# Development of a New Advanced Process for Manufacturing Polyacetal Resins. Part I. Development of a New Process for Manufacturing Highly Concentrated Aqueous Formaldehyde Solution by Methylal Oxidation

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## SYNOPSIS

A new technology for the production of highly concentrated aqueous formaldehyde was developed by oxidizing methylal. Whereas the oxidation of methanol yields 1 mol of water per 1 mol of formaldehyde, methylal oxidation produces only 1 mol of water for every 3 mol of formaldehyde. Thus, the output from methylal oxidation is more than 70% formaldehyde compared with 55% from methanol oxidation. For this purpose, basic research for methylal synthesis was tried and the world's first commercial production of methylal was accomplished. Using this methylal, the world's first technology of methylal oxidation for manufacturing highly concentrated aqueous formaldehyde was established by development of a new methylal oxidation catalyst composed of iron, molybdenum, and a third component. This highly concentrated aqueous formaldehyde is then fed to the acetal homopolymer and copolymer plant whose combined capacity is 35,000 tons/years. © 1993 John Wiley & Sons, Inc.

## 1. INTRODUCTION

In 1972, Asahi Chemical started to produce the acetal homopolymer by utilizing the world's third type of polyacetal technology,[1] the other being those of DuPont (homopolymer) and Celanese (copolymer). Since its starting raw material is methanol, which is very cheap, acetal resin has a very promising future.

Asahi Chemical already has a process for making the acetal homopolymer. However, convinced of the further potential of the acetal resin in addition to the acetal homopolymer, Asahi decided to also develop the acetal copolymer.

There are two important points to be considered in Asahi's development: First, polyacetal production requires a significant amount of energy, and the conversion cost from formalin to polyacetal is high. The main reason why acetal resin needs so much

energy is the high-energy requirement to obtain purified monomer, i.e., purified formaldehyde and purified trioxane from formalin. Second, in the polymer-stabilizing step, several units of the polymer are lost.

The targets in developing an advanced process at Asahi Chemical were as follows:

1. A monomer process using highly concentrated aqueous formaldehyde solution. Asahi changed the formalin manufacturing process from a methanol-based oxidation process to a methylal oxidation process. The concentration of formaldehyde was increased from 55% in the methanol process to 70% in the methylal process. This new process reduced the energy requirement for production of purified formaldehyde and trioxane and also reduced plant construction costs for the trioxane synthesis step.
2. The use of highly purified monomer and end-capping during polymerization.[2,3] Develop-

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ment for the second target will be discussed in Part II of this series.[4]

## 2. BACKGROUND FOR DEVELOPMENT

Formaldehyde is conventionally produced by methanol oxidation. During the methanol oxidation, 1 mol of formaldehyde is formed with 1 mol of water [eq. (1)]:

$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow CH_2O + H_2O \qquad (1)$$

The maximum formaldehyde concentration industrially achievable today is 55%.

This methanol oxidation process is used industrially, but it has two problems to obtain final products:

1. Much energy is required to volatilize the water; half of the formalin is water.
2. Formaldehyde is volatilized with water, and the recovery of volatilized formaldehyde is very complicated.

To better understand these points, these two problems for producing acetal resin are explained using the flow sheet shown in Figure 1:

Methanol is oxidized and the thus-formed formaldehyde is absorbed as 55% formalin. From this formalin, in the case of the acetal homopolymer, water is removed and purified formaldehyde gas is obtained. This is polymerized to polyoxymethylene. In this case, a large amount of energy is needed to remove the water from the aqueous formaldehyde to produce purified formaldehyde gas. This is the first problem.

