

# DEVELOPMENT OF METHYLAL SYNTHESIS BY REACTIVE DISTILLATION

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The world's first technology for the commercial production of methylal is the reactive distillation method. Its application to a new formaldehyde process has also been investigated. Whereas the oxidation of methanol yields one mole of water per mole of formaldehyde, methylal oxidation produces only one mole of water for every three moles of formaldehyde. Thus, the output by methylal oxidation is more than 70 % formaldehyde compared with 55 % by methanol oxidation.

For this purpose, basic research on methylal synthesis was conducted and the world's first commercial production of methylal using reactive distillation was accomplished. Using this methylal, the world's first methylal oxidation technology for manufacturing highly concentrated aqueous formaldehyde was established.

This highly concentrated aqueous formaldehyde is then fed to an acetal homopolymer and copolymer plant having a combined capacity of 35,000 tons/year.

## Introduction

In 1972, Asahi Chemical began producing acetal homopolymer by the world's third type of polyacetal technology<sup>1)</sup>, the others being those of Du Pont (homopolymer) and Celanese (copolymer).

Since its raw material is methanol, which is very cheap, acetal resin has a very promising future.

We previously developed a process for making the acetal homopolymer. Convinced of the further potential of acetal resin in addition to the acetal homopolymer, we decided to develop the acetal copolymer as well. There are two important points to be considered in this development.

First, polyacetal production requires a significant amount of energy, and the cost of conversion 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.

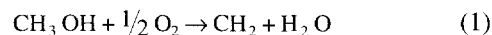
The targets in developing an advanced process were as follows:

1. We 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 the production of purified formaldehyde and trioxane, and also reduced plant construction cost for the trioxane synthesis step.
2. We developed highly purified monomer and end-capping during polymerization<sup>2, 3)</sup>. Development of the second target will be discussed in a future report.

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## 1. Background of Development

Formaldehyde is conventionally produced by methanol oxidation. During the oxidation, one mole of formaldehyde is formed with one mole of water (Eq. (1)):



The maximum formaldehyde concentration industrially achievable today is 55 %.

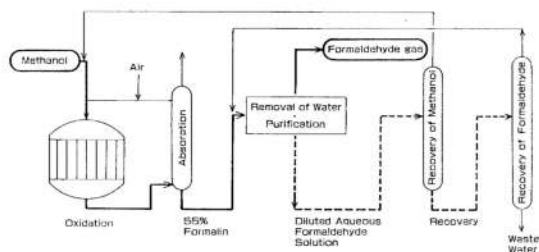
This methanol oxidation process is used industrially, but it has two problems in obtaining final products:

1. A significant amount of 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.

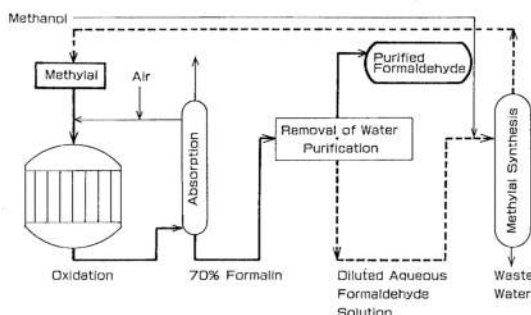
To better understand these points, these two problems for producing acetal resin are explained using the flow sheet shown in **Fig. 1**:

Methanol is oxidized and the formaldehyde produced is absorbed as 55 % formalin. From this formalin, in the case of the acetal homopolymer, water is removed and purified formaldehyde gas is obtained. It 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 other 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, the recovery of formaldehyde, has several problems. Pure formaldehyde is a substance whose boiling point is 254 K, but in aqueous solution it forms methylene glycol. In aqueous solution, the volatilities of formaldehyde and water are very close,



**Fig. 1** Flow sheet of methanol-oxidation formaldehyde process for the production of acetal resin



**Fig. 2** Flow sheet of methylal-oxidation formaldehyde process for the production of acetal resin

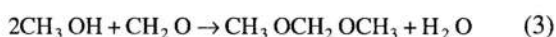
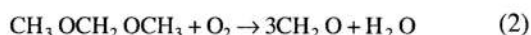
and therefore it is very difficult to separate these two substances. Formaldehyde and water are separated at a temperature over 413 K under a pressure of about 4 atmospheres in a process that needs a significant amount of energy. Moreover, a constant problem is the generation of formic acid in an unwanted side reaction. This acid induces metal corrosion, which poses a very serious problem for an operating plant.

