Optimal Design of a Benzyl Alcohol Process*

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Summary: A new three stage process to produce benzyl alcohol from toluene has been developed as a semi-pilot scale plant. The third stage, that is the hydrogenation of methyl benzoate to benzyl alcohol, is discussed in this article.

Thus the study for the optimal design of the hydrogenation stage has been made on the basis of experimental process data and collected cost data. Consequently, distinguishing features of hydrogenation of methyl benzoate in commercial operation are found as shown below:

1. Reactor, hydrogen bubbling column
2. Catalyst used, copper chromium type
3. Solvent, constant b.p. mixture of methanol/toluene
4. Catalyst recovery, pressure drum filter
5. Reaction temperature, 140°C
6. Reaction pressure, 250 kg/cm²·G
7. Solvent ratio, 1.96 kg/benzoate kg
8. Catalyst ratio, 0.132 kg/benzoate kg
9. Hydrogen superficial velocity, 1.0 cm/sec
10. Conversion, ca. 30%
11. Selectivity, 95%

The new process produces benzyl alcohol of 99.9% purity at a price less than 200 yen/kg at a production capacity of 600 tons/30 days.

1 Introduction

Nowadays a rather limited amount of benzyl alcohol is being used in soap, perfume, flavour, medical and some other industries¹⁾. The alcohol with high solvent properties, however, will be used in a large amount in paint and dyeing industries as well, provided the price of the alcohol comes down to the level of conventional solvents.

A new basic technology producing benzyl alcohol from toluene has been developed to semi-pilot scale at the Technical Research Center of Nippon Mining Co., Ltd.^{2),3)}, in an effort to offer cheaper benzyl alcohol. The new process consists of three stages. The first stage is oxidation of toluene to benzoic acid in the presence of cobalt catalyst. The second stage is esterification of benzoic acid to methyl benzoate. The final stage is hydrogenation of the benzoate to benzyl alcohol in the presence of our newly developed catalyst⁴⁾.

There are several commercial technologies that have been introduced for the first and second stage reactions, but none for the final stage reaction. Moreover, the final stage reaction is responsible to large proportion (as high as seventy percent) of the production cost of benzyl alcohol. Thus, the discussion in this paper is concentrated mainly on the final stage reaction, though the investment costs for oxidation and esterification processes which may be slightly affected by the selectivity of benzyl alcohol are taken into consideration.

The hydrogenation stage consists of three sections, namely, reaction section, catalyst recovery section for catalyst separation and recovery, and distillation section for solvent recovery and purification of the product. Each section is shown in **Figs. 1~3**, respectively.

A backmixing type bubbling column is used as a reactor because of its high-mixing properties. Feed slurry (methyl benzoate and catalyst) and

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Fig. 1 Schematic Diagram of Hydrogenation Process

Fig. 2 Schematic Diagram of Catalyst Recovery Section

the solvent are pumped to the reactor continuously. Hydrogen gas is blown into the column at the bottom and recycled to suspend the catalyst powder in the reactive solution.

The reaction is usually carried out at a temperature in the range of 130 to 170°C under pressure higher than 100 kg/cm²·G. The overall yield of this reaction is very high and the product does not contain any chlorides (99.9 wt% purity).

The reactor effluent is sent to the continuous drum filter, and separated catalyst cake is dried and reactivated in the stirred fluidized bed cal-

Fig. 3 Schematic Diagram of distillation section

ciner and then recycled to the feed. The filtrate is led to a distillation section to purify the product and to recover the solvent. Recovered solvent is recycled to the feed.

2 Preliminary Process Optimization

Simply stated, the present problem is to carry out the optimal design for the catalytic hydrogenation of methyl benzoate. The variables to be optimized include reactor type and dimensions, reaction temperature, reaction pressure, conversion, solvent demand, catalyst demand, filter type and size, system configuration and size of distillation columns, etc.

While the process system of the oxidation and esterification stages is fixed as in pre-designed suitable manner, only the capacity and materials and utilities consumptions in those stages might be somewhat affected by the design of the hydrogenation stage.

