



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Criteria of Screening Degradation Inhibitors

In Chapters 1 and 2, it was shown that amine degradation is caused by impurities such as O_2 and SO_2 present in the flue gas stream under conditions typically encountered in a CO_2 absorption process. There are several options as to how to prevent amine degradation. A scavenger could be added to the amine solution to react competitively with O_2 . The scavenger can absorb dissolved O_2 or can consume O_2 rather than O_2 consuming the amine. Also, a stabilizing agent can be added to the amine solution to react with degradation reaction intermediates or bind with free radicals that are generated along the reaction pathway and prevent them from further participating in the reaction mechanism. Furthermore, a chelating agent could also be added to the amine solution to protect it against degradation by reacting with dissolved O_2 or binding with oxidized form of metals and prevent them from further participating in the reaction mechanism. Table 4.1 shows the degradation inhibitors examined in this study. They are categorized as scavenger, stabilizing agent and chelating agent. This section presents the results obtained with the three categories of degradation inhibitors.

The inhibition of the oxidative degradation of MEA is achieved by introducing additions of degradation inhibitors to the MEA solution during the absorption of CO_2 in the presence of O_2 and SO_2 . The effectiveness of any degradation inhibitor is determined by how much the decrease of MEA concentration over time or the MEA degradation rate is minimized.

Table 4.1 Possible degradation inhibitors for minimizing the MEA degradation rate

Scavenger	Stabilizing agent	Chelating agent
Inhibitor UR-A Inhibitor UR-D	Inhibitor UR-B	Inhibitor UR-C

The experiments were conducted under conditions typically encountered in CO₂ capture process, most especially using flue gas streams from a coal fired power plant. The simulated flue gas used was 6% O₂, 6 and 196 ppm SO₂. For applications, typical composition of coal-fired power plant flue gas contains approximately 2-400 ppm SO₂, after SO₂ scrubbing and 2-12% O₂. For 6 and 196 ppm SO₂ being conducted in this study represents the low and high level of SO₂ in the flue gas streams.

4.2 Visual Observation of Degraded Samples

After the collected samples had been withdrawn from the liquid sampling valve of the reactor, they were observed visually to record any color change and change in turbidity from the initial conditions.

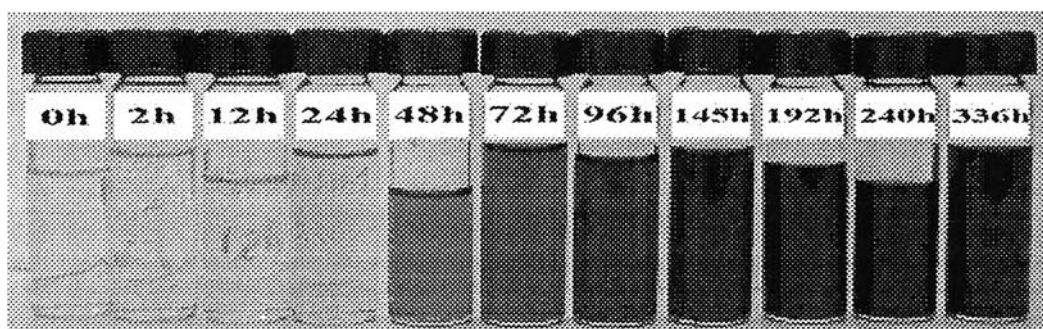


Figure 4.1 Appearance of the MEA samples after being contacted with 100% O₂ at various times (5 kmol/m³ MEA, 100% O₂, and 120°C).

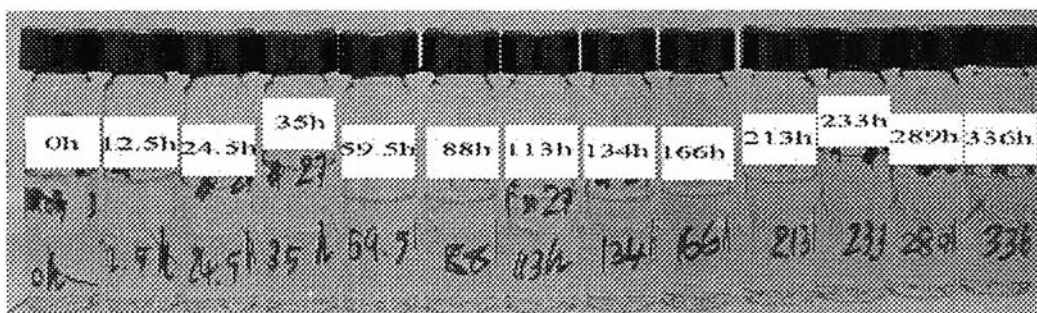


Figure 4.2 Appearance of the MEA samples with inhibitor after being contacted with 6% O_2 at various times (5 $kmol/m^3$ MEA, 6% O_2 , with inhibitor UR-B, and 120°C).

In terms of color, the collected samples change from clear to light yellow, then to dark yellow, and eventually to almost opaque dark brown color. This indicates that the composition of original MEA solution has been changed after being contacted with the impurities (O_2 and SO_2). For systems containing no inhibitors, the MEA solution darkened with time. Upon adding the inhibitors, the MEA solution did not change color. Figure 4.1 shows the appearance of the collected samples degraded with 100% O_2 for the indicated times, whereas Figure 4.2 shows MEA samples with inhibitor after being contacted with 6% O_2 .

4.3 The Performance of Inhibitor UR-A

Inhibitor UR-A is widely used as a scavenger that can react fast with dissolved O_2 . The mechanism of the inhibiting action of inhibitor UR-A is to react competitively with dissolved O_2 ; it can react faster than MEA with dissolved O_2 . Therefore, dissolved O_2 in this system is not able to degrade MEA. It is a strong reducing agent and reacts with dissolved O_2 in the solution to form reaction products of inhibitor UR-A with O_2 . When inhibitor UR-A reacts with O_2 , it donates electrons instead of MEA to reactive O_2 thereby reducing the concentration of dissolved O_2 in the system.

4.3.1 Determination of Optimum Concentration of Inhibitor UR-A in MEA-H₂O-O₂ Degradation System

The MEA-H₂O-O₂ system is first used to determine the optimum concentration of inhibitor UR-A necessary for minimizing the MEA degradation rate. The experiments were conducted by adding increasing concentrations of 0.05, 0.1 and 0.3 kmol/m³ of UR-A in separate tests in 5 kmol/m³ of MEA solution and 6%O₂ simulated flue gas stream. The degradation temperature was chosen to be 120°C to mimic the extreme condition in the regenerator column.

Figures 4.3 and 4.4 show the effects of concentration of inhibitor UR-A on its performance for MEA oxidative degradation. It was found that inhibitor UR-A at a concentration of 0.05 kmol/m³ yielded the lowest MEA degradation rate of 1.19×10^{-4} kmol/m³.h which was approximately 4 times lower than that of the run carried out in the absence of inhibitor UR-A (i.e. 4.48×10^{-4} kmol/m³.h). The percentage of degradation inhibition of inhibitor UR-A in MEA-H₂O-O₂ degradation system was found to be 73.