The next problem is the recovery of the diluted aqueous formaldehyde solution. The first step is to recover the unreacted methanol from the diluted aqueous formaldehyde solution. This step is easy and presents no problem. The second step is the recovery of formaldehyde. This step has problems: Pure formaldehyde is a substance whose boiling point is −19°C, but in aqueous solution, it forms methylene glycol. The vapor equilibrium of methylene glycol and water are very close and, therefore, it is very difficult to separate these two substances. Therefore, formaldehyde and water are separated at a temperature over 140°C under pressure. This separation process needs a significant amount of energy, and, moreover, the troublesome problem is the generation of formic acid in a side reaction. This formic acid induces metal corrosion. This is a very big problem for an operating plant.

This problem was demonstrated in the case of the production of the acetal homopolymer. In the case of the acetal copolymer, purified formaldehyde is substituted by trioxane, and similar problems also occur.

In this light, Asahi Chemical launched a project to develop a new formaldehyde manufacturing process as an effective substitute for the methanol-oxidation process.[5] Their research has led to the es-
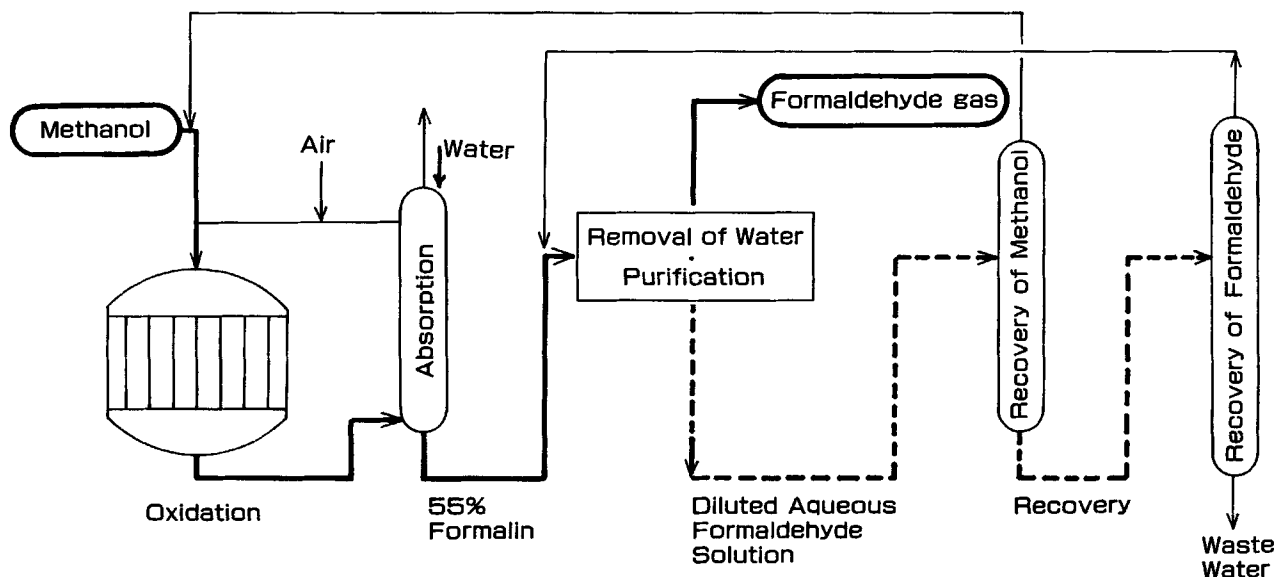


**Figure 1** Example of methanol-oxidation formaldehyde (production of acetal resin).

tablishment of a process for manufacturing highly concentrated aqueous formaldehyde solution by methylal oxidation.

## 3. DETAILS OF DEVELOPMENT

Now, we will introduce Asahi Chemical's new formaldehyde process in more detail:

In the methylal oxidation, only 1 mol of water forms for every 3 mol of formaldehyde [eq. (2)]:

$$CH_3OCH_2OCH_3 + O_2 \rightarrow 3CH_2O + H_2O$$

$$2CH_3OH + CH_2O \rightarrow CH_3OCH_2OCH_3 + H_2O \quad (2)$$
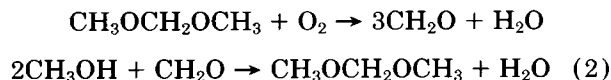
Hence, a significantly increased formaldehyde concentration can be attained. Methylal is manufactured from methanol and the dilute aqueous formaldehyde solution that is produced as a by-product in the production of purified formaldehyde.