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

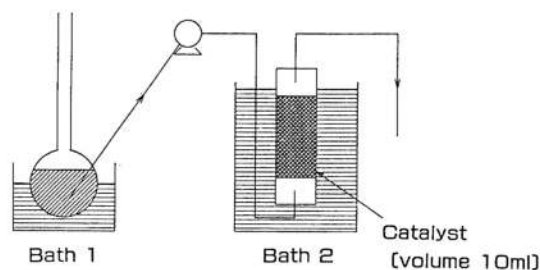
In this light, we launched a project to develop a new formaldehyde manufacturing process as an effective substitute for the methanol oxidation process<sup>4)</sup>. Our research has led to the establishment of a process for manufacturing highly concentrated aqueous formaldehyde solution by methylal oxidation. This paper mainly concerns the development of the methylal synthesis process by reactive distillation and its application to the new formaldehyde process.

## 2. Details of Development

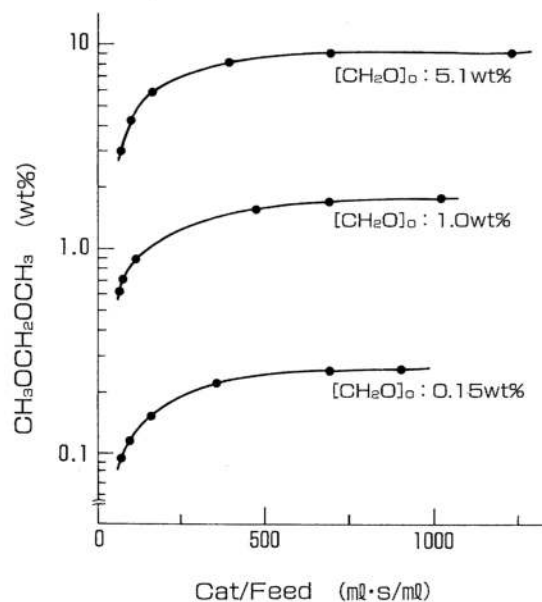
During the methylal oxidation, only one mole of water is formed for every three moles of formaldehyde (Eq. (2)):



Hence, a significantly increased formaldehyde concentration can be attained. Methylal is manufactured from methanol and the dilute aqueous formaldehyde



**Fig. 3** Apparatus for basic research in methylal synthesis. The catalyst volume is 10 ml



**Fig. 4** Effects of formaldehyde concentration on methylal formation. Initial methanol concentration: 40 wt%; Temperature: 333 K

solution that is produced as a by-product during the production of purified formaldehyde (Eq. (3)).

Merits of the methylal oxidation formaldehyde process are as follows.

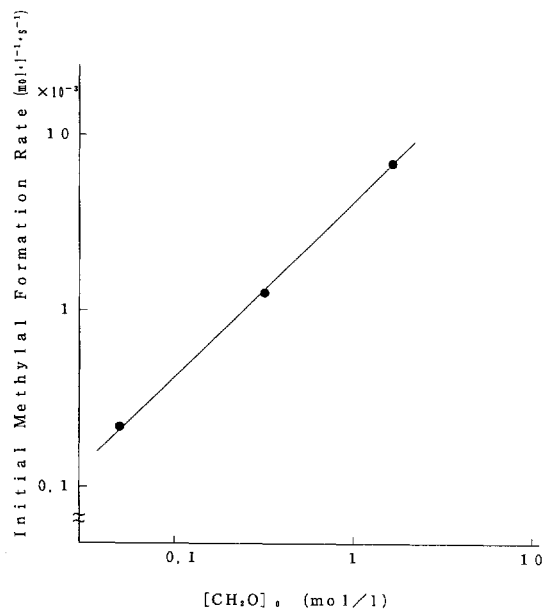
1. The energy requirement for evaporation of water is low because the water content in formalin is low.
2. Since the formaldehyde concentration is high, the yield of synthesized trioxane is also high.
3. The recovery step for the diluted aqueous formaldehyde solution can be omitted.

