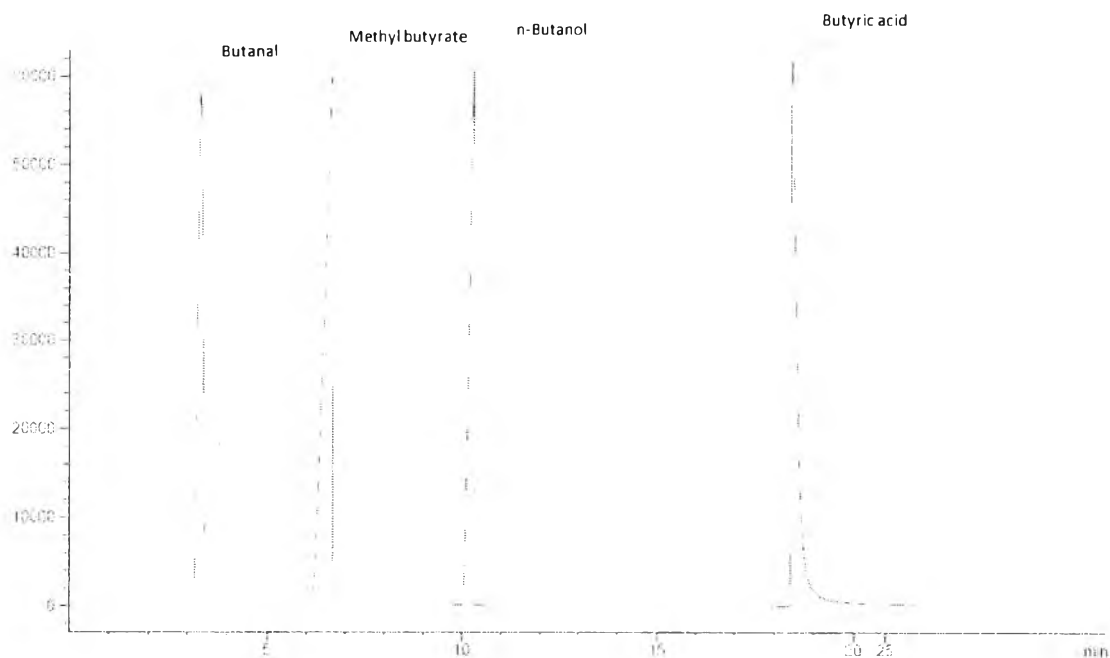
To find out the response factor value of each compound, the n-octane was used as the reference. Table 4.1 shows the response factor of each substance in the reference standard which contains methanol, n-butanol, butanal, butyric acid, methyl butyrate, dibutyl ether, 4-heptanone, and butyl butyrate.



**Figure 4.1** Chromatogram of standard gas mixture from TCD detector.



**Figure 4.2** Chromatogram of standard gas mixture from FID detector.



**Figure 4.3** Chromatogram of standard liquid mixture analyzed by FID.

**Table 4.1** Response factors of each substance in the reference standard

Substances	Response factor
Methanol	0.5353
n-Butanol	0.6205
Butanal	0.5674
Butyric acid	0.5905
Methyl butyrate	0.7054
Dibutyl ether	0.5278
4-Heptanone	0.6374
Butyl butyrate	0.6745

## 4.2 Hydrogenation of Oxygen-containing C4 Compounds over Pd/C Catalyst

### 4.2.1 Hydrogenation of Methyl Butyrate over Pd/C Catalyst

#### *4.2.1.1 Effect of Reaction Temperature*

To study the effect of the reaction temperature, the hydrogenation of methyl butyrate was conducted at 400 psig, LHSV of 2.0 h<sup>-1</sup>, and H<sub>2</sub>/feed molar ratio of 2.5. The results in Table 4.2 revealed that conversion of methyl butyrate was dramatically increased with reaction temperature (from 25.85% at 300°C to 70.92% at 350°C). It was also observed the change in product selectivity as propane and CO increased with increasing reaction temperature. But selectivities to butyric acid and butyl butyrate were found to decrease. The side-products from hydrolysis, methanol and its condense product, dimethyl ether in gas phase were also increased with reaction temperature. In addition, C<sub>3</sub>/C<sub>4</sub> ratio was found to increase with reaction temperature, revealed that hydrodecarbonylation on Pd/C is prefer to undergo at high reaction temperature. Moreover, the deactivation of active sites of hydrodeoxygenation was also observed since the ratio of C<sub>3</sub>/C<sub>4</sub> was increased and selectivity to hydrodeoxygenated product, butane was decreased as a function of time on stream which possibly cause by coking since CO from hydrodecarbonylation can be occurred in competitive adsorption onto Pd surface, resulting in a loss of catalytic activity (Resasco *et al.*, 2008).

**Table 4.2** Product distribution from methyl butyrate over Pd/C at various reaction temperatures (Reaction condition : pressure = 400 psig, H<sub>2</sub>/Feed ratio = 2.5, and LHSV = 2 h<sup>-1</sup>)

Reaction Temperature (°C)	300		350	
Time on stream (h)	1	6	1	6
Conversion	25.85	25.13	70.92	70.05
Selectivity (%)				
Carbon monoxide	10.41	10.18	21.82	20.81
Methanol	24.14	24.21	22.23	22.84
Dimethyl ether	2.82	2.17	4.65	4.23
Propane	16.12	15.55	32.71	31.33
Butane	2.29	1.14	3.63	2.44
Butanal	1.68	1.70	0.44	0.47
n-Butanol	0.98	0.99	1.08	1.37
Heptane	0.14	0.14	0.98	0.85
4-Heptanone	1.30	1.32	4.19	3.74
Butyric acid	30.52	32.41	6.87	10.21
Butyl butyrate	9.46	9.72	1.29	1.38
Others	0.14	0.47	0.11	0.33
C <sub>3</sub> /C <sub>4</sub> ratio	7.04	13.64	9.01	12.84

#### 4.2.1.2 Effect of Reaction Pressure

To study the effect of the reaction temperature, the hydrogenation of methyl butyrate was conducted at 350°C, LHSV of 2.0 h<sup>-1</sup>, and H<sub>2</sub>/feed molar ratio of 2.5. The results in Table 4.3 showed that reaction pressure affects conversion of methyl butyrate adversely (from 72.64% at 200 psig to 60.25% at 600 psig). Selectivities to hydrodecarbonylated products (propane and carbon monoxide) were found to decrease with reaction pressure. By contrast, selectivities to butane, n-butanol, butanal which are hydrogenated product and intermediates were increased with reaction pressure indicating that hydrodeoxygenation over Pd/C is slightly prefer at higher pressure. The increase in reaction pressure also resulted in higher amount of butyric acid and coupling ester, butyl butyrate. Selectivities to side-

product from hydrolysis, methanol and its condense counter part, dimethyl ether in gas phase went inversely. Furthermore,  $C_3/C_4$  ratio was decreased with reaction pressure. Nevertheless, reaction pressure insignificantly affects the reaction pathway of Pd/C, since Pd/C prefers hydrodecarbonylation path resulting in propane and carbon monoxide as the main products even at elevated pressure.