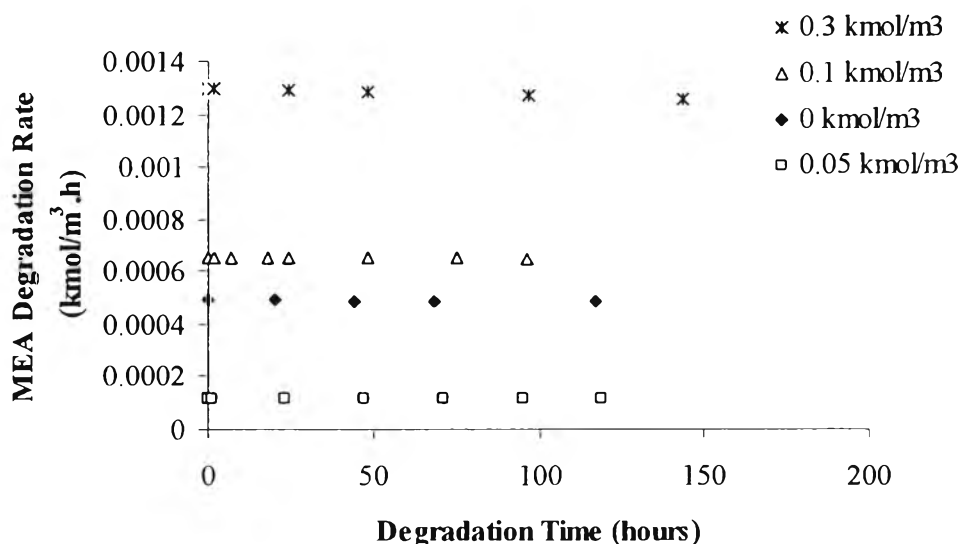


Figure 4.3 Effects of concentration of inhibitor UR-A on MEA-H₂O-O₂ degradation system (5 kmol/m³ MEA, 6% O₂, and 120°C).

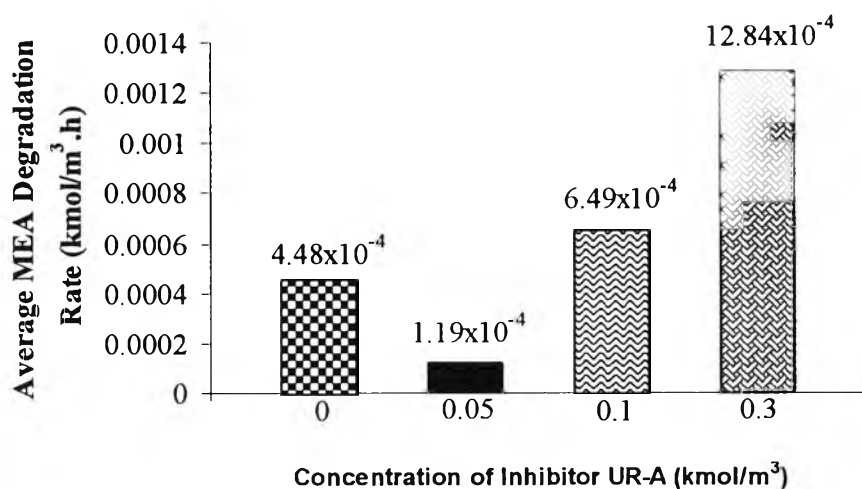


Figure 4.4 The performance of inhibitor UR-A on MEA-H₂O-O₂ degradation system (5 kmol/m³ MEA, 6% O₂, and 120°C).

Further experiments were conducted by using the higher inhibitor UR-A concentrations of 0.1 and 0.3 kmol/m³. At 0.1 kmol/m³ of inhibitor UR-A concentration, the average MEA degradation rate was 6.49×10^{-4} kmol/m³.h which was 1.4 times higher than that of the run without any inhibitor. A higher degradation rate of 12.84×10^{-4} kmol/m³.h was also observed when the concentration of inhibitor UR-A was increased to 0.3 kmol/m³. The rate was 2.9 times as fast as that for the run conducted in the absence of any inhibitor. One drawback of inhibitor UR-A is the solubility limit. The solubility limit of inhibitor UR-A is reached between 0.1-0.3 kmol/m³.

An optimum concentration of inhibitor is necessary for inhibition of the oxidative degradation of MEA. Based only on the experiments conducted, the optimum concentration of inhibitor UR-A was 0.05 kmol/m³ and it gave the greatest reduction in the oxidative degradation of MEA.

Further increase in the concentration of this inhibitor resulting in increases the MEA degradation rate. The adverse effect of excess concentrations of inhibitor UR-A on MEA degradation could be explained as follows: first, in 1929 Vorlander et al. studied the effect of inhibitor UR-A and O₂ in aqueous solutions.

These authors state that the reaction rate of O_2 with inhibitor UR-A increases linearly with inhibitor UR-A concentration. Beyond the optimum concentration, the excess amount of inhibitor UR-A reacts with MEA instead of just O_2 . The latter is an undesired reaction that facilitates MEA degradation. Secondly, a more than stoichiometric amount of inhibitor UR-A will lead to the excess amount to trigger additional degradation itself. The unreacted inhibitor UR-A can either catalyze the reaction between O_2 and MEA or catalyze the decomposition of the molecules of MEA resulting in a faster rate of degradation.

In view of the foregoing, an optimum amount of inhibitor UR-A to control MEA degradation must be determined based on the operating conditions used as excessive amounts can cause significant additional damage to MEA. Moreover, it becomes obvious that not only does an increase in the concentration of inhibitor UR-A increase the degradation rate, it also adds up the cost of the chemical and operation.

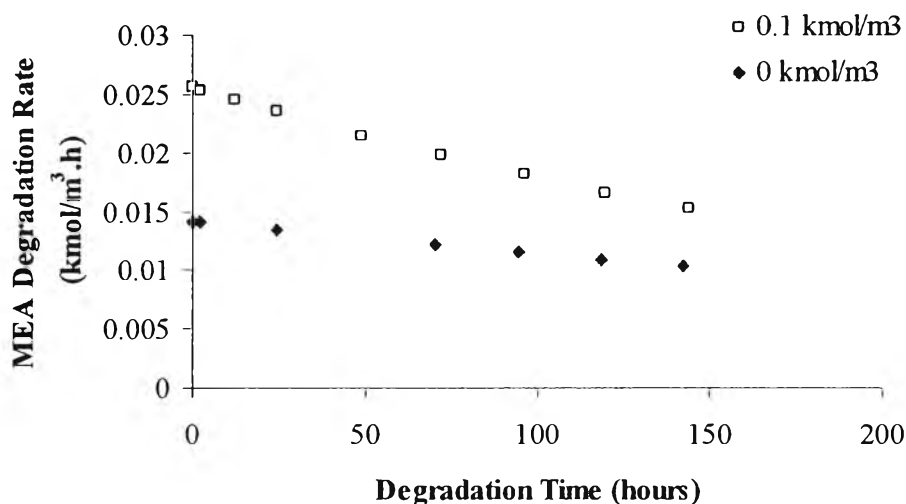


Figure 4.5 Negative effect of excess inhibitor UR-A on MEA- H_2O - O_2 degradation system (7 kmol/m^3 MEA, 100% O_2 , and 120°C).

Figure 4.5 shows the negative effect of excess inhibitor UR-A. This experiment was conducted by adding inhibitor UR-A in the concentration of 0.1

kmol/m³ in 7 kmol/m³ MEA solution and 100%O₂ at 120°C. This extreme condition was carried out to show the detrimental effects in terms of oxidative degradation rate of MEA. At this concentration, the average oxidative degradation rate was 2.11×10^{-2} kmol/m³.h which was 1.7 times higher than that of the run without inhibitor UR-A (i.e. 1.23×10^{-2} kmol/m³.h).

The optimum concentration of inhibitor UR-A of 0.05 kmol/m³ was the best in minimizing the degradation rate of MEA in the presence of O₂. This concentration was then selected for further evaluation using a more realistic system consisting of MEA-H₂O-O₂-SO₂-UR-A.