The methylal-oxidation formaldehyde process can be described using the flow sheet shown in **Fig. 2**:

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 methylal thus formed 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.



**Fig. 5** Relationship between initial formaldehyde concentration and initial methylal formation rate. Initial methanol concentration: 40 wt%; Temperature: 333 K

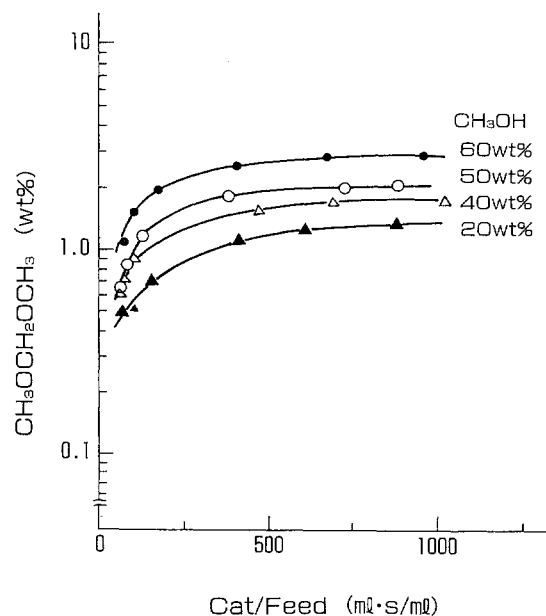
A more detailed description of the methylal synthesis process is as follows. It is generally known that methylal can be obtained by heating methanol and aqueous formaldehyde solution in the presence of an acid catalyst such as sulfuric acid, but there was previously no established technology for the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

The methylal-oxidation formaldehyde process development work sought to establish a commercially feasible process for methylal synthesis. The basic research for the methylal synthesis was thus begun.

The experimental apparatus is shown in **Fig. 3**. A solid acid catalyst was used in this work. The glass vessel, which contains aqueous formaldehyde and methanol, was immersed in bath 1 and the temperature was adjusted. From this vessel, reactants (methanol, formaldehyde and water) were fed to a reactor which contained 10 ml solid acid and was immersed in bath 2. The temperature was then adjusted. In each experiment, the flow rate of reactants was varied. Reaction products were sampled using a microsyringe and analyzed by gas chromatography. "Porapak" was used as the column chromatography packing agent, and reactants were determined using  $H_2$  as the carrier gas.

The effects of formaldehyde concentration on methylal formation were first investigated. The results are shown in **Fig. 4**. The vertical axis is the log scale of methylal concentration, and the horizontal axis is the "catalyst by reactants fed", which is the so-called contact time.

The initial formaldehyde concentration was varied from 0.15 to 5.1 wt%. The behavior of the methylal formation curves are quite similar to one another, though the initial formaldehyde concentration is changed nearly



**Fig. 6** Effects of methanol concentration on methylal formation Initial formaldehyde concentration: 1.0 wt%; Temperature: 333 K

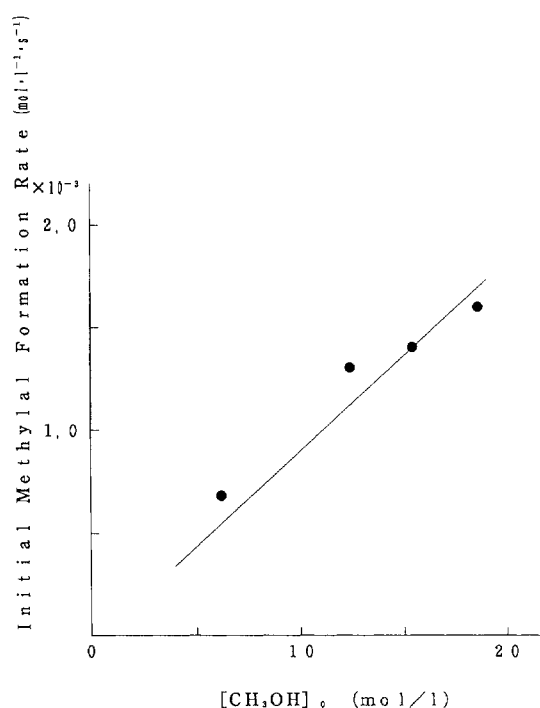
40 times. This suggests that the methylal formation rate is proportional to the first order of the formaldehyde concentration. Considering Eq. (3), since "one mole of formaldehyde and two moles of methanol make one moles of methylal and one mole of water, the fact that methylal formation is proportional to the first order of formaldehyde concentration is plausible. The precise mechanism will be discussed later.

