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# Production of benzaldehyde: a case study in a possible industrial application of phase-transfer catalysis

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**Abstract**

The conventional method of producing benzaldehyde by direct oxidation of toluene has a major drawback: low conversion to achieve high selectivity. Phase-transfer catalysis (PTC) may be used as an alternative route for benzaldehyde production. In the present study, routes to produce benzaldehyde from benzyl chloride in the liquid phase by using PTC have been examined based on the kinetic data obtained. Using the results of this study and the available information on the conventional route, process design simulations have been carried out for all the routes. While PTC-based processes offer advantages, the study shows that the conventional route appears to be the preferred one for this relatively large-scale organic intermediate with current conversions, selectivities, and chemical costs. However, even minor improvements in one or two PTC steps can greatly enhance the prospects of the PTC route. In general, as the processes get increasingly chemistry intensive, the PTC route becomes increasingly the preferred candidate. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Benzaldehyde; Direct oxidation; Catalysis; Phase transfer catalysis

## 1. Introduction

Phase-transfer catalysis (PTC), a technique to bring reactants in two immiscible phases together by adding a phase-transfer (PT) catalyst, is often an attractive alternative to conventional processes which can be inefficient due to high pressure and temperature requirements or due to low conversions or product selectivities. PTC offers mild reaction conditions, such as lower reaction temperatures and pressures, which enhance process reliability and flexibility. Furthermore, the PTC method often reduces or even eliminates the need for organic solvents in the reaction.

The use of PT catalysts has grown significantly in the past few decades. It is reported that there are several commercial processes which use approximately 1 million pounds of PT catalyst per year [1].

Benzaldehyde, $C_6H_5CHO$, is one of the most industrially useful members of the family of aromatic aldehydes. Its most important use is in organic synthesis, where it is the raw material for a large number of products (including perfumery chemicals). A considerable amount of benzaldehyde is utilized to produce various other aldehydes, such as cinnamic, methylcinnamic, amylcinnamic, and hexylcinnamic.

Two industrially important processes for the synthesis of benzaldehyde involve the hydrolysis of benzal chloride and the air-oxidation of toluene [2]. Other processes, such as the oxidation of benzyl alcohol, the reduction of benzoyl chloride, and the reaction of carbon monoxide and benzene, have been utilized in the past, but are no longer industrially useful. Today, the air-oxidation of toluene, both in the vapor and liquid phases, is the source of most of world's synthetic benzaldehyde. The process, however, requires rather high temperatures and pressures and gives low yields due to the formation of by-products. Alternative processes that can overcome these disadvantages would be attractive.

PTC is an attractive alternative method of synthesizing benzaldehyde. Studies have been reported in the literature on the synthesis of benzaldehyde under PTC conditions using various starting materials and PT catalysts. It has been reported that, under PTC conditions, benzaldehyde can be synthesized through direct oxidation of benzyl chloride by using chromium compounds [3–7]. Other studies reported the synthesis of benzaldehyde by oxidizing benzyl alcohol by using oxidizing agents such as hypochlorite anion [8–13].

## 2. Objective of present study

Although PT catalysts have been used extensively in industry, to the best of the authors' knowledge, there has not been any study reported in public journals which discusses

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the use of a PT catalyst in any industrially important chemical synthesis process from the process engineering point of view. The goal of the present study is to use the synthesis of benzaldehyde as a case study for the application of the PTC method in an industrially important medium-volume intermediate. Several PTC routes to produce benzaldehyde from benzyl chloride were investigated and kinetic data for these routes were obtained. Based on the results of this kinetic study and the available information on the conventional route, process design simulations of these routes were carried out to assess the commercial feasibility of these processes. From this simulation study, advantages and disadvantages of a commercial scale PTC-based benzaldehyde plant using PTC were assessed in comparison with a plant using the conventional method. Plausible ways to improve the economic feasibility of this PTC-based process were investigated.

## 3. Selection of starting organic material

Selection of the starting material used in benzaldehyde synthesis using PTC is crucial. Toluene is the ideal starting material since it is one of the most common raw materials available commercially. However, direct conversion of toluene to benzaldehyde using the PTC method is very difficult if not impossible. Toluene must undergo one treatment, for instance, chlorination to form benzyl chloride, before it can be converted to benzaldehyde efficiently. Currently, most of the benzyl chloride is commercially manufactured by the thermal or photochemical chlorination of toluene at 65–100°C [2]. There have been reports that benzyl chloride can be produced from toluene via PTC [14,15]. However, since the present conventional process for chlorinating toluene to produce benzyl chloride is already a mild process, utilizing a PT catalyst for converting toluene to benzyl chloride does not seem to be attractive.

For synthesizing benzaldehyde via PTC, potential raw materials that would be attractive are benzyl alcohol and benzyl chloride. Benzyl chloride as raw material would be a more attractive choice since it is only a one-step process from toluene which is the main raw material for synthesizing benzaldehyde using conventional methods. From the process point of view, benzyl alcohol is the preferred starting material since it can be converted easily to benzaldehyde by using a single oxidation step. However, from the economic point of view, benzyl alcohol is not an attractive choice since it is much more expensive than benzyl chloride. Currently, benzyl alcohol is almost universally manufactured from toluene which is first converted to benzyl chloride before being subsequently hydrolyzed to benzyl alcohol via treatment with aqueous sodium carbonate [2]. Thus, since benzyl alcohol is produced from benzyl chloride anyway, benzyl chloride would be the more attractive choice of raw material for producing benzaldehyde assuming that the process involved is neither more difficult nor more expensive than that with benzyl alcohol as the raw material.

## 4. Theoretical basis for determining reaction routes

Theoretically, the simplest way of converting benzyl chloride to benzaldehyde would be by a single-step reaction, i.e. by contacting benzyl chloride with an oxidizing agent such as permanganate, chromate, or hypochlorite ions. In this study, hypochlorite ion is selected to be the oxidizing agent of choice. Hypochlorite ion is selected since it is relatively less expensive compared with the other oxidizing agents. It is thought that the reaction between benzyl chloride and hypochlorite anion takes place according to the single-step reaction

$$\begin{aligned}&\mathrm{PhCH_2Cl_{org}} + (\mathrm{OCl^-})_{aq}\\&\quad\rightarrow \mathrm{PhCHO_{org}} + (\mathrm{HCl})_{aq} + (\mathrm{Cl^-})_{aq}\end{aligned} \tag{1}$$

The possible PTC mechanism of this single-step oxidation reaction is shown in Fig. 1. As shown therein, contact between benzyl chloride and hypochlorite anion may take place both with and without the assistance of a PT catalyst.

From a kinetic study of the PTC-enhanced oxidation of benzyl chloride to benzaldehyde with chromate salts as the oxidizing agents, it was reported that the main PTC route for benzaldehyde synthesis from benzyl chloride is through the formation of benzyl alcohol as an intermediate product, whereas the direct PTC-assisted oxidation of benzyl chloride to benzaldehyde is insignificant [16]. This study suggests that, in order to achieve good benzaldehyde yields, benzyl chloride must be initially converted to benzyl alcohol before conversion to benzaldehyde. Benzyl alcohol is obtained from benzyl chloride via a hydrolysis reaction with hydroxide anion. It is then oxidized by hypochlorite anion to form the final product, benzaldehyde. Thus, the overall reaction of benzyl chloride's conversion to benzaldehyde consists of the following two reaction steps:

*Step* 1. Hydrolysis of benzyl chloride by hydroxide anion to form benzyl alcohol intermediate:

$$\mathrm{PhCH_2Cl_{org}} + (\mathrm{OH^-})_{aq} \rightarrow \mathrm{PhCH_2OH_{org}} + (\mathrm{Cl^-})_{aq} \tag{2}$$

*Step* 2. Oxidation of the benzyl alcohol intermediate by hypochlorite anion to form benzaldehyde:

$$\mathrm{PhCH_2OH_{org}} + (\mathrm{OCl^-})_{aq} \rightarrow \mathrm{PhCHO_{org}} + (\mathrm{Cl^-})_{aq} + \mathrm{H_2O} \tag{3}$$