4.3.2 Inhibition Performance of Optimum Concentration of UR-A as a Function of SO₂ Concentration in MEA-H₂O-O₂-UR-A Degradation System

As stated earlier, flue gas streams not only contain CO₂ and O₂ but also, SO₂ is often present as well. SO₂ reacts irreversibly with MEA to produce a heat stable salt (HSS) which is not steam regenerable. For this reason, processes of CO₂ capture require that, as much as possible, SO₂ should be removed before the flue gas is treated in the absorber for CO₂ capture. Moreover, it is less expensive to install an SO₂ scrubber than to accept the MEA losses when the flue gas streams contain very high SO₂ concentrations. SO₂, in addition to being an acid, can react with a hydroxyl group of MEA to form sulfonic acid, which is a strong acid and therefore will form heat stable salts.

Since both O₂ and SO₂ are present in the systems in industrial applications, any degradation inhibitor added to the system need to be effective in the presence of both O₂ and SO₂. Therefore, it was essential to determine the effect of SO₂ concentration in the system containing MEA-H₂O-O₂-UR-A.

In order to simulate flue gas streams at low and high levels of SO₂ concentration, the experiments were conducted by adding SO₂ in series of increasing SO₂ concentrations 0, 6 and 196 ppm. In 5 kmol/m³ MEA solution, 6%O₂ simulated flue gas stream and an addition of 0.05 kmol/m³ inhibitor UR-A (the optimum concentration determined earlier). All the experiments were carried out at 120°C (regenerator condition).

Figures 4.6 and 4.7 show the inhibition performance of inhibitor UR-A in MEA degradation inhibition as a function of SO₂ concentration (i.e. the performance of inhibitor UR-A in the MEA-H₂O-O₂-SO₂-UR-A degradation system). For the run without SO₂ and inhibitor UR-A (0 ppm SO₂, 0 kmol/m³ UR-A), the degradation rate was 4.48×10^{-4} kmol/m³.h. The rate decreased drastically to 1.19×10^{-4} kmol/m³.h when 0.05 kmol/m³ of inhibitor UR-A was added in this system. For the runs with 6 ppm SO₂ and without inhibitor UR-A (6 ppm SO₂, 0 kmol/m³ UR-A), the degradation rate was 4.86×10^{-4} kmol/m³.h. The rate decreased sharply to 1.43×10^{-4} kmol/m³.h when 0.05 kmol/m³ of inhibitor UR-A was added in this system. Also, for the 196 ppm SO₂ system with the addition of inhibitor UR-A at the same concentration resulted in a low degradation rate of 0.46×10^{-4} kmol/m³.h. The percentage of degradation inhibition of inhibitor UR-A at 0.05 kmol/m³ in 0, 6, and 196 ppm SO₂ concentrations calculated using Equation (3.1) were 73, 71, and 84, respectively.

Without degradation inhibitors in 0, 6, and 196 ppm SO₂ systems, an increase in the SO₂ concentration in the gas phase resulted in an increase in the degradation rate. This is because SO₂ reacts quickly with O₂ in the MEA solutions to form sulfate (SO₄⁻²), forming a heat stable salt with MEA (Kohl and Nielsen, 1997). These results were confirmed in an earlier study by Uyanga and Idem (2007).

With the concentration of inhibitor UR-A of 0.05 kmol/m³ in 0, 6, and 196 ppm SO₂ systems, a slightly increase in the SO₂ concentration (i.e. 6 ppm) in the gas phase resulted in an increase in the degradation rate because 0.05 kmol/m³ of inhibitor UR-A is not the optimum concentration for 6 ppm SO₂. This inhibitor concentration needs to be optimized as the SO₂ concentrations have been changed.

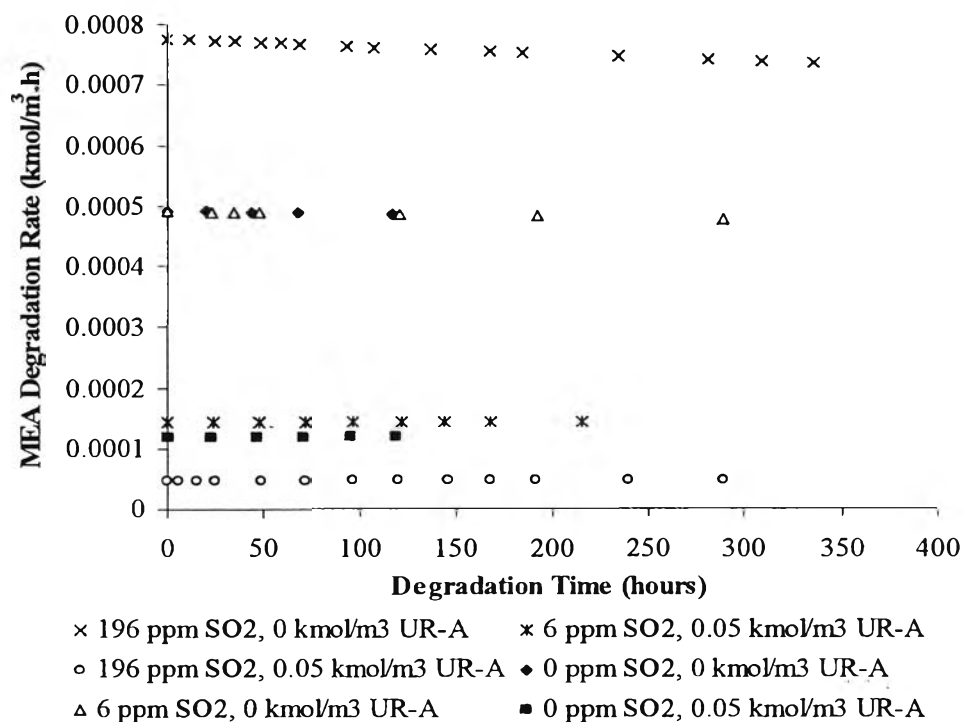


Figure 4.6 The inhibition performance of inhibitor UR-A on MEA degradation as a function of SO₂ concentration in the MEA-H₂O-O₂-SO₂-UR-A degradation system (5 kmol/m³ MEA, 6% O₂, 0,6,196 ppm SO₂, and 120°C).

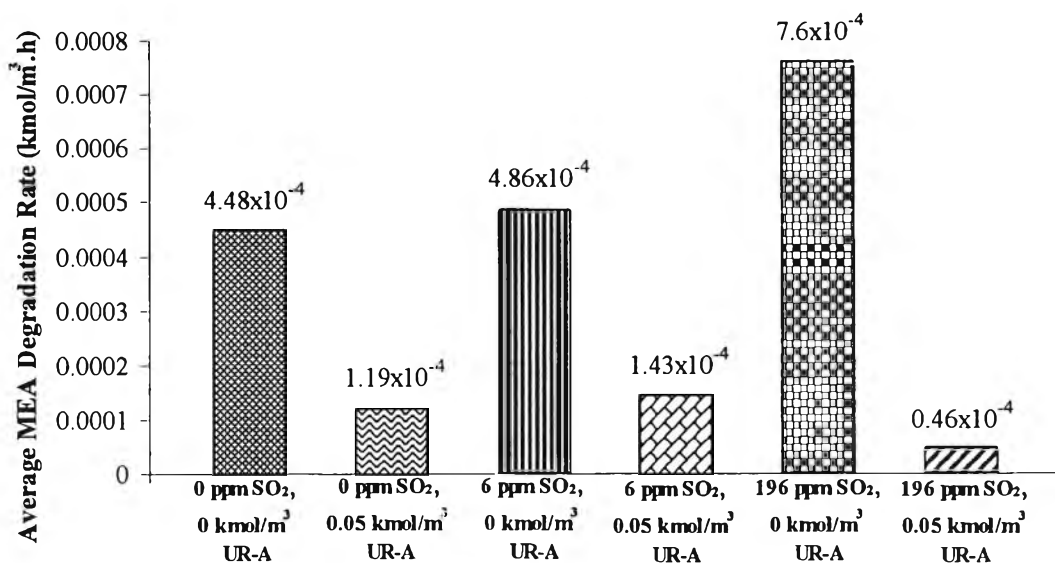


Figure 4.7 The performance of inhibitor UR-A in the MEA-H₂O-O₂-SO₂ degradation system (5 kmol/m³ MEA, 6% O₂, 0,6,196 ppm SO₂, and 120°C).

