Intrinsic Kinetics of Methanol Dehydration over Al$_2$O$_3$ Catalyst

Liang Zhang, Hai-Tao Zhang, Wei-Yong Ying, Ding-Ye Fang

Abstract—Dehydration of methanol to dimethyl ether (DME) over a commercial Al$_2$O$_3$ catalyst was studied in an isothermal integral fixed bed reactor. The experiments were performed on the temperature interval 513-613 K, liquid hourly space velocity (*LHSV*) of 0.9-2.1h^{-1}, pressures between 0.1 and 1.0 MPa. The effect of different operation conditions on the dehydration of methanol was investigated in a laboratory scale experiment. A new intrinsic kinetics equation based on the mechanism of Langmuir-Hinshelwood dissociation adsorption was developed for the dehydration reaction by fitting the expressions to the experimental data. An activation energy of 67.21 kJ/mol was obtained for the catalyst with the best performance. Statistic test showed that this new intrinsic kinetics equation was acceptable.

Keywords—catalyst, dimethyl ether, intrinsic kinetics, methanol

I. INTRODUCTION

DURING the past few years, DME has received growing attention due to its potential use as a multi-purpose fuel [1]. It is a colorless, nontoxic, non-corrosive, non-carcinogenic and environmentally friendly substance with a boiling point of −25°C [2]. DME can be used as an aerosol propellant in the cosmetics industry to replace chlorofluorocarbons and liquefied petroleum gas. Furthermore high-purity DME can also be used to make hair sprays and dyes, personal care mousses, antiperspirants, and room air fresheners. Then there would be a growing requirement to produce DME on a large scale, to meet the future market. Dehydration of methanol over an acidic catalyst is an important reaction for the production of DME [3]. DME can be obtained according to the following reaction:

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$$
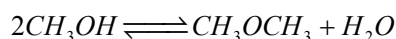
Gas-solid reactors were popularly used for dehydration of methanol to DME in chemical plant. When one designs methanol dehydration reactor, the kinetics of the dehydration reaction is important in sizing the reactor. The kinetics of methanol dehydration on acidic catalysts has been studied extensively resulting in different kinetics equations. A list of

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published kinetic models for methanol dehydration to DME is given in Table I. Equations (1-3) have been derived from the experiments conducted in conditions not found in an industrial reactor. Since methanol dehydration is a reversible single reaction, equations (1-3) without reversible term are not suitable for the industrial reactor design, where reaction takes place at high conversion levels. Then, screening of the kinetics equations (4-6) using our experimental data showed that a new kinetics equation should be derived to obtain more accurate results.

In this study，the effect of different operation conditions including temperature, *LHSV*, pressure on methanol conversion was studied. The intrinsic kinetics of methanol dehydration reaction was studied, and the kinetic expressions were tested against experimental data that were obtained on the commercial Al$_2$O$_3$ catalyst. A new kinetics equation was derived based on the mechanism of Langmuir-Hinshelwood dissociation adsorption, and the kinetics parameters were determined.

II. EXPERIMENTAL SECTION

The scheme of the laboratory-scaled system employed in this study is illustrated in Fig.1. Pure methanol was pumped from methanol container at certain *LHSV* to a super-heater before entering the reactor. The superheated methanol was sent to an isothermal integral fixed bed reactor. The catalyst bed is in the isothermal zone. The axial reactor temperature at any point of the catalyst bed was measurable via a thermo-well using a thermocouple. The reactor outlet products were passed through a check valve and counterbalance valve to the gas-liquid separator. Water, methanol from reactor were cooled down and weighed at regular intervals, and outlet gas from gas-liquid separator was measured by a soap film flowmeter. A small portion of gas from separator was subjected to gas chromatography (GC) for on-line analysis. The gas chromatograph (Agilent Technologies, model 7890A) was equipped with TCD and FID. It had a capillary column (HP-PlotQ, 30 m × 0.53 mm × 40 μm) for separating methanol, DME, water. The reaction performance results including Methanol conversion and DME selectivity were calculated subsequently. According to the preliminary experiment, a small amount of by-products such as CO, H$_2$ as well as CH$_4$ can be detected when reaction temperature is above 633K. Essentially, only methanol, DME, and water were detected in the reactor effluent mixture at temperatures below 613K.

