Iron waste was dissolved in a sulfuric acid to form a concentrated FeSO₄-H₂SO₄ solution. This research was conducted by catalytic oxidation of ferrous sulfate using manganese dioxide as catalyst to form a ferric sulfate. Catalytic oxidation reaction using a catalyst of manganese dioxide is a three-phase heterogeneous reaction. This reaction kinetics is quite complex. This study aims to develop a mathematical modeling of reaction kinetics for three phases, gas, liquid, and solid. Oxidation was undertaken on the condition of isothermal and isobaric in the three-neck flask as reactor. Experiment was run in the temperature range of 313 K to 363 K and catalyst concentration of 4.16 x 10⁻³ g L⁻¹ to 25 x 10⁻³ g L⁻¹.

Results indicated that the oxidation rate increased with the increase of temperature and catalyst concentration. Reaction kinetics can be approached with quasi steady state model and chemical reactions on the surface of the catalyst are a step controls the reaction kinetics. The relation between reaction rate constant and temperature in the following Arrhenius form:

\[ k_r = 2182 \exp \left( -\frac{17613}{RT} \right), \text{L g eq}^{-1} \text{min}^{-1} \]

Manganese dioxide as catalyst can increase a reaction rate and reduce the activated energy which can be expressed in the following equation:

\[ E = 20129.025 \exp(-0.0472m_r), \text{J mol}^{-1} \]

Activated energy was found from 14414 J mol⁻¹ to 19747 J mol⁻¹ and maximum ferrous sulfate conversion was of 97.20%. Those values were similar result with the literature available.

**Keywords:** kinetics, catalytic oxidation, heterogeneous, mathematical modeling, iron waste, quasi steady state

**INTRODUCTION**

Iron waste was produced from industries which used iron as material. It can cause the environment damage due to discharged around the plant area. Iron waste can be dissolved in sulfuric acid to produce ferrous sulfate according to the following reaction.
The oxidation rate was increased by raising sulphate and chlorides. Ferric sulfate can be used to separation by settling. The most commonly used organic substances, it can use coagulants and solids, inorganic species, micro organism and waste water treatment, the removal of suspended reaction processes. Furthermore, ferrous sulfate can be oxidized in acidic condition to form ferric sulfate with the overall reaction.

\[ \text{Fe} + \text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{H}_2 \]  
(1)

Ferrous sulphate oxidation can be investigated in the presence of catalyst such as phosphoric acid, cupric sulfate, and active carbon. Manganese dioxide (Cher and Davidson 1955, King and Davidson 1958, Ronnholm et al. 1999a, Sulistyo et al. 2003a). Sulistyo et al. (2003b) investigated the catalyzed oxidation of dissolved iron waste ion as ferrous sulfate to ferric sulfate with phosphoric acid, cupric sulfate as catalyst. Meanwhile Sulistyo and Yuwono (2003) also used the heterogeneous catalyst namely manganese dioxide. The benefit of the using heterogeneous catalyst is that it is easier to separate the catalyst from the product. The rate oxidation was first order with respect to ferrous ion (Cher and Davidson 1955, King and Davidson 1958). The oxidation rate was increased by raising temperature and pressure (Chmielewski and Charewic 1984, Ronnholm et al. 2002). In using cupric ion as catalyst, Cher and Davidson (1955) expressed that at lower cupric ion concentration the rate of oxidation increased by increasing the cupric ion concentration. The reaction order will be changed from the first order and the oxidation rate will be decreased as the reaction processes.

In the process water as well as industrial waste water treatment, the removal of suspended solids, inorganic species, micro organism and organic substances, it can use coagulants and flocculants to promote agglomeration and then separation by settling. The most commonly used coagulant materials are iron and alumina as sulphate and chlorides. Ferric sulfate can be used to produce a floc that is more dense enhances the floc settling. Ronnholm et al. (1999a) mentioned that coagulant effect of ferric ion was 11 times higher than that of alumina ion.