In hypochlorite salt solution, theoretically the hydroxide anion will be available from the interaction between the hypochlorite anion with water according to the equilibrium

$$(\mathrm{OCl^-}) + \mathrm{H_2O} \rightleftarrows (\mathrm{HOCl}) + (\mathrm{OH^-}) \tag{4}$$

A plausible PTC mechanism of this hydrolysis–oxidation reaction can be seen in Fig. 2. Based on this mechanism, it is

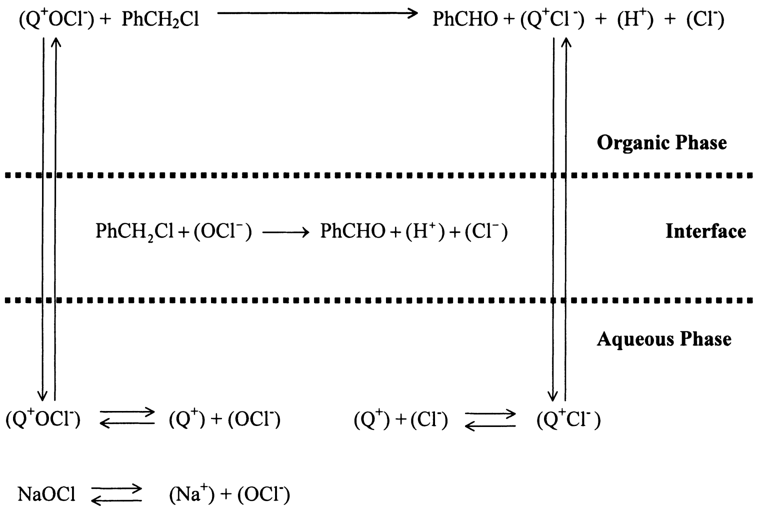

Fig. 1. Diagram of the single-step PTC mechanism of the synthesis of benzaldehyde from benzyl chloride by oxidation with hypochlorite ion.

thought that adding a hydroxide-containing compound, such as sodium hydroxide, will increase the formation of benzyl alcohol intermediate which subsequently will increase the formation of benzaldehyde.

Theoretically, the hydrolysis of alkyl/aromatic halides to produce alkyl/aromatic alcohols can be accomplished by using a single hydroxide anion displacement step with the assistance of a PT catalyst. However, it has been reported that this direct hydrolysis method results in low selectivity to alcohols since ethers are the preferred products [17,18]. To obtain pure alkyl alcohols from alkyl halides it has been suggested that an esterification step is necessary [19]. With an esterification step coming into the picture, alkyl halide undergoes a displacement step with a carboxylate salt such as sodium acetate or sodium formate, to form a carboxylate ester. The carboxylate ester formed is then easily hydrolyzed to alkyl alcohol. Thus, based on this additional information on the conversion of benzyl chloride to benzaldehyde, it is thought that higher yield of benzaldehyde may be obtained by first converting benzyl chloride to a benzyl carboxylate such as benzyl acetate. Benzyl acetate then can be used as the intermediate raw material to form benzaldehyde. The reaction scheme for the conversion of benzyl chloride to benzaldehyde then will consist of the following three steps:

*Step* 1. Esterification of benzyl chloride with acetate anion to form benzyl acetate intermediate:

$$\mathrm{PhCH_2Cl_{org}} + (\mathrm{OAc^-})_{aq} \rightarrow \mathrm{PhCH_2OAc_{org}} + (\mathrm{Cl^-})_{aq} \quad (5)$$

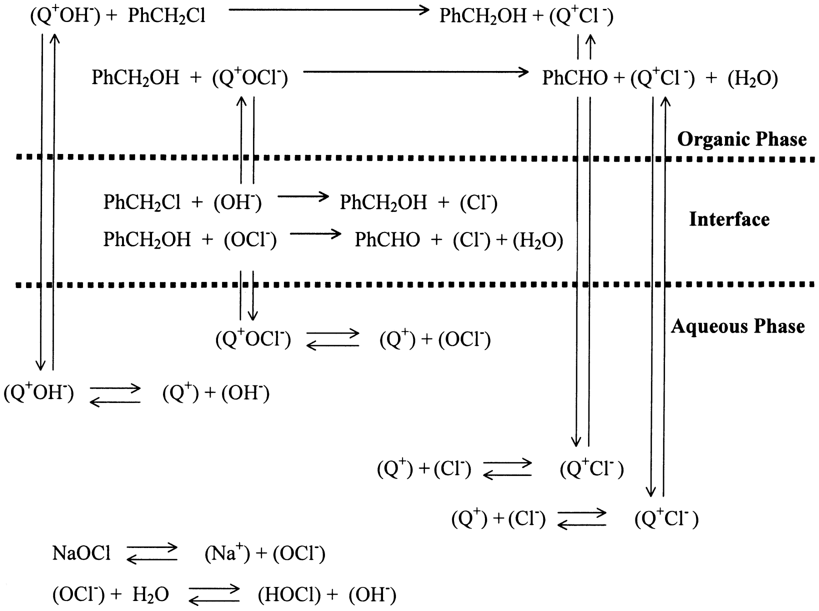

Fig. 2. Diagram of the two-step PTC mechanism of the synthesis of benzaldehyde from benzyl chloride.

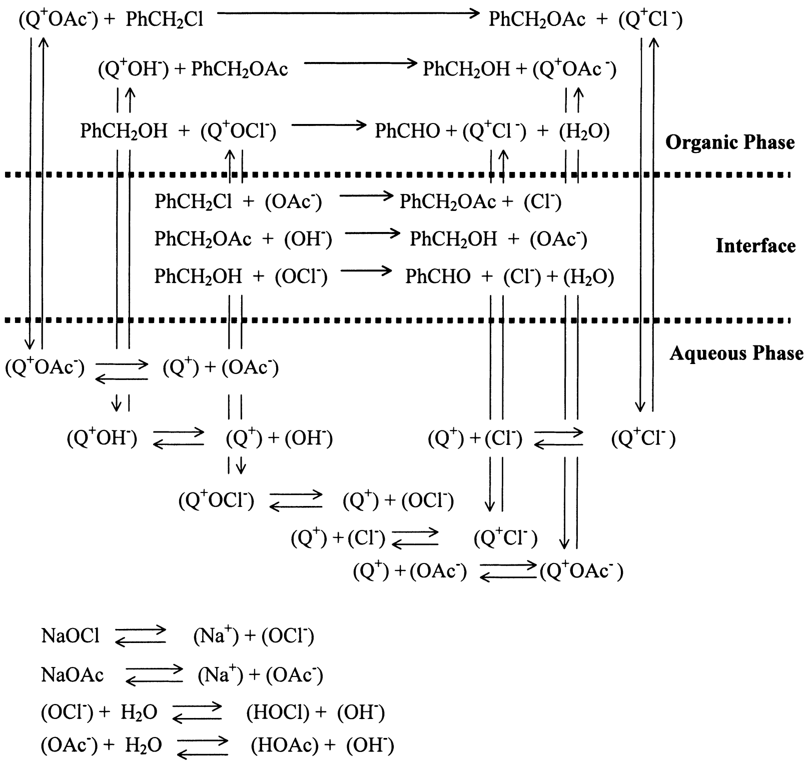

Fig. 3. Diagram of the three-step PTC mechanism of the synthesis of benzaldehyde from benzyl chloride.