4.4 The Performance of Inhibitor UR-B

Inhibitor UR-B is used as a stabilizing agent (Gornall et al., 1948) and could inhibit the oxidative degradation of MEA. Inhibitor UR-B is added to the MEA solution to react with intermediate or bind with free radicals in the reaction mechanism and prevent them from participating in the reaction mechanism.

4.4.1 Determination of Optimum Concentration of Inhibitor UR-B in MEA-H₂O-O₂-SO₂ Degradation System

A realistic system consisting of MEA-H₂O-O₂-SO₂ was used to determine the optimum concentration of inhibitor UR-B. The experiments were performed by adding inhibitor UR-B in a series of increasing concentrations of 0.005, 0.01, 0.06, 0.1 and 0.3 kmol/m³ into 5 kmol/m³ MEA solution with O₂ and SO₂ concentrations fixed at 6% and 6 ppm, respectively. The degradation temperature was fixed at 120°C. The degradation rate-time profiles are given in Figure 4.8, whereas the performances of inhibitor UR-B for these degradation systems are shown in Figure 4.9.

It was found that at 0.01 kmol/m^3 of inhibitor UR-B yielded the lowest MEA degradation rate and the average MEA degradation rate was $4.66 \times 10^{-6} \text{ kmol/m}^3 \cdot \text{h}$ which was approximately 104 times lower than that of the run carried out in the absence of inhibitor UR-B (i.e. $4.86 \times 10^{-4} \text{ kmol/m}^3 \cdot \text{h}$). The percentage of degradation inhibition of inhibitor UR-B in MEA-H₂O-O₂-SO₂ degradation system was found to be 99. Due to the cost of the chemical, a low concentration of inhibitor UR-B of 0.005 kmol/m^3 should provide a good economic scenario. However, at 0.005 kmol/m^3 of inhibitor UR-B, the average MEA degradation rate was $3.31 \times 10^{-4} \text{ kmol/m}^3 \cdot \text{h}$ which was approximately 1.5 times lower than that of the run carried out in the absence of inhibitor UR-B. The percentage of degradation inhibition of inhibitor UR-B of 0.005 kmol/m^3 was found to be 32. This concentration does not sufficiently inhibit MEA degradation.

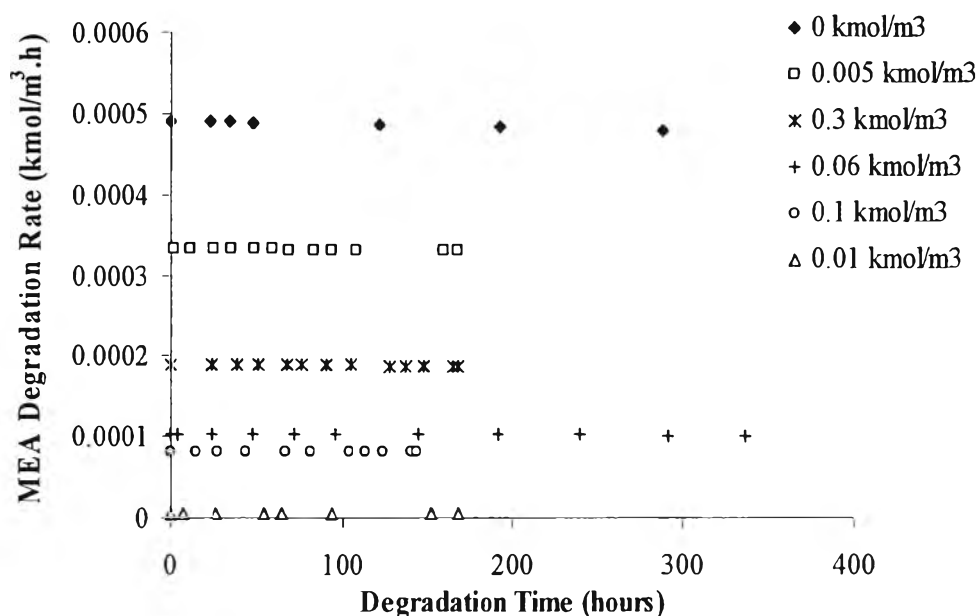


Figure 4.8 Effects of concentration of inhibitor UR-B on MEA-H₂O-O₂-SO₂ degradation system (5 kmol/m^3 MEA, 6% O₂, 6 ppm SO₂, and 120°C).

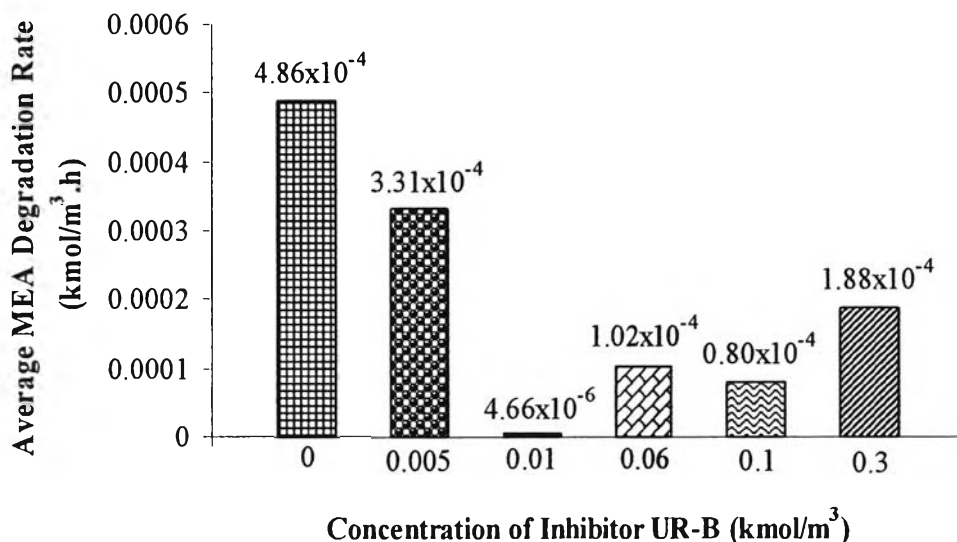


Figure 4.9 The performance of inhibitor UR-B on MEA-H₂O-O₂-SO₂ degradation system (5 kmol/m³ MEA, 6% O₂, 6 ppm SO₂, and 120°C).

The MEA degradation rate also decreased with a higher inhibitor UR-B concentration in the MEA solution up to 0.3 kmol/m³. At concentrations of inhibitor UR-B at 0.06, 0.1, and 0.3 kmol/m³, the average MEA degradation rates were 1.02, 0.80, and 1.88×10^{-4} kmol/m³.h which were approximately 4.8, 6, and 2.6 times lower than that of the run carried out in the absence of inhibitor UR-B, respectively. The percentage of degradation inhibition of inhibitor UR-B of 0.06, 0.1, and 0.3 kmol/m³ were found to be 79, 84, and 61, respectively. However, the inhibition effects of increased inhibitor UR-B concentrations were less than that for the concentration of 0.01 kmol/m³. Upon the addition of higher concentration of inhibitor UR-B, the average MEA degradation rate decreased and increased again. This would indicate that inhibitor UR-B is participating in the MEA oxidation mechanism.

