



## Kinetics of Reaction between Dimethyl Sulfide and Hydrogen in Black Liquor Gasification Gas with ZnO Catalyst

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Black liquor gasification gas contains a small amount of dimethyl sulfide, which needs to be removed before the gasification gas combusting in the gas turbine in black liquor integrated gasification combined cycle (BLIGCC). A desulphurization method has been carried experimentally in the conditions of high temperature and ZnO catalyst, where dimethyl sulfide and hydrogen reacted to produce methane and hydrogen sulfide, then the hydrogen sulfide was absorbed with alkali solution. The current investigation was carried out to find the kinetics of reaction between dimethyl sulfide and hydrogen in black liquor gasification gas with ZnO catalyst. The reaction was studied in a pipe reactor at various temperatures and concentrations of dimethyl sulfide and hydrogen. The reaction rate was evaluated by analyzing the consumption of dimethyl sulfide and then the rate law was established. The reaction has been found 0.963 and 1.098 order with respect to dimethyl sulfide and hydrogen, respectively and the activation energy was 31737.19 J mol with frequency factor 16747.32.

**Key Words:** Black liquor, Gasification, Desulphurization, Dimethyl sulfide, Hydrogen and kinetics.

### INTRODUCTION

Black liquor, the remaining solution contains inorganic material and organic degradation products in the conventional pulping process in pulp mills, has large number of chemical oxidation demand (COD)<sup>1</sup> and can be a significant source of water pollution. In the other hand, it is a kind of renewable energy resource containing heat value of 14-16.5 kJ/g. Therefore, appropriate treatment of black liquor is a major concern of pulp mills, where the black liquor is concentrated to about 55-70 % solids and then burned in a Tomlinson-type recovery boiler (RB) to recover alkali and energy and at the same time that the COD is significantly reduced<sup>2</sup>. However, the relatively low energy recovery (50-63 %)<sup>3</sup> of the recovery boilers, coupled with the emissions of polluting gases has stimulated the search for improved methods for treating black liquor<sup>4</sup>.

There has been a great deal of interest in integrated gasification combined cycle (IGCC) technology in the past two decades<sup>5,6</sup>. When applied to treat black liquor in pulp mills, it was called black liquor integrated gasification combined cycle (BLIGCC) technology. The black liquor integrated gasification combined cycle technology is undergoing intense development, because it offers potential advantages in energy recovery, as well as environmental benefits. Specifically, the potential for power generation by black liquor integrated gasification combined cycle is up to 2.5 times that of the conventional system, having a caloric efficiency of 74-81 %<sup>5-7</sup>, compared

to the 50-63 % efficiency of conventional recovery boilers system noted above. And compared with the conventional recovery boilers the emission of net CO<sub>2</sub> from black liquor integrated gasification combined cycle is lower, which will benefit the environment<sup>7,8</sup>.

Despite the great potential advantages associated with black liquor integrated gasification combined cycle technology, there are many technical problems have to be resolved before industrialization, including methods for gas desulphurization. Black liquor gasification gas contains CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> and a small amount of sulfide<sup>9-11</sup>, including hydrogen sulfide, methyl mercaptan and dimethyl sulfide. Current methods of gasification gas desulphurization are mainly alkali absorption method, organic amine absorption method and high temperature reaction method<sup>12-14</sup>. A deep desulphurization method has been carried experiment in the condition of high temperature and ZnO catalyst, where dimethyl sulfide and hydrogen reacted to produce methane and hydrogen sulfide, then the hydrogen sulfide was absorbed with alkali solution<sup>15</sup>. The current investigation was carried out to find the kinetics of reaction between dimethyl sulfide and hydrogen in black liquor gasification gas with ZnO catalyst.

### EXPERIMENTAL

**Experimental device:** The experimental device consisted of gas mixing chamber, reaction tube and absorber, shown in Fig. 1. Marked graduated scale, the gas mixing chamber's

bottom (3) connected to the water storage tank (1) and its top export connected to a three-way valve (5), those other two interfaces connected to the reaction tube (12) and the nitrogen tank (or hydrogen tank). The reaction tube in order connected to an air cooling pipe (16), a hydrogen sulfide absorber (17) and a dimethyl sulfide absorber (19). Finally the exhaust gas was collected by an air bag.