Hydrogenation is taken place as the following consecutive reactions.

where MB stands for methyl benzoate, BA for benzyl alcohol, MeOH for methanol, and TL for toluene, respectively.

Several variables are optimized *a priori* within some specified regions from the limitations of the process and from reaction conditions.

Our experimental studies have shown that the overall rate of the first reaction is second order with respect to the concentration of MB, and that of the second reaction is first order of BA. Activation energy of the first step is ca. 12 kcal/mol and that of the second is ca. 30 kcal/mol.

High reaction temperatures lead to high reaction rate, reducing the reactor volume and its cost, but cause adverse effects on BA selectivity and the utilities.

The rate constant K_1 increases in proportion to the hydrogen pressure while K_2 is assumed to be independent of it. A higher pressure increases installation cost of the reactor and the compressors. Thus, the reaction temperature and pressure are selected *a priori* considering preliminary results in the range of 130°C to 170°C, and under the range of 150 to 250 kg/cm²·G.

Usually surface reaction is controlling. The superficial velocity of hydrogen gas, v does not affect the overall reaction rate. Therefore v is

fixed as low as possible to suspend catalyst, *i.e.* at 1 cm/sec. MB conversion is important on the point of the capacity of the recovery sections. Higher conversion makes cost of reactor section higher and that of the recovery sections lower. Solvent ratio and catalyst ratio, which are weight ratio to MB in the feed slurry, have also great effect on K_1 and K_2 , as well as the recovery costs.

The catalyst is such a fine particle size that the usual solid-liquid separators, such as centrifuges, auto-filter press, cannot be operated efficiently in our process. Several experiment led us to choose Fest filter, which gives pressure driving filtration under 3 kg/cm²·G.

The initial and the running costs in the distillation section depend on the flow rate and the composition of the reactor effluent. The flow scheme of the section is, at first, determined by preliminary calculations as shown in Fig. 3 to minimize heat consumptions and the number of columns. Then vapor-liquid equilibriums are studied experimentally to give basis of more exact considerations which are included in the optimal design calculation.

The separation of MB and BA is best carried out under vacuum, ca. 60 mmHg, since the relative volatility increases with decrease in temperature, and low temperature prevents the formation of benzyl benzoate in the columns.

3 Permissible Region of the Variables

These initial studies, followed by tentative design calculations, determined the region of variables to be optimized finally as follows (explained later).

Solvent ratio

$$S_R \quad 1.954 \sim 4.303 \quad \text{kg/MBkg} \\ -1 \leq x_1 \leq 1$$

Reaction temperature

$$T \quad 140 \sim 160 \quad ^\circ\text{C} \\ -1 \leq x_2 \leq 1$$

Solvent composition

$$S_C \quad 0.044 \sim 0.13 \quad \text{TLmol/MeOHmol} \\ -1 \leq x_3 \leq 1$$

Catalyst ratio

$$C_R \quad 0.132 \sim 0.263 \quad \text{kg/MBkg} \\ -1 \leq x_4 \leq 1$$

Reaction pressure

$$P \quad 150 \sim 250 \quad \text{kg/cm}^2 \cdot \text{G} \\ -1 \leq x_5 \leq 1$$

where, x_i ($i=1 \sim 5$), are the dimensionless variables whose absolute values are unity at the

both limits of each of the variables.

It is restricted to make the region wider by considering the errors of the experimental data and of its formulation.

The objective function, O_F , is defined as total production cost of BA, which covers oxidation, esterification and hydrogenation stages. O_F consists of fixed charge, E_q , utilities cost, U_t and materials cost, M_t (Refer Eq. (20)).

The minimum point of the objective function is explored by the steepest decent method^(5),6), as well as by the Box-Wilson method⁽⁷⁾, while keeping the following variables constant: H_2 velocity v ($=1.0$ cm/sec) and production capacity C_{ap} ($=333$ and $1,000$ kg/hr.).

