# The One-Step Synthesis of Methyl Isobutyl Ketone via Catalytic Distillation: Kinetics of the Selective Hydrogenation of Mesityl Oxide

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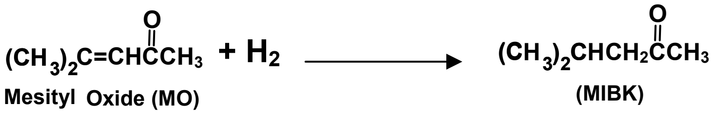
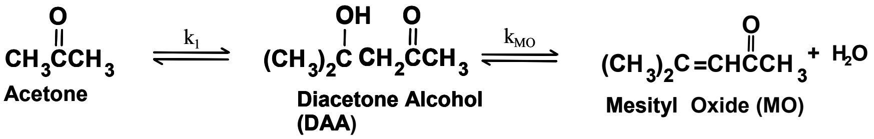
## Introduction

Methyl isobutyl ketone (MIBK) is a valuable industrial solvent produced commercially in a three-stage process from an acetone feedstock. First, acetone is dimerized to produce diacetone alcohol (DAA) (eqn. 1.). Second, DAA undergoes a condensation reaction to produce mesityl oxide (MO) and water (eqn. 1). Third, the carbon-carbon double bond of MO is selectively hydrogenated to produce MIBK (eqn 2). The conventional process for the production of MIBK, illustrated in Figure 1, involves several unit operations resulting in high capital and operating costs and inherent inefficiencies. Consequently, it is desirable to produce MIBK from acetone in a single stage. It has been recently reported that MIBK can be produced from acetone and hydrogen in one step in a catalytic distillation reactor (Figure 2).[1]



$$\underset{\text{Mesityl Oxide (MO)}}{(CH_3)_2C{=}CH\overset{O}{\overset{\|}{C}}CH_3} + H_2 \longrightarrow \underset{\text{(MIBK)}}{(CH_3)_2CHCH_2\overset{O}{\overset{\|}{C}}CH_3} \qquad (1)$$



$$\underset{\text{Acetone}}{CH_3\overset{O}{\overset{\|}{C}}CH_3} \overset{k_1}{\rightleftharpoons} \underset{\text{Diacetone Alcohol (DAA)}}{(CH_3)_2\overset{OH}{\overset{|}{C}}\,CH_2\overset{O}{\overset{\|}{C}}CH_3} \overset{k_{MO}}{\rightleftharpoons} \underset{\text{Mesityl Oxide (MO)}}{(CH_3)_2C{=}CH\overset{O}{\overset{\|}{C}}CH_3} + H_2O \qquad (2)$$

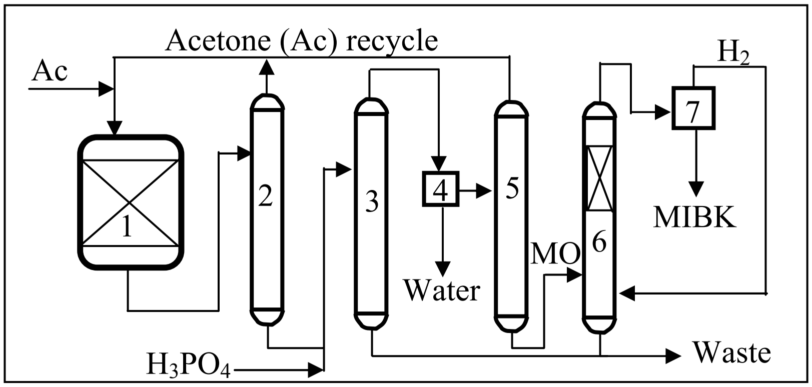


Figure 1 A conventional three-step process for the proeduction of MIBK
1- DAA reactor; 2,5-distillation columns; 3-MO reactor;
4,7-phase separators; 6-hydrogenation reactor

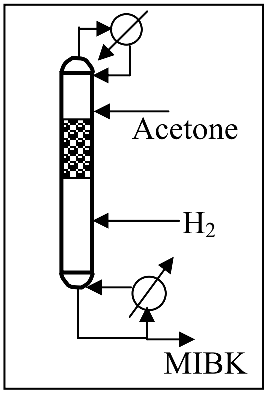


Figure 2 One-Step CD process for MIBK production

In previous work in our group, a catalytic distillation process was developed for the production of DAA from acetone [2]. The effects of CD process parameters on the

DAA and MO production rates were established and the kinetics of the aldol condensation of acetone using an anion exchange resin were characterized.[2,3] The synthesis of MIBK from acetone in a CD reactor is an extension of the CD process for DAA production developed previously. However, the introduction of hydrogen to this system opens up numerous possible reaction pathways. Consequently, a detailed knowledge of the effects of the unique transport phenomena observed in CD reactors as well as the physico-chemical properties of the catalyst materials on product yield and selectivity is required. In this work, the selective hydrogenation of MO with a 0.5 wt% $Pd/Al_2O_3$ catalyst was studied in the liquid phase to obtain a fundamental understanding of this step of the MIBK synthesis including the development of a robust kinetic model that can be incorporated into existing computer models for subsequent use in process simulation and design of the one-step synthesis of MIBK via catalytic distillation. The interactions of mesityl oxide and MIBK with the Pd catalyst were studied via in-situ diffuse reflectance infrared spectroscopy in order to gain insight into the reaction mechanism.

## Results and Discussion

Kinetic data was obtained from over a broad range of mesityl oxide concentrations in acetone solvent and over a range of pressures that may be realized in a catalytic distillation process. Standard tests were employed to ensure that the effects of external mass transfer, including the rate of gas absorption, were not influencing the observed rate of reaction. The experimental results showed a high degree of repeatability with a typical experimental error of about 3%. The catalyst showed a very high selectivity to MIBK production, typically in excess of 93%. Based on the kinetic and spectroscopic studies, it was postulated that hydrogen is adsorbed dissociatively on the catalyst surface and that mesityl oxide coordinates to the catalyst as an $\eta_4$ diadsorbed species in which the olefinic group forms an $\eta_2\pi(C,C)$ pi complex and the carbonyl group is coordinated at an adjacent site. The Langmuir-Hinshelwood approach was utilized to develop a mechanistic kinetic model of the selective hydrogenation of mesityl oxide in acetone at 100°C. The proposed kinetic model was validated by nonlinear regression analysis of the kinetic data obtained and was found to fit the data very well with a very strong model significance. The validity of the proposed kinetic model indicates that the assumptions inherent in the model are correct. Specifically, that the surface reaction is controlling, that hydrogen is adsorbed dissociatively on the metal surface and that mesityl oxide exists as a diadsorbed species on the catalyst surface. The results of this study will be used for design and simulation of a CD process for the one-step synthesis of MIBK.

## References

1. K.H. Lawson and B. Nkosi, US Patent 6,008, 416
2. G.G. Podrebarac, F.T.T. Ng and G.L. Rempel, *Chemical Engineering Science*, Vol. 53, No. 5, pp. 1067-1075, (1998).
3. G.G. Podrebarac, F.T.T. Ng and G.L. Rempel, *Chemical Engineering Science*, Vol. 52, No. 17, pp. 2991-3002, (1997).