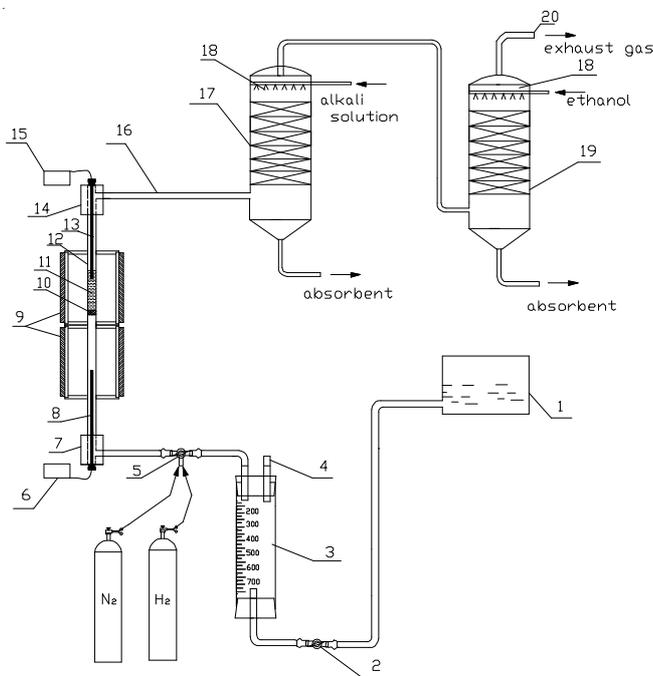


Fig. 1. Schematic diagram of experimental apparatus 1:water storage tank; 2:Two-way valve; 3:gas mixing chamber; 4:Import Management Sealed with rubber; 5:Three-way valve; 6:Preheat temperature controller; 7:1#tee; 8: Preheat temperature probe; 9: Heating units; 10: Metal grille; 11:catalyst; 12:reaction tube; 13: reaction temperature probe;14:2#tee;15:reaction temperature controller; 16:air cooling pipe; 17:H<sub>2</sub>S absorber; 18: Absorbent distributor; 19: CH<sub>3</sub>SCH<sub>3</sub> absorber; 20: Gas discharge outlet.

**Preparation of mixed gas:** In order to import hydrogen gas and nitrogen gas into the gas mixing chamber filled with water in proportion and then, puncturing rubber seal set of import management, CH<sub>3</sub>SCH<sub>3</sub> solution was injected into the chamber by an injector. After that, the chamber was heated to 40 °C to evaporate CH<sub>3</sub>SCH<sub>3</sub> completely.

**Experiment process:** After mixing gas preparation, the knob of three-way valve would be turned to let the nitrogen gas join into the reaction tube, which would be heated to the reaction temperature in nitrogen atmosphere. After heated to the reaction temperature, again, the knob was turned into another way to connect the mixing gas chamber and a certain flow rate mixing gas joined into the reaction tube where reactions take place.

**Collection, analysis and calculation of the remaining CH<sub>3</sub>SCH<sub>3</sub>:** The main remaining CH<sub>3</sub>SCH<sub>3</sub> was absorbed by ethanol solution in an absorber, while a little mass of CH<sub>3</sub>SCH<sub>3</sub> still stayed in the final exhaust gas. Then, the absorption was determined by gas chromatography (GC), and the standard curve was shown in Fig. 2 and the ratio between mass of CH<sub>3</sub>SCH<sub>3</sub> absorbed in liquid and stayed in the exhaust air in absorber was shown in Table-1, which resulted equations (1).

$$\text{mass}_{\text{CH}_3\text{SCH}_3,(\text{g})} = 0.061\text{mass}_{\text{CH}_3\text{SCH}_3,(\text{l})} \quad (1)$$