**Table 4.3** Product distribution from methyl butyrate over Pd/C at various reaction pressures (Reaction condition : temperature = 350°C,  $H_2$ /Feed ratio = 2.5, and LHSV = 2  $h^{-1}$ )

Reaction Pressure (psig)	200		400		600	
Time on stream (h)	1	6	1	6	1	6
Conversion	72.64	72.19	70.92	70.05	60.25	58.74
Selectivity (%)						
Carbon monoxide	22.86	22.01	21.82	20.81	17.02	16.35
Methanol	20.67	20.91	22.23	22.84	24.87	25.09
Dimethyl ether	5.43	5.21	4.25	4.23	2.77	2.81
Propane	34.82	33.61	29.71	29.33	25.52	24.58
Butane	1.52	1.26	3.63	2.44	3.12	2.32
Butanal	0.43	0.45	0.44	0.47	0.49	0.53
n-Butanol	0.28	0.30	1.08	1.37	1.70	1.82
Heptane	0.35	0.76	0.58	0.85	0.73	0.78
4-Heptanone	3.22	3.44	4.19	3.74	3.70	3.06
Butyric acid	9.52	10.97	10.17	12.21	17.02	19.26
Butyl butyrate	0.70	0.74	1.29	1.38	2.85	3.06
Others	0.20	0.34	0.61	0.33	0.21	0.34
$C_3/C_4$ ratio	22.91	26.68	8.19	12.02	8.18	10.59

## 4.2.2 Hydrogenation of Butyric Acid over Pd/C Catalyst

### 4.2.2.1 Effect of Reaction Temperature

To study the effect of the reaction temperature, the hydrogenation of butyric acid was conducted at 400 psig, LHSV of 2.0  $h^{-1}$ , and  $H_2$ /feed molar ratio of 2.5. The reaction temperature was varied from 250 to 350°C.

The results in Table 4.4 revealed that conversion of butyric acid was significantly increased with increasing reaction temperature (from 4.65% at 250°C to 57.38% at 350°C). The increase in reaction temperature also resulted in the hydrodecarbonylated products which are propane and carbon monoxide. However, the ketonic decarboxylated product and its hydrogenated product which are 4-heptanone and heptane were also slightly increased with reaction temperature. On other hand, selectivities to hydrogenated intermediates and product, butanal, n-butanol and butane were found in rather small amount, assert a hydrodecarbonylation performance of Pd/C which generally undergo via hydrodecarbonylation path. In addition, selectivity to coupling ester, butyl butyrate was decreased with reaction temperature. Nevertheless, C<sub>3</sub>/C<sub>4</sub> ratio was significantly increased with reaction temperature, revealed that reaction tends to undergo hydrodecarbonylation path at elevated reaction temperature.

**Table 4.4** Product distribution from butyric acid over Pd/C at various reaction temperatures (pressure = 400 psig, H<sub>2</sub>/Feed ratio = 2.5, and LHSV = 2 h<sup>-1</sup>)

Reaction Temperature (°C)	250		300		350	
Time on stream (h)	1	6	1	6	1	6
Conversion	4.65	4.23	45.42	42.56	57.38	53.65
Selectivity (%)						
Carbon monoxide	17.54	16.94	26.51	27.58	29.91	30.23
Propane	25.51	25.01	40.75	41.98	46.52	47.85
Butane	6.00	5.78	3.32	3.54	1.75	1.63
Butanal	3.23	3.30	3.63	3.55	1.67	1.55
n-Butanol	4.34	4.11	3.13	3.34	1.56	1.45
Dibutyl ether	0.27	0.34	0.98	0.88	1.24	1.11
Heptane	0.25	0.18	0.54	0.47	1.27	1.34
4-Heptanone	1.25	1.35	2.06	2.12	2.58	2.32
Butyl butyrate	41.38	42.78	19.05	16.85	13.86	13.08
Others	0.48	0.39	0.57	0.16	0.91	0.78
C <sub>3</sub> /C <sub>4</sub> ratio	4.25	4.32	12.27	11.85	26.58	29.35

#### 4.2.2.2 Effect of Reaction Pressure

To study the effect of the reaction pressure, the hydrogenation of butyric acid was conducted at 300°C, LHSV of 2.0 h<sup>-1</sup>, and H<sub>2</sub>/feed molar ratio of 2.5. The results in Table 4.5, revealed that reaction pressure slightly affect the conversion of butyric acid (from 47.81% at 200 psig to 40.32% at 600 psig). Selectivities to hydrodecarbonylated products, propane and carbon monoxide, were found to decrease with reaction pressure. By contrast, selectivities to hydrodeoxygenated products were increased with reaction pressure. That is, an increase in reaction pressure resulted in the formation of hydrodeoxygenated products together with coupling ester, while suppress hydrodecarbonylation reaction. Furthermore, C<sub>3</sub>/C<sub>4</sub> ratio was decreased with reaction pressure (from 26.02% at 200 psig to 6.22% at 600 psig) indicating that hydrodeoxygenation is preferred at elevated reaction pressure. But however, Pd/C was selective to hydrodecarbonylation path as propane and carbon monoxide were found as the main product.



**Table 4.5** Product distribution from butyric acid over Pd/C at various reaction pressures (Reaction condition : temperature = 300°C, H<sub>2</sub>/Feed ratio = 2.5, and LHSV = 2 h<sup>-1</sup>)

Reaction Pressure (psig)	200		400		600	
Time on stream (h)	1	6	1	6	1	6
Conversion	47.81	45.23	45.42	42.56	40.32	37.65
Selectivity (%)						
Carbon monoxide	31.61	30.98	26.51	27.58	21.32	21.11
Propane	48.65	47.92	40.75	41.98	32.70	32.26
Butane	1.87	1.78	3.32	3.54	5.26	5.45
Butanal	2.15	2.05	3.63	3.55	4.14	4.23
n-Butanol	1.75	1.67	3.13	3.34	4.15	4.01
Dibutyl ether	0.37	0.28	0.98	0.88	1.22	1.12
Heptane	0.29	0.31	0.54	0.47	0.62	0.59
4-Heptanone	2.31	2.41	2.06	2.12	1.99	1.78
Butyl butyrate	11.07	12.57	19.05	16.85	28.30	29.44
Others	0.22	0.34	0.57	0.16	0.92	0.60
C <sub>3</sub> /C <sub>4</sub> ratio	26.02	26.92	12.27	11.85	6.22	5.92