4 Formulation of the Equations

4.1 Reaction Rate

The consecutive reactions, mentioned previously are expressed by the following equations.

$$-\frac{d(\text{MB})}{d\theta} = k_1 P_{H_2}^l (\text{MB})^m \quad (1)$$

$$\frac{d(\text{BA})}{d\theta} = k_1 P_{H_2}^l (\text{MB})^m - k_2 P_{H_2}^j (\text{BA})^n \quad (2)$$

$$(\text{MB}) = (\text{MB})_0, \quad (\text{BA}) = 0, \quad \text{at } \theta = 0$$

It was found $l=1$, $m=2$, $j=0$ and that $n=1$, from batchwise experiments⁽⁸⁾. Thus, Eqs. (1) and (2) are rewritten as,

$$-\frac{d(\text{MB})}{d\theta} = k_1 P_{H_2} (\text{MB})^2 \quad (3)$$

$$\frac{d(\text{BA})}{d\theta} = k_1 P_{H_2} (\text{MB})^2 - k_2 (\text{BA}) \quad (4)$$

Eqs. (3) and (4) are reformed to Eqs. (5) and (6) by using some of the following definitions.

$$\text{Conversion: } C = 1 - \frac{(\text{MB})}{(\text{MB})_0}$$

$$\text{Selectivity: } S = \frac{(\text{BA})}{(\text{MB})_0 - (\text{MB})}$$

$$K_1 = k_1 P_{H_2} (\text{MB})_0$$

$$K_2 = k_2$$

$$\frac{dC}{d\theta} = K_1 (1-C)^2 \quad (5)$$

$$\frac{d(CS)}{d\theta} = K_1 (1-C)^2 - K_2 CS \quad (6)$$

$$C=0 \quad S=1, \quad \text{at } \theta=0$$

These are basic equations. The integration of Eq. (5) is expressed by,

$$K_1 \theta = C/(1-C) \quad (7)$$

Dividing Eq. (6) by Eq. (5), the following equation, then Eq. (8) is obtained.

$$\frac{d(CS)}{dC} = \frac{K_1 (1-C)^2 - K_2 CS}{K_1 (1-C)^2}$$

$$C \frac{dS}{dC} + K \frac{CS}{(1-C)^2} + S = 1 \quad (8)$$

where $K=K_2/K_1$, and is considered to be a kind of selectively parameter. Eq. (8) can be solved analytically as,

$$S = \frac{1}{C} \left[C - 1 + \exp\left(\frac{K}{C-1}\right) \left\{ KEi\left(\frac{K}{1-C}\right) - KEi(K) + \exp(K) \right\} \right]^{*} \quad (9)$$

The curves in **Fig. 4** which show the relation among C , S and K are obtained by Eq. (9).

K_1 and K_2 are obtained by wide range of batchwise experimental data in such a way that at first K_1 is calculated by Eq. (7), and then K is found in **Fig. 4**, finally K_2 is determined.

Then using the symmetrical composite design method⁽⁹⁾, K_1 and K_2 are formulated in the following manner as functions of four variables (which are stated in 3)⁽¹⁰⁾.

$$\begin{aligned} K_1 = & (0.2363 + 0.0251x_1 + 0.0318x_2 - 0.0079x_3 \\ & + 0.0798x_4 - 0.0053x_1^2 + 0.0027x_2^2 - 0.0068x_3^2 \\ & - 0.0112x_4^2 + 0.0141x_1x_2 - 0.0010x_1x_3 \\ & + 0.0202x_1x_4 + 0.0093x_2x_3 + 0.0134x_2x_4 \\ & + 0.0163x_3x_4) \times (1.340 + 0.333x_5) \end{aligned} \quad (10)$$

$$\begin{aligned} K_2 = & 0.0571 - 0.0072x_1 + 0.00219x_2 + 0.0045x_3 \\ & + 0.0053x_4 - 0.0003x_1^2 + 0.0027x_2^2 \\ & - 0.0042x_3^2 - 0.0020x_4^2 - 0.0043x_1x_2 \\ & - 0.0031x_1x_3 - 0.0051x_1x_4 + 0.0022x_2x_3 \\ & + 0.0069x_2x_4 + 0.0012x_3x_4 \end{aligned} \quad (11)$$

Fig. 4 Relation between C and S When Parameter, $K=K_2/K_1$ is Constant in Batchwise Reaction

$$*) \quad Ei(x) = \int_{-\infty}^x e^x x^{-1} dx$$

Table 1-a Data for Filtration¹²⁾

Average specific cake resistance	α	10^{13}	m/kg
Resistance of filter cloth	K_m	2×10^{12}	1/m
Pressure difference	ΔP	3	kg/cm ²

κ and μ are decided in process condition.