For the remaining CH<sub>3</sub>SCH<sub>3</sub> including the mass of CH<sub>3</sub>SCH<sub>3</sub> absorbed in the ethanol solution and the mass of CH<sub>3</sub>SCH<sub>3</sub> remaining in the exhaust air, their mass balance equation was:

$$\text{mass}_{\text{CH}_3\text{SCH}_3,\text{remaining}} = \text{mass}_{\text{CH}_3\text{SCH}_3,(\text{l})} \quad (2)$$

Submission of eqn. (1) into (2), yield eqn. (3)

$$\text{mass}_{\text{CH}_3\text{SCH}_3,\text{remaining}} = 1.061\text{mass}_{\text{CH}_3\text{SCH}_3,(\text{l})} \quad (3)$$

where,  $\text{mass}_{\text{CH}_3\text{SCH}_3,(\text{g})}$  was the mass of CH<sub>3</sub>SCH<sub>3</sub> remaining in the exhaust air (g);  $\text{mass}_{\text{CH}_3\text{SCH}_3,(\text{l})}$  was the mass of CH<sub>3</sub>SCH<sub>3</sub> absorbed in the ethanol solution (g);  $\text{mass}_{\text{CH}_3\text{SCH}_3,\text{remaining}}$ : mass of remaining CH<sub>3</sub>SCH<sub>3</sub> (g).

**Calculation reaction rate of CH<sub>3</sub>SCH<sub>3</sub>:** The reaction rate of CH<sub>3</sub>SCH<sub>3</sub> was calculated by eqn. (4):

$$r = \frac{m_{\text{CH}_3\text{SCH}_3,\text{reacted}}}{V_{\text{total}} \times t \times 62} \quad (4)$$

where, r: reaction rate of CH<sub>3</sub>SCH<sub>3</sub>, mol L<sup>-1</sup> S<sup>-1</sup>;  $m_{\text{CH}_3\text{SCH}_3,\text{reacted}}$ : mass of reacted CH<sub>3</sub>SCH<sub>3</sub>, g;  $V_{\text{total}}$ : total reacted volume, L, which is equal to the volume size of mixing gas chamber; t: contact time, s.

The mass of reacted CH<sub>3</sub>SCH<sub>3</sub> was calculated by eqn. (5):

$$m_{\text{CH}_3\text{SCH}_3,\text{reacted}} = m_{\text{CH}_3\text{SCH}_3,\text{injected}} - m_{\text{CH}_3\text{SCH}_3,\text{remaining}} \quad (5)$$

where,  $m_{\text{CH}_3\text{SCH}_3,\text{injected}}$ : was the mass of injected CH<sub>3</sub>SCH<sub>3</sub>, g.

**Calculation of contact times:** The contact times between the reactant and catalyst was calculated by eqn. (6):

$$t = \frac{l}{v} \quad (6)$$

where, t: contact time, s; l: length of catalyst layer, cm; v: the apparent linear rate of gas flow, cm/s. The apparent linear rate of gas flow was calculated by eqn. (7):

$$v = \frac{q_v}{\epsilon S} \quad (7)$$

where,  $q_v$ : volume flow rate of gas, cm<sup>3</sup> s;  $\epsilon$ : catalyst porosity, g cm<sup>3</sup>; In here, porosity was 0.38 for the 40 mesh catalyst particles put in a reaction tube with diameter of 6.0 mm; S: the cross-sectional area of reaction tube, cm<sup>2</sup>. Submission of equation (6) into (5), yield eqn. (8)

$$t = \frac{l\epsilon S}{q_v} \quad (8)$$

## RESULTS AND DISCUSSION

**Standard curve:** The standard solutions of dimethyl sulfide were prepared in different concentration of 42.4, 84.7, 169.4, 338.8, 508.2 and 677.6 (mg/L); those were measured by gas chromatography, respectively. The curve related between peak area and concentration of CH<sub>3</sub>SCH<sub>3</sub> was shown in Fig. 2.