### 4.2.3 Hydrogenation of Butanal over Pd/C Catalyst

#### 4.2.3.1 Effect of Reaction Temperature

To study the effect of the reaction temperature, the hydrogenation of butanal was conducted at 400 psig, LHSV of 2.0 h<sup>-1</sup>, and H<sub>2</sub>/feed molar ratio of 2.5. The results in Table 4.6 showed that the conversion of butanal was high compared to those of butyric acid, and methyl butyrate, which close to 100% conversion even at 300°C. This indicates the high reactivity of aldehyde group in butanal. Selectivities to propane, carbon monoxide, and butane were found to increase with reaction temperature, while the selectivities of condensed product and hydrodeoxygenated intermediate; in this case, dibutyl ether and n-butanol, were significantly decreased when reaction temperature is increased. Since, selectivity to ketonic decarboxylated products (heptane and 4-heptanone) were unnoticeable

changed, and  $C_3/C_4$  ratio was slightly decreased, but reaction still prefer to undergo hydrodecarbonylation path, it can point out that reaction temperature does not affect the reaction pathway of butanal over Pd/C.

**Table 4.6** Product distribution from butanal over Pd/C at various reaction temperatures (Reaction condition : pressure = 400 psig,  $H_2$ /Feed ratio = 2.5, and LHSV =  $2\text{ h}^{-1}$ )

Reaction Temperature (°C)	250		300		350	
Time on Stream (h)	1	6	1	6	1	6
Conversion	77.25	77.35	95.3	93.17	99.46	98.49
Selectivity (%)						
Carbon monoxide	7.22	6.51	14.70	14.90	29.40	28.00
Propane	7.65	6.69	19.50	19.30	44.00	40.70
Butane	1.63	1.44	5.02	4.08	12.70	10.00
n-Butanol	29.20	30.90	17.23	16.81	2.45	3.63
Dibutyl ether	38.93	38.34	28.40	29.10	3.76	6.64
Heptane	8.03	7.65	8.01	8.97	4.89	7.12
4-Heptanone	0.49	0.49	0.31	0.35	0.57	0.94
Butyl butyrate	6.36	7.41	6.30	6.28	1.63	2.42
Others	0.49	0.57	0.53	0.21	0.60	0.55
$C_3/C_4$ ratio	4.69	4.64	3.88	4.73	3.46	4.07

#### 4.2.3.2 Effect of Reaction Pressure

To study the effect of the reaction pressure, the hydrogenation of butanal was conducted at  $300^\circ\text{C}$ , LHSV of  $2.0\text{ h}^{-1}$ , and  $H_2$ /feed molar ratio of 2.5. The results in Table 4.7, revealed that reaction pressure slightly affect the conversion of butanal (from 99.46% at 200 psig to 96.32% at 600 psig). Selectivities to hydrodecarbonylated products were found to significantly decrease with reaction pressure. On other hand, selectivities to dibutyl ether, heptane, 4-heptanone, and butyl butyrate were found to increase with increasing reaction pressure. Interestingly,  $C_3/C_4$  ratio for hydrogenation of butanal went adversely, the

explanation for this phenomenon is that when the reaction pressure increased, n-butanol from hydrogenation of butanal might not undergo via dehydration to form 1-butene and butane but it tends to react with nearby n-butanol molecule to form dibutyl ether resulting in abundant increase in dibutyl ether (from 5.85% at 200 psig to 32.80% at 600 psig) leading to the lower in butane product.

**Table 4.7** Product distribution from butanal over Pd/C at various reaction pressures (Reaction condition : temperature = 300°C, H<sub>2</sub>/Feed ratio = 2.5, and LHSV = 2 h<sup>-1</sup>)

Reaction Pressure (psig)	200		400		600	
Time on Stream (h)	1	6	1	6	1	6
Conversion	99.46	98.49	95.30	93.17	96.32	91.89
Selectivity (%)						
Carbon monoxide	32.10	31.10	14.70	14.90	12.30	12.80
Propane	49.80	48.50	19.50	19.30	15.40	15.90
Butane	5.75	5.15	5.02	4.08	4.44	4.10
n-Butanol	3.80	4.60	17.23	16.81	11.60	9.84
Dibutyl ether	5.85	7.30	28.40	29.10	32.80	32.20
Heptane	1.54	1.55	8.01	8.97	11.50	12.30
4-Heptanone	0.11	0.39	0.31	0.35	0.49	0.84
Butyl butyrate	0.86	1.21	6.30	6.28	11.26	11.37
Others	0.19	0.20	0.53	0.21	0.21	0.65
C <sub>3</sub> /C <sub>4</sub> ratio	8.66	9.41	3.88	4.73	3.46	3.87

#### 4.2.4 Hydrogenation of n-Butanol over Pd/C Catalyst

##### 4.2.4.1 Effect of Reaction Temperature

To study the effect of the reaction temperature, the hydrogenation of n-butanol was conducted at 400 psig, LHSV of 2.0 h<sup>-1</sup>, and H<sub>2</sub>/feed molar ratio of 2.5. The results revealed that reaction temperature affects the products distribution and conversion as shown in Table 4.8. As expected, the conversion of n-butanol was substantially increased with reaction temperature (from 41.00 % at 250°C to 89.51 % at 350°C). Selectivities to hydrodecarbonylated and

hydrodeoxygenated products, propane, carbon monoxide and butane were considerably increased, while Selectivity of condensed product, dibutyl ether was significantly decreased with reaction temperature. The results indicated that the condensation reaction is preferred to undergo at lower reaction temperature, but when reaction temperature is increased n-butanol tends to undergo hydrodecarbonylation and hydrodeoxygenation path. Interestingly, that  $C_3/C_4$  ratio of hydrogenation of n-butanol over Pd/C was lower than 1, indicating that n-butanol prefers hydrodeoxygenation path which inconsistent with the previous study with methyl butyrate, butyric acid and butanal. It can be explained that, normally Pd/C should undergo hydrodecarbonylation path, this reaction require dehydrogenation of n-butanol to butanal first. But in this case, hydrogenation of n-butanol was done under hydrogen pressure, it means dehydrogenation is hardly to occur, so that reaction pathway is selective to hydrodeoxygenation resulting in  $C_3/C_4$  ratio was lower than 1. However, reaction temperature unlikely to affect the  $C_3/C_4$  ratio, since it rather constant under investigated condition.