Table 1-b Data for Distillation

	TW-1	TW-2	TW-3
Operation Pressure	760	760	60 mmHg
Average Relative Volatility (between key components)	59.1	1.7	2.5
Feed Condition (liquid/feed)	0	1.0	1.0
Separation Condition (limit of key components in Top and Bottom streams)	Top MB 0.001 Bot. H ₂ O 0.001	H ₂ O 0.001 MeOH 0.05	BA 0.005 MB 0.01 mole fraction
Plate Efficiency (overall)	0.6	0.5	0.5
Tray Spacing, m	Diameter of columns, m		
0.30	less than 0.75		
0.45	0.75~1.2		
0.60	more than 1.2		

Table 1-c Data for Calcination

Type	Stirred fluidized bed
Temperature	450±20°C in air
Air Velocity	0.80 cm/sec
Solid Retention Time	2.5 hrs
Bed Height/Diameter	1.6
Number of Impellers	1
Stirring Speed	50 rpm

4.2 Other Technical Data and Equations

The rate of filtration of the slurry can be expressed as the following equation.

$$\frac{dv}{d\theta} = \frac{k}{2(v+c)} \quad (12)$$

where,

$$\left. \begin{aligned} k &= \frac{2\Delta P g_c}{\alpha \mu} \\ c &= \frac{K_m \kappa}{\alpha} \end{aligned} \right\} \quad (13)$$

The symbols α and K_m represent the average specific cake resistance and the resistance of unit area of filter cloth, respectively. Solving Eq. (12) filter size can be determined¹¹⁾ using the values shown in **Table 1-a**.

For the distillation columns activity coefficients are studied in the approximate compositions near the feed, top and bottom positions, and then formulated to equations. The number of trays and reflux ratios for distillation columns can be determined by a well known calculation method using Fenske equation, Underwood equation and Gilliland correlation. In this step reflux ratios are specified as 1.5 times the minimum reflux ratios. Plate efficiencies of the columns are assumed to be suitable values between 0.5 and

0.6 on the basis of comparing similar existing towers. Then the diameters of the columns are calculated by the limitation of the allowable vapor rate which relates to tray spacing¹³⁾. Main design factors required for calculation are shown in **Table 1-b**.

From the result of pilot plant test, the type and design factors of the calciner are determined as given in **Table 1-c**. The size of calciner can be estimated by solid retention time and height/diameter ratio.

4.3 Cost Data

The following eight items are basic to initial investment of the hydrogenation process: reactor, feed compressor, recycle compressor, vessels and pumps, heat exchangers, calciner, filter and distillation columns. All costs were calculated on the basis that equipment purchased and built in the Pacific coast of Japan for the year 1970. For purpose of machine computation, the following are applied to obtain the various initial costs in 10⁶ yen.

The costs $C_1 \sim C_8$ are determined in the interpolation method: the logarithm of the cost and that of the cost variable are assumed to be in linear

Table 2 Cost Variables and Pressure Correction Factors

<i>j</i>	Equipment	Cost Variables A_j	Pressure Correction F_j Factors
1	Reactor	Internal volume (m^3)	Ratio of the thickness of cylindrical wall
2	Recycle Compressor	Recycle H_2 ($Nm^3/hr \times 10^{-3}$)	Ratio of power
3	Feed Compressor	Feed H_2 (Nm^3/hr)	Ratio of power
4	Vessels and Pumps	Feed weight (t/hr)	Ratio of pressure
5	Heat Exchangers	Feed enthalpy ($kcal/^\circ C \cdot hr \times 10^{-3}$)	—

Table 3 Practical Cost Data

<i>j</i>	Cost C_j 10 ⁶ yen			Cost Variable A_j		
	Case 1	Case 2	Case 3	Case 1	Case 2	Case 3
1	10.58	91.7	197.4	1.58	23.1	56.7
2	9.33	56.4	87.3	1.15	19.0	48.0
3	5.64	28.2	45.1	8.98	150	374
4	2.50	9.31	13.3	0.32	5.34	13.4
5	0.63	8.60	17.8	0.23	3.86	9.65

relation. In **Table 2** are illustrated the nature of the selected cost variables and the pressure correction factors, meanwhile practical data are shown in **Table 3**. At first the reaction pressure is assumed at 200 kg/cm²·G and the apparent cost is given by interpolation; then, multiplying pressure factors, the real cost can be obtained.