*Step* 2. Hydrolysis of the benzyl acetate intermediate by hydroxide anion to form benzyl alcohol:

$$\mathrm{PhCH_2OAc_{org}} + (\mathrm{OH^-})_{aq} \rightarrow \mathrm{PhCH_2OH_{org}} + (\mathrm{OAc^-})_{aq} \tag{6}$$

*Step* 3. Oxidation of benzyl alcohol by hypochlorite anion to form the final product benzaldehyde:

$$\mathrm{PhCH_2OH_{org}} + (\mathrm{OCl^-})_{aq} \rightarrow \mathrm{PhCHO_{org}} + (\mathrm{Cl^-})_{aq} + \mathrm{H_2O} \tag{7}$$

In the presence of sodium acetate in the aqueous phase, hydroxide anion is also generated from the reaction of the acetate anion with water:

$$(\mathrm{OAc^-}) + \mathrm{H_2O} \rightleftarrows (\mathrm{HOAc}) + (\mathrm{OH^-}) \tag{8}$$

Thus, step 2 can take place with the addition of acetate anion in the aqueous phase. Adding hydroxide anion from an external source such as sodium hydroxide will increase the formation of benzyl alcohol. Theoretically, the reactions can take place in a single reactor, i.e. the three inorganic anions (acetate, hydroxide, and hypochlorite) present at the same time. The PTC mechanism of the formation of benzaldehyde from benzyl chloride involving all the steps is shown in Fig. 3.

## 5. Plausible synthesis routes

Based on the theory discussed above, several routes to convert benzyl chloride to benzaldehyde can be proposed. The classification of these routes is based on the number of reaction steps required for the conversion: one-step reaction system, i.e. oxidation step only; two-step reaction system, i.e. hydrolysis + oxidation; and three-step reaction system, i.e. esterification + hydrolysis + oxidation. As shown in Fig. 4, various routes can be proposed by varying the manner in which these steps are carried out.

## 6. PT catalyst selection

As with other syntheses, the selection of a suitable catalyst for benzaldehyde synthesis is crucial. Ideally, the selected catalyst should be able to catalyze all the steps involved in the reaction. This may make the catalyst selection more complex.

Various types of PT catalysts are available for selection. However, in this study the selection of catalyst is limited to the quaternary ammonium salt type since it is generally inexpensive, easy to prepare, and less toxic compared to the other PT catalyst types. The principal criteria in selecting the catalyst are reactivity and separation of catalyst from the product. Based on their hydrophilic/organophilic properties, two homogeneous quaternary ammonium salts were selected:

1. benzyltributyl ammonium chloride (BTBAC): a hydrophilic PT catalyst;
2. trioctylmethyl ammonium chloride (TOMAC): a strongly organophilic PT catalyst.

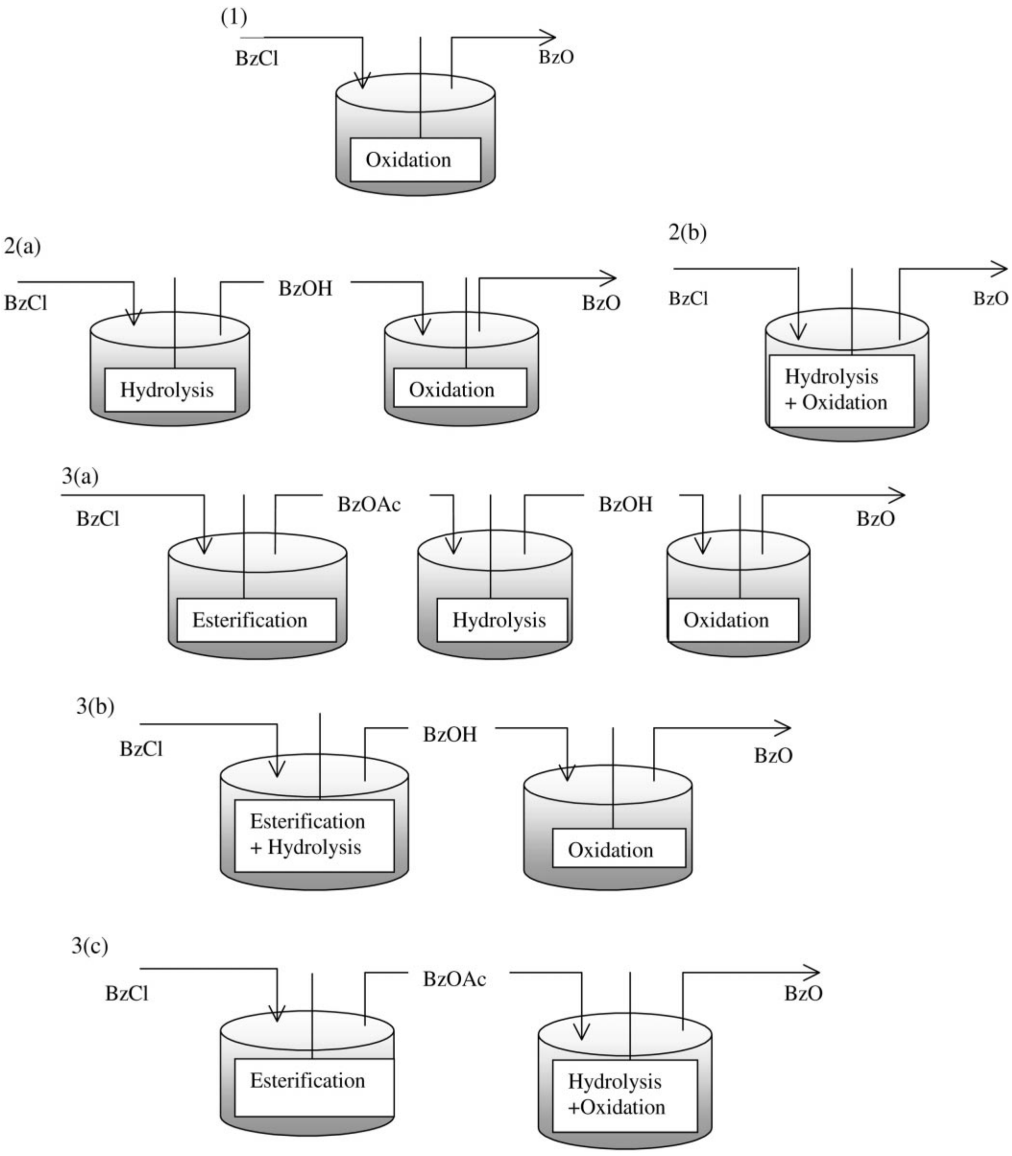

Fig. 4. Schematic of routes for benzaldehyde synthesis from benzyl chloride.

An organophilic PT catalyst generally will have higher reactivity since it resides more in the organic phase which increases the amount of inorganic anion being transferred to the organic phase to react with the organic reactant. However, catalyst separation from product may be more difficult if the latter is soluble in the organic phase, as in benzaldehyde synthesis. A hydrophilic PT catalyst such as BTBAC may provide an easier separation since it naturally prefers to reside in the aqueous phase. Since the aqueous phase has a high ionic strength, especially at high salt concentrations, the hydrophilic PT catalyst can be salted out and thus made to reside in the organic phase. Separation can be done easily by washing the organic phase, usually with water, after separating the organic phase from the aqueous phase. From this point of view, for this benzaldehyde synthesis process, BTBAC may be a better choice than TOMAC catalyst provided the reactivities are comparable.

## 7. Kinetic study

Extensive kinetic studies on the reactions involved in the benzaldehyde synthesis routes considered have been conducted and reaction modeling has been attempted. Results of the kinetics and modeling of these reactions are being reported separately. A summary of these results is presented below.

### 7.1. Experimental procedure

In the kinetic study the concentrations of the organic reactant and products versus time data were obtained.

Table 1
Experimental results of direct oxidation of benzyl chloride to benzaldehyde[a]

| Reactant concentrations | | Catalyst | Final organic phase composition (mol%) | | |
|---|---|---|---|---|---|
| BzCl (mol/$l_{org}$) | NaOCl (mol/$l_{aq}$) | | BzO | BzCl | BzOH |
| 0.5 | 0.8 | None | 0.0 | 100.0 | 0.0 |
| 0.5 | 0.8 | BTBAC | 0.0 | 100.0 | 0.0 |
| 0.5 | 0.8 | TOMAC | 2.1 | 97.9 | 0.0 |

[a] Reaction conditions — organic/aqueous phase volume: 70/70 ml; agitation speed: 700 rpm; temperature: 90°C; reaction time: 3 h; catalyst concentration: 5 mol% of organic reactant concentration.