**Table 4.8** Products distribution of n-butanol over Pd/C at various reaction temperatures (Reaction condition : pressure = 400 psig,  $H_2$ /Feed ratio = 2.5, and LHSV =  $2\text{ h}^{-1}$ )

Reaction temperature (°C)	250		300		350	
Time on stream (h)	1	6	1	6	1	6
Conversion	41.00	38.23	64.32	63.14	89.51	87.69
Selectivity (%)						
CO	2.41	2.26	8.31	7.86	14.61	14.11
Propane	3.83	3.72	13.23	12.92	23.13	22.41
Butane	11.43	11.61	35.56	35.91	54.74	54.34
Dibutyl ether	82.02	81.98	42.31	42.95	6.69	8.61
Others	0.31	0.43	0.59	0.36	0.83	0.53
$C_3/C_4$ ratio	0.34	0.32	0.37	0.36	0.42	0.41

#### 4.2.4.2 Effect of Reaction Pressure

To study the effect of the reaction pressure, the hydrogenation of n-butanol was performed at 300°C, LHSV of 2.0 h<sup>-1</sup>, and H<sub>2</sub>/feed molar ratio of 2.5. The reaction pressure was varying from 200 to 600 psig. The results in Table 4.9 showed that the conversion of n-butanol tend to decrease with increasing reaction pressure (from 76.32% at 200 psig to 47.41% at 600 psig) and tend to form condensed product, dibutyl ether, whereas selectivity to both hydrodecarbonylated and hydrodeoxygenated products were decreased, indicated that the condensation reaction is preferred to undergo at higher reaction pressure while hydrodecarbonylation and hydrodeoxygenation likely to be suppressed. However, the higher in reaction pressure led to lower C<sub>3</sub>/C<sub>4</sub> ratio, revealed that n-butanol prefer to undergo hydrodeoxygenation path than hydrodecarbonylation path at elevated pressure. In addition, the C<sub>3</sub>/C<sub>4</sub> ratio of hydrogenation of n-butanol over Pd/C was lower than 1 due to aforementioned reasons in effect of reaction temperature.

**Table 4.9** Products distribution of n-butanol over Pd/C at various reaction pressures (Reaction condition : temperature = 300°C, H<sub>2</sub>/Feed ratio = 2.5, and LHSV = 2 h<sup>-1</sup>)

Reaction pressure (psig)	200		400		600	
Time on stream (h)	1	6	1	6	1	6
Conversion	76.32	74.47	64.32	63.14	47.41	46.54
Selectivity (%)						
CO	12.42	11.47	8.31	7.86	3.41	3.11
Propane	19.34	18.18	13.23	12.92	5.24	4.92
Butane	23.23	22.56	35.56	35.91	18.13	18.34
Dibutyl ether	44.28	47.39	42.31	42.95	72.43	73.04
Others	0.73	0.40	0.59	0.36	0.79	0.59
C <sub>3</sub> /C <sub>4</sub> ratio	0.83	0.81	0.37	0.36	0.28	0.26

### 4.3 Hydrogenation of Oxygen-containing C4 Compounds over NiMo/Al<sub>2</sub>O<sub>3</sub> Catalyst

#### 4.3.1 Hydrogenation of Methyl Butyrate over NiMo/Al<sub>2</sub>O<sub>3</sub> Catalyst

##### *4.3.1.1 Effect of Reaction Temperature*

To study the effect of the reaction temperature, the hydrogenation of methyl butyrate was conducted at 400 psig, LHSV of 2.0 h<sup>-1</sup>, and H<sub>2</sub>/feed molar ratio of 2.5. The results in Table 4.10 revealed that conversion of methyl butyrate was increased with reaction temperature (from 25.95% at 300°C to 34.86% at 350°C). It was also observed the change in product selectivity as hydrodecarbonylated products (propane, carbon monoxide), hydrodeoxygenated product (butane), and butyric acid increased with increasing reaction temperature while selectivity to coupling ester, butyl butyrate was decreased. Others hydrodeoxygenated intermediate which are butanal and n-butanol together with side-products from hydrolysis, methanol and its condense product, dimethyl ether were fairly constant under investigated conditions. In addition, C<sub>3</sub>/C<sub>4</sub> ratio was slightly decreased with reaction temperature, indicating that hydrodeoxygenation is preferred even at elevated temperature. However, deactivation of active sites for hydrodeoxygenation was also observed since the C<sub>3</sub>/C<sub>4</sub> ratio was increased and selectivity to butane was decreased as a function of time on stream which likely to cause by coking.

**Table 4.10** Product distribution from methyl butyrate over NiMo/Al<sub>2</sub>O<sub>3</sub> at various reaction temperatures (Reaction condition : pressure = 400 psig, H<sub>2</sub>/Feed ratio = 2.5, and LHSV = 2 h<sup>-1</sup>)

Reaction Temperature (°C)	300		350	
Time on stream (h)	1	6	1	6
Conversion	25.95	21.53	36.56	32.96
Selectivity (%)				
Carbon monoxide	2.36	2.44	2.44	2.44
Methanol	27.61	28.61	26.25	27.31
Dimethyl ether	0.90	0.96	1.49	1.38
Propane	4.89	5.11	5.92	6.06
Butane	8.43	4.17	11.62	5.98
Butanal	0.77	0.93	0.36	0.53
n-Butanol	3.06	2.76	2.17	1.95
Heptane	0.19	0.23	0.44	0.53
4-Heptanone	0.27	0.33	0.36	0.43
Butyric acid	29.14	27.71	31.22	32.41
Butyl butyrate	21.81	26.25	16.92	20.21
Others	0.57	0.50	0.81	0.77
C <sub>3</sub> /C <sub>4</sub> ratio	0.58	1.23	0.51	1.01

#### 4.3.1.2 Effect of Reaction Pressure

To study the effect of the reaction pressure, the hydrogenation of methyl butyrate was conducted at 350°C, LHSV of 2.0 h<sup>-1</sup>, and H<sub>2</sub>/feed molar ratio of 2.5. The results in Table 4.11 showed that reaction pressure slightly affects the conversion of methyl butyrate (from 34.86% at 200 psig to 37.23% at 600 psig). However, Selectivity to hydrodeoxygenated product, butane was increased, while selectivities to propane and carbon monoxide were found to decrease, indicating that hydrodeoxygenation is preferred at elevated reaction pressure. However, selectivities to hydrogenated intermediates, which are n-butanol and butanal were slightly increased with increasing reaction pressure. Nevertheless, selectivities to ketonic decarboxylated products, 4-heptanone and heptane were

slightly decreased whereas coupling ester, butyl butyrate was increased. Additionally,  $C_3/C_4$  ratio was significantly decreased with reaction pressure (from 2.47 at 200 psig to 0.41 at 600 psig) indicating that reaction is prefer hydrodeoxygenation path at elevated reaction pressure.