Other costs $C_6 \sim C_8$ are formulated as follows:
Calcliner and other solid handling device:

$$C_6 = 2.69C_L^{0.45} \quad (14)$$

where

C_L = catalyst load (kg/hr)

Filter:

$$\left. \begin{array}{l} A \geq 2m^2 \\ C_7 = 8.0A^{0.63} \end{array} \right\} \quad (15)$$

$$\left. \begin{array}{l} A < 2m^2 \\ C_7 = 10.4A^{0.29} \end{array} \right\} \quad (16)$$

where

A = filtration area (m^2)

Distillation columns:

$$C_{8i} = 0.4f_i N_i D_{Ti}^{0.4} \quad (17)$$

$$C_8 = \sum_i C_{8i} \quad (18)$$

where

N_i = number of plates in each column (—)

D_{Ti} = diameter of each column (m)

f_i = type factor depending on the column (—)

Thus total initial investment of the process, which produces 200 tons of BA in a month, T_C is expressed by,⁸⁾

$$T_C = (1 - 0.252) \sum_{j=0}^8 C_j + 95.6 \quad (19)$$

$$C_0 = 96.5S^{-0.56}$$

where 0.252 is a compensation factor for administrative expense such as engineering cost, insurance, contingency, etc.; 95.6 is a compen-

sation constant for common installation cost such as storage tank, service pump, etc. C_0 stands for the total initial investment of the oxidation and esterification processes, which may be affected slightly by BA selectivity S .

Therefore the fixed charge on production cost, E_q is given below

$$E_q = 0.1124T_C \quad (20)$$

where 0.1124 is a factor corresponding to depreciation rate, maintenance cost ratio, etc.

Other costs M_i and U_i for materials and utilities requirement, are directly estimated by the material and energy balances (as illustrated in **Tables 5** and **6**).

5 Computation

A HITAC 8400 digital computer was used in this investigation. The computer program consists of two parts. The first part, dealing with any given set of variables, calculates the objective function, that is, the total installations, utilities and materials costs, on the basis of above mentioned data and formulation. In this step various technics of chemical engineering calculation are quite useful. The process includes many recycle loops; therefore, material balance which gives flow rate and composition of the streams is given as the solution of simultaneous equations.

The second part carries out the exploration of the minimum point of the objective function. The first part is built in the second, and is operated as a subroutine program. The flow charts for these two parts are shown in **Figs. 5** and **6**.

6 Computation Results

6.1 Preliminary Computation

To avoid the possibility of missing the true minimum, and to give a direction for experimental studies, a wider range was selected for the first trial, so that the desired minimum point is purposely included. The base point is not considered as an optimum in an industrial scale, but best known from prior laboratory work. In this

Fig. 5 Subroutine Program for Design and Cost estimation of the process

Fig. 6 Optimization Program Based on Steepest Decent Method

preliminary step, an approximate solution to the problem was obtained by assuming that the solvent is pure MeOH, that BA selectivity is constant at 0.90, and the installation costs except for reactor, filter and solvent recovery tower, are considered to be constant.

The composite design method proposed by Box and Wilson was used in this part of the investigation, and result was obtained as a response equation of the following canonical form.

$$O_F = 152.8 + 5.2x_1^2 + 4.5x_2^2 + 7.5x_3^2 + 6.1x_4^2 + 3.0x_5^2 \quad (21)$$

As the coefficients of the variables in the above equation are all positive, moving away from the optimal point in any direction will cause an increase in cost. The coefficients also represent sensitivity of each variable; Ψ .