In **Fig. 5**, the relationship between initial formaldehyde concentration and initial methylal formation rate is shown. We obtained the initial methylal formation rate by plotting methylal formed versus contact time. The initial slope gave the initial methylal formation rate. We confirmed that methylal formation is proportional to the first order of the formaldehyde concentration.

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

In **Fig. 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 the methylal formation rate is proportional to the first order of the methanol concentration. Referring to the chemical reaction (Eq. (3)), since two moles of methanol and one mole of formaldehyde make one mole of methylal and one mole of water, the methylal formation rate is expected to be proportional to the second order of the 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.

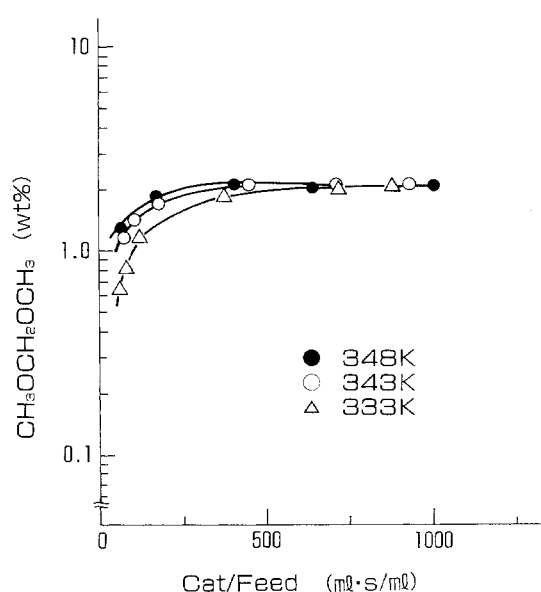
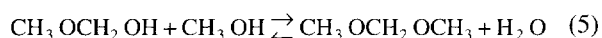
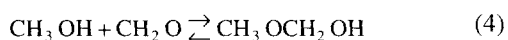


**Fig. 7** Relationship between initial methanol concentration and initial methylal formation rate. Initial formaldehyde concentration: 1.0 wt%; Temperature: 333 K

**Figure 8** shows the effects of temperature on the methylal formation rate. Temperature was varied from 333 to 348 K. The methylal formation rate increased with reaction temperature, but the final methylal concentrations at equilibrium were nearly equal to one another. This means that the heat of reaction is very small.

From these experiments, the reaction rate formula shown in **Table 1** was developed. Each reaction rate constant for these experimental conditions can also be estimated as shown in Table 1. 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 produce hemiacetal (Eq. (4)). The reaction rate of this step is very fast. Second, methanol and hemiacetal produce methylal and water (Eq. (5)). The reaction between methanol and hemiacetal is the rate-determining step for the total reaction. Thus, the methylal formation rate is proportional to the first order of methanol concentration and hemiacetal concentration. In our experimental conditions there is excess methanol to formaldehyde, so the hemiacetal concentration is thought to be nearly equal to the formaldehyde concentration. Therefore, the methylal formation rate is proportional to the first order of methanol concentration and formaldehyde concentration:



**Fig. 8** Effects of temperature on methylal formation. Initial formaldehyde concentration: 1.0 wt%; Initial methanol concentration: 50 wt%,  $\Delta$  333 K,  $\circ$  343 K,  $\bullet$  348 K

**Table 1.** Kinetics of methylal synthesis

$\frac{d[\text{CH}_3\text{OCH}_2\text{OCH}_3]}{dt} = k_1[\text{CH}_3\text{OCH}_2\text{OH}][\text{CH}_3\text{OH}] - k_2[\text{CH}_3\text{OCH}_2\text{OCH}_3][\text{H}_2\text{O}]$			
	$k_1$ [l.mol <sup>-1</sup> .s <sup>-1</sup> ]	$k_2$ [l.mol <sup>-1</sup> .s <sup>-1</sup> ]	$K$
333 K	$1.6 \times 10^{-4}$	$0.55 \times 10^{-4}$	3.0
343 K	$2.6 \times 10^{-4}$	$0.80 \times 10^{-4}$	3.2
348 K	$3.2 \times 10^{-4}$	$1.0 \times 10^{-4}$	3.2

$k_1 = 395 \times \exp [40,600/RT]$ ,  $k_2 = 38.1 \times \exp [-37,200/RT]$   
 $K = k_1/k_2 = 10.4 \times \exp [-3,300/RT]$

From these basic experimental results, the industrial methylal synthesis technology was developed<sup>4</sup>.