**Table 4.11** Product distribution from methyl butyrate over NiMo/Al<sub>2</sub>O<sub>3</sub> at various reaction pressures (Reaction condition : temperature = 350°C, H<sub>2</sub>/Feed ratio = 2.5, and LHSV = 2 h<sup>-1</sup>)

Reaction Pressure (psig)	200		400		600	
Time on stream (h)	1	6	1	6	1	6
Conversion	34.86	29.08	36.56	32.96	37.23	31.57
Selectivity (%)						
Carbon monoxide	4.42	4.08	2.44	2.44	1.98	1.95
Methanol	25.35	25.21	26.25	27.31	27.23	27.71
Dimethyl ether	1.57	1.72	1.49	1.38	0.86	0.93
Propane	8.43	7.80	5.92	6.06	5.07	5.30
Butane	3.41	1.70	11.62	5.98	12.31	5.45
Butanal	0.80	0.88	0.36	0.53	0.34	0.49
n-Butanol	0.43	0.47	2.17	1.95	2.03	1.79
Heptane	0.78	0.84	0.44	0.53	0.41	0.30
4-Heptanone	0.73	0.80	0.36	0.43	0.26	0.31
Butyric acid	38.84	39.17	31.22	32.41	30.81	33.62
Butyl butyrate	14.91	16.95	16.92	20.21	17.91	21.32
Others	0.33	0.38	0.81	0.77	0.79	0.83
$C_3/C_4$ ratio	2.47	4.58	0.51	1.01	0.41	0.97

### 4.3.2 Hydrogenation of Butyric Acid over NiMo/Al<sub>2</sub>O<sub>3</sub> Catalyst

#### 4.3.2.1 Effect of Reaction Temperature

To study the effect of the reaction temperature, the hydrogenation of butyric acid was conducted at 400 psig, LHSV of 2.0 h<sup>-1</sup>, and H<sub>2</sub>/feed molar ratio of 2.5. The reaction temperature was varied from 250 to 350°C.



The results in Table 4.12, revealed that conversion of butyric acid was significantly increased with increasing reaction temperature (from 9.45% at 250°C to 58.37% at 350°C). It was observed the change in product selectivity as selectivities to hydrodecarbonylated and hydrodeoxygenated products which are propane, carbon monoxide and butane increased with increasing reaction temperature. However, the products from ketonic decarboxylation reaction, 4-heptanone and heptane were found in trace amount under investigated conditions. Nevertheless, selectivities to hydrodeoxygenated intermediates, butanal and n-butanol likely to increase with reaction temperature but it decrease when the reaction temperature further increased which can be explained by the highly increasing of selectivity to butane. Additionally, selectivity to condensed products, both dibutyl ether and butyl butyrate were slightly decreased with reaction temperature. Nevertheless, C<sub>3</sub>/C<sub>4</sub> ratio was slightly decreased with reaction temperature, indicating that hydrodeoxygenation is preferred even at elevated temperature for NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst.

**Table 4.12** Product distribution from butyric acid over NiMo/Al<sub>2</sub>O<sub>3</sub> at various reaction temperatures (Reaction condition : pressure = 400 psig, H<sub>2</sub>/Feed ratio = 2.5, and LHSV = 2 h<sup>-1</sup>)

Reaction Temperature (°C)	250		300		350	
Time on stream (h)	1	6	1	6	1	6
Conversion	9.45	7.83	42.15	36.58	58.37	50.21
Selectivity (%)						
Carbon monoxide	3.57	3.93	5.75	7.75	8.67	9.41
Propane	5.13	6.61	7.79	9.24	11.43	12.55
Propylene	0.16	0.75	0.60	1.28	0.56	1.49
Butane	7.56	5.26	14.16	9.82	21.54	11.01
1-Butene	0.27	0.79	0.31	0.90	0.62	1.11
Butanal	0.43	0.56	1.70	1.75	0.59	0.64
n-Butanol	1.58	1.76	2.57	2.21	1.53	1.64
Dibutyl ether	0.67	0.59	0.55	0.61	0.24	0.34
Heptane	trace	trace	trace	trace	trace	trace
4-Heptanone	trace	trace	trace	trace	trace	trace
Butyl Butyrate	79.86	78.91	66.03	66.00	54.26	61.17
Others	0.77	0.84	0.54	0.44	0.56	0.64
C <sub>3</sub> /C <sub>4</sub> ratio	0.68	1.22	0.58	0.98	0.54	1.16

#### 4.3.2.2 Effect of Reaction Pressure

To study the effect of the reaction temperature, the hydrodeoxygenation of butyric acid was conducted at 350°C, LHSV of 2.0 h<sup>-1</sup>, and H<sub>2</sub>/feed molar ratio of 2.5. The results in Table 4.13 showed that reaction pressure slightly affect the conversion of butyric acid (from 41.06% at 200 psig to 44.13% at 600 psig). Selectivities to hydrodecarbonylated products, propane, propylene and carbon monoxide were decreased with increasing reaction pressure. By contrast, selectivities to hydrodeoxygenated products, butane, butanal, n-butanol were found to increase with increasing reaction pressure, but the formation of 1-butene was

reduced revealed that increasing of reaction pressure can lowering the formation of unsaturated hydrocarbon by enhancement of hydrogenation activity. Nevertheless, an increasing in reaction pressure was also led to the formation of coupling ester, butyl butyrate as selectivity increased. Additionally,  $C_3/C_4$  ratio was significantly decreased with reaction temperature (from 1.30 at 200 psig to 0.35 at 600 psig). Moreover, the active site for hydrodeoxygenation is found to deactivate as a function of time on stream, resulting in lower  $C_3/C_4$  ratio at 6 h of time on stream.

**Table 4.13** Product distribution from butyric acid over NiMo/Al<sub>2</sub>O<sub>3</sub> at various reaction pressures (Reaction condition : temperature = 300°C, H<sub>2</sub>/Feed ratio = 2.5, and LHSV = 2 h<sup>-1</sup>)

Reaction Pressure (psig)	200		400		600	
Time on stream (h)	1	6	1	6	1	6
Conversion	41.06	34.87	42.15	36.58	44.13	35.43
Selectivity (%)						
Carbon monoxide	9.89	10.57	5.75	7.75	3.12	4.54
Propane	12.98	14.09	7.79	9.24	5.09	6.88
Propylene	2.10	3.42	0.60	1.28	0.21	0.62
Butane	10.54	7.54	14.16	9.82	14.98	9.98
1-Butene	1.09	2.10	0.31	0.90	0.15	0.42
Butanal	0.98	0.88	1.70	1.75	2.09	1.98
n-Butanol	1.19	1.02	2.57	2.21	4.42	3.98
Dibutyl ether	0.59	0.46	0.55	0.61	0.63	0.58
Heptane	0.78	0.57	trace	trace	trace	trace
4-Heptanone	1.03	1.54	trace	trace	trace	trace
Butyl Butyrate	58.37	57.53	66.03	66.00	69.03	70.53
Others	0.46	0.28	0.54	0.44	0.28	0.49
$C_3/C_4$ ratio	1.30	1.82	0.58	0.98	0.35	0.72