They are in the following order. $\Psi_3 > \Psi_4 > \Psi_1 > \Psi_2 > \Psi_5$. The more the sensitivity that is observed in a variable, the more careful consideration is required for the variable.

Apparently Ψ also depends on the width of each variable range and the region of each variable is determined by taking this into consideration.

6.2 Approach to Optimization

Eq. (21) suggests that the response surface is not a saddle type but very monotonous. This leads us to say that the steepest decent method is quite adequate to find an optimum. Therefore in the following part, this method is solely employed.

6.2.1 Case of Wider Region ($-2 \leq x_i \leq 2$, $i=1,2,\dots,5$)

In the case of the wider region ($-2 \leq x_i \leq 2$, $i=1,2,\dots,5$), the optimal point is given as shown in Table 4. This result is obtained with none of those assumptions in the preceding section.

The optimal point, however, is quite far from the base point and the reliability of the formula is now open to question. In fact the experiment

Table 4 Optimal Point in Case of Wider Region
 $C_{ap} = 333.3 \text{ kg/hr}$

x_1	(S_R)	-2	(0.814)
x_2	(T)	-2	(130)
x_3	(S_C)	-0.888	(0.488)
x_4	(C_R)	-1.723	(0.084)
x_5	(P)	-0.010	(200)
O_F		131.2	

Table 5 Performance and Costs at Optimal Condition

			Case 1 BA 200 t/mo	Case 2 600 t/mo	Case 3 200 t/mo (with cat. pretreatment)
Dimensionless Variables					
x_1			-1	-1	-1
x_2			-1	-1	-1
x_3			-0.649	-0.700	-0.744
x_4			-1	-1	-1
x_5			-1	-1	-1
Process Variables					
S_R	Solvent Ratio	(kg/MBkg)	1.961	1.960	1.960
T	Reaction Temperature	(°C)	140	140	140
S_C	Solvent Composition	(TLmol/MeOHmol)	0.0591	0.0569	0.0550
C_R	Catalyst Ratio	(kg/MBkg)	0.132	0.132	0.132
P	Reaction Pressure	(kg/cm ² ·G)	250	250	250
v	H ₂ Velocity	(cm/sec)	1.0	1.0	1.0
C_{ap}	Capacity	(BAkg/hr)	333.3	1,000	333.3
θ	Residence Time	(hr)	2.05	2.00	1.96
C	Conversion		0.282	0.279	0.308
S	Selectivity		0.941	0.943	0.945
K_1	Rate Constant	(hr ⁻¹)	0.265	0.269	0.328
K_2	Rate Constant	(hr ⁻¹)	0.0306	0.0301	0.0296
Cost Variables and Others					
A_1			14.81	43.70	12.88
A_2			5.37	11.04	4.89
A_3			4.69	14.16	4.26
A_4			3.16	9.54	2.87
A_5			151.0	451.47	150.0
D	Dea. of Reactor	(m)	1.208	1.732	1.150
V	Slurry Flow Rate	(m ³ /hr)	6.01	18.13	5.47
θ	Time for Filtration	(hr)	41.28	41.28	41.28
n	Rev. Vel. of Filter	(rph)	5	5	5
A	Filter Size	(m ²)	108.5	327.2	100.1
A'	Filter Size, for Catalyst Washing	(m ²)	—	—	43.0
N_1	No. of Trays, TW-1		12	12	12
N_2	TW-2		76	84	74
N_3	TW-3		27	27	27
D_{T1}	Diameter TW-1	(m)	1.04	1.58	0.993
D_{T2}	TW-2	(m)	0.985	1.44	0.952
D_{T3}	TW-3	(m)	0.844	1.29	0.798
R_1	Reflux Ratio TW-1		0.172	0.172	0.171
R_2	TW-2		0.094	0.050	0.118
R_3	TW-3		0.914	0.912	0.955
Utility Consumptions					
	Steam	(t/hr)	7.25	20.66	8.33
	Power	(kW)	818	2,457	795
	Cooling Water	(t/hr)	323	943	301
Raw Materials					
TL		(kg/BAkg)	0.9498	0.9495	0.9488
H ₂			0.0405	0.0403	0.0436
MeOH			0.0268	0.0271	0.0246
Cat ₁ +Cat ₂ *)			0.0219	0.0219	0.0218
Cat ₃ **)			0.0313	0.0315	0.0285
Initial Costs					
		(10 ⁶ yen)			
C_1			82.24	204.32	73.45
C_2			24.70	39.14	23.28
C_3			10.94	17.63	10.46
C_4			7.13	17.61	6.53
C_5			33.74	59.28	33.63
C_6			42.51	70.11	46.28
C_7			151.92	307.21	231.17
C_8			85.62	149.75	85.62
C_9			99.72	180.10	99.49
T_C			773.09	1,492.73	859.26
Production Costs					
		(yen/BAkg)			
U_t	Total Utilities		28.00	27.25	29.76
	Steam		14.46	13.74	16.62
	Power		10.24	10.25	9.95
	Cooling Water		1.66	1.61	1.54
M_t	Total Materials		39.11	39.17	38.37
	TL		23.74	23.74	23.74
	H ₂		2.67	2.66	2.88
	MeOH		0.80	0.81	0.74
	Cat ₁ +Cat ₂		2.50	2.50	2.49
	Cat ₃		9.40	9.46	8.54
E_q	Fixed Charges		86.93	55.95	96.62
O_F	Objective Function, $E_q + U_t + M_t$		154.04	122.37	164.75