Merits of the methylal process are as follows:

1. The energy requirement for evaporation of water is low because the water content in formalin is low.
2. Since the formaldehyde concentration is high, the yield of synthesized trioxane is also high.
3. The recovery step for the diluted aqueous formaldehyde solution can be omitted.

Now, we will explain the methylal-oxidation formaldehyde process using the flow sheet shown in Figure 2:
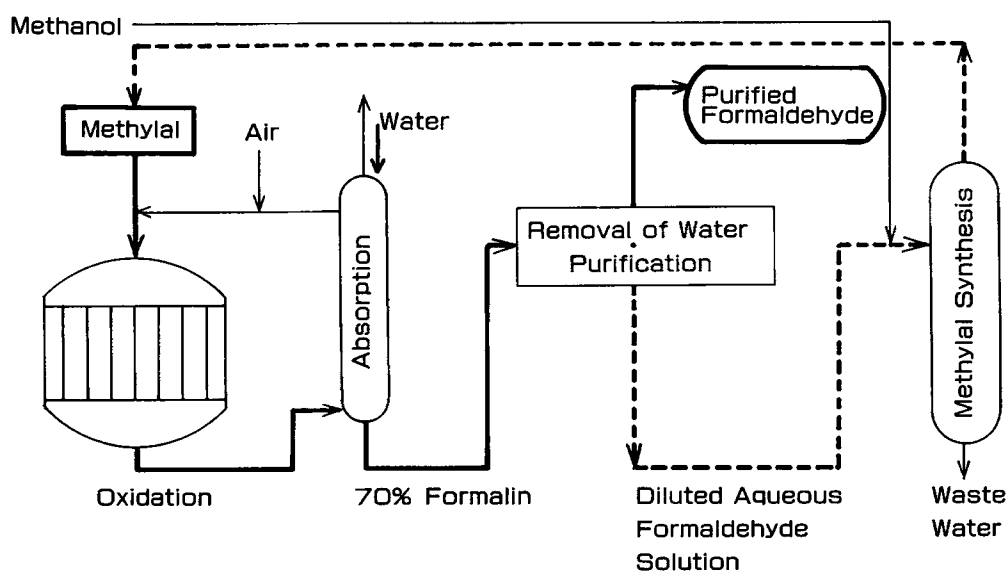
At first, methylal is oxidized and the formaldehyde thus formed is absorbed as 70% aqueous formaldehyde. From this aqueous formaldehyde solution, in the case of the acetal homopolymer, purified formaldehyde is obtained.

Diluted formaldehyde solution is fed to the methylal synthesis section with methanol. The thus-formed methylal is then fed to the methylal oxidation section.

The methylal-oxidation formaldehyde process to produce highly concentrated aqueous formaldehyde solution consists of three steps: (1) methylal synthesis, (2) methylal oxidation, and (3) formaldehyde absorption.

### 3.1. Methylal Synthesis

It is generally known that methylal can be obtained by heating methanol and aqueous formaldehyde solution in the presence of an acid catalyst such as sulfuric acid, but there is no established technology for the commercial production of methylal.

Methylal-oxidation formaldehyde process development activities sought to establish a commercially feasible process for methylal synthesis. First, basic research for the methylal synthesis was begun.

The experimental apparatus is shown in Figure 3. A solid acid catalyst was used in this experiment. Reaction products were analyzed by gas chromatography.