### 4.3.3 Hydrogenation of Butanal over NiMo/Al<sub>2</sub>O<sub>3</sub> Catalyst

#### *4.3.3.1 Effect of Reaction Temperature*

To study the effect of the reaction temperature, the hydrodeoxygenation of butanal was conducted at 400 psig, LHSV of 2.0 h<sup>-1</sup>, and H<sub>2</sub>/feed molar ratio of 2.5. The results in Table 4.14 showed that the conversion of butanal was significantly increased when the reaction temperature was changed from 250°C to 300°C, but the conversion of butanal was slightly increased when reaction temperature further increase to 350°C. However, the selectivities to hydrodecarbonylated and hydrodeoxygenated products, propane, carbon monoxide and butane were found to increase with reaction temperature. At the same time, the selectivity to hydrogenated intermediate, n-butanol was significantly decreased when reaction temperature was increased but selectivity to dibutyl ether was increased. However, selectivity to butyl butyrate was likely to increase with reaction temperature, but it rapidly dropped when reaction temperature was further increased to 350°C which can be explained by an abruptly increase in amount of butane product. In addition, selectivities to ketonic decarboxylated products, 4-heptanone and heptanes were slightly increased with reaction temperature. Moreover, the decreasing of conversion and the increasing of C<sub>3</sub>/C<sub>4</sub> ratio with time on stream indicating that the catalyst deactivation which occurred by coking, especially the active site for hydrodeoxygenation path.

**Table 4.14** Product distribution from butanal over NiMo/Al<sub>2</sub>O<sub>3</sub> at various reaction temperatures (Reaction condition : pressure = 400 psig, H<sub>2</sub>/Feed ratio = 2.5, and LHSV = 2 h<sup>-1</sup>)

Reaction Temperature (°C)	250		300		350	
Time on Stream (h)	1	6	1	6	1	6
Conversion	39.14	27.88	81.67	63.67	82.83	68.98
Selectivity (%)						
Carbon monoxide	0.22	0.30	0.69	1.48	1.65	5.10
Propane	0.35	0.47	0.55	1.39	2.06	6.11
Propylene	trace	trace	0.13	0.25	0.25	0.51
Butane	2.03	2.01	8.94	3.08	55.24	45.66
1-Butene	trace	trace	0.43	1.05	3.67	5.05
n-Butanol	81.20	83.10	36.67	36.63	7.68	10.21
Dibutyl ether	4.28	2.90	8.42	6.21	20.51	9.60
Heptane	trace	trace	0.68	0.62	0.72	0.78
4-Heptanone	trace	trace	0.39	0.98	1.82	2.67
Butyl Butyrate	11.51	11.09	42.4	48.21	6.13	13.90
Others	0.41	0.13	0.70	0.10	0.27	0.41
C <sub>3</sub> /C <sub>4</sub> ratio	0.17	0.23	0.07	0.40	0.04	0.13

#### 4.3.3.2 Effect of Reaction Pressure

To study the effect of the reaction pressure, the hydrogenation of butanal was conducted at 400 psig, LHSV of 2.0 h<sup>-1</sup>, and H<sub>2</sub>/feed molar ratio of 2.5. The summary results in Table 4.15 showed that reaction pressure slightly affect the conversion of butanal (from 80.42% at 200 psig to 85.69% at 600 psig). Selectivities to hydrodecarbonylated products were found to slightly decrease with reaction pressure. On other sides, selectivities to hydrodeoxygenated intermediates and hydrodeoxygenated product were found to increase with reaction pressure. However, the increasing of reaction pressure also led to the higher in selectivity to dibutyl ether, the condensed product of n-butanol. Interestingly, the amount of butyl butyrate went adversely to those of dibutyl ether, because the increasing in reaction

pressure led to the higher selective to hydrodeoxygenation path, while suppressed dehydrogenation of butanal to butyric acid, it means, lower amount of butyric acid can react with n-butanol to form butyl butyrate. In addition,  $C_3/C_4$  ratio was found to decrease with increasing reaction pressure indicating that reaction prefers hydrodeoxygenation path. Moreover, a decreasing of conversion and an increasing of  $C_3/C_4$  ratio with time on stream revealed the catalyst deactivation which occurred by coking, especially the active site for hydrodeoxygenation path.

**Table 4.15** Product distribution from butanal over NiMo/Al<sub>2</sub>O<sub>3</sub> at various reaction pressures (Reaction condition : temperature = 300°C, H<sub>2</sub>/Feed ratio = 2.5, and LHSV = 2 h<sup>-1</sup>)

Reaction Pressure (psig)	200		400		600	
Time on Stream (h)	1	6	1	6	1	6
Conversion	80.42	63.80	81.67	63.67	85.69	64.63
Selectivity (%)						
Carbon monoxide	1.57	1.93	0.69	1.48	0.28	0.58
Propane	1.97	2.48	0.55	1.39	0.35	0.71
Propylene	0.46	0.55	0.13	0.25	trace	trace
Butane	4.45	2.32	8.94	3.08	18.41	13.2
1-Butene	0.65	0.98	0.43	1.05	0.19	0.25
n-Butanol	30.72	25.31	36.67	36.63	43.71	40.05
Dibutyl ether	7.15	5.35	8.42	6.21	20.04	17.95
Heptane	0.62	0.47	0.68	0.62	0.56	0.38
4-Heptanone	0.95	2.04	0.39	0.98	0.33	0.99
Butyl Butyrate	50.92	58.07	42.4	48.21	15.51	25.54
Others	0.54	0.50	0.70	0.10	0.62	0.35
$C_3/C_4$ ratio	0.48	0.92	0.07	0.40	0.02	0.05

#### 4.3.4 Hydrogenation of n-Butanol over NiMo/Al<sub>2</sub>O<sub>3</sub> Catalyst

##### *4.3.4.1 Effect of Reaction Temperature*

To study the effect of the reaction temperature, the hydrogenation of n-butanol was conducted at 400 psig, LHSV of 2.0 h<sup>-1</sup>, and H<sub>2</sub>/feed molar ratio of 2.5. The results revealed that reaction temperature significantly affects on conversion of n-butanol and products selectivity as shown in Table 4.16. Selectivities to hydrogenated products which are butane and 1-butene tend to increase with increasing reaction temperature whereas selectivity to condensed product, dibutyl ether was found to dramatically decrease. Hence, it can be reported that the increase in reaction temperature enhances both hydrodecarbonylation and hydrodeoxygenation reaction resulting in the higher in selectivities to propane and butane. Meanwhile, formation of dibutyl ether which occurs via dehydration between molecules of n-butanol is likely to reverse to n-butanol at higher reaction temperature, it also led to the decreasing in selectivity dibutyl ether while selectivity to hydrodeoxygenated products were increased. Nevertheless, C<sub>3</sub>/C<sub>4</sub> ratio was slightly increased with reaction temperature, proved that NiMo/Al<sub>2</sub>O<sub>3</sub> prefers to undergo hydrodeoxygenation even at elevated temperature.