**Mathematical modeling**

The reaction between a ferrous sulfate and oxygen take place on a solid catalyst surface. The reaction system is called slurry reaction. It is assumed that in the slurry reactor, the liquid phase is well mixed and the catalyst particles are evenly distributed. The gas phase is in a plug flow. The reaction mechanism can be displayed in the following steps (Smith 1981, Fogler 2006):

a. mass transfer A from bulk gas to bubble interface \( r_1 \)
\[ r_1 = k_g a_g (P_A - P^*) = k_g a_g (P_A - H C_{ILA}) = k_g a_g H_A (P_A/C_{ILA}) \]  
(4)

b. mass transfer A from bubble interface to bulk liquid \( r_2 \)
\[ r_2 = k_L a_g (C_{ILA} - C_A) \]  
(5)

c. mass transfer A from bulk liquid to catalyst surface \( r_3 \)
\[ r_3 = k_c a_c (C_A - C_{SA}) \]  
(6)

d. mass transfer B from bulk liquid to catalyst surface \( r_4 \)
\[ r_4 = k_c a_c (C_B - C_{SB}) \]  
(7)

e. catalytic surface reaction \( r_5 \)
\[ r_5 = k_r \eta C_{SB} C_{SA} - k_r \eta C_{SAB} \]  
(8)

f. mass transfer AB from catalyst surface to bulk liquid \( r_6 \)
\[ r_6 = k_{AB} a_c (C_{SAB} - C_{AB}) \]  
(9)

No ferric sulfate (AB) adsorbed into catalyst and \( r_6 \) to be assumed very fast. So \( C_{AB} \approx 0 \). The catalyst diameter is small (0.5mm), then effectiveness factor equal to one and the catalytic surface reaction can be expressed as the following equation:

\[ r_5 = k_r C_{SB} C_{SA} \]  
(10)

To find the controlling step, the mathematical modeling was proposed for quasi steady state. Mathematical equation in each step (step a to f) followed the reaction coefficient, and it can be
From the equation \( (14) \) will be found the square root of equation\((-r_B)\), the value which is in accordance with \( C_B \approx 0 \) and \((-r_B) \approx 0 \) is \((-r_B)^2\) then equation \((14)\) can be expressed:

\[
(-r_B) = 2\alpha \beta \left( \frac{P_A}{\beta H_A} + \frac{C_B}{4\alpha} + \frac{1}{k_R} \right) \pm \sqrt{\left( \frac{P_A}{\beta H_A} + \frac{C_B}{4\alpha} + \frac{1}{k_R} \right)^2 - \frac{P_A C_B}{\alpha \beta H_A}}
\]

\((15)\)

2. If \( \alpha \) or \( \beta \) is large. Then \( \frac{1}{4\alpha \beta} (-r_B)^2 \) can be neglected. Then equation \((12)\) can be simplified to the following equation:

\[
-r_B = \frac{P_A C_B}{\frac{P_A}{\beta H_A} + \frac{H_A C_B}{4\alpha} + \frac{H_A}{k_R}} \quad \text{(16)}
\]

**EXPERIMENTAL**

**Material**

An iron waste powder has a Fe content of 67%. Sulfuric acid (98%) and Manganese dioxide has average diameter of 0.5 mm as catalyst were purchased from E-merck.

**Apparatus**

The reactor was a three necked bottle (500 mL) and equipped with agitator and constant stirring rate. The reactor was installed; the cooler water used was as cooling medium and electrical heating mantel was used as heat source. Experiments were undertaken in a isothermal and at atmospheric pressure reactor.

**Procedure**

An iron waste powder was dissolved in sulfuric acid (± 2 M) when heated at 348K until the iron waste powder dissolved. Thereafter the remaining iron waste powder was separated by filtration and the solution was analyzed the ferrous ion content by volumetric analyzing using potassium permanganate solution (Vogel. 1951). Water was added to form a ferrous sulfate solution contained approximately 0.2 M FeSO₄.