The effects of formaldehyde concentration on methylal formation was first investigated. The results are shown in Figure 4. The vertical axis is the
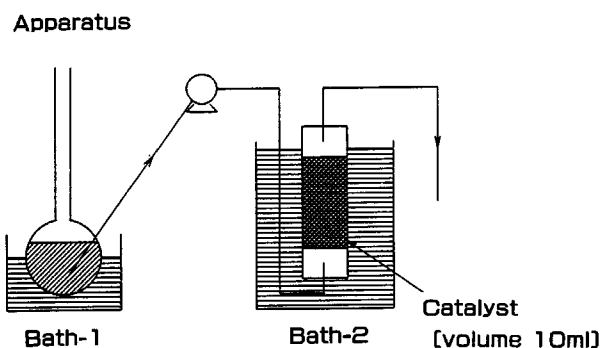


**Figure 2**   Example of methylal-oxidation formaldehyde (production of acetal resin).

**Apparatus**



**Figure 3**   Basic research for methylal synthesis.

log scale of methylal formation, and the horizontal axis is the "catalyst by reactants fed," which is the so-called contact time.

Initial formaldehyde concentration was varied from 0.15 to 5.1 wt %. The methylal formation curves are quite similar to each other, though the initial formaldehyde concentration is changed nearly 40 times. This suggests that methylal formation is proportional to the first order of formaldehyde concentration.

In Figure 5, the relationship between initial formaldehyde concentration and initial methylal formation rate is shown. We confirmed that methylal formation is proportional to the first order of formaldehyde concentration.
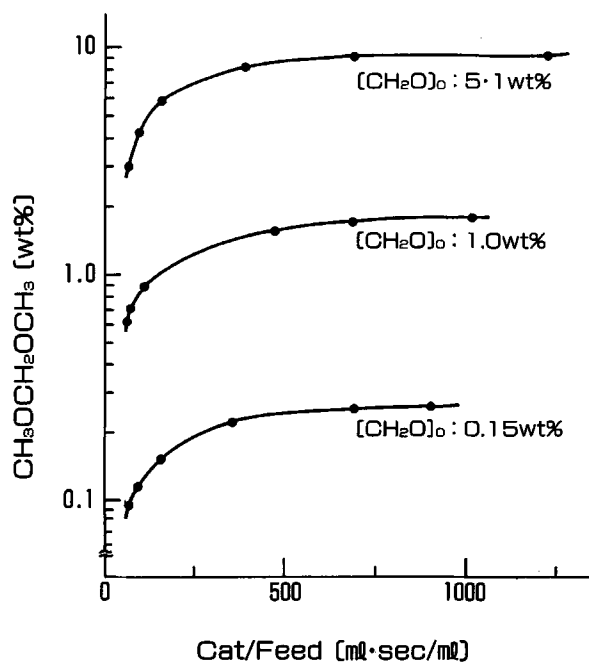


**Figure 4**   Effects of formaldehyde concentration on methylal formation [$CH_3OH$]$_0$: 40 wt %, temperature: 60°C.



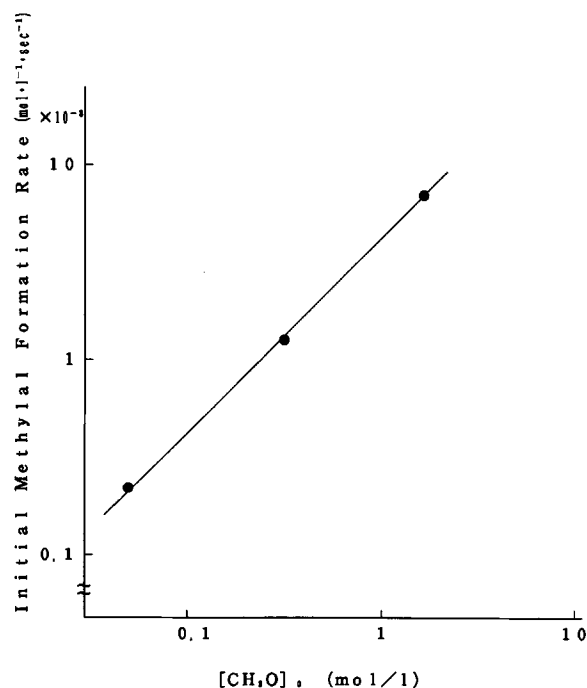**Figure 5**   Relationship between initial formaldehyde concentration and initial methylal formation rate: [$CH_3OH$]$_0$: 40 wt %; temperature: 60°C.