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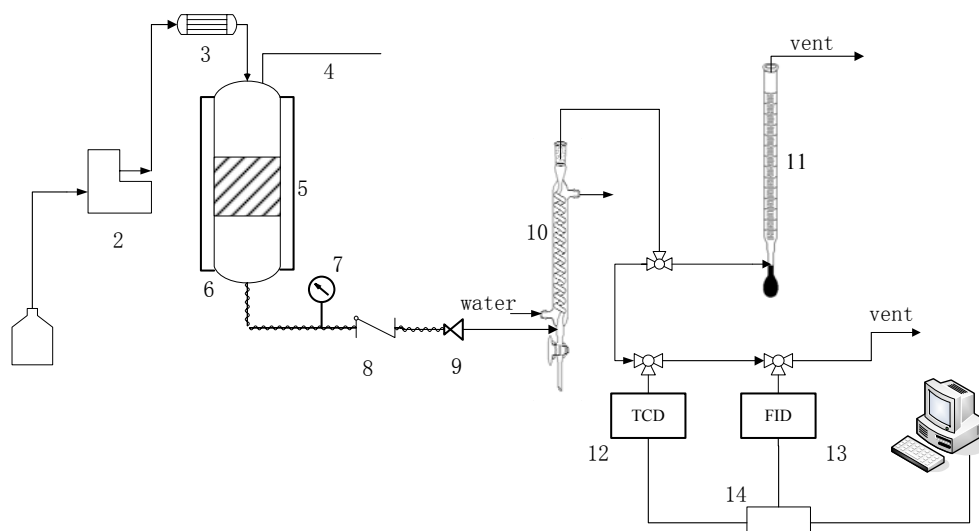International Journal of Chemical and Molecular Engineering
Vol:5, No:11, 2011

Fig. 1 Schematic diagram of intrinsic kinetics experiment: (1) Methanol vessel.(2) Free pump. (3) Preheater. (4) Thermocouple. (5) Heating furnace. (6) Reactor. (7)Press gauge. (8) Check valve. (9) Counterbalance valve. (10) Gas-liquid separator. (11) Soap bubble flowmeter. (12-13) Gas chromatograph. (14) Chromatographic working station

TABLE I
SUMMARY OF THE PUBLISHED KINETIC MODELS

Equation	No.	Catalyst	Reference source
$-r_M = \dfrac{k_1 P_M^{1/2}}{P_M^{1/2} + k_2 P_W}$	(1)	Al_2O_3	Kallo and Knozinger [4], 1967
$-r_M = \dfrac{k K_M P_M^{1/2}}{1 + K_M P_M^{1/2} + K_W P_W}$	(2)	Al_2O_3	Figueras et al [5]. 1971
$-r_M = \dfrac{k K_M P_M}{[1 + 2(K_M P_M)^{1/2} + K_W P_W]^2}$	(3)	Acidic ion exchange resin	Klusacek and Schneider [6], 1982
$-r_M = \dfrac{k K_M^2 [P_M^2 - (P_W P_D / K_{eq})]}{[1 + 2(K_M P_M)^{1/2} + K_W P_W]^4}$	(4)	γ-Al_2O_3	Bercic and Levec [7], 1992
$-r_M = \dfrac{k[P_M^2 / P_W - (P_D / K_{eq})]}{(1 + K_M P_M + K_W P_W)^2}$	(5)	HZSM-5	Lu et al.[8] , 2004
$-r_M = \dfrac{k P_M [1 - (P_D P_W / K_{eq} P_M^2)]}{1 + K_M P_M + P_W / K_W}$	(6)	γ-Al_2O_3	Mollavali et al. [9], 2008

The size of the reactor is Φ 24 mm × 6 mm ×600 mm. The amount of catalyst is 4.0015g. The operation conditions are as follows: temperature ranging from 513 to 613K, pressure ranging from 0.1 to 1.0MPa, and liquid hourly space velocity (*LHSV*) from 0.9 to 2.1h^{-1}. These operation conditions were identified with the conditions in commercial methanol dehydration plant.