The next step was that 150 mL ferrous
sulfate and 0.5M sulfuric acid was put into the reactor, then the temperature was elevated gradually to the desired temperature and maintained at a constant level. After the desired temperature attained, the reaction was started by adding manganese dioxide and flowing an air as oxidizing agent into the system. Samples were periodically withdrawn for chemical analysis to measure the remaining concentration of ferrous sulfate by volumetric analysis with 0.1 N KMnO₄.

Parameter evaluation

Ferrous sulfate concentration data at various times and certain temperature was put to equation (15) and (16). Then it was solved by numerical with Runge-Kutta method (Jenson and Jeffreys 1977). The value of Henry constant was obtained from Table 3. While the parameters \( \alpha \), \( k_R \), and \( \beta \) can be obtained with the multi-variable optimization with the sum of square of error (SSE) using the method of Hooke-Jeeves (Sediawan and Prasetya 1997).

RESULTS AND DISCUSSION

This research studied the effect of temperature in the range 313 K to 363 K. The concentration of catalyst in the range of 4.16 gL⁻¹ to 25 gL⁻¹ stirred speed of 290 rpm and air flow rate of 2.415 Lmin⁻¹.

Effect of temperature

Table I. presents the experimental result and evaluated parameters at various temperatures. It shows that the average deviation and the sum of square error at each temperature is quite small. The highest average deviation was found at temperature of 353K around of 9.01% with SSE value of 1.088 \( 10^3 \). This result shows that the proposed model of mathematics was similar to the experimental result. The parameters value of \( \alpha \), \( \beta \) and \( k_R \) increased by raising the temperature. Hence, the controlling step is the chemical reaction on the surface of the catalyst.

**Figure 1.** \( \ln(k_R) \) versus 1/T

The relationship between reaction rate constant \( k_R \) and temperature (T) was expressed in the Arrhenius form with the following equation:

\[
 k_R = 2182 \exp \left( -\frac{17613}{RT} \right) \text{ L g eq}^{-1}\text{min}^{-1}
\]  

(17)

To ensure the rate of controlling step, it was evaluated by comparing of the value of each kinetics parameter. Equation (16) can be expressed in the form of

\[
 -r_R = k_{ov} C_B
\]  

(18)

\[
 \frac{1}{k_{ov}} = \frac{1}{\beta} + \frac{H_A C_B}{4P_A \alpha} + \frac{H_A}{P_A k_R}
\]  

(19)

The result of each kinetics parameter values was presented in Table 2. The parameters showed that the both mass transfer step namely \( \alpha \) and \( \beta \) have very small value and closed to zero while the reaction step was the highest value. It can be concluded that reaction step was the control of reaction kinetics.

The reaction rate constant at various temperature was presented in Figure 1.

Effect of catalyst concentration

The result of effect of catalyst concentration on ferrous sulphate conversion was presented in Table 3. It was noted that the ferrous sulphate conversion increased by increasing catalyst concentration. In addition, with increasing catalyst concentration, activated energy will reduce and reaction rate will be faster.
The value of reaction rate constant \( k_R \) in Table 3 and \( k_0 = 2128.77 \) and using equation (17), the value of activated energy was calculated and presented in Table 4.

The effect of catalyst concentration on activated energy can be presented in Table 4. The relationship between activated energy and catalyst concentration can be expressed in the following equation.

\[
E = 20128.028 \exp(-0.01416 mk), \text{ Jmol}^{-1}
\] (20)

By using equation (19), the controlling step can be evaluated and the result was presented in Table 5. The contribution of each kinetics parameter can be evaluated from Table 5. The highest contribution was chemical reaction parameter while the mass transfer parameters were closed to zero. It can also be concluded that chemical reaction was the controlling step.