**Data of absorbed balance:** The high purity hydrogen and nitrogen were join into the gas mixing chamber by volume ratio of 4:6 and 2, 4, 8, 16 mL of (v %) 5 % CH<sub>3</sub>SCH<sub>3</sub>, respected to 84.7, 169.4, 254.1 and 338.8 mg, were injected into the 900 mL chamber, respectively. The mixing gas passes through the reaction tube, the cooling pipe and the absorber with ethanol absorbent at atmosphere temperature. Then, the absorption was determined by gas chromatography and the

TABLE-1  
DATA OF ABSORBED BALANCE IN THE CH<sub>3</sub>SCH<sub>3</sub> ABSORBER

Number	Injected mass (mg)	Absorbent volume (mL)	Concentration of absorbent (mg/L)	Mass in liquid (mg)	Mass in gas (mg)	Mass(g)/mass(l)
1	84.7	484.5	166.85	80.84	3.86	0.0477
2	169.4	512.3	310.85	159.15	10.25	0.0644
3	254.1	503.7	474.32	238.92	15.18	0.0635
4	338.8	462.8	685.22	317.12	21.68	0.0684
Average						0.061

TABLE-2  
CONVERSION OF CH<sub>3</sub>SCH<sub>3</sub> IN DIFFERENT TEMPERATURE

Temperature (K)	573	623	673	723	753	773	823	873
Conversion (%)	5.18	8.10	9.69	11.24	84.52	95.69	97.38	97.86

TABLE-3  
CALCULATION OF CONTACT TIMES BETWEEN THE REACTANT AND CATALYST

Mass of catalyst (g)	Stacked volume of catalyst (cm <sup>3</sup> )	Cross-sectional area of tube (cm <sup>2</sup> )	Length of catalyst layer (cm)	Volume flow rate (cm <sup>3</sup> /s)	Catalyst porosity	Apparent linear rate of gas flow (cm/s)	Contact time (s)
2.0	1.89	0.28	6.68	6.67	0.38	62.69	0.107

mass of CH<sub>3</sub>SCH<sub>3</sub> stayed in the final exhaust gas was calculated by subtraction between the injected mass and the absorbed mass of CH<sub>3</sub>SCH<sub>3</sub> in liquid. The data was shown in Table-1.

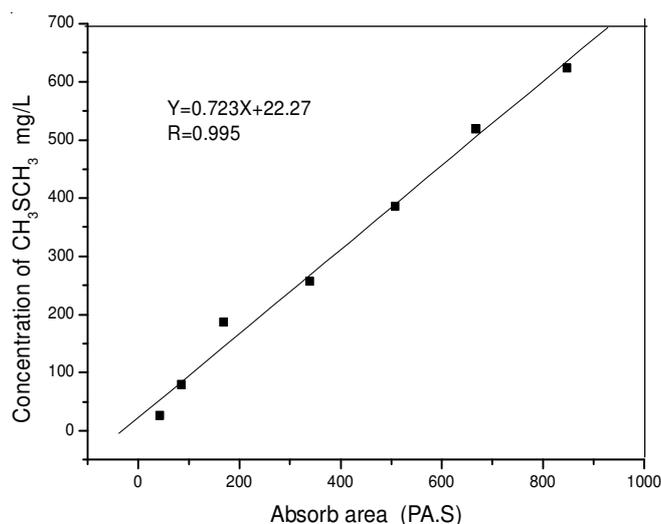


Fig. 2. Curve related between peak area and concentration of CH<sub>3</sub>SCH<sub>3</sub>

From data (Table-1),

$$\text{mass}_{\text{CH}_3\text{SCH}_3(\text{g})} = 0.061 \text{mass}_{\text{CH}_3\text{SCH}_3(\text{l})} \quad (1)$$

where,  $\text{mass}_{\text{CH}_3\text{SCH}_3(\text{g})}$  was the mass of CH<sub>3</sub>SCH<sub>3</sub> remaining in the exhaust air (g);  $\text{mass}_{\text{CH}_3\text{SCH}_3(\text{l})}$  was mass of CH<sub>3</sub>SCH<sub>3</sub> absorbed in the ethanol solution (g);  $m_{\text{CH}_3\text{SCH}_3, \text{remaining}}$  was the mass of remaining CH<sub>3</sub>SCH<sub>3</sub> (g), which including the mass of CH<sub>3</sub>SCH<sub>3</sub> absorbed in the ethanol solution and the mass of CH<sub>3</sub>SCH<sub>3</sub> remaining in the exhaust air.