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 reactive 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. We developed a sulfonated, crosslinked polystyrene<sup>4</sup>. A well-known catalyst like sulfuric acid has the problem of corrosion. A solid acid catalyst with a high selectivity of nearly 100 % and a long-life catalytic activity was therefore developed.

The second point is the development of the reactive distillation system<sup>4</sup>. Distillation was conducted using a distillation tower and multi-reaction units<sup>4</sup>. The middle portion of the distillation tower was furnished with stages from which the liquid components were withdrawn and pumped to the reactor units. Each reactor unit was filled with a solid acid catalyst. The liquid components were circulated to provide a solid-liquid contact

with the catalyst. The reactive solutions containing the resulting methylal, which emerged from each of the reactor units, were returned to the distillation tower where they made gas-liquid contact with the vapor ascending from the bottom of the tower to its top so that the concentration of methylal would progressively increase. 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, using the extractive distillation system<sup>4</sup>.

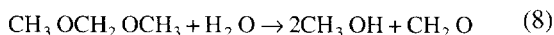
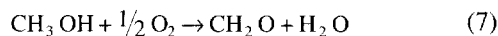
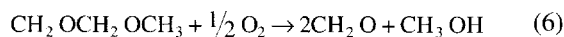
As a result of these refinements, 99 % pure methylal was obtained from the top of the distillation column and waste water was taken out from the bottom.

Thus, the world's first technology for commercial production of methylal was established.

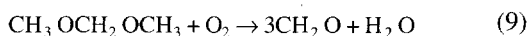
Methylal thus manufactured is fed to the oxidation step to produce highly concentrated aqueous formaldehyde<sup>4</sup>.

Summarizing the methylal oxidation, three elementary reactions—methylal partial oxidation (Eq. (6)), methanol oxidation (Eq. (7)), and methylal hydrolysis (Eq. (8)) occur simultaneously. Therefore, the reaction behavior is very complicated.

Individual reactions:



Total reaction:



The use of a conventional methanol oxidation catalyst ( $\text{MoO}_3\text{-Fe}_2\text{O}_3$  complex catalyst) for methylal oxidation resulted in a short catalyst life.

An important step in our work was therefore the development of a more durable catalyst. We developed a catalyst, composed of iron, molybdenum, and a third component that can withstand long-term use for over one year of methylal oxidation processing<sup>4</sup>.

Methylal is then oxidized to give 70 wt% aqueous formaldehyde<sup>4</sup>. This highly concentrated aqueous solution is then fed to the acetal homopolymer and copolymer plants of Asahi Chemical, the combined capacity of which is 35,000 tons/year<sup>5</sup>.

## Conclusions

For the commercial production of methylal, basic research on the its synthesis from methanol and formaldehyde was investigated using a sulfonated cross-linked polystyrene as the solid acid catalyst. The methylal formation rate was found to be proportional to the first order of formaldehyde concentration and methanol concentration.

Considering the results of the basic reaction of methanol and formaldehyde to methylal, we completed the world's first development and commercialization of a new process for manufacturing methylal by reactive distillation. This methylal is then oxidized to give 70 wt% aqueous formaldehyde, which is fed to the acetal homopolymer and copolymer plants of Asahi Chemical.

## Nomenclature

$[\text{CH}_2\text{O}]_0$	= initial formaldehyde concentration	[mol/l]
$[\text{CH}_3\text{OH}]_0$	= initial methanol concentration	[mol/l]
$K$	= equilibrium constant	[-]
$k_1$	= rate constant of methyl formation	[l/mol·S]
$k_2$	= rate constant of methylal hydrolysis	[l/mol·S]
$R$	= gas constant	[J/mol·K]
$T$	= reaction temperature	[K]

## <Subscripts>

O = initial

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