Unless stated otherwise, all reagents were of analytical grade and not further purified. The soluble PT catalysts used in this study, BTBAC and TOMAC, were obtained from Fluka Chemical Corp. The organic reactants (i.e. benzyl chloride, benzyl alcohol and benzyl acetate) were dissolved in toluene and the solid inorganic reactants (sodium acetate, sodium hydroxide and calcium hypochlorite) in deionized water.

The kinetic experiments were carried out in a 300 ml stainless steel reactor from PARR Instruments. The vessel was lined with a Teflon insert and equipped with a two-blade paddle. The temperature could be controlled to within 1°C. For all reactions, the total volume of the mixture was 140 ml with equal volume fractions of the liquid phases. The concentrations of the organic reactants and products were measured by using a Perkin-Elmer gas chromatograph (Model 3000 Autosystem with FID). A packed column (Carbopack, 10% SP-2250 from Supelco Inc.) with a length of 2.0 m and a diameter of 1/8 in. was used for the analysis. An external standard was used.

### 7.2. *Summary of results*

#### 7.2.1. *One-step reaction system*

Several experimental results on the direct reaction between benzyl chloride and sodium hypochlorite are shown in Table 1. Up to 3 h of reaction time no conversion of benzyl chloride was observed even for the reaction in the presence BTBAC as catalyst. A small amount of benzaldehyde was formed after 3 h in the reaction with TOMAC. No formation of benzyl alcohol was observed in any of the reactions.

These results indicate that the PTC oxidation mechanism suggested in Fig. 1 does not take place. Thus, it was concluded that the one-step reaction system for synthesizing benzaldehyde from benzyl chloride by oxidation with sodium hypochlorite (i.e. route 1 in Fig. 4) is not technically feasible.

#### 7.2.2. *Two-step reaction system*

In the two-step reaction, benzyl chloride is first converted to benzyl alcohol which is subsequently oxidized to benzaldehyde. It has been reported in the literature that the oxidation of benzyl alcohol to benzaldehyde by $OCl^-$ (hypochlorite) anion in the presence of PT catalyst can easily take place at room temperature. High conversion with high selectivity to benzaldehyde can be obtained in a short time. Laboratory experimental results confirm this finding.

On the contrary, the conversion of benzyl chloride to benzyl alcohol is more difficult and takes a longer time. Experimental results, Table 2, show that the hydrolysis of benzyl chloride to benzyl alcohol is significantly affected by the PT catalyst type, $OH^-$ anion concentration, and addition of sodium iodide “co-catalyst”. High conversion of benzyl chloride is obtained in the reaction in the presence of TOMAC, but the selectivity to benzyl alcohol is very low since the preferred product is benzyl ether. Reaction in the presence of BTBAC results in a significantly lower conversion of benzyl chloride, but the selectivity to benzyl alcohol can be as high as 100%. It was observed that adding a small amount of sodium iodide to the aqueous phase increases the conversion of benzyl chloride but decreases the selectivity to benzyl alcohol. This enhancing effect of sodium iodide has been previously reported by other workers [18,20]. In reactions using both types of PT catalysts the selectivity to benzyl alcohol becomes lower when a higher concentration of sodium hydroxide is used. With TOMAC, the selectivity is as low as 25%.

To reduce the number of actual reactors required for the reactions, it is possible to combine the $OH^-$ anion and $OCl^-$ anion in the aqueous phase in order for the hydrolysis and oxidation steps to take place simultaneously. However, as shown in Table 3, the reactions using this combination of

Table 2
Selected experimental results on hydrolysis of benzyl chloride to benzyl alcohol[a]

| NaOH concentration (mol/$l_{aq}$) | “Co-catalyst” (mol/$l_{aq}$) | PT catalyst | BzCl conversion (mol%) | Selectivity to BzOH (mol%) | Selectivity to by-products (mol%) |
|---|---|---|---|---|---|
| 0.8 | None | BTBAC | 42.4 | 100 | 0.0 |
| 0.8 | NaI (0.1) | BTBAC | 72.3 | 57.7 | BzEther (23.6); BzI (17.2) |
| 0.8 | None | TOMAC | 69.7 | 29.7 | BzEther (71.3) |
| 1.5 | None | BTBAC | 57.6 | 81.1 | BzEther (17.3) |
| 1.5 | NaI (0.025) | BTBAC | 71.8 | 52.3 | BzEther (42.2); BzI (5.5) |
| 1.5 | None | TOMAC | 82.3 | 25.6 | BzEther (74.4) |

[a] Reaction conditions — organic/aqueous phase volume: 70/70 ml; agitation speed: 700 rpm; temperature: 90°C; reaction time: 4 h; catalyst concentration: 5% of initial benzyl chloride concentration (0.025 mol/$l_{org}$).

Table 3
Experimental results on direct conversion of benzyl chloride to benzaldehyde by combination of hydrolysis and oxidation[a]

| NaOCl/NaOH concentration (mol/$l_{aq}$) | Catalyst | BzCl conversion (mol%) | Selectivity to BzO (mol%) | Selectivity to BzOH (mol%) |
|---|---|---|---|---|
| 0.8/2.4 | None | 18.1 | 45.3 | 54.7 |
| 0.8/2.4 | BTBAC | 49.5 | 33.1 | 66.9 |
| 0.8/2.4 | TOMAC | 27.3 | 40.3 | 59.7 |
| 1.6/2.4 | None | 10.8 | 45.2 | 54.8 |
| 1.6/2.4 | BTBAC | 40.4 | 38.9 | 57.5 |

[a] Reaction conditions — benzyl chloride concentration: 0.5 mol/$l_{org}$; organic/aqueous phase volume: 70/70 ml; temperature: 90°C; speed: 700 rpm; reaction time: 3 h; catalyst concentration: 5% of initial benzyl chloride concentration (0.025 mol/$l_{org}$).

hydrolysis and oxidation steps suffer from both low benzyl chloride conversion and, more importantly, low selectivity to benzaldehyde. By using BTBAC as catalyst, up to 50% of benzyl chloride could be converted within 3 h at 90°C temperature; however, the selectivity to benzaldehyde was less than 40%. The low conversion and benzaldehyde selectivity may be due to the following two reasons. First, $OCl^-$ anion is not a stable anion, particularly at high temperature. There was evidence that during reaction at 90°C this anion decomposed, which reduced the availability of hypochlorite anion for reaction. Second, the presence of OCl in the aqueous phase interferes with the hydrolysis step. Compared to the $OH^-$ anion, the $OCl^-$ anion has a relatively strong affinity to the PT catalyst cation. When both anions are present in the aqueous phase, the PTC cation tends to attach more to the $OCl^-$ anion which makes it difficult for the $OH^-$ anion to be transferred to the organic phase to react with benzyl chloride. Thus, it is concluded that simultaneous hydrolysis and oxidation by combining hydroxide and hypochlorite anions is not technically feasible. This conclusion essentially eliminates route 2(b) and hence route 3(c) in Fig. 4 from further consideration.

### 7.2.3. Three-step reaction system

In order to improve the selectivity, the benzyl chloride esterification step is brought into the picture which makes the benzyl chloride conversion to benzyl alcohol take place in two steps: (1) benzyl chloride esterification to benzyl acetate, and (2) hydrolysis of benzyl acetate to benzyl alcohol. Experimental results on these steps, obtained separately, show that, between the two steps, esterification is the slower one. While benzyl acetate is almost completely hydrolyzed by the $OH^-$ anion to form benzyl alcohol with 100% selectivity even without a PT catalyst at a reaction temperature as low as 40°C in 30 min of reaction time, the esterification of benzyl chloride to benzyl acetate is much slower. Complete conversion of benzyl chloride to benzyl acetate is obtained in 5 h in the presence of TOMAC and sodium iodide co-catalyst. A longer reaction time is needed for reaction with BTBAC. Thus, since complete conversion and high selectivity of each step can be obtained, a three-step system in which the steps are conducted separately with esterification as the limiting step can give a high conversion of benzyl chloride with high selectivity to benzaldehyde. This system is shown as route 3(a) in Fig. 4.