Based only on our experimental results, the optimum concentration of inhibitor UR-B is 0.01 kmol/m³, and this gives rise to the lowest MEA degradation rate. This concentration in the degradation system is sufficient to inhibit the oxidative degradation of MEA. 0.01 kmol/m³ of Inhibitor UR-B was selected for further evaluation using a more realistic system consisting of MEA-H₂O-O₂-SO₂-UR-B.

Increased concentrations of inhibitor UR-B slightly increased the average MEA degradation rate. Inhibitor UR-B concentrations of 0.06, 0.1 and 0.3 kmol/m³ increased the oxidative degradation rate. This can be explained on the basis of the acid-catalysis of the oxidative degradation of MEA. An increase in the concentration of inhibitor UR-B increases the acidity (Gnedkov et al., 2000) of the system, thus, resulting in a more rapid MEA degradation. This implies that any amount of inhibitor UR-B in excess of the stoichiometric amount for inhibition will have a deleterious effect on the MEA degradation rate.

4.4.2 Inhibition Performance of Optimum Concentration of UR-B as a Function of SO₂ Concentration in MEA-H₂O-O₂-UR-B Degradation System

This system represents an evaluation of the effects of SO₂ concentration on MEA degradation. The results are reported based on experimental data using 5 kmol/m³ MEA solutions with SO₂ concentrations of 0, 6, and 196 ppm, an O₂ concentration fixed at 6%, and an addition of 0.01 kmol/m³ inhibitor UR-B, which was the optimum concentration determined earlier. The degradation temperature was fixed at 120°C. Figures 4.10 and 4.11 show the inhibition performance of inhibitor UR-B on MEA degradation as a function of SO₂ concentration and the overall performance of inhibitor UR-B in the MEA-H₂O-O₂-SO₂-UR-B degradation system.

For the run without SO₂ and inhibitor UR-B (0 ppm SO₂, 0 kmol/m³ UR-B), the degradation rate was 4.48×10^{-4} kmol/m³.h. The rate decreased drastically to 0.31×10^{-4} kmol/m³.h when 0.01 kmol/m³ of inhibitor UR-B was added in this system. The percentage of degradation inhibition of 0.01 kmol/m³ inhibitor UR-B was found to be 93. An increase in the concentration of inhibitor UR-B to 0.1 kmol/m³ only decreased the degradation rate by a factor of 2. The average MEA degradation rate was 2.26×10^{-4} kmol/m³.h and the percentage of degradation inhibition was found to be 49; this result was not as good as that with 0.01 kmol/m³ of inhibitor UR-B.

For the runs with 6 ppm SO₂ and without inhibitor UR-B (6 ppm SO₂, 0 kmol/m³ UR-B), the degradation rate was found to be 4.86×10^{-4} kmol/m³.h. The rate decreased sharply to 4.66×10^{-6} kmol/m³.h when 0.01 kmol/m³ of inhibitor

UR-B was added in this system. Also, for the 196 ppm SO₂ system with the addition of inhibitor UR-B at the optimum concentration resulted in a low degradation rate of 0.65×10^{-4} kmol/m³.h. The percentage of degradation inhibition of inhibitor UR-B at 0.01 kmol/m³ in 6 and 196 ppm SO₂ concentrations calculated using Equation (3.1) were 99 and 91, respectively.

Inhibitor UR-B is an additive that effectively minimizes the MEA degradation rate because, at any concentration of inhibitor UR-B, it can reduce MEA degradation rate, especially at concentration of 0.01 kmol/m³. This makes inhibitor UR-B a potential additive for industrial applications.

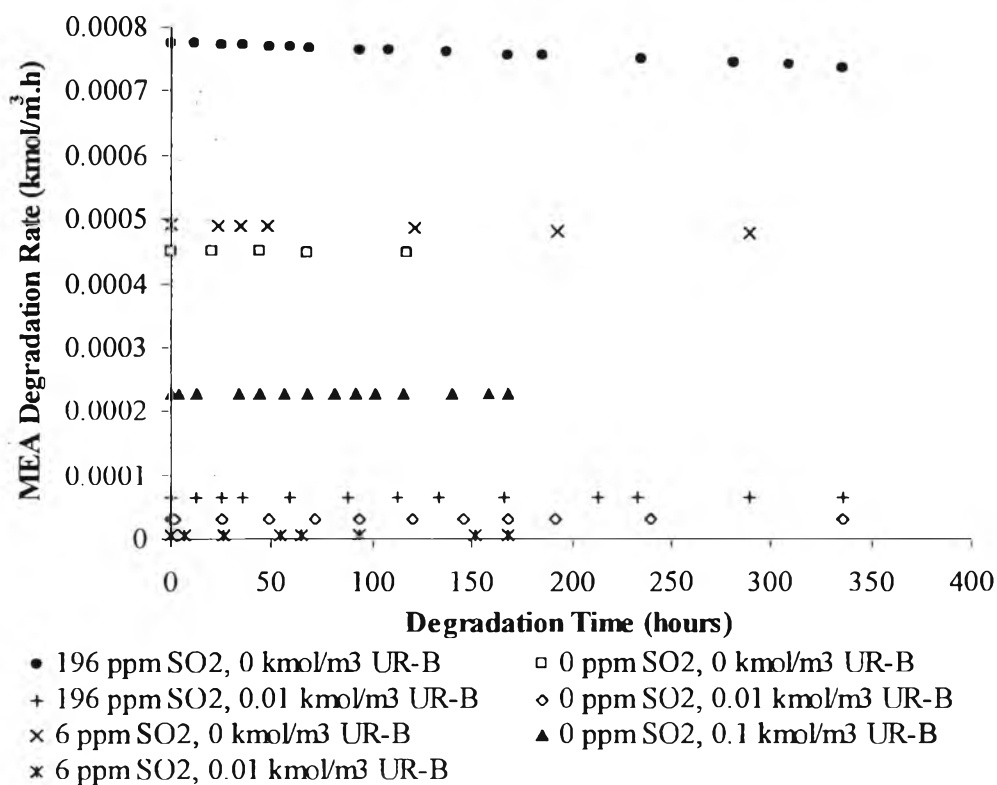


Figure 4.10 The inhibition performance of inhibitor UR-B on MEA degradation as a function of SO₂ concentration in the MEA-H₂O-O₂-SO₂-UR-B degradation system (5 kmol/m³ MEA, 6% O₂, 0,6,196 ppm SO₂, and 120°C).