To check for internal diffusion resistance, 4g of samples of four different sizes, namely 0.83, 0.38, 0.25 and 0.18 mm, were loaded under similar conditions. The influence of the internal diffusion was investigated by performing experiments on catalyst pellets of above different sizes in identical working conditions. The results, presented in Fig.2, showed that the influence of internal diffusion on the process kinetics is practically avoided for catalyst pellets with the diameter smaller than 0.38 mm. Consequently, all the kinetic experiments were performed with catalyst pellets having the average diameter around 0.154mm-0.198mm. Besides, to check for external transport resistance, several tests were carried out at different methanol feed flow rates, keeping constant the ratio of catalyst weight to methanol flow rate. The measured methanol conversions showed that, during the working domain, the influence of external mass transfer on process kinetics is not obvious. So, the internal and external diffusion effects were eliminated at these experimental conditions.
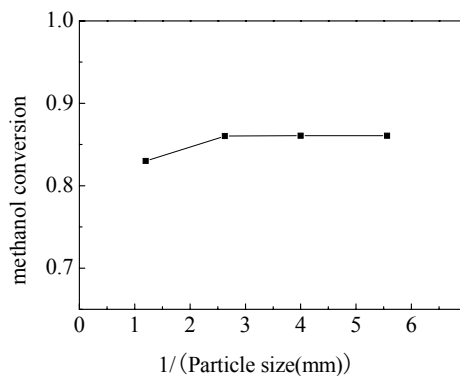

Fig. 2 Methanol conversion versus the pellet dimension (Conditions: *T* =563 K, *P* =0.1 MPa, *LHSV* =0.9 h^{-1}.)

III. RESULTS AND DISCUSSION

TABLE II
Textural Properties of the Fresh Catalysts

Sample	Surface area S_{BET} (m^2/g)	Total volume V_p (cm^3/g)	Average pore diameter (nm)
Al_2O_3	237	0.48	6.9

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A. Catalyst Characterization

The BET surface area, pore volume, and average pore diameter of the catalysts are given in Table II.

The commercial Al_2O_3 catalyst mainly existed with mesopore sizes of 10nm as shown in Fig.3.
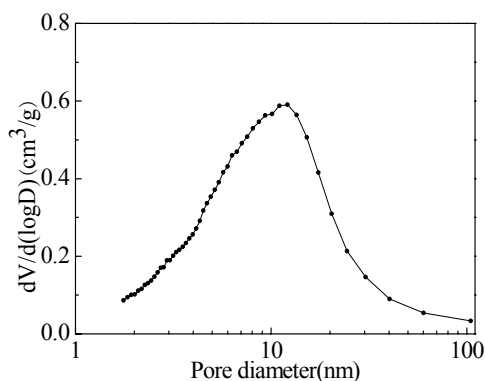

Fig. 3 Pore size distribution curve of catalyst obtained by N_2 adsorption at 77 K

The XRD pattern of sample (Fig.4) clearly indicates that the catalyst is highly amorphous in nature, with a low level of crystallinity in the form of cubic aluminum oxide (JCPDS File Card Nos.10-0425).
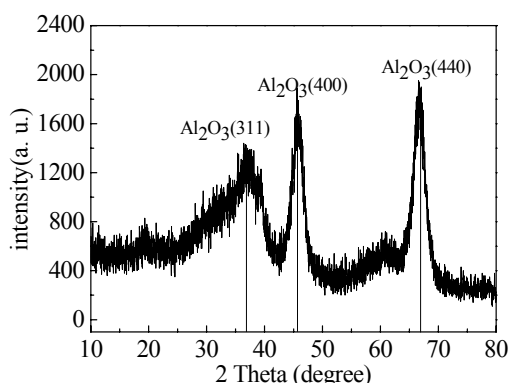

Fig. 4 X-ray diffraction (XRD) pattern of catalyst

B. Influence of temperature on methanol conversion

The effect of the temperature ranging from 513 K to 613 K on the methanol conversion was studied under the condition of atmospheric pressure and *LHSV* range from 0.9 h^{-1} to 2.1h^{-1}. The effect of temperature is shown in Fig.5, which reveals that with the increase of temperature, there exists an optimum temperature for methanol conversion between 563 K and 583 K. The existence of optimum temperature is mainly due to the declining equilibrium value of methanol conversion with temperature increasing. Besides, the methanol conversion at *LHSV*=2.1 h^{-1} was lower in the temperature range of 513 -533 K. A fraction of methanol which passed the catalyst bed with high flow rate would not be reacted timely, due to the relatively lower reaction rate at temperatures below 533 K.
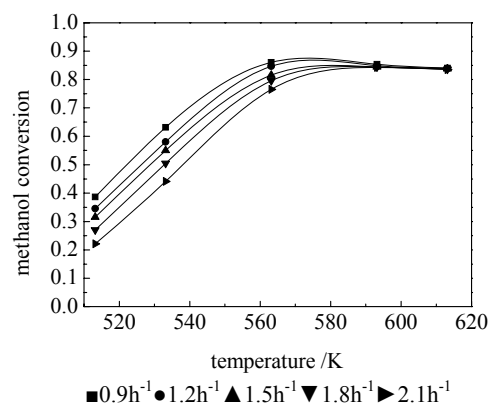