**Table 4.16** Product distribution from n-butanol over NiMo/Al<sub>2</sub>O<sub>3</sub> at different reaction temperatures (Reaction condition : pressure = 400 psig, H<sub>2</sub>/Feed ratio = 2.5, and LHSV = 2 h<sup>-1</sup>)

Reaction temperature (°C)	250		300		350	
Time on stream (h)	1	6	1	6	1	6
Conversion	41.42	35.76	73.62	70.17	90.63	86.32
Selectivity (%)						
CO	1.11	0.52	1.41	0.61	4.43	3.51
Propane	2.57	1.21	3.47	1.87	5.91	4.28
Propylene	0.21	0.76	0.72	0.83	1.12	1.25
Butane	33.54	29.43	44.41	43.45	65.67	62.52
1-Butene	0.35	0.44	0.37	0.46	0.72	0.89
Dibutyl ether	61.81	67.16	49.11	52.15	21.91	27.12
Others	0.41	0.48	0.51	0.63	0.24	0.43
C <sub>3</sub> /C <sub>4</sub> ratio	0.082	0.066	0.094	0.062	0.106	0.087

#### 4.3.4.2 Effect of Reaction Pressure

To study the effect of the reaction pressure, the deoxygenation of n-butanol was performed at 300°C, LHSV of 2.0 h<sup>-1</sup>, and H<sub>2</sub>/feed molar ratio of 2.5. The reaction was varying from 200 to 600 psig. The summary results in Table 4.17 shown that reaction pressure strongly affect on conversion of n-butanol and products selectivity similarly to the effect of reaction pressure on hydrogenation of n-butanol over Pd/C, that is, conversion of n-butanol tends to decrease with increasing reaction pressure. Additionally, the increase in reaction pressure also led to a higher in selectivity to condensed product, dibutyl ether indicating that hydrodeoxygenation and hydrodecarbonylation reaction was decreased by formation of dibutyl ether via dehydration reaction. However, the increasing of reaction pressure also led to the lower in C<sub>3</sub>/C<sub>4</sub> ratio, indicating that NiMo/Al<sub>2</sub>O<sub>3</sub> prefers hydrodeoxygenation path at elevated reaction pressure. Moreover, the lower hydrogenation activity is observed at lower reaction pressure as



the amount of the unsaturated products, propylene and 1-butene were increased especially at time on stream of 6 h.

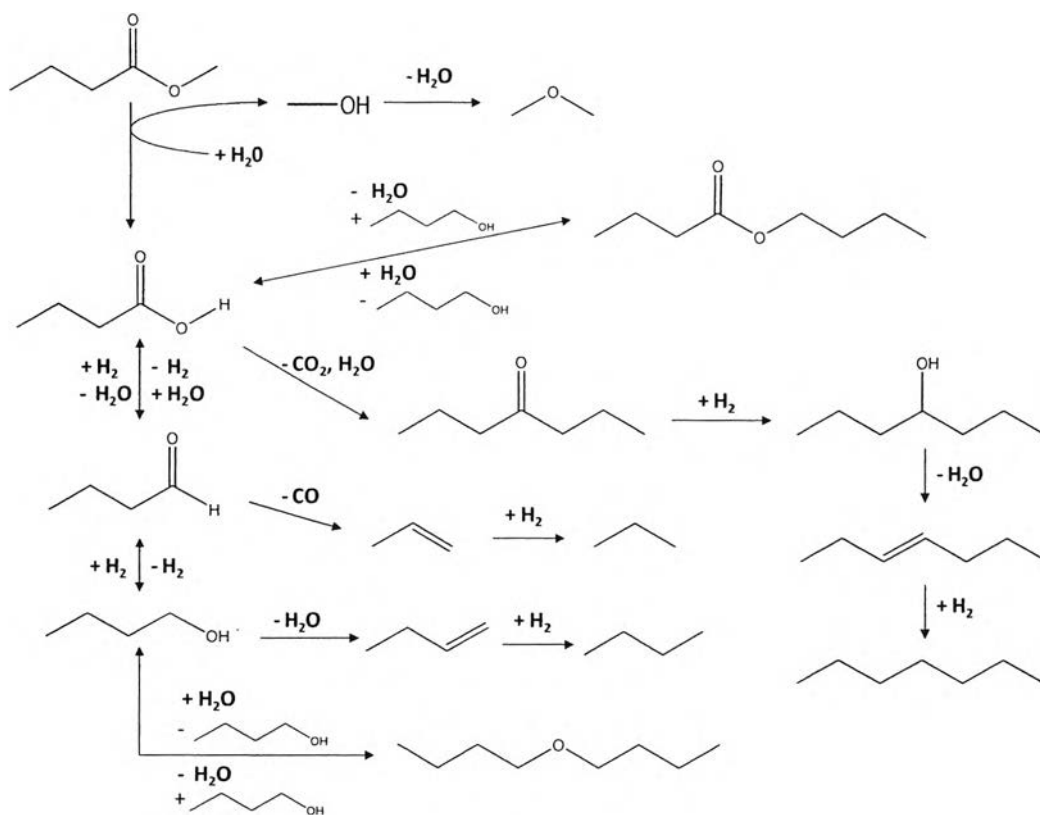
**Table 4.17** Product distribution from n-butanol over NiMo/Al<sub>2</sub>O<sub>3</sub> at different reaction pressures (Reaction condition : temperature = 300°C, H<sub>2</sub>/Feed ratio = 2.5, and LHSV = 2 h<sup>-1</sup>)

Reaction pressure (psig)	200		400		600	
Time on stream (h)	1	6	1	6	1	6
Conversion	96.90	90.40	73.62	70.17	49.00	45.80
Selectivity (%)						
CO	4.51	2.86	1.41	0.61	1.03	0.61
Propane	10.56	5.76	3.47	1.87	2.52	1.47
Propylene	3.13	7.12	0.72	0.83	0.09	1.23
Butane	71.53	60.68	44.41	43.45	47.32	44.87
1-Butene	2.21	5.56	0.37	0.46	0.13	0.45
Dibutyl ether	7.64	17.75	49.11	52.15	48.56	50.81
Others	0.42	0.27	0.51	0.63	0.35	0.56
C <sub>3</sub> /C <sub>4</sub> ratio	0.186	0.194	0.094	0.062	0.055	0.060