Figure 6 shows the effects of methanol concentration on methylal formation. In this experiment, the initial formaldehyde concentration is 1.0 wt %, and the methanol concentration is varied from 20 to 60 wt %.

In Figure 7, the relationship between initial methanol concentration and initial methylal formation rate is shown. An approximately linear relationship is observed.

From this experiment, we found that methylal formation is proportional to the first order of methanol concentration. Referring to the chemical reaction [eq. (3)],

$$2CH_3OH + CH_2O \rightarrow CH_3OCH_2OCH_3 + H_2O \quad (3)$$

"2 mol of methanol and 1 mol of formaldehyde make 1 mol of methylal and 1 mol of water"; therefore, methylal formation is expected to be proportional to the second order of methanol concentration, but in the actual experiment, the results are first order in methanol concentration. The difference between the experimental analysis and theoretical expectation will be discussed later.

Figure 8 shows the effects of temperature on methylal formation. Temperature was varied from 60 to 75°C. The higher the reaction temperature,
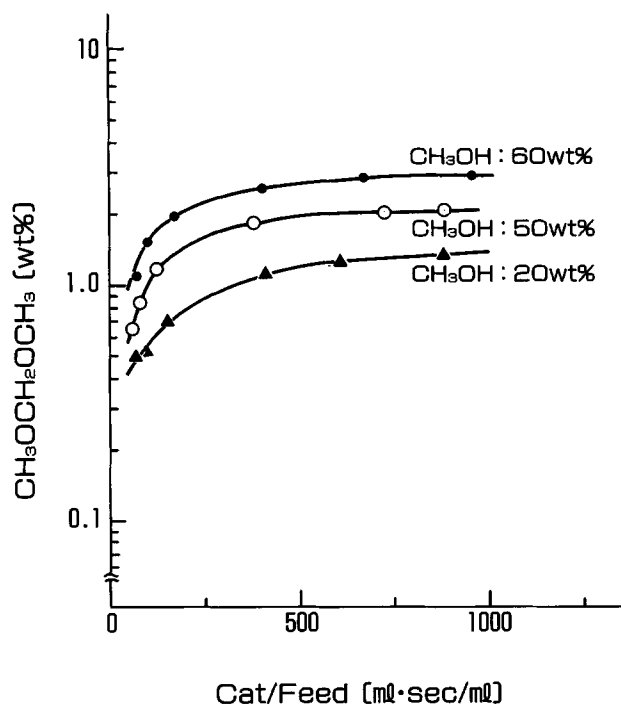
**Figure 6** Effects of methanol concentration on methylal formation: [$CH_2O$]$_0$: 1.0 wt %; temperature: 60°C.

the faster the reaction velocity, but the equilibrium methylal concentration is nearly equal to each other. This means that the heat of reaction is almost zero.

From these experiments, a reaction velocity formula as shown in Table I can be developed. Each reaction velocity constant for these experimental conditions can also be estimated as shown in Table I. The equilibrium constant, $K$, is nearly 3.0.