#### Conversion and reaction rates in different temperature:

Prepared mixing gas in 47.06, 94.11, 141.17, 188.22 and 235.28 (mg/L) of CH<sub>3</sub>SCH<sub>3</sub> with (v %) 40 % of H<sub>2</sub>, respectively, the mixing gas was conducted in flow rate of 400 mL/min into the reacted tube, where 2 g catalyst in 40 mesh was fed and the reaction temperature was 300, 350, 400, 450, 480, 500, 550, 600 °C, respectively. The relationship between

conversion of CH<sub>3</sub>SCH<sub>3</sub> and temperature was shown in Table-2. Calculated by equation (8), the contact time between the reactant and catalyst was 0.107 s (Table-3). The relationship between reaction rate of CH<sub>3</sub>SCH<sub>3</sub> and temperature was shown in Fig. 3.

The conversion of CH<sub>3</sub>SCH<sub>3</sub> increased with the increasing temperature (Table-2). While temperature was over 773 K, the conversion of CH<sub>3</sub>SCH<sub>3</sub> was over 95 %.

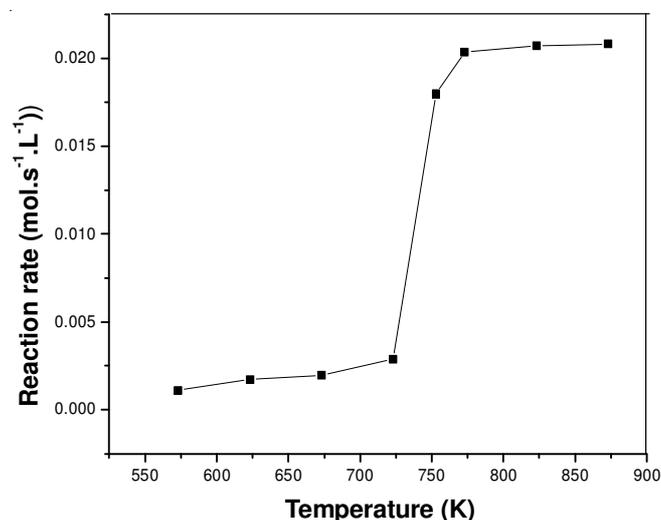


Fig. 3. Relationship between reaction rate and temperature

The reaction rate curve is divided into three sections with increasing temperature (Fig. 3). At the first section of 573-723 K, the reaction rate increased slowly with increasing temperature, where the reaction rate was less than 0.001 mol L<sup>-1</sup> s<sup>-1</sup> and was mainly control by temperature. The reaction rate increased rapidly at the second section of 723-773 K and was mainly control by temperature. The reaction rate was quick but increasing slowly with increasing temperature at third section of 773-873 K, where the reaction rate was mainly control by concentration and the reaction rate was over 0.0075 mol L<sup>-1</sup> s<sup>-1</sup>.

**Determination of dimethyl sulfide order:** Prepared maxing gas in 47.06, 94.11, 141.17, 188.22 and 235.28 (mg/L) of  $\text{CH}_3\text{SCH}_3$  with (v %) 40 % of  $\text{H}_2$ , respectively, the maxing gas conducted in flow rate of 400 mL/min into the reacted tube, in where 2 g catalyst in 40 mesh was feed and reaction temperature 480 °C. The relationship between reaction rate and concentration of  $\text{CH}_3\text{SCH}_3$  was shown in Table-4 and the relationships between  $\ln r$  and  $\ln c$  was shown in Fig. 4.

C (mol/L)	0.000759	0.00152	0.00228	0.00303	0.00380
Conversion (%)	85.97	85.30	84.52	82.85	80.42
Reaction rate (mol/L.s)	0.00230	0.00458	0.00679	0.00886	0.0108

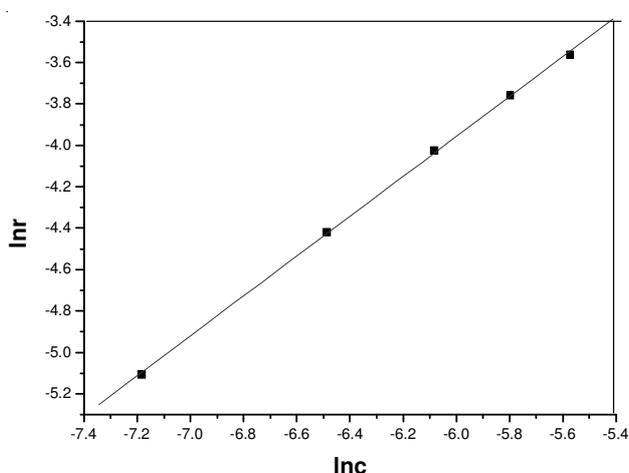


Fig. 4. Relationship between  $\ln r$  and  $\ln c$

Analysis by origin software, the linear slope was 0.963 and the intercept was 1.821, so the linear equation was:

$$\ln r = 0.963 \ln c + 1.821 \quad (10)$$

As the rate law

$$r = K[\text{CH}_3\text{SCH}_3]^a[\text{H}_2]^b \quad (11)$$

$$\ln r = \ln K + a \ln [\text{CH}_3\text{SCH}_3] + b \ln [\text{H}_2] \quad (12)$$

For the concentration of hydrogen, C is constant in the experiments, so

$$C = \ln K + b \ln [\text{H}_2]$$

$$\ln r = a \ln [\text{CH}_3\text{SCH}_3] + C \quad (13)$$

Comparing the equation (10) and (13), yield,  $a = 0.963$ . It meant the order of dimethyl sulfide was 0.963.

**Determination of hydrogen order:** Prepared maxing gas in 141.17 mg/L of  $\text{CH}_3\text{SCH}_3$  with (v %) 10, 20, 30, 40 and 50 % of  $\text{H}_2$ , respectively, the maxing gas conducted in flow rate of 400 mL/min into the reacted tube, in where 2 g catalyst in 40 mesh was feed and reaction temperature 480 °C. The relationship between reaction rate and hydrogen was shown in Table-5 and the relationship between  $\ln r$  and  $\ln c$  was linear.

Analysis by origin software, the linear slope was 1.0983 and the intercept was 1.493, so the linear equation was:

$$\ln r = 1.098 \ln c + 1.493 \quad (14)$$

As the rate law

$$r = K[\text{CH}_3\text{SCH}_3]^a[\text{H}_2]^b \quad (11)$$

$$\ln r = \ln K + a \ln [\text{CH}_3\text{SCH}_3] + b \ln [\text{H}_2] \quad (12)$$

As the concentration of dimethyl sulfide was a constant in experiment:

$$C = \ln K + a \ln [\text{CH}_3\text{SCH}_3]$$

$$\ln r = b \ln [\text{H}_2] + C \quad (15)$$

Comparing the eqns. (14) and (15), yield,  $b = 1.098$ , it meant the order of hydrogen was 1.098.

**Calculation of activation energy  $E_a$  and K value:** On analysis of Fig. 3, the reaction rate was control by temperature at the first and second section and those experiment data may be the basis for calculating the activation energy  $E_a$ . For the reaction rate data at second section (723-773 K) was deviation from the system data and should be given up, exact experiments at 673-723 K were carried to gain accurate data to calculate the activation energy (Table-6). The value of K was calculated in regression equation at different temperature, (Table-6).

Analysis by origin software, the linear slope was -3819.18 and the intercept was 9.726, so the linear equation was:

$$\ln K = -3819.18 T^{-1} + 9.726 \quad (16)$$

As,

$$K = A e^{\left(\frac{E_a}{RT}\right)} \quad (17)$$

$$K = -\ln K = -\left(\frac{E_a}{R}\right)T^{-1} + \ln A \quad (18)$$

Comparing the equation (16) and (18), yield,

$$-E_a/R = -3819.18,$$

$$E_a = 31737.39 \text{ J mol.}$$

And,  $\ln A = 9.726$ ,

$$A = 16747.32$$

C (mol/L)	0.004464286	0.008928571	0.013392857	0.017857143	0.022321429
Reaction rate, mol/(L.s)	0.0116	0.0253	0.0395	0.0532	0.0680

Temperature (K)	Concentration of $\text{CH}_3\text{SCH}_3$ (mol/L)	Concentration of $\text{H}_2$ (mol/L)	Order of $\text{CH}_3\text{SCH}_3$	Order of $\text{H}_2$	Average reaction rate (mol/L.s)	K value
673	0.00228	0.0179	0.963	1.098	0.00197	57.11
683	0.00228	0.0179	0.963	1.098	0.00214	62.18
693	0.00228	0.0179	0.963	1.098	0.00233	67.73
703	0.00228	0.0179	0.963	1.098	0.00259	75.20
713	0.00228	0.0179	0.963	1.098	0.00273	79.46
723	0.00228	0.0179	0.963	1.098	0.00288	83.54

## Conclusion

For the reaction between dimethyl sulfide and hydrogen with ZnO catalyst, it has been found 0.963 and 1.098 order with respect to dimethyl sulfide and hydrogen, respectively and the activation energy was 31737.19 J mol with frequency factor 16747.32. The reaction rate equation was:

$$r = 16747.32 \times e^{\left(\frac{31737.19}{8.31 \times T}\right)} [\text{H}_2]^{1.098} [\text{CH}_3\text{SCH}_3]^{0.963}$$

## Nomenclature

A	Pre-exponential Arrhenius parameter
a	The order of
BLIGCC	Black liquor integrated gasification combined cycle
COD	Chemical oxidation demand (mg/L)
b	The order of
C	Constant
[CH <sub>3</sub> SCH <sub>3</sub> ]	Concentration of dimethyl sulfide (mol/L)
E <sub>a</sub>	Activation energy (J/mol)
[H <sub>2</sub> ]	Concentration of hydrogen (mol/L)
k	Rate constant
l	Length of catalyst layer (cm)
r	Reaction rate of dimethyl sulfide (mol L <sup>-1</sup> S <sup>-1</sup> )
R	Gas constant (8.314 J K <sup>-1</sup> mol <sup>-1</sup> )
RB	Recovery boiler
S	The cross-sectional area of reaction tube (cm <sup>2</sup> )
t	Contact time (s)
T	Temperature (K)
v	The apparent linear rate of gas flow (cm/s)
e	Catalyst porosity
62	Molecular weight of CH <sub>3</sub> SCH <sub>3</sub>
0.061	The ratio between mass of CH <sub>3</sub> SCH <sub>3</sub> absorbed in liquid and stayed in the air

## Subscript

m <sub>CH<sub>3</sub>SCH<sub>3</sub> (g)</sub>	Mass of dimethyl sulfide stayed in the exhaust air (g)
m <sub>CH<sub>3</sub>SCH<sub>3</sub> (l)</sub>	Mass of dimethyl sulfide absorbed in ethanol (g)
m <sub>CH<sub>3</sub>SCH<sub>3</sub>, injected</sub>	Mass of injected dimethyl sulfide (g)
m <sub>CH<sub>3</sub>SCH<sub>3</sub>, reacted</sub>	Mass of reacted dimethyl sulfide (g)
m <sub>CH<sub>3</sub>SCH<sub>3</sub>, remaining</sub>	Mass of remaining CH <sub>3</sub> SCH <sub>3</sub> (g)
q <sub>v</sub>	Volume flow rate of gas (cm <sup>3</sup> /s)
V <sub>total</sub>	Total reacted volume (L)

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