#### 4.4 Proposed Mechanism for Hydrogenation of Oxygen-containing C4 Compounds

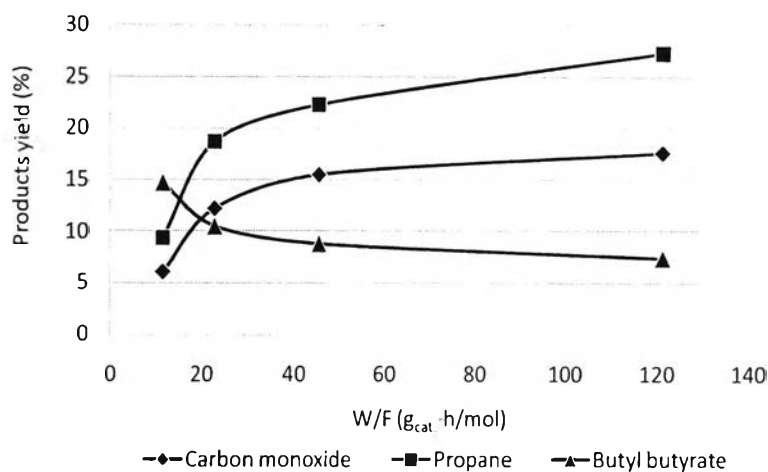
The possible reaction pathway of hydrogenation reaction of oxygen-containing C4 compounds namely, methyl butyrate, butyric acid, butanal and n-butanol, over Pd/C and NiMo/Al<sub>2</sub>O<sub>3</sub> were investigated under various reaction conditions. The obtained products in gas phase were identified as carbon monoxide (CO), methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), dimethyl ether (CH<sub>3</sub>OCH<sub>3</sub>), propane (C<sub>3</sub>H<sub>8</sub>), propylene (C<sub>3</sub>H<sub>6</sub>), 1-butene (C<sub>4</sub>H<sub>8</sub>) and butane (C<sub>4</sub>H<sub>10</sub>). The liquid products were identified as methanol (CH<sub>3</sub>OH), butanal (C<sub>3</sub>H<sub>7</sub>CHO), n-butanol (C<sub>4</sub>H<sub>9</sub>OH), dibutyl ether (C<sub>4</sub>H<sub>9</sub>OC<sub>4</sub>H<sub>9</sub>), 4-heptanone (C<sub>3</sub>H<sub>7</sub>COC<sub>3</sub>H<sub>7</sub>), n-heptane (C<sub>7</sub>H<sub>16</sub>), and

butyl butyrate ( $C_3H_7COOC_4H_9$ ). The reaction pathways have been proposed as shown in Fig.4.4

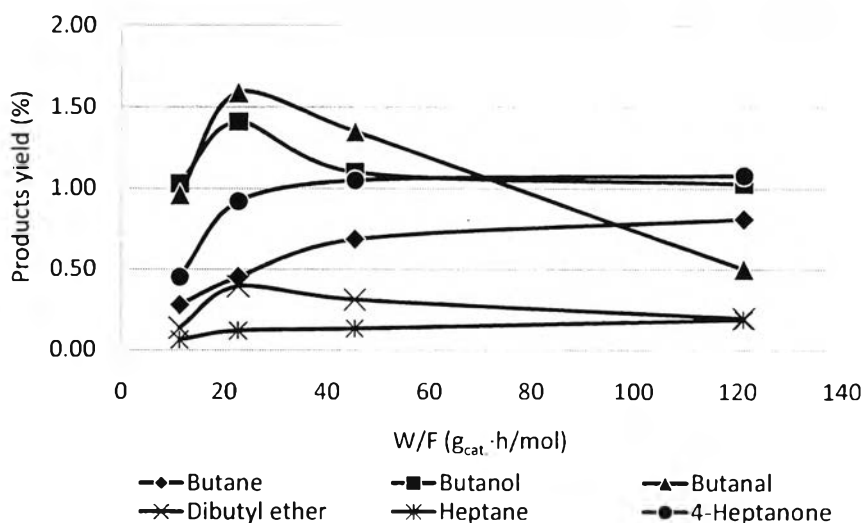


**Figure 4.4** Proposed reaction pathways of hydrogenation of methyl butyrate.

The plot of product yield product yield as function of W/F is shown in Fig. 4.5. In Fig 4.5, a), yield of butyl butyrate decreased, while propane and carbon monoxide increased with contact time. Meanwhile, in Fig.4.5, b) yield of butanal, n-butanol and dibutyl ether increased, and then decreased with W/F. However, slope butanal is higher than n-butanol, and slope of n-butanol is higher than dibutyl ether suggesting that butanal is a primary product of n-butanol, and n-butanol and dimethyl ether are secondary and tertiary products, respectively. However, yield of butane is also increased with W/F indicating that butane is an product derived from butanal, n-butanol, and dibutyl ether.



a)



b)

**Figure 4.5** Plot of products yield, (a) major product, (b) minor product, as a function of W/F of butyric acid over Pd/C at 300°C, 400 psig, H<sub>2</sub>/feed ratio of 2.5.

The hydrogenation of oxygen-containing C4 compounds resulted in different products depending on reaction condition. At the condition tested, there are two main hydrogenated products, propane and butane, which resulted from

hydrodecarbonylation and hydrodeoxygenation reaction, respectively, depending on catalyst type. In hydrodecarbonylation, methyl butyrate will be converted to butyric acid, then further convert to butanal by means of hydrogenation, then butanal will be undergo decarbonylated by cleavage carbonyl group to unsaturated hydrocarbons, which is propylene, after that the propylene was further hydrogenated to its corresponding saturated hydrocarbon, propane. For hydrodeoxygenation path, methyl butyrate will be converted to butanal by hydrolysis and hydrogenation, and the obtained butanal will be further hydrogenated to n-butanol, then alcohols can yield unsaturated hydrocarbons by means of dehydration reaction, which takes place by the protonation at hydroxyl group of alcohol followed by splitting of water from protonated butanol forms a 1-butene via acid-catalyzed followed by hydrogenation to butane (Senol *et al.*, 2007). Since butyl butyrate was found with high amount at low W/F, this suggested that formation of butyl butyrate was fast, especially on NiMo/Al<sub>2</sub>O<sub>3</sub>. This reaction can be explained in terms of reverse hydrolysis reaction, i.e. esterification, of butanol and butyric acid to form corresponding an ester and water. Others side-product such as heptane, 4-heptanone, dimethyl ether, and dibutyl ether were also observed. The formation of 4-heptanone can be explained by ketonic decarboxylation reaction, this reaction is believed to occur by carbanion, formed by decarboxylation from a carboxylate, is attack onto adjacent carboxylic group to form symmetry ketone and its side-product (Renz *et al.*, 2005), which are 4-heptanone and water, after that 4-heptanone will be reduced to alcohol followed by dehydration to heptene, then further hydrogenated to heptane. In addition, the formation of this symmetry ketone via ketonic decarboxylation over Pd/C and activated alumina were also found when ethyl stearate (Murzin *et al.*, 2007) and butyric acid (Leung *et al.*, 1995) were used as reactant. The formation of ether compound, dimethyl ether and dibutyl ether by the means of dehydration or so called “etherification” between two alcohol groups were also observed in gas and liquid product, respectively.