*) Catalyst for oxidation and esterification.

**) For hydrogenation.

failed to trace a value of K_1 from the formula on the optimal point. Therefore, the region is reduced, and the formulas are corrected as Eqs. (10) and (11) for further studies.

6.2.2 Case of Limited Region ($-1 \leq x_i \leq 1$, $i=1,2,\dots,5$)

The final result, an optimal set of variables, accompanied by other major parameters are obtained and shown in **Table 5**. At the optimal condition, calculated kinetic rate data were verified by experiment.

The variables except x_3 slip the true minimum point out of their limited range, however, the terminal point may be still regarded as an optimum due to certain process restrictions, such as catalyst life and ease or stability of the plant operation. The nature of response surface in

Fig. 7 Cost Contours Near the Optimal Point (S_R , T , P , Constant)

Fig. 8 Cost Contours Near the Optimal Point (S_R , T , C_R , Constant)

Fig. 9 Cost Contours Near Optimal Point (S_R , T , S_C , Constant)

Table 6 Production Cost Estimate

Plant Scale BA t/mo		Case 1 200 No Pretreatment	Case 2 600 No Pretreatment	Case 3 200 Cat. Pretreatment
Initial Investment	(10 ⁶ yen)	914	1,765	1,015
BL	(")	773	1,493	859
OBL	(")	141	272	156
Materials Cost	(yen/kg)	39.11	39.17	38.37
Utilities Cost	(")	28.00	27.25	29.76
Labour	(")	13.54	4.51	13.54
Fixed Charge*)	(")	86.93	55.95	96.62
Production Cost	(")	167.58	126.88	178.29
Direct Overhead	(")	7.25	5.32	7.78
Selling Expense	(")	4.60	4.60	4.60
Interest for Operation	(")	6.04	4.43	6.48
Total Production Cost	(")	185.5	141.2	197.2
Profit	(")	56.0	36.1	62.1
Rate of Return on Investment	(%/yr)	30	30	30
Selling Price	(yen/kg)	241.5	177.3	259.3

*) Total of such fixed charges as Maintenance (3%/yr of BL), Depreciation (11.25%/yr of BL, 5%/yr of OBL), Interest for construction (5%/yr of BL+OBL) and Administrative expense (5%/yr of BL+OBL).

Fig. 10 Dependence of Production Cost O_F on rate Constant K_1 Around the Optimal Point

Fig. 11 Dependence of Production Cost O_F on Filtration Resistance α Around the Optimal Point

Furthermore, the experimental study showed that hydrogen pretreatment of the catalyst raises its activity as much as 20%, but the effect is temporary, so that a process with such device doubles the filter and reactor requirement and is expensive. This is also considered (Table 5).

The production cost and the selling price for 200 tons/month and 600 tons/month capacities are illustrated in Table 6. The larger plant allows 25% reduction in the selling price.