When benzyl chloride in the organic solvent is contacted with an aqueous phase containing sodium acetate and sodium hydroxide in the presence of a PT catalyst, the result is esterification followed by hydrolysis in series. Theoretically the inorganic component involved in the hydrolysis does not interfere with the esterification step, and vice versa. The esterification reaction naturally takes place first. Compared to the $OH^-$ anion, the acetate ($OAc^-$) anion is easier to transfer into the organic phase due its stronger affinity to the PTC cation. The benzyl acetate formed then readily reacts with the $OH^-$ anion to form benzyl alcohol. Several experimental results are shown in Table 4. The conversion of benzyl chloride and its selectivity to benzyl alcohol are affected by the type of PT catalyst, sodium acetate concentration in the aqueous phase, and the manner of NaOH addition. The highest benzyl chloride conversion and highest selectivity to benzyl alcohol are obtained in the presence of TOMAC and at high sodium acetate concentration, while the concentration of NaOH is kept low by adding it slowly during the reaction. As expected, reaction with BTBAC gives lower conversions; however, in the reaction with high sodium acetate concentration, the conversion is almost as high as that in the reaction with TOMAC.

## 7.3. Conclusions from kinetic study

### 7.3.1. Selection of reaction route

From the results of the kinetic study, it may be concluded that in order to obtain high benzyl chloride conversion with high selectivity to benzaldehyde a three-step reaction route is necessary. The three steps can be carried out separately or esterification and hydrolysis can be carried out simultaneously with a separate oxidation step (routes 3(a) and 3(b) in Fig. 4).

### 7.3.2. Selection of PT catalyst

Homogenous BTBAC is selected to be the catalyst of choice. The use of a high concentration of salt in the aqueous phase enables this hydrophilic PT catalyst to have a reactivity that is almost as high as that of TOMAC which is more organophilic. The hydrophilic property of BTBAC makes

Table 4
Selected experimental results on reaction of benzyl chloride to benzyl alcohol via combination of esterification and hydrolysis[a]

| NaOAc/NaOH concentration (mol/$l_{aq}$) | PT catalyst | BzCl conversion (mol%) | Selectivity to BzOH (mol%) | Selectivity to BzEther/BzOAc/BzI (mol%) |
|---|---|---|---|---|
| 2.0/0.5[b] | BTBAC | 40.7 | 84.2 | 8.7/1.33/5.72 |
| 4.0/0.5[c] | BTBAC | 64.6 | 76.7 | 14.8/4.2/4.3 |
| 6.0/0.5[c] | BTBAC | 87.7 | 84.6 | 9.5/3.7/2.2 |
| 2.0/0.5[b] | TOMAC | 91.2 | 63.3 | 34.4/1.6/0.6 |
| 2.0/0.5[c] | TOMAC | 90.1 | 75.3 | 22.4/1.7/2.3 |
| 0.5/0.5[c] | TOMAC | 78.4 | 52.7 | 44.4/2.1/0.9 |
| 4.0/0.5[c] | TOMAC | 88.2 | 86.4 | 11.7/1.1/0.5 |
| 6.0/0.5[c] | TOMAC | 94.6 | 88.6 | 6.0/4.8/0.2 |
| 6.0/0.5[b] | TOMAC | 95.5 | 79.0 | 19.6/1.0/0.23 |

[a] Reaction conditions — organic/aqueous phase volume: 70/70 ml; agitation speed: 700 rpm; temperature: 90°C; reaction time: 4 h; catalyst concentration: 5% of initial benzyl chloride concentration (0.025 mol/$l_{org}$); NaI co-catalyst concentration: 0.025 mol/$l_{aq}$.

[b] Manner of NaOH addition: added at once in the beginning of reaction.

[c] Manner of NaOH addition: added slowly throughout the reaction time.

the catalyst more attractive since catalyst separation from the product is potentially much easier.

## 8. Development of a commercial scale benzaldehyde plant

### 8.1. Experimental data

For design purposes, experimental data on benzaldehyde synthesis using routes 3(a) and 3(b) at reaction conditions (i.e. reactant concentrations) appropriate for commercial-scale operation were obtained. The basis of the selection of reactant concentrations is the concentrations of the salts in the aqueous phase which should be made as high as possible while still maintaining good solubility in water at reaction temperature. For the esterification step, 70 g of benzyl acetate were dissolved in 100 g of water to make up an aqueous phase with a concentration of approximately 6 mol/$l_{aq}$. For the oxidation step, calcium hypochlorite was used to supply the hypochlorite anion. The maximum concentration of hypochlorite anion that can be obtained is 2 mol/$l_{aq}$. Reaction conditions for each reaction step are listed in Table 5. Note that for the oxidation step, the organic phase volume was doubled to reduce the organic phase reactant concentration to be equal to the hypochlorite anion concentration in the aqueous phase. This is also necessary in order to obtain better control on conversion.

Figs. 5 and 6 show the experimental results from reactions in which benzyl chloride undergoes the complete three-step schedule. Fig. 5 shows the composition plots of the components from a reaction in which the organic phase product is separated from the aqueous phase and used as the organic phase feed for the next reaction step. In a 4 h esterification step at 90°C, about 94% of benzyl chloride reacted with approximately 94% selectivity to benzyl acetate. By-products are benzyl alcohol, benzyl ether and benzyl iodide (with selectivities of 4.5, 1 and 0.5%, respectively). It was observed that a third phase in the form of a viscous oily liquid was formed between the aqueous and organic phases. A GC analysis of the oily liquid indicated that it consists of mainly toluene, benzyl alcohol and the catalyst. The organic phase is

Table 5
Reaction conditions for the proposed commercial scale reaction system

| Esterification step | Hydrolysis step | Oxidation step |
|---|---|---|
| Organic phase | Organic phase | Organic phase: |
| Reactant: benzyl chloride (4 mol/$l_{org}$) | Organic phase from the esterification step | Organic phase form the hydrolysis step |
| Solvent: toluene | Aqueous phase | Additional toluene is added to double organic phase volume |
| | Reactant: sodium hydroxide (4 mol/$l_{aq}$) | |
| Aqueous phase | | Aqueous phase |
| Reactant: sodium acetate (6 mol/$l_{aq}$) | Organic/aqueous phase volume ratio: 1.0 | Reactant: calcium hypochlorite 2 mol/$l_{aq}$ |
| Reactant: sodium iodide (0.04 mol/$l_{aq}$; 1 mol% of organic reactant) | Reaction temperature: 70°C | Organic/aqueous phase volume ratio: 1.0 |
| PT catalyst | Reaction time: 20 min | Reaction temperature: 25°C |
| Homogeneous BTBAC (0.2 mol/$l_{org}$; 5 mol% of organic reactant) | | Reaction time: 30 min |
| Organic/aqueous phase volume ratio: 1.0 | | |
| Reaction temperature: 90°C | | |
| Reaction time: 4 h | | |