### Table 1. Effect of Temperature

\( (m_k = 8.33 \text{ gL}^{-1}, Qu = 40.264 \text{ mLmin}^{-1}, N = 290 \text{ rpm}, \text{solution volume} = 300 \text{ mL}) \)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>( C_B) (g.eq/L) at Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.2278</td>
</tr>
<tr>
<td>10</td>
<td>0.1702</td>
</tr>
<tr>
<td>20</td>
<td>0.1306</td>
</tr>
<tr>
<td>30</td>
<td>0.1165</td>
</tr>
<tr>
<td>40</td>
<td>0.1088</td>
</tr>
<tr>
<td>50</td>
<td>0.1011</td>
</tr>
<tr>
<td>60</td>
<td>0.0986</td>
</tr>
<tr>
<td>70</td>
<td>0.0934</td>
</tr>
<tr>
<td>80</td>
<td>0.0858</td>
</tr>
<tr>
<td>90</td>
<td>0.0832</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>( k_R ), ( 2.40 )</th>
<th>Deviation</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>723.00</td>
<td>335.75</td>
<td>82.2326</td>
<td>5.81%</td>
<td>0.0004771</td>
</tr>
<tr>
<td>854.128</td>
<td>402.348</td>
<td>82.2240</td>
<td>7.25%</td>
<td>0.0006952</td>
</tr>
<tr>
<td>885.15</td>
<td>436.25</td>
<td>69.9143</td>
<td>7.52%</td>
<td>0.0005165</td>
</tr>
<tr>
<td>917.3</td>
<td>455.55</td>
<td>69.9085</td>
<td>7.52%</td>
<td>0.00048757</td>
</tr>
<tr>
<td>952</td>
<td>502.5</td>
<td>69.9085</td>
<td>7.52%</td>
<td>0.00108867</td>
</tr>
<tr>
<td>1108</td>
<td>529.75</td>
<td>69.9085</td>
<td>7.52%</td>
<td>0.00042193</td>
</tr>
</tbody>
</table>

### Table 2. Effect of Temperature on Each Parameter Values

<table>
<thead>
<tr>
<th>( T ) (°C)</th>
<th>( \frac{1}{k_{ov}} )</th>
<th>( \frac{1}{\beta} )</th>
<th>( \frac{H_A C_B}{4 P_A \alpha} )</th>
<th>( \frac{H_A}{P_A k_R} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>82.2326</td>
<td>0.0030</td>
<td>0.004 %</td>
<td>82.2240</td>
</tr>
<tr>
<td>50</td>
<td>73.9220</td>
<td>0.0025</td>
<td>0.003 %</td>
<td>73.9143</td>
</tr>
<tr>
<td>60</td>
<td>59.0422</td>
<td>0.0023</td>
<td>0.004 %</td>
<td>59.0356</td>
</tr>
<tr>
<td>70</td>
<td>56.8787</td>
<td>0.0022</td>
<td>0.004 %</td>
<td>56.8723</td>
</tr>
<tr>
<td>80</td>
<td>44.4619</td>
<td>0.0020</td>
<td>0.004 %</td>
<td>44.4567</td>
</tr>
<tr>
<td>90</td>
<td>44.4577</td>
<td>0.0019</td>
<td>0.004 %</td>
<td>44.4534</td>
</tr>
</tbody>
</table>
### Table 3. Effect of Catalyst Concentration