$\blacksquare 0.9h^{-1}\bullet 1.2h^{-1} \blacktriangle 1.5h^{-1} \blacktriangledown 1.8h^{-1} \blacktriangleright 2.1h^{-1}$
Fig. 5 Effect of temperature on methanol conversion

C. Influence of LHSV on methanol conversion

The effect of the *LHSV* ranging from 0.9 h^{-1} to 2.1h^{-1} on the methanol conversion was studied under the condition of atmospheric pressure and temperature range from 513 K to 613 K. The results are show in Fig.6. It was obviously found that the methanol conversion decreased with an increase in the methanol feed at temperatures below 563 K. It can be attributed to that the methanol conversion is very close to the equilibrium conversion at temperatures above 563 K.
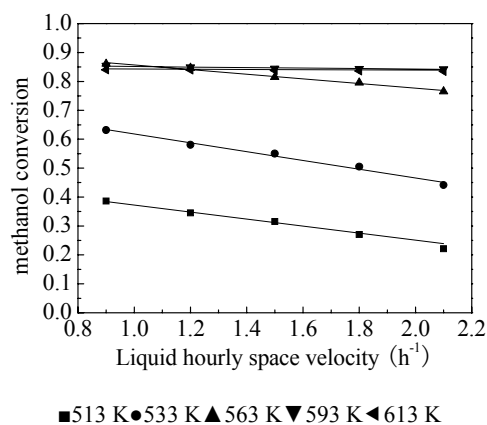

$\blacksquare 513$ K$\bullet 533$ K$\blacktriangle 563$ K$\blacktriangledown 593$ K$\blacktriangleleft 613$ K
Fig. 6 Effect of *LHSV* on methanol conversion

D. Influence of pressure on methanol conversion

The effect of the pressure on the methanol conversion was studied under the condition of *LHSV* in 1.5h^{-1} and temperature at 593 K. As shown in Fig.7, the methanol conversion was nearly unaltered by pressure. The experiment result was coincided with the fact that reaction of methanol dehydration to DME is equimolar.

TABLE III
COMPARISON OF THE CALCULATED VALUES WITH THE EXPERIMENTAL VALUES OF THE METHANOL CONVERSION UNDER DIFFERENT OPERATION CONDITIONS