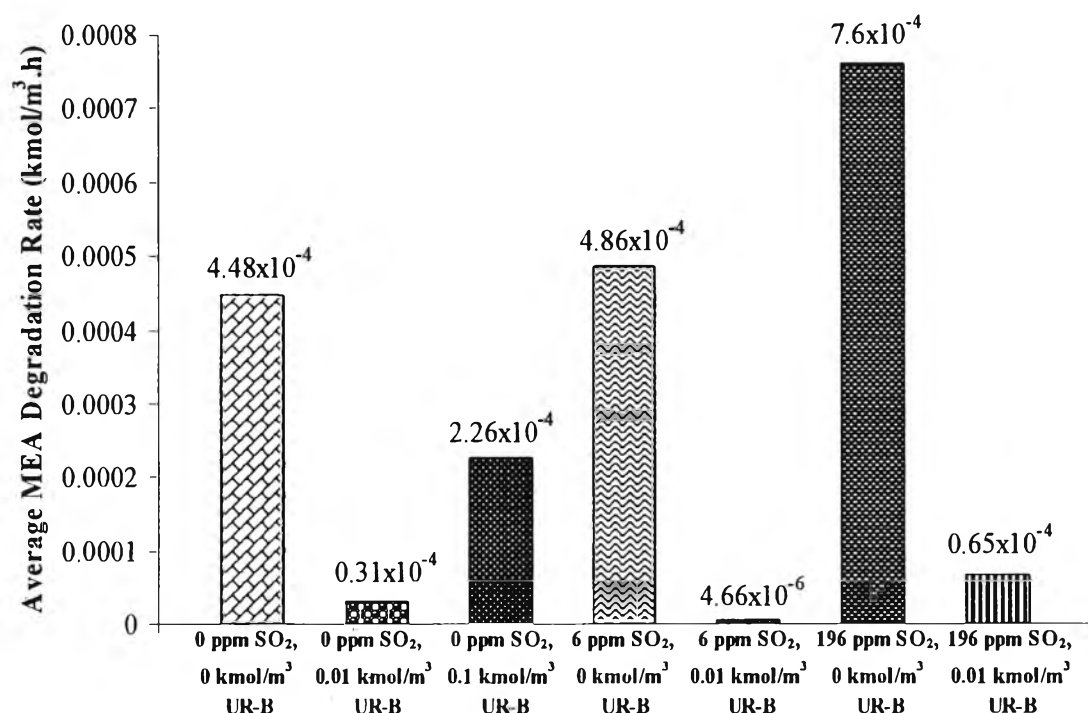


Figure 4.11 The performance of inhibitor UR-B in the MEA-H₂O-O₂-SO₂ degradation system (5 kmol/m³ MEA, 6% O₂, 0,6,196 ppm SO₂, and 120°C).

0.01 kmol/m³ of inhibitor UR-B seemed to be optimum for 6 ppm SO₂ because it decreases the degradation rate of MEA. For the system without the SO₂ concentration in the gas phase resulted in an increase in the degradation rate. The inhibitor concentration needs to be optimized as the SO₂ concentrations have been changed.

4.5 The Performance of Inhibitor UR-C

From the competitive effect, it appears that inhibitor UR-C acts as an electron donor (Bhattacharyya et al., 1994) to form stable products of inhibitor UR-C with reactive O₂ instead of the O₂ reacting with MEA solution. Inhibitor UR-C reacts rapidly with O₂ (Robinson et al., 1999) and is sometimes used as a reducing agent

(Heelis, 1982 and Fife et al., 1989), thus creating the possibility that inhibitor UR-C can inhibit the oxidative degradation of MEA.

4.5.1 Determination of Optimum Concentration of Inhibitor UR-C in MEA-H₂O-O₂-SO₂ Degradation System

The system consisting of MEA-H₂O-O₂-SO₂ was used to determine the optimum concentration of inhibitor UR-C. The experiments were conducted by adding inhibitor UR-C at concentrations of 0.00125, 0.0025, 0.005, and 0.1 kmol/m³ into 5 kmol/m³ MEA solution with O₂ and SO₂ concentrations fixed at 6% and 6 ppm, respectively. The degradation temperature was fixed at 120°C. The degradation rate-time profiles obtained from these experiments are given in Figure 4.12, whereas the performances of inhibitor UR-C for these degradation systems are shown in Figure 4.13.

Based on our experiments, it was found that inhibitor UR-C at the concentration of 0.0025 kmol/m³ yielded the lowest MEA degradation rate of 1.09×10^{-4} kmol/m³.h. This value was approximately 4.5 times lower than that of the run carried out in the absence of inhibitor UR-C (i.e. 4.86×10^{-4} kmol/m³.h). The percentage degradation inhibition of inhibitor UR-C at this concentration in MEA-H₂O-O₂-SO₂ degradation system was 78. Further experiments were conducted using higher concentrations of inhibitor UR-C of 0.005 and 0.1 kmol/m³. This served to determine the optimum concentration needed for best minimizing the oxidative degradation of MEA. At 0.005 kmol/m³ of inhibitor UR-C the average oxidative degradation rate was calculated as 4.55×10^{-4} kmol/m³.h which was 1.1 times lower than that of the run carried out in the absence of inhibitor UR-C. The percentage of degradation inhibition was found to be 6.

An opposite trend was obtained with an increase in the concentration of inhibitor UR-C to 0.1 kmol/m³. The average oxidative degradation rate was calculated as 14.7×10^{-4} kmol/m³.h which was approximately 3 times higher than that of the run without inhibitor UR-C.

Due to the cost of the chemical, a lower concentration of inhibitor UR-C, for example 0.00125 kmol/m³ could become an opportunity if it could yield a good performance. The average MEA degradation rate was 1.77×10^{-4} kmol/m³.h

which was approximately 2.7 times lower than that of the run carried out in the absence of inhibitor UR-C. Also, the percentage degradation inhibition was found to be 64; this result was not as good as the one with 0.0025 kmol/m^3 inhibitor UR-C concentration.

At the optimum concentration 0.0025 kmol/m^3 of inhibitor UR-C causes the lowest MEA degradation rate. Thus, this concentration in the degradation system is sufficient to inhibit the oxidative degradation of MEA. Further evaluation of inhibitor UR-C was done using a more realistic system consisting of MEA-H₂O-O₂-SO₂-UR-C. Upon the addition of increasing concentrations of inhibitor UR-C, the average MEA degradation rate decreased and then increased again. This would indicate that inhibitor UR-C is participating in the MEA oxidation mechanism.

It is also evident that the addition of higher concentrations of inhibitor UR-C (i.e. 0.005 and 0.1 kmol/m^3) also substantially accelerates the average MEA degradation rate. Explanation for the results obtained can be given as follows: an increase in the concentration of inhibitor UR-C beyond the optimum concentration causes side reactions. The side reactions may involve reactions of O₂ with the excess concentration of inhibitor UR-C leading to form the undesired degradation of MEA by inhibitor UR-C (Gambardella et al., 2005), and thus, a more rapid degradation rate of MEA. The degradation products with inhibitor UR-C and side reaction products during the addition of inhibitor UR-C cannot be identified due to the limitation of the HPLC technique that it was set. This technique is suitable for determination of MEA concentration. An excess amount of inhibitor UR-C has a very negative effect on inhibitor UR-C because there is the probability of increasing the collision and activity of inhibitor molecules with MEA molecules thereby increasing the oxidative degradation rate of MEA. It is important to point out that with increased inhibitor UR-C concentrations beyond the optimum; the effectiveness of inhibitor UR-C is more effective in accelerating in the MEA degradation rather than reducing.