(T = 60 °C, Qu = 40.264 mLs\(^1\), N = 290 rpm, solution volume = 300 mL)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>C(_B) (gek/mL)</th>
<th>Catalyst concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.2273</td>
<td>4.16</td>
</tr>
<tr>
<td>10</td>
<td>0.1774</td>
<td>8.33</td>
</tr>
<tr>
<td>20</td>
<td>0.1529</td>
<td>12.5</td>
</tr>
<tr>
<td>30</td>
<td>0.1476</td>
<td>16.66</td>
</tr>
<tr>
<td>40</td>
<td>0.1402</td>
<td>20.83</td>
</tr>
<tr>
<td>50</td>
<td>0.1338</td>
<td>25</td>
</tr>
<tr>
<td>60</td>
<td>0.1285</td>
<td>825.00</td>
</tr>
<tr>
<td>70</td>
<td>0.1253</td>
<td>885.15</td>
</tr>
<tr>
<td>80</td>
<td>0.1211</td>
<td>1217</td>
</tr>
<tr>
<td>90</td>
<td>0.1179</td>
<td>1514.5</td>
</tr>
<tr>
<td>α</td>
<td>825.00</td>
<td>1514.5</td>
</tr>
<tr>
<td>β</td>
<td>443.00</td>
<td>1609.50</td>
</tr>
<tr>
<td>k(_R)</td>
<td>1.70</td>
<td>1699.59</td>
</tr>
</tbody>
</table>

### Table 4. Effect on Catalyst Concentration on Activated Energy

(T = 333 K, k\(_o\) = 2128.77)

<table>
<thead>
<tr>
<th>m(_k), g L(^{-1})</th>
<th>k(_o), L g.eq(^{-1}) min(^{-1})</th>
<th>E/R, K</th>
<th>E, J mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.16</td>
<td>1.70</td>
<td>2375.180</td>
<td>19747.18</td>
</tr>
<tr>
<td>8.13</td>
<td>3.93</td>
<td>2096.122</td>
<td>17427.10</td>
</tr>
<tr>
<td>12.50</td>
<td>5.60</td>
<td>1978.197</td>
<td>16446.68</td>
</tr>
<tr>
<td>16.66</td>
<td>7.30</td>
<td>1889.917</td>
<td>15712.71</td>
</tr>
<tr>
<td>20.83</td>
<td>9.40</td>
<td>1805.722</td>
<td>15012.71</td>
</tr>
<tr>
<td>25.00</td>
<td>11.67</td>
<td>1733.734</td>
<td>14414.26</td>
</tr>
</tbody>
</table>

### Table 5. Effect of Catalyst Concentration on Each Parameter Values

<table>
<thead>
<tr>
<th>m(_k) (g)</th>
<th>1(\frac{m}{k_{ovw}})</th>
<th>1(\frac{1}{\beta})</th>
<th>(H_{A}C_{B})</th>
<th>(\frac{H_{A}}{4PA\alpha})</th>
<th>(\frac{H_{A}}{P_{A}k_{R}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.16</td>
<td>136.4869</td>
<td>0.0023</td>
<td>0.002 %</td>
<td>0.0083</td>
<td>0.006 %</td>
</tr>
<tr>
<td>8.13</td>
<td>59.0422</td>
<td>0.0023</td>
<td>0.004 %</td>
<td>0.0043</td>
<td>0.007 %</td>
</tr>
<tr>
<td>12.50</td>
<td>41.4332</td>
<td>0.0016</td>
<td>0.004 %</td>
<td>0.0013</td>
<td>0.003 %</td>
</tr>
<tr>
<td>16.66</td>
<td>31.7846</td>
<td>0.0015</td>
<td>0.005 %</td>
<td>0.0010</td>
<td>0.003 %</td>
</tr>
<tr>
<td>20.83</td>
<td>24.6833</td>
<td>0.0011</td>
<td>0.004 %</td>
<td>0.0004</td>
<td>0.002 %</td>
</tr>
<tr>
<td>25.00</td>
<td>19.8847</td>
<td>0.0010</td>
<td>0.005 %</td>
<td>0.0002</td>
<td>0.001 %</td>
</tr>
</tbody>
</table>
Comparison with the previous work

