Mitsubishi Chemical 1,4-Butandiol & Tetrahydrofuran Technology

1,4-Butandiol (14BDO(BG)) & Tetrahydrofuran (THF)
14BDO (BG) is generally manufactured from acetylene, 1,3-butadiene, propylene, and n-butane. 14BDO is a valuable chemical intermediate used in the production of high performance polymers, solvents and fine chemicals. 14BDO (BG) is industrially utilized in the production of polybutylene terephthalate (PBT), thermoplastic polyurethanes (TPU) and copolyester ether (COPE).
THF is produced in conjunction with 14BDO (BG) by the utilizing process to 1,3-butadiene and n-butane as feedstock. THF is utilized as pharmaceutical solvent and in the manufacture of polytetraethylene ether glycol (PTMEG).

Introduction of Mitsubishi 14BDO (BG) & THF Technology
Mitsubishi Chemical (MCC) process can manufacture 14BDO (BG) and THF by butadiene process. For more than 30 years, MCC has run 14BDO (BG) & THF business (Production and Sales). MCC currently runs 60,000 ton/year 14BDO (BG) & THF plant in Japan. MCC has developed its own State-of-Art technology and offers Process Technology together with Mitsubishi high performance catalyst. MCC has offered license to South Korea and Taiwan, and these production capacities are 50,000 ton/year (’99), 40,000 ton/year (’00), and 60,000 ton/year (’07).

Feature of Mitsubishi 14BDO (BG) & THF process
Mitsubishi 14BDO (BG) & THF process uses 1,3-butadiene as feedstock, and proceeds via acetoxylation followed by hydrogenation and hydrolysis.
Features of this process are as follows;
(1) Being able to produce 14BDO (BG) & THF at any ratio
(2) Advantaged low costs
   /MCC original high performance catalysts
   /Low construction costs
(3) Safety and stable process by mild operating conditions
   /Being able to continue full-load operation for two years
(4) Stable and high quality products (low moisture and low impurity) which is highly valued from many manufacturer of TPU and PBT or PTMEG
(5) Green process
   /Less waste water amount because of consuming the raw water
   /Energy recovery system from waste oil and waste gas
Chemistry of this process

• Acetoxylation reaction

\[
\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 + 2\text{ACOH} + \frac{1}{2}\text{O}_2 
\rightarrow \text{AcO-CH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{-OAc} + \text{H}_2\text{O}
\]

• Hydrogenation reaction

\[
\text{AcO-CH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{-OAc} + \text{H}_2 
\rightarrow \text{AcO-CH}_2-\text{CH}_2-\text{CH}_2\text{-CH}_2\text{-OAc}
\]

• Hydrolysis reaction

\[
\begin{align*}
\text{AcO-CH}_2-\text{CH}_2-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-OAc} + \text{H}_2\text{O} 
& \rightarrow \text{AcO-CH}_2-\text{CH}_2-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-OH} + \text{AcOH} \\
\text{AcO-CH}_2-\text{CH}_2-\text{CH}_2\text{-CH}_2\text{-OH} + \text{H}_2\text{O} 
& \rightarrow \text{HO-CH}_2-\text{CH}_2-\text{CH}_2\text{-CH}_2\text{-OH} + \text{AcOH}
\end{align*}
\]

• Deacetocyclization reaction

\[
\begin{align*}
\text{AcO-CH}_2-\text{CH}_2-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-OH} & \rightarrow \text{THF} + \text{AcOH} \\
\text{HO-CH}_2-\text{CH}_2-\text{CH}_2\text{-CH}_2\text{-OH} & \rightarrow \text{THF} + \text{H}_2\text{O}
\end{align*}
\]

Simplified block flow

Air \quad 1,3-Butadiene \quad Acetic acid

Acetoxylation reaction 

Hydrogenation reaction 

Hydrolysis reaction 

Deacetocyclization reaction 

Distillation

Distillation

THF 

14BDO (BG)
World 1,4BDO (BG) & THF Plant Capacity
In 2011, world 1,4BDO production capacity is around 2,100,000 ton/year.

World Butanediol capacity by country (2011)

- US: 17%
- Taiwan: 12%
- China: 27%
- Germany: 14%
- Japan: 5%
- Netherland: 6%
- Others (Asia): 19%
- World: 27%

World Butanediol capacity by process (2011)

- Butadiene: 39%
- Acetylene: 28%
- Butane: 23%
- Propylene: 10%
- World: 10%