| No.	LHSV h^{-1}	P MPa	T K	$x_{M,exp}$	$x_{M,cal}$ Eq6	$\frac{x_M - x_{MC}}{x_M}$ %	$x_{M,cal}$ Eq7	$\frac{x_M - x_{MC}}{x_M}$ %
1	1.5	0.2	593.15	0.8444	0.8567	-1.46	0.8568	-1.47
2	1.5	0.4	593.15	0.8439	0.8567	-1.52	0.8568	-1.53
3	1.5	0.6	593.15	0.8446	0.8567	-1.43	0.8568	-1.44
4	1.5	0.8	593.15	0.8443	0.8567	-1.47	0.8568	-1.48
5	1.5	1.0	593.15	0.8442	0.8567	-1.48	0.8568	-1.49
6	1.5	0.1	633.15	0.8356	0.8400	-0.53	0.8400	-0.53
7	1.2	0.1	513.15	0.3452	0.3332	3.46	0.3438	0.41
8	1.5	0.1	513.15	0.3156	0.2712	14.08	0.2885	8.60
9	1.8	0.1	513.15	0.2703	0.2284	15.50	0.2485	8.08
10	2.1	0.1	513.15	0.2213	0.1972	10.88	0.2182	1.40
11	1.5	0.1	533.15	0.5506	0.5684	-3.23	0.5191	5.73
12	1.8	0.1	533.15	0.5050	0.4962	1.75	0.4594	9.03
13	2.1	0.1	533.15	0.4390	0.4117	0.54	0.4117	6.72
14	0.9	0.1	563.15	0.8607	0.8693	-1.00	0.8682	-0.87
15	1.8	0.1	563.15	0.7958	0.8192	-2.94	0.7952	0.07
16	2.1	0.1	563.15	0.7655	0.7846	-2.50	0.7548	1.40
17	0.9	0.1	593.15	0.8542	0.8568	-0.30	0.8568	-0.30
18	1.2	0.1	593.15	0.8490	0.8568	-0.91	0.8568	-0.92
19	1.5	0.1	593.15	0.8444	0.8565	-1.44	0.8568	-1.46
20	1.8	0.1	593.15	0.8438	0.8556	-1.40	0.8566	-1.51
21	0.9	0.1	613.15	0.8403	0.8482	-0.95	0.8483	-0.95
22	1.2	0.1	613.15	0.8396	0.8482	-1.02	0.8483	-1.03
23	1.5	0.1	613.15	0.8380	0.8482	-1.22	0.8483	-1.23
24	1.8	0.1	613.15	0.8358	0.8481	-1.47	0.8483	-1.49
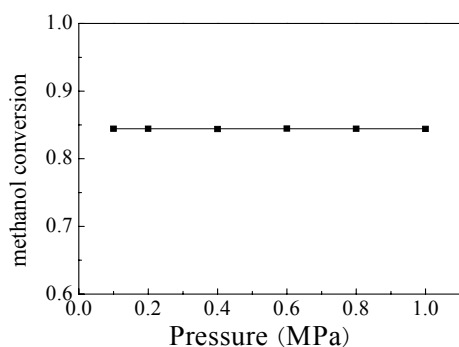
Fig. 7 Effect of pressure on methanol conversion

IV. INTRINSIC KINETICS OF METHANOL DEHYDRATION

To obtain the rate equation, a reaction mechanism should be adopted. Generally, almost all catalytic surface reactions proceed via the Langmuir-Hinsheldwood mechanism [10]. Besides, it is evident that in almost all rate equations for dehydration the reaction rate is proportional to the square root of the methanol concentration in Table I. This indicates that the dehydration reaction undergoes dissociative adsorption of methanol on the catalyst surface. In the derivation of rate equations for the dehydration of methanol, the Langmuir-Hinsheldwood mechanism was applied. With the assumption that surface reaction is the controlling step and the dissociative adsorption of methanol on the surface of Al_2O_3 is taking place, the Langmuir-Hinsheldwood model can be represented in the following form:

$$-r_M = \frac{kP_M(1 - P_D P_W / K_P P_M^2)}{[1 + (K_M P_M)^{1/2} + K_W P_W]^2} \quad (7)$$

A. Intrinsic Kinetics Data and Results

Discrimination of the kinetic models and estimation of the values of the kinetic parameters was performed by fitting the experimental data of the methanol conversion to the kinetics equations (4-7). Screening of the kinetics equations using the experimental data in Table II found that the equation (6) showed better fit to the experimental data. Equation (6) contained reversible term, besides it was based on Langmuir-Hinsheldwood mechanism in which the dehydration reaction undergoes molecular adsorption of methanol. Then it was chose to compare with equation (7).

The intrinsic kinetics data and the comparison of the calculated values with the experimental values of the methanol conversion under different operation conditions were shown in Table III. The equation (7) displayed better fit with the experimental data compared with equation (6) due to the smaller relative error.

B. Estimation of the kinetics parameters

The temperature dependencies of the rate constant, k, and adsorption equilibrium constants K_M and K_W were expressed by the Arrhenius and Van't Hoff equations:

$$k = k_0 \exp(-\frac{E}{R_g T}) \quad (8)$$

$$K_i = A_{0,i} \exp(-\frac{\Delta H_i}{R_g T}) \quad (9)$$

The intrinsic reaction rate was tested in an isothermal integral fixed bed reactor. Reaction rate $r_M = -\frac{dN_M}{dw} = -\frac{N_M^0 dx_{MC}}{dw}$, then methanol conversion in the reactor outlet $x_{MC} = \int_0^w \frac{r_M}{N_M^0} dw$ can be obtained by integrating. The activation energy of the reaction and heat of

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adsorption of methanol and water can be obtained using the Levenberg-Marquardt algorithm. The objective function was to minimize the sum of the square of residuals $S = \sum_{j=1}^{M}(x_{M,j} - x_{MC,j})^2$ corresponding to differences between the experimental data and those calculated for the kinetic model. The values of activation energy and heat of adsorption for methanol and water were presented in Table IV.