From these experiments, the elementary reaction of methylal formation from methanol and formaldehyde can be deduced as follows: First, methanol and formaldehyde make hemiacetal. Second, methanol and hemiacetal make methylal and water [eq. (4)]. The hemiacetal concentration is thought to be nearly equal to the formaldehyde concentration; therefore, methylal formation is proportional to the first order of methanol concentration and formaldehyde concentration:

$$CH_3OH + CH_2O \rightleftharpoons CH_3OCH_2OH$$

$$CH_3OCH_2OH + CH_3OH \rightleftharpoons$$

$$CH_3OCH_2OCH_3 + H_2O \quad (4)$$
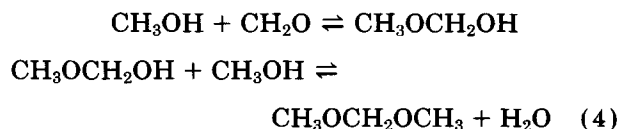
From these basic experimental results, the industrial methylal synthesis technology was developed[5]:
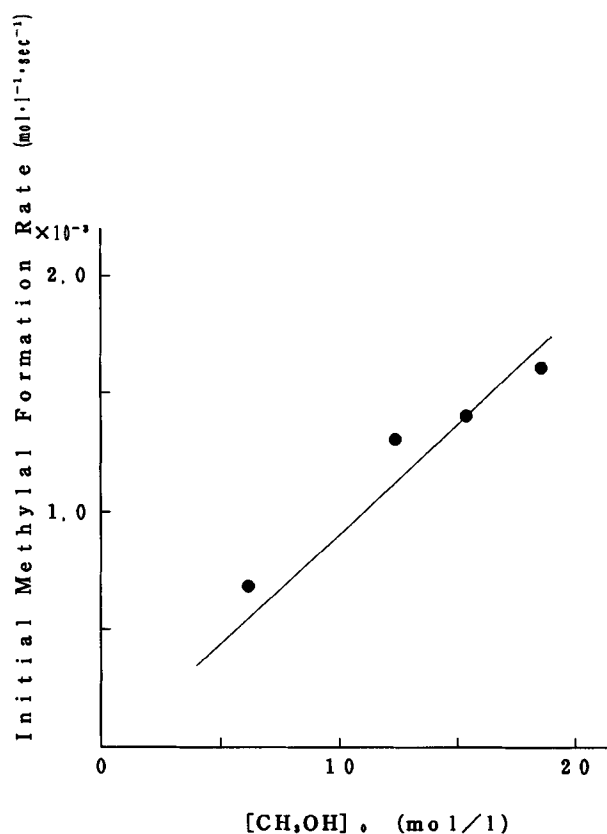


**Figure 7** Relationship between initial methanol concentration and initial methylal formation rate: [$CH_2O$]$_0$: 1.0 wt %; temperature: 60°C.
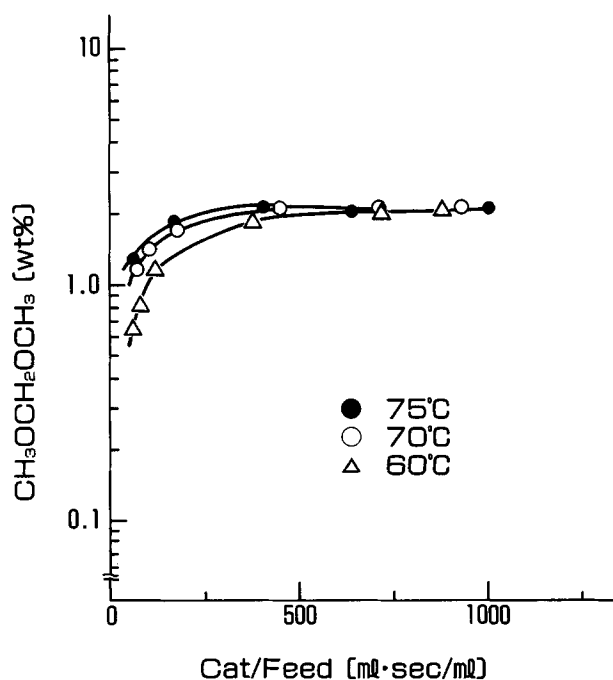