6.3 Important Process Factors

Among the various process factors, rate constant K_1 and filtration resistance α have the greatest effect on the production cost. If these are improved, the cost can be reduced as illustrated in Figs. 10 and 11.

Further experimental studies are expected.

7 Conclusions

As the results of this investigation, features of design and operation of a process for the liquid phase hydrogenation of methyl benzoate have been obtained. These are given as follows:

1. Reactor, hydrogen bubbling column
2. Catalyst used, copper-chromium type
3. Solvent, constant b.p. mixture of MeOH/TL
4. Catalyst recovery, high pressure drum filter
5. No catalyst pretreatment
6. Reaction temperature, 140°C
7. Reaction pressure, 250 kg/cm²·G
8. Solvent ratio, 1.96 kg/MBkg
9. Hydrogen superficial velocity, 1.0 cm/sec
10. Conversion, ca. 30%
11. Selectivity, 95%
12. Diameter of reactor, 1.73 m
13. Height of reactor, 17 m

The flow sheets are shown in Figs. 1 to 3.

A new benzyl alcohol process with toluene as raw material, in which catalytic hydrogenation occupies the major role, can offer benzyl alcohol at a price less than 200 yen/kg at a production capacity of 600 tons/30 days.

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Nomenclature

- A : Filtration area of filter, m²
 A_i : Cost variables, $i=1\sim5$
 C : MB Conversion
 C_{ap} : BA Production rate, kg/hr
 C_i : Initial cost of equipment, $i=0\sim8$, 10⁶ yen
 C_L : Catalyst load, kg/hr
 C_R : Catalyst ratio, kg/MB kg
 c : Parameter of filtration defined in Eq. (13), m
 D : Diameter of reactor, m
 D_T : Diameter of distillation tower, m
 Eq : Fixed charge on production cost, yen/BA kg
 F_i : Pressure correction factors, $i=1\sim4$
 f_i : Type Factors of each tower, $i=1\sim4$
 j : Order of reaction, BA→TL respect to H₂
 K : Selectivity parameter, K_2/K_1
 K_1 : Rate constant, $k_1 P_{H_2}$ (MB)₀, 1/hr
 K_2 : Rate constant, same as k_2 , 1/hr
 K_m : Resistance of unit area of filter medium, 1/m
 k : Parameter of filtration defined in Eq. (13), m²/sec
 k_1 : Rate constant MB→BA, l/mol·hr⁻¹·cm²/kg
 k_2 : Rate constant BA→TL, 1/hr

- l : Order of reaction, MB→TL respect to H_2
 M_f : Materials cost, yen/BA kg
 m : Order of reaction, MB→BA, respect to MB
 N : Number of trays in tower
 n : Order of reaction, BA→TL, respect to BA or Revolution velocity of filter, rph
 O_F : Objective function—production cost of BA
 P : Reaction pressure, kg/cm²·G
 P_{H_2} : Partial pressure of hydrogen, kg/cm²·G
 ΔP : Driving pressure difference for filtration, kg/cm²
 R : Reflux ratio
 S : BA Selectivity
 S_c : Solvent composition, TL mol/MeOH mol
 S_R : Solvent ratio, kg/MB kg
 T : Reaction temperature, °C
 T_c : Total initial investment within battery limit, 10⁶ yen
 U_f : Utilities cost, yen/BA kg
 V : Slurry flow rate, m³/hr
 v : Filtrate volume per unit area of filter, m or Hydrogen superficial velocity through reactor, cm/sec
 X_i : Standardized variables after transformation of coordinates, $i=1\sim 5$
 x_i : Dimensionless process variables, $i=1\sim 5$

Greek letters

- α : Specific cake resistance of filtration, m/kg
 θ : Reaction time for batch reactor, hr or Time for filtration, hr
 $\bar{\theta}$: Mean residence time in continuous reactor, hr
 κ : Diluteness of slurry, m³/kg

- μ : Viscosity of filtrate, kg/m sec
 Ψ : Sensitivity of variable to production cost

Abbreviations

- BA: Benzyl Alcohol
 MB: Methyl Benzoate
 MeOH: Methanol
 TL: Toluene

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