Activated energy in this present investigation was obtained of 17,613 Jmol\(^{-1}\) with MnO\(_2\) catalyst concentration 8.33 gL\(^{-1}\) while Ronnholm et al. (1999b) using active carbon catalyst with a catalyst concentration of 80 gL\(^{-1}\) obtained the activated energy of 12,969 Jmol\(^{-1}\). Meanwhile, when she used the phosphoric acid as catalyst Megawati (2004) obtained the activated energy 22,156 Jmol\(^{-1}\). Type of catalyst will effect ferrous sulfate conversion. The maximum conversion obtained in the present investigation was of 97.20%, using MnO\(_2\) as catalyst synthesized e-Merck at atmospheric pressure. Sulistyo and Yuwono (2003) used the catalyst MnO\(_2\) which was made from MnSO\(_4\) and ammonium hydroxide. The conversion was obtained of 35.24%. Megawati (2004) used phosphoric acid as catalyst. The conversion of ferrous sulfate was of 86.67%. The highest conversion was found of 98.86% with used technical grade of oxygen and above the atmospheric pressure (Ronnholm et al. 1999b).

CONCLUSION

Based on the results of research and discussion, the conclusion can be drawn as follows:

1. Reaction kinetics of the catalytic oxidation process of ferrous sulfate can be approached by using quasi steady state model and the mathematical model in the form:

\[
(-r_B) = 2\alpha\beta \left[ 1 - \sqrt{\frac{1}{k_R}} \right] \frac{a_P C_B}{\alpha \beta H_A} \left( \frac{P_A}{\beta H_A} + \frac{C_B}{4a} + \frac{1}{k_R} \right) - \sqrt{\left( \frac{P_A}{\beta H_A} + \frac{C_B}{4a} + \frac{1}{k_R} \right) - \frac{P_A C_B}{\alpha \beta H_A}}
\]

2. Ferrous sulfate catalytic oxidation reaction to form ferric sulfate was faster by the addition of catalyst concentration and increasing temperature.

3. Chemical reaction step was the controlling step and mathematical model can be simplified as follows:

4. The highest conversion and activated energy obtained was similar to those in literature available.

NOTATION

\[
\begin{align*}
A &= \text{Oxygen} \\
AB &= \text{Ferric sulfate} \\
a_c &= \text{External area of catalyst particles per unit volume of liquid bubble free, cm}^{-1} \\
a_g &= \text{gas bubble-liquid interfacial area per unit volume of liquid bubble free, cm}^{-1} \\
B &= \text{ferrous sulfate} \\
C_A &= \text{oxygen concentration in bulk liquid, g.eq L}^{-1} \\
C_S &= \text{concentration at outer surface of catalyst particle, g.eq L}^{-1} \\
C_{IL} &= \text{equilibrium concentration at the bubble-liquid interface, g.eq L}^{-1} \\
D &= \text{sulfuric acid} \\
E &= \text{water (H}_2\text{O)} \\
H_A &= \text{Henry constant, Pa g.eq L}^{-1} \\
k_c &= \text{liquid to particle mass transfer coefficients, cm min}^{-1} \\
k_g &= \text{bulk gas to bubble interface mass transfer coefficient, g.eq cm}^{-2} \text{min}^{-1} \text{Pa}^{-1} \\
k_L &= \text{bubble interface to bulk liquid mass transfer coefficient, cm min}^{-1} \\
k_R &= \text{intrinsic reaction rate constant, L g.eq}^{-1} \text{min}^{-1} \\
m_k &= \text{catalyst concentration, g.L}^{-1} \\
P_A &= \text{oxygen pressure, Pa} \\
P^* &= \text{equilibrium oxygen pressure, Pa} \\
r_B &= \text{reaction rate of ferrous sulfate, g.eq L}^{-1} \text{min}^{-1} \\
\alpha &= \text{total resistance of oxygen side, min}^{-1} \\
\beta &= \text{total resistance of ferrous sulfate side, min}^{-1} \\
\eta &= \text{effectiveness factor}
\end{align*}
\]

ACKNOWLEDGMENTS

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REFERENCES