**Figure 8** Effects of temperature on methylal formation [$CH_2O$]$_0$: 1.0 wt %; [$CH_3OH$]$_0$: 50 wt % °C.

**Table I   Kinetics of Methylal Synthesis:**
$(d[CH_3OCH_2OCH_3])/dt = k_1 [CH_3OCH_2OH]$
$[CH_3OH] - k_2 [CH_3OCH_2OCH_3] [H_2O]$

|       | $k_1$ [L mol$^{-1}$ s$^{-1}$] | $k_2$ [L mol$^{-1}$ s$^{-1}$] | $K$ |
|-------|------------------------|------------------------|-----|
| 60°C  | $1.6 \times 10^{-4}$   | $0.55 \times 10^{-4}$  | 3.0 |
| 70°C  | $2.6 \times 10^{-4}$   | $0.80 \times 10^{-4}$  | 3.2 |
| 75°C  | $3.2 \times 10^{-4}$   | $1.0 \times 10^{-4}$   | 3.2 |

$K_1 = 395 \times \exp[-9,700/RT]$, $K_2 = 38.1 \times \exp[-8,900/RT]$,
$K = k_1/k_2 = 10.4 \times \exp[-800/RT]$.

Methylal is synthesized in a quaternary reaction system involving formaldehyde, methanol, methylal, and water. Productivity was found to be determined by their reaction equilibrium. Therefore, a reaction distillation system was adopted. There are two main factors concerning this industrial methylal synthesis process:

The first point is the development of a solid acid catalyst. A well-known catalyst like sulfuric acid has the problem of corrosion. A solid acid catalyst with a high selectivity, nearly 100%, and a long-life catalytic activity was developed.

The second point is the development of the reaction distillation system. Nearly 100% conversion of formaldehyde and methanol into methylal was achieved. A technique for breaking the methylal-to-methanol ratio of 93 to 7 (weight ratio) in the azeotropic mixture was also devised.[5]

As a result of these refinements, 99% pure methylal was obtained from the top of the distillation column, and wastewater was taken out from the bottom. Thus, the world's first technology for the commercial production of methylal was established by Asahi.
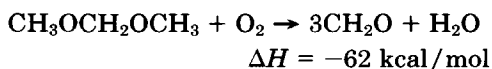
## 3.2. Methylal Oxidation

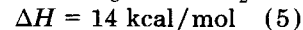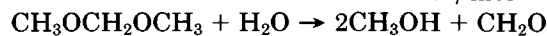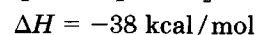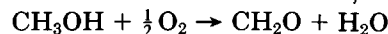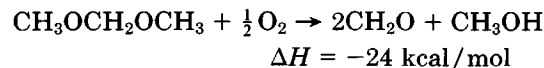The same oxidation reactor was used for both the methylal oxidation and methanol oxidation.

The methylal oxidation reaction is shown as follows [eq. (5)]:

The total reaction is 1 mol of methylal being oxidized by 1 mol of oxygen with 3 mol of formaldehyde and 1 mol of water being formed. The $\Delta H$ is calculated to be $-62$ kcal per mol.[6] However, the elementary reactions are complicated. There are three reactions:

Total reaction:

$$CH_3OCH_2OCH_3 + O_2 \rightarrow 3CH_2O + H_2O$$
$$\Delta H = -62 \text{ kcal/mol}$$

(Individual) reactions:

$$CH_3OCH_2OCH_3 + \tfrac{1}{2}O_2 \rightarrow 2CH_2O + CH_3OH$$
$$\Delta H = -24 \text{ kcal/mol}$$
$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow CH_2O + H_2O$$
$$\Delta H = -38 \text{ kcal/mol}$$
$$CH_3OCH_2OCH_3 + H_2O \rightarrow 2CH_3OH + CH_2O$$
$$\Delta H = 14 \text{ kcal/mol} \quad (5)$$

The first reaction is the methylal partial oxidation. One mole of methylal and 0.5 mol of oxygen produces 2 mol of formaldehyde and 1 mol of methanol. This reaction is exothermic. In the early stage of methylal oxidation in the absence of water with reduction of methylal, appearance of formaldehyde and methanol are observed. This phenomenon suggests the methylal partial oxidation.