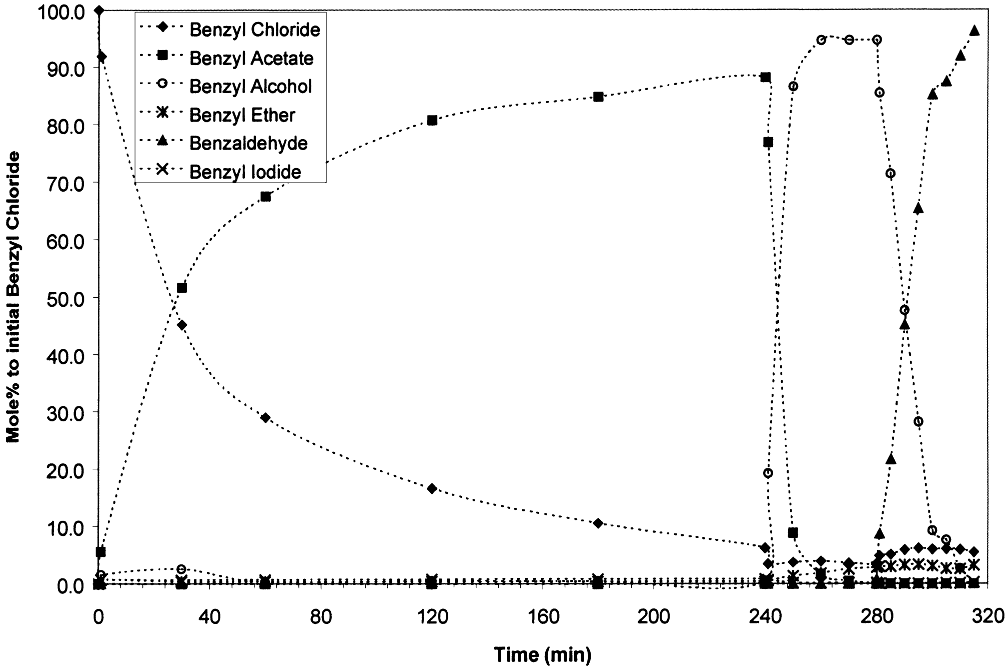

Fig. 5. Actual composition plots of the components from a reaction scheme in which benzyl chloride undergoes the complete three-step schedule with phase separation between reaction steps.

separated from the aqueous phase and used for the hydrolysis step. Within 20 min of hydrolysis at 70°C, 98% of benzyl chloride was converted to benzyl alcohol. It was noted that benzyl chloride was also further reacted, as well as benzyl iodide. At the end of the reaction, the overall benzyl chloride conversion was 97% with selectivity to benzyl alcohol of approximately 97%. The organic phase product was further separated, diluted by addition of solvent and reacted in the oxidation step for 30 min at 25°C. Approximately 97% of benzyl alcohol was converted with selectivity to benzalde-

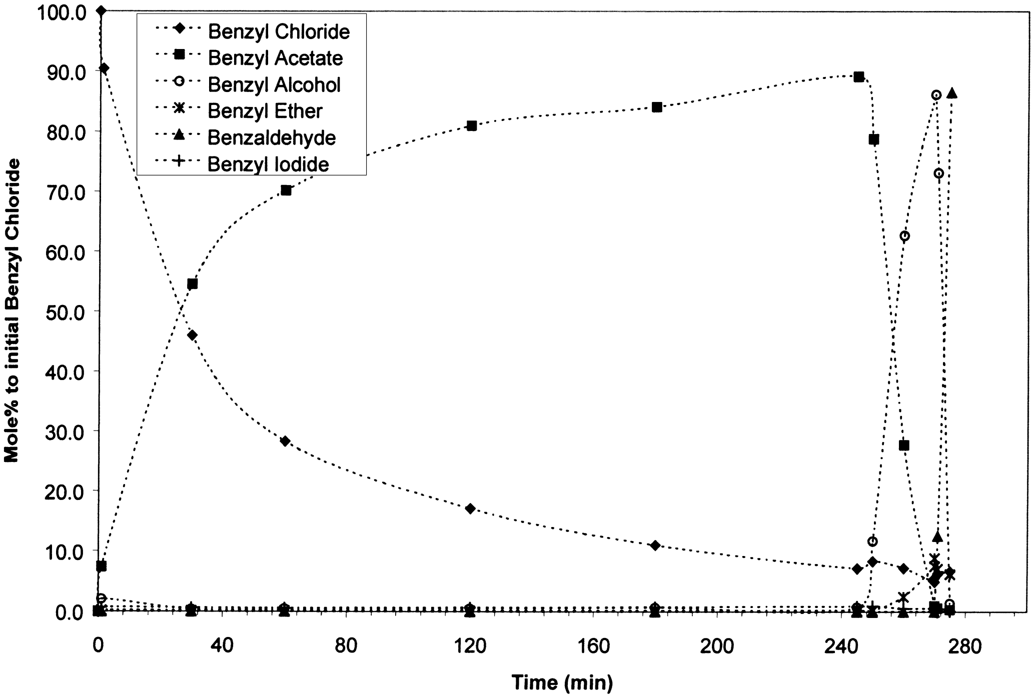

Fig. 6. Actual composition plots of the components from a reaction scheme in which benzyl chloride undergoes the complete three-step schedule without phase separation between esterification and hydrolysis steps.

hyde of 98%. It was noted that a small amount of benzyl chloride was regenerated in this phase. By the end of the oxidation step, the overall conversion of benzyl chloride was 95% with selectivity to benzaldehyde of 96%.

Fig. 6 shows the composition plots of the components from a reaction scheme in which the hydrolysis conducted immediately after esterification without separating the organic phase from the aqueous phase. At the end of the 4 h esterification step, the overall conversion of benzyl chloride was 93% with 95% selectivity to benzyl acetate. After 20 min of hydrolysis step, 98% of benzyl acetate is converted to benzyl alcohol. The overall conversion of benzyl chloride increased to 95%; however, the selectivity to benzyl alcohol is only 90% due to more significant formation of benzyl ether. The organic phase product then underwent the oxidation reaction step. It was observed that the reaction was very fast. Within 5 min of reaction, 97% of benzyl alcohol was converted to benzaldehyde. Further reaction caused benzaldehyde to be oxidized further to benzoic acid. By the end of the 5 min oxidation step, the overall conversion of benzyl chloride was 94% with selectivity to benzaldehyde of approximately 92%.

From these experimental data, it can be seen that routes 3(a) and 3(b) give comparable benzyl chloride conversion and selectivity to benzaldehyde. The fact that the oxidation step in route 3(b) is very fast, which make it difficult to control the reaction, indicates that the amount of PT catalyst in the organic phase is too high. Prior to the oxidation step, a step to remove some of the PT catalyst from the organic phase may have to be incorporated. The separation may be accomplished by washing the organic phase with water. The need for this extra step in route 3(b) makes route 3(a) (i.e. three separate reaction steps) more attractive. In the reaction scheme using route 3(a), most of the catalyst (mostly in the third liquid phase) is naturally separated from the organic phase when the phase is separated from the aqueous phase. No further catalyst separation is needed down the process stream. Furthermore, by using route 3(a) in which the esterification step is separated from the hydrolysis step, sodium acetate regenerated from the hydrolysis reaction may be easily recycled for use in the esterification step without further separation.

### 8.2. Design basis

Based on the experimental data obtained in the benzaldehyde synthesis using route 3(a), the basic design of a plant with a capacity of 3000 metric tonnes of benzaldehyde per year is now attempted. The plant will operate in a batch-continuous mode, i.e. the reactors are operated in the batch mode while the product purification steps are operated in the continuous mode. A PFD of the plant is shown in Fig. 7.

The plant basically will consist of two main sections: the reactor section and the purification section. The reactor section, operated in batch mode, consists of two reactors equipped with agitators. The first reactor is used for conducting reaction step 1, i.e. the esterification step, and the second reactor is used for conducting reaction steps 2 and 3, i.e. hydrolysis and oxidation steps, respectively. Since the operating temperatures of these two reactions are different, the second reactor will be designed to operate with two different heat transfer media. The time required to complete a batch cycle is dependent on the time required to complete the esterification step since compared to the other two steps it takes the longest time to complete. It is calculated that it will take 6 h per batch to complete the esterification step; thus, per day of operation, four batches can be completed. The time schedule of the reactors' operation per batch cycle is shown in Table 6.

The purification section of the plant will consist of two distillation columns. The first column mainly functions to recover the organic solvent (i.e. toluene) which can be recycled. The solvent is recovered as distillate product while the bottom product consisting of organic product mixture is fed to the second column which functions to recover ben-

Table 6
Scenario of operation schedule per batch with production rate of four batches per operation day

| Reactor 1 | | Reactor 2 | |
|---|---|---|---|
| Activity | Time (min) | Activity | Time (min) |
| Reaction step 1: filling | 30 | Reaction step 2: filling | 30 |
| Reaction step 1: reaction | 240 | Reaction step 2: reaction | 20 |
| Reaction step 1: emptying | 30 | Reaction step 2: emptying | 30 |
| Down time | 60 | Down time | 35 |
| | | Reaction step 3: filling (# 1) | 30 |
| | | Reaction step 3: reaction | 30 |
| | | Reaction step 3: emptying | 30 |
| | | Down time | 30 |
| | | Reaction step 3: filling (# 2) | 30 |
| | | Reaction step 3: reaction | 30 |
| | | Reaction step 3: emptying | 30 |
| | | Down time | 35 |
| Total | 360 | Total | 360 |

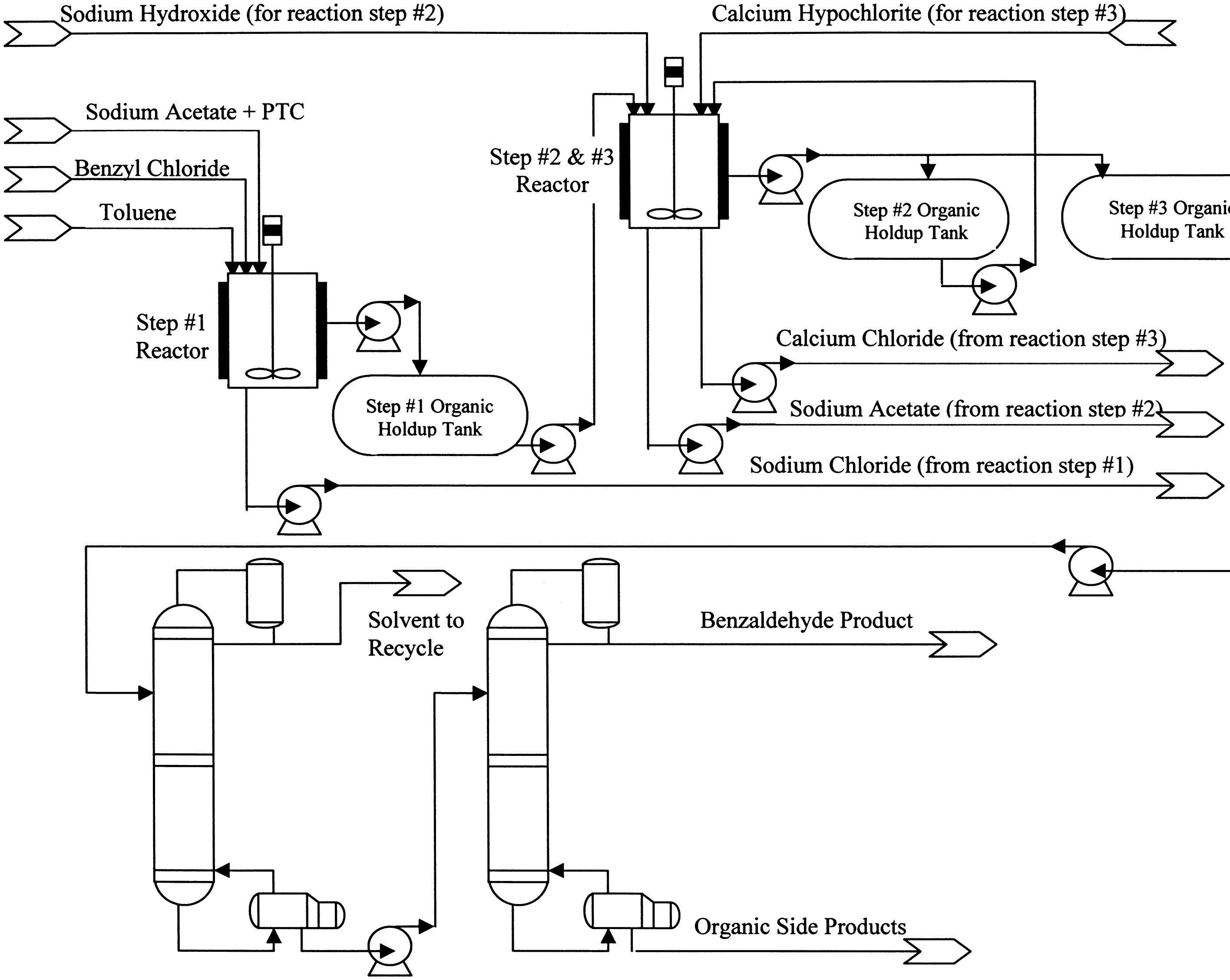

Fig. 7. Process flow diagram of a PTC-based benzaldehyde plant.

Table 7
Estimated capital cost of a PTC-based benzaldehyde plant[a]

| Equipment identification | Capacity/size specification | Actual BM cost (US$)[b] |
|---|---|---|
| Jacketed reactors | | |
| Reactor 1 | $17\,\mathrm{m}^3$ | 148571 |
| Reactor 2 | $17\,\mathrm{m}^3$ | 148571 |
| Agitators | | |
| Reactor 1 | 200 kW | 1238095 |
| Reactor 2 | 200 kW | 1238095 |
| Distillation columns | | |
| Tower 1 | No. of trays = 20<br>$L \times D = 12\,\mathrm{m} \times 1\,\mathrm{m}$ | 74905 |
| Tower 2 | Packed column<br>$L \times D = 20\,\mathrm{m} \times 0.4\,\mathrm{m}$ | 141762 |
| Heat exchangers | | |
| Tower 1 condenser | $8.5\,\mathrm{m}^2$ | 14114 |
| Tower 2 condenser | $4.0\,\mathrm{m}^2$ | 4705 |
| Tower 1 reboiler | $4.5\,\mathrm{m}^2$ | 37638 |
| Tower 2 reboiler | $15\,\mathrm{m}^2$ | 94095 |
| Pumps (two units each) | | |
| Organic phase 1 | 40 GPM, 700 W | 21667 |
| Aqueous phase 1 | 40 GPM, 700 W | 21667 |
| Organic phase 2 | 80 GPM, 1400 W | 30333 |
| Aqueous phase 2 | 80 GPM, 1400 W | 30333 |
| Organic phase 3 | 80 GPM, 1400 W | 30333 |
| Aqueous phase 3 | 80 GPM, 1400 W | 30333 |
| Storage/holdup vessels | | |
| Organic phase 1 | $20\,\mathrm{m}^3$ | 72429 |
| Organic phase 2 | $20\,\mathrm{m}^3$ | 72429 |
| Organic phase 3 | $34\,\mathrm{m}^3$ | 100286 |
| Benzaldeyde product | $70\,\mathrm{m}^3$ | 183486 |
| Side product | $12\,\mathrm{m}^3$ | 49400 |
| Total BM cost | | 3783248 |
| Contingency and fee (30%) | | 1134974 |
| Total fixed capital | | 4918222 |

[a] Capacity: 3000 metric tonnes per year benzaldehyde.

[b] Equipment price estimation was obtained from cost data charts provided by Ulrich [22] using cost index value of 390 for the year 2000.

zaldehyde from the organic product mixture. Simulation by using the HYSIS-Process computer program on this separation section shows that a benzaldehyde product stream of 99 wt.% purity is obtained as a distillate product, while the bottom stream consists of an organic mixture, mainly of benzyl ether and benzyl chloride (approximately 40 wt.% each).