The calculated value of activation energy(67.21 kJ/mol) is lower than the one estimated theoretically by P. Grigore [11] for methanol dehydration on the H-SAPO-34 (80.10 kJ/mol) but in agreement with the value obtained by Schmitz [12](66.60kJ/mol). The estimated heat of adsorption for the

TABLE IV
VALUES OF THE ACTIVATION ENERGY AND THE HEAT OF
ADSORPTION FOR METHANOL AND WATER FOR KINETICS MODEL

activation energy E_a (J/mol)	heat of adsorption for methanol H_M (J/mol)	heat of adsorption for water H_W (J/mol)
$-r_M = \dfrac{kP_M(1 - P_D P_W / K_P P_M^2)}{[1 + (K_M P_M)^{1/2} + K_W P_W]^2}$		
67214.4	-60614.3	-40308.0

methanol molecule (60.61kJ/mol) is close to the value for HZSM-5 zeolite published by B. Solange [13] (65kJ/mol). Furthermore, the estimated heat of adsorption for water molecules (40.31kJ/mol) is approximately equal to the adsorption energy reported by the K. Klusacek [6] for the reaction product (40.70kJ/mol).

C. Verification of the model

It is stated that the intrinsic kinetics model was suitable when $F > 10 \times F_{0.05}$、$\rho^2 > 0.9$. Statistic results in Table V showed that equation（7）meet the requirements above. This proved that the intrinsic kinetics model based on the mechanism of Langmuir-Hinshelwood dissociation adsorption was appropriate for this catalyst.

V. CONCLUSIONS

The effect of different operation conditions on the dehydration of methanol was analyzed in a laboratory scale experiment. It was showed that the temperature and flow rate have significant effect on the methanol conversion. However,

TABLE V
Statistic Results for the Kinetic Model

	M_P	$N-M_P$	ρ^2	F	$F_{0.05} \times 10$
Equation (7)	6	18	0.9995	8374.76	26.6

the pressure had little effect on the methanol conversion in the range of this experiment. Experimental data obtained through a fixed bed catalytic reactor were used to select a kinetic model of the catalytic process. These two kinetics equations derived from different mechanism both showed comparable and good agreement with the experimental data. However, this new intrinsic kinetics equation based on the mechanism of

Langmuir-Hinshelwood dissociation adsorption was much more proper compared with the equation derived by Mollavali. The calculated values of activation energy, the estimated heat of adsorption for methanol and heat of adsorption for water calculated were compared with values obtained by previous authors. It is demonstrated that this new kinetics equation can be used to simulating and enlarging fixed bed reactor for methanol dehydration.

APPENDIX

E_a = activation energy of reaction [J·mol^{-1}]

k_0 = pre-exponential factor

k = reaction rate constant

K_P = reaction equilibrium constant

K_M = methanol adsorption equilibrium constant

K_W = water adsorption equilibrium constant

H_M = heat of adsorption for methanol molecule

H_W = heat of adsorption for water molecule

R_g = ideal gas constant [J·mol^{-1}·K^{-1}]

T = temperature [K]

P = pressure [MPa]

N = number of experiment

M_P = number of kinetics parameter

N_M = instantaneous mole flow rate

N_M^0 = initial mole flow rate

w = weight

$x_{M,exp}$ = calculated methanol conversion

$x_{M,exp}$ = experimental methanol conversion

$LHSV$ = liquid hourly space velocity

$$F = \frac{\left[\sum_{j=1}^{N} x_{M,j}^2 - \sum_{j=1}^{N}(x_{M,j} - x_{MC,j})^2\right] / M_P}{\sum_{j=1}^{N}(x_{M,j} - x_{MC,j})^2 / (N - M_P)}$$

$$\rho^2 = 1 - \sum_{j=1}^{M}(x_{M,j} - x_{MC,j})^2 / \sum_{j=1}^{M} x_{M,j}^2$$

i = M, W

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