The second reaction is methanol oxidation. One mole of methanol and 0.5 mol of oxygen produces 1 mol of formaldehyde and 1 mol of water. This reaction is also exothermic and a conventional methanol oxidation reaction.

The third reaction is methylal hydrolysis. One mole of methylal and 1 mol of water produce 2 mol of methanol and 1 mol of formaldehyde. This reaction is endothermic. In the early stage of methylal oxidation in the presence of water, with the reduction of water, the appearance of methanol and formaldehyde are observed, and lowering of the reaction temperature is also observed. This phenomenon suggests methylal hydrolysis.

Summarizing the methylal oxidation, three elementary reactions—methylal partial oxidation, methanol oxidation, and methylal hydrolysis, occur simultaneously and, therefore, the reaction behavior is very complicated. The use of a conventional methanol oxidation catalyst ($MoO_3 \cdot Fe_2O_3$ complex catalyst) for methylal oxidation resulted in a short catalyst life.
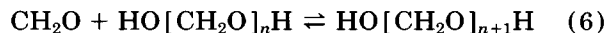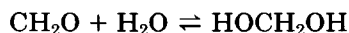
Asahi Chemical has developed the industrial methylal oxidation technology.[5,7-11] A main factor was development of a catalyst. Asahi developed a catalyst, composed of iron, molybdenum, and a third component that can withstand long-term use for over 1 year of methylal oxidation.[7,11] A high conversion of over 98%, a high selectivity of over 94%, and a long continuous operation have been attained.

As a result of this methylal oxidation technology, Asahi increased the capacity of oxidation over 70% compared to methanol oxidation in the same oxidation reactor.

## 3.3. Formaldehyde Absorption

This section discusses formaldehyde absorption. Aqueous formaldehyde is a very complex mixture of

soluble oligomers of formaldehyde, free water, and a small amount of free formaldehyde. These are the results of the reaction equilibrium [eq. (6)]:

$$CH_2O + H_2O \rightleftharpoons HOCH_2OH$$

$$CH_2O + HOCH_2OH \rightleftharpoons HO[CH_2O]_2H$$

$$CH_2O + HO[CH_2O]_nH \rightleftharpoons HO[CH_2O]_{n+1}H \quad (6)$$

The distribution of the soluble oligomer in aqueous formaldehyde can be calculated, and the result was demonstrated by Thompson and Bryant[12] of the DuPont group. Oligomer distribution shows that the high degree of oligomer increased with the concentration of formaldehyde. A high degree of oligomer is said to cause precipitation.

The storage stability limit and thermodynamic equilibrium concentration line was given by Thompson and Bryant[12] of the DuPont group. The nucleation of precipitants reduces the storage stability limit to the thermodynamic equilibrium concentration line.

An aqueous formaldehyde solution with a concentration higher than 55% is liable to form scale, and it has been an agreed view in this trade that formaldehyde concentrations higher than this level are industrially impossible to achieve.

Thorough studies were, therefore, made on the scale-forming mechanism and contributive factors, which finally led to the development of a specially structured absorption column free from scale-causative factors and the technology for scale-free processing of highly concentrated formaldehyde solution.[10] Thus, Asahi Chemical has established a stable operation, steadily turning out an aqueous formaldehyde solution of high concentrations around 70%.

## 4. CONCLUSIONS

Asahi Chemical completed the world's first development and commercialization of a new process for manufacturing formaldehyde.[13] This highly concentrated aqueous formaldehyde solution is the feed for the acetal homopolymer and copolymer plants of Asahi Chemical, whose combined capacity is 35,000 T/Y.[14]

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