### 8.3. Preliminary economic evaluation

To evaluate the profitability of the plant design, the capital costs and the manufacturing costs are estimated. They are shown in Tables 7 and 8, respectively. Table 8 also provides the calculations for estimating the sale price of benzaldehyde. It is estimated that the total fixed capital cost of the 3000 metric tonnes per year plant is US$ 5 million. Note that cost for providing the two agitators required for the reactors comprises about half of the total cost.

Table 8 shows a manufacturing cost of US$ 6.36/kg benzaldehyde produced. Close to 90% of the cost comes from the cost of raw chemicals. Based on these capital and manufacturing costs, it is estimated that in order to obtain a 20% return on investment (ROI), benzaldehyde has to be sold at the price of US$ 6.69/kg.

### 8.4. Comparison with conventional method-based benzaldehyde plant

To assess the feasibility of the PTC-based process, the economics of this process is compared with that of a benzaldehyde plant with the same capacity using the conventional method, i.e. by the air-oxidation method. The process design of a liquid phase air-oxidation-based benzaldehyde plant with a capacity of 3000 metric tonnes per year was developed. Experimental kinetic data obtained from the literature were used [21]. Reaction conditions of the process are listed in Table 9. Similar to the PTC-based plant, the liquid phase air-oxidation-based plant is also operated in the batch-continuous mode, whereas in the reactor section consists of two bubble column reactors operated in parallel

Table 8
Price estimation benzaldehyde from a PTC-based benzaldehyde plant (in US$)

| | | | | |
|---|---|---|---|---|
| Assume a rate of return on investment (ROI) of 20% (before tax) | | Fixed capital, $C_{FC}$ | 5000000 | |
| Net income before tax per year | 1000000 | Working capital (10% $C_{FC}$) | 500000 | |
| Cost of manufacture per year | 19298000 | Total capital investment, $C_{TC}$ | 5500000 | |
| Benzaldehyde sale per year | 20298000 | | | |
| Sale price of benzaldehyde/kg | 6.69 | | | |
| | Quantity/h | Cost per unit | Cost/h operation | Cost/kg product |
| Chemicals | | | | |
| Benzyl chloride | 500.7 kg | 1.50/kg | 760.50 | 1.98 |
| Sodium acetate | 324.3 kg | 1.56/kg | 505.91 | 1.32 |
| Sodium hydroxide | 150.3 kg | 3.74/kg | 562.12 | 1.47 |
| Calcium hydroxide | 268.6 kg | 1.56/kg | 419.02 | 1.09 |
| Sodium iodide | 5.9 kg | 36.00/kg | 214.17 | 0.56 |
| PT catalyst | 63.0 kg | 2.35/kg | 148.05 | 0.39 |
| Credit NaOAc recycle | 292 kg | 1.56/kg | (455.36) | (1.19) |
| Total material cost | | | 2154.40 | 5.62 |
| Utilities | | | | |
| Cooling water | 42 $m^3$ | 0.013/$m^3$ | 0.55 | 0.00 |
| 10 bar steam | 1000 kg | 8.80/tonne | 8.8 | 0.02 |
| Electricity | 420 kW | 0.04/kW h | 16.28 | 0.04 |
| Process water | 3.4 $m^3$ | 0.13/$m^3$ | 0.45 | 0.00 |
| Total utility cost | | | 26.08 | 0.07 |
| Labor related costs | | | | |
| Labor, two men per shift | 2 labors | 38.00 per labor hour | 76.00 | 0.20 |
| Technical assistance | | 52000 per labor year | 6.57 | 0.02 |
| Control laboratory | | 57000 per labor year | 7.20 | 0.02 |
| Total labor related cost | | | 89.76 | 0.23 |
| Other fixed costs | | | | |
| Maintenance | | 10% $C_{FC}$ per year | 63.13 | 0.16 |
| General overhead | | 20% maintenance + operation costs | 30.58 | 0.09 |
| Local taxes and insurance | | 1.5% $C_{FC}$ per year | 9.47 | 0.03 |
| Depreciation | | 10% $C_{FC}$ per year | 63.13 | 0.16 |
| Total other fixed costs | | | 166.31 | 0.43 |
| Cost of manufacture | | | 2436.56 | 6.36 |

at 2 h per batch cycle. The purification section consists of two fractional distillation columns operated continuously to separate benzaldehyde from by-products and the unreacted toluene.

Summaries of the preliminary economic estimation of the conventional-method-based plant are shown in Table 10. The

Table 9
Reaction conditions for liquid phase air-oxidation of toluene

Reactor operation mode: batch
Raw material: toluene
Solvent: acetic acid
Toluene concentration in solvent: 30 wt.%
Catalysts: cobalt acetate/sodium bromide (0.02/0.16 gmol/l)
Air volumetric flow per minute: 10 times of total liquid volume
Reaction temperature and pressure: 110°C, 10 $kg/cm^2$
Reaction time: 30 min
Toluene conversion: 20%

Product distribution
Benzaldehyde: 40%
Benzoic acid: 60%

Table 10
Liquid phase toluene-oxidation plant[a]

| | US$/h | US$/kg product |
|---|---|---|
| Manufacturing costs | | |
| Chemical cost[b] | 599.85 | 1.57 |
| Utility cost | 65.80 | 0.17 |
| Fixed cost (labor, taxes, depreciation, etc.) | 291.68 | 0.76 |
| Total manufacturing cost | 957.33 | 2.50 |
| Assume 20% ROI | | |
| Net income before tax | 1240000 | |
| Cost of manufacture per year | 7583000 | |
| Benzaldehyde sales per year | 8823000 | |
| Sale price of benzaldehyde/kg | 2.91 | |

[a] Basis: 3000 metric tonnes per year benzaldehyde production; operation: 330 days per year; fixed capital investment: US$ 6.2 million.

[b] Chemical cost does not include the credit comes from the sale of benzoic acid by-product.

fixed capital cost for this plant is estimated to be US$ 6.2 million. The manufacturing cost per kg of benzaldehyde produced is estimated to be US$ 2.50. In order to obtain a 20% ROI goal, without considering credit from benzoic acid by-product, benzaldehyde product will have to be sold at a price of US$ 2.91/kg.

Economic comparison between the two plants clearly shows that although the fixed capital cost for the PTC-based benzaldehyde plant is lower than that for the conventional plant, benzaldehyde from the PTC-based plant must be sold at a price that is slightly over twice the cost by the conventional process. The price disparity can improve if the present raw materials being used, for examples sodium hydroxide, sodium acetate, and calcium hypochlorite, can be replaced with less expensive materials which can perform the same functions without sacrificing reactivity and product selectivity.

## 9. Conclusion

The utilization of the PTC method for the synthesis of benzaldehyde shows that, technically, PTC can provide an alternative approach that is elegant and simpler to operate, with the advantage of significantly higher conversion and selectivity at much milder reaction conditions. Further, the PTC method dispenses with the need for high operating pressure and a large reactant recycle. However, the PTC-based process tends to be highly chemistry intensive that makes the product price heavily dependent on the prices of the raw materials used. Thus, the PTC method can be an attractive alternative only for syntheses that are already chemistry intensive, such as those in the pharmaceutical and fine chemical industries.

Generally it will be difficult for the PTC method to compete as an alternative to one that is engineering intensive for many medium scale processes. The air-oxidation of toluene to benzaldehyde is an engineering intensive process that uses relatively inexpensive raw materials (toluene and air). The high operating pressure and temperature in the process elevate the operating cost, i.e. utility costs. However, the large-scale production involved makes the overall production cost more economical.

In conclusion it would appear that the PTC route is not an automatic panacea for many processes. Indeed, for the medium scale process selected for the present study, it is more expensive in spite of the increased conversion and selectivity obtained. The PTC-based processes should find their greatest applications in the manufacture of chemicals that can be regarded directly as consumer items or of higher level intermediates in the synthetic chain. Thus, industries like the pharmaceutical industry should be the most obvious beneficiaries of PTC.

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