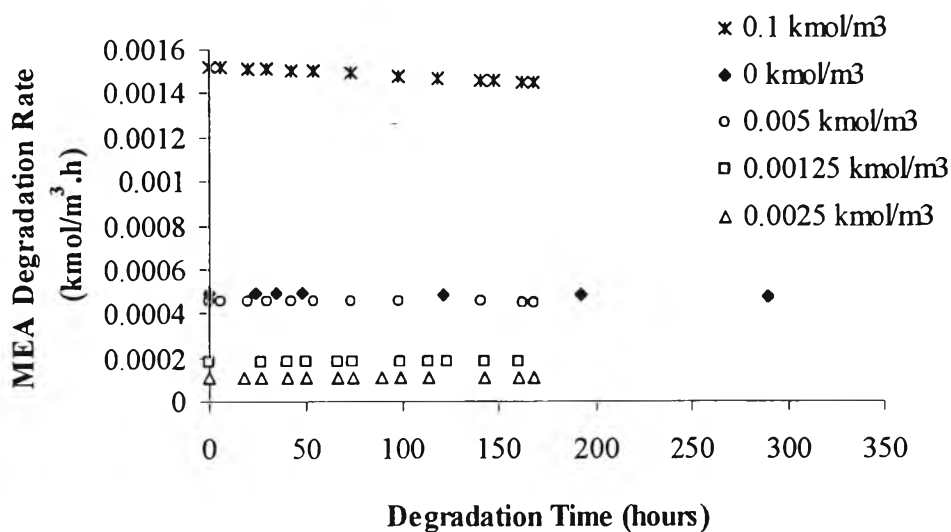


Figure 4.12 Effects of concentration of inhibitor UR-C on MEA-H₂O-O₂-SO₂ degradation system (5 kmol/m³ MEA, 6% O₂, 6 ppm SO₂, and 120°C).

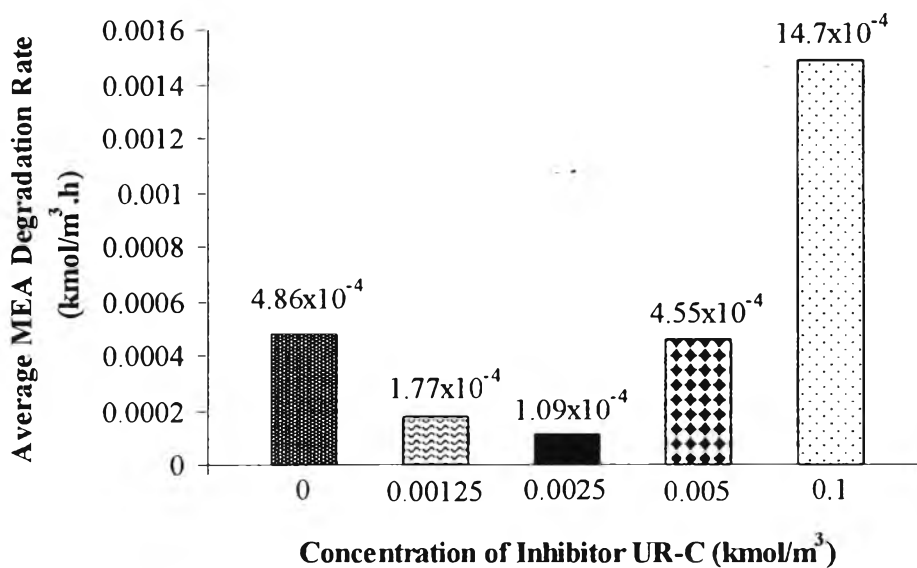


Figure 4.13 The performance of inhibitor UR-C on MEA-H₂O-O₂-SO₂ degradation system (5 kmol/m³ MEA, 6% O₂, 6 ppm SO₂, and 120°C).

4.5.2 Inhibition Performance of Optimum Concentration of UR-C as a Function of SO₂ Concentration in MEA-H₂O-O₂-UR-C Degradation System

The experiments were conducted by adding SO₂ in series of increasing SO₂ concentrations 0, 6 and 196 ppm in 5 kmol/m³ MEA solution, 6%O₂ simulated flue gas stream and an addition of 0.0025 kmol/m³ inhibitor UR-C, which was the optimum concentration determined earlier. All the experiments were carried out at 120°C. The inhibition performance of inhibitor UR-C on MEA degradation as a function of SO₂ concentration for these systems are shown in Figure 4.14, whereas the performance of inhibitor UR-C in the MEA-H₂O-O₂-SO₂-UR-C degradation system is given in Figure 4.15.

In the runs without SO₂ and inhibitor UR-C (0 ppm SO₂, 0 kmol/m³ UR-C), the degradation rate was 4.48×10^{-4} kmol/m³.h. The rate decreased drastically to 0.84×10^{-4} kmol/m³.h when 0.0025 kmol/m³ of inhibitor UR-C was added in this system. In the run with 6 ppm SO₂ and without inhibitor UR-C (6 ppm SO₂, 0 kmol/m³ UR-C), the degradation rate was 4.86×10^{-4} kmol/m³.h. The rate decreased sharply to 1.09×10^{-4} kmol/m³.h when 0.0025 kmol/m³ of inhibitor UR-C was added in this system. The 196 ppm SO₂ system with the addition of inhibitor UR-C at the same concentration also resulted in a low degradation rate of 0.9×10^{-4} kmol/m³.h. This rate was even much lower than that of 0 and 6 ppm SO₂ runs without the inhibitor indicating a strong inhibition effect of inhibitor UR-C in reducing the degradation rate. The percentage of degradation inhibition of inhibitor UR-C in 0, 6 and 196 ppm SO₂ systems calculated using Equation (3.1) were approximately 81, 78, and 88, respectively. This makes inhibitor UR-C a potential additive for industrial applications.

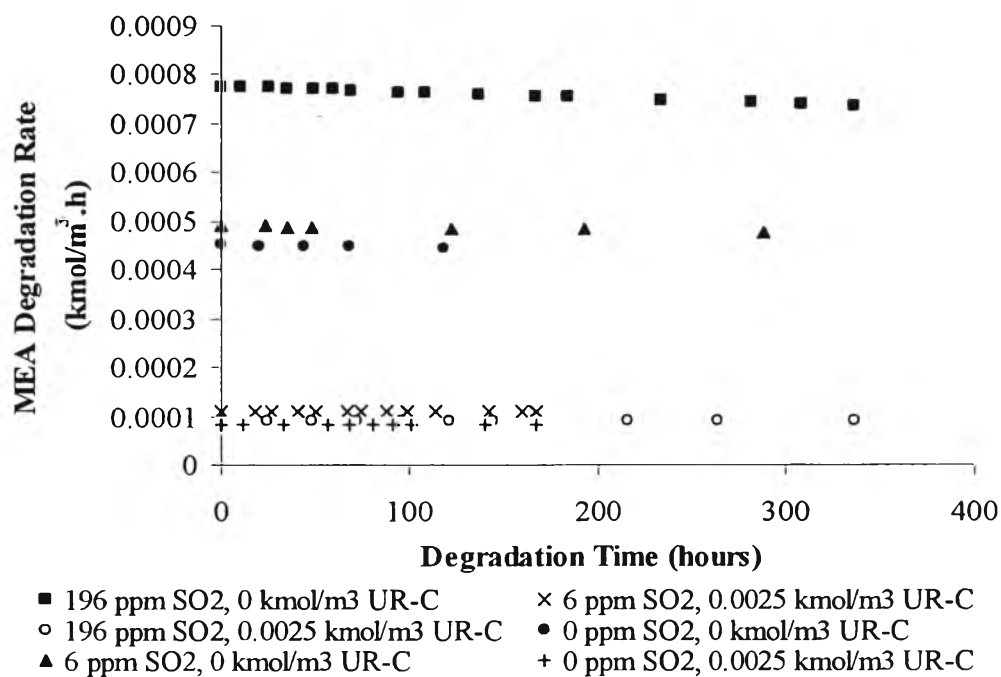


Figure 4.14 The inhibition performance of inhibitor UR-C on MEA degradation as a function of SO₂ concentration in the MEA-H₂O-O₂-SO₂-UR-C degradation system (5 kmol/m³ MEA, 6% O₂, 0,6,196 ppm SO₂, and 120°C).

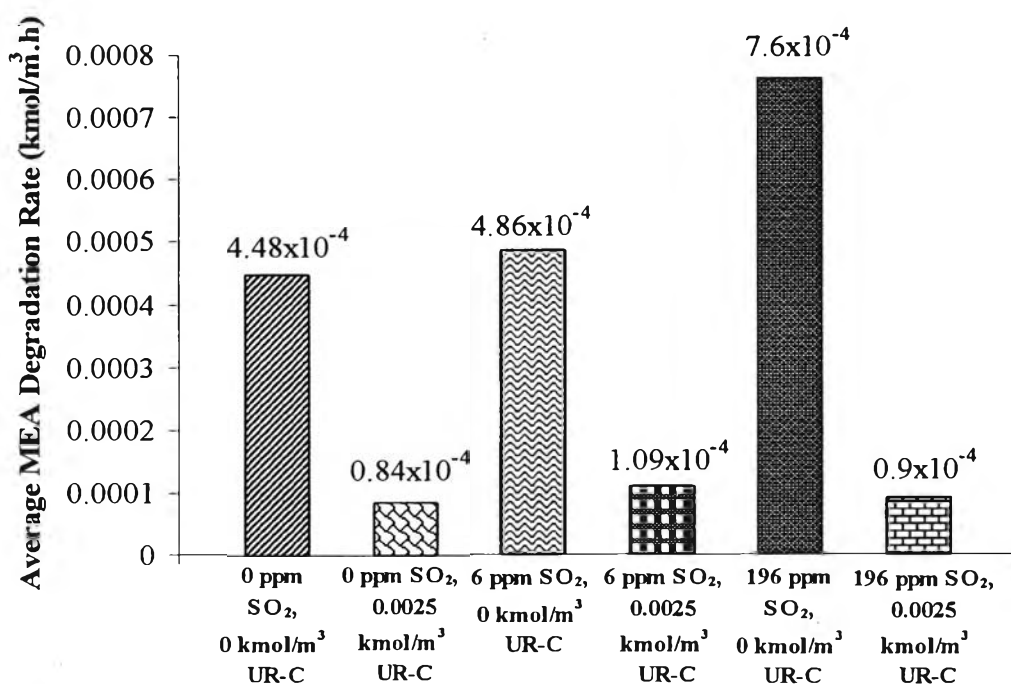


Figure 4.15 The performance of inhibitor UR-C in the MEA-H₂O-O₂-SO₂ degradation system (5 kmol/m³ MEA, 6% O₂, 0,6,196 ppm SO₂, and 120°C).

4.6 The Performance of Inhibitor UR-D

Inhibitor UR-D is a scavenger that can react fast with dissolved O₂. Inhibitor UR-D is added to the degradation systems in order to react competitively with dissolved O₂; it can react faster than MEA with dissolved O₂. Therefore, dissolved O₂ in this system cannot further degrade MEA. It is also a strong reducing agent and reacts with dissolved O₂ in the solution to form reaction products of inhibitor UR-D and O₂. When inhibitor UR-D reacts with O₂, it donates electrons rather than MEA to reactive O₂ and thereby reduces the dissolved O₂ in the systems.

4.6.1 Determination of Optimum Concentration of Inhibitor UR-D in MEA-H₂O-O₂-SO₂ Degradation System

The final degradation inhibitor examined inhibitor UR-D as a potential additive for oxidative degradation of MEA. The system consisting of MEA-H₂O-O₂-SO₂ was used to determine the optimum concentration of inhibitor UR-D.

The experiments were conducted by adding inhibitor UR-D at 0.025 and 1 kmol/m³ into 5 kmol/m³ MEA solution with O₂ and SO₂ concentrations fixed at 6% and 6 ppm, respectively. The degradation temperature was fixed at 120°C. The degradation rate-time profiles obtained from these experiments are given in Figure 4.16, whereas the performances of inhibitor UR-D for these degradation systems are shown in Figure 4.17.

It was found that both 0.025 and 1 kmol/m³ of inhibitor UR-D can inhibit the MEA degradation rate. The inhibitor UR-D at the concentration of 0.025 kmol/m³ yielded the lowest MEA degradation rate, based only on our experiments. Without the addition of inhibitor UR-D, the average MEA degradation rate reached about 4.86×10^{-4} kmol/m³.h. In the presence of 0.025 kmol/m³ of inhibitor UR-D, the average MEA degradation rate decreased to 0.6×10^{-4} kmol/m³.h which was approximately 8.1 times lower than that of the run carried out in the absence of inhibitor UR-D. The percentage degradation inhibition of 0.025 kmol/m³ inhibitor UR-D in MEA-H₂O-O₂-SO₂ degradation system was 88.

Further experiment was conducted using a higher concentration of inhibitor UR-D of 1 kmol/m³. At this concentration, the average oxidative degradation rate was calculated as 2.14×10^{-4} kmol/m³.h which was 2.3 times lower than that of the run carried out in the absence of inhibitor UR-D. The percentage degradation inhibition was found to be 56.

The limited experiments conducted showed that the concentration 0.025 kmol/m³ of inhibitor UR-D gave the lowest MEA degradation rate. Upon the addition of increasing amounts of inhibitor UR-D to the MEA solution, the average MEA degradation rate decreased and then increased again. This would indicate that inhibitor UR-D is participating in the MEA oxidation mechanism.

The average MEA degradation rate did increase slightly after the addition of inhibitor UR-D (i.e. 1 kmol/m³) beyond the optimum concentration. This slight increase in the average MEA degradation rate can be explain as follows: the increased in concentration of inhibitor UR-D increases the acid product which is sulfamic acid (Sisler et al., 1939 and Gomiscek et al., 1981) in the presence of SO₂. This means that at this concentration of inhibitor UR-D, it will serve to catalyze

MEA degradation. Secondly, as the concentration of inhibitor UR-D increases beyond the optimum, inhibitor UR-D can generate acids such as nitric acid when it is added and reacts with dissolved oxygen in the system, thereby reducing its inhibition effect.

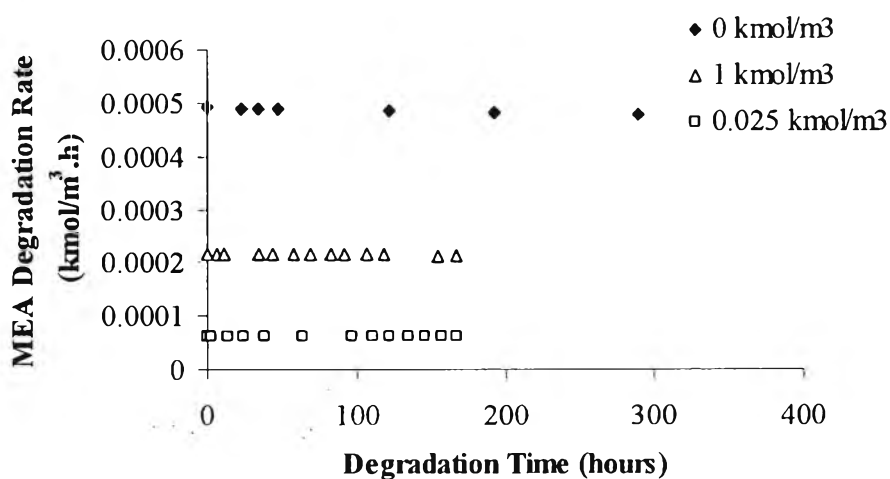


Figure 4.16 Effects of concentration of inhibitor UR-D on MEA-H₂O-O₂-SO₂ degradation system (5 kmol/m³ MEA, 6% O₂, 6 ppm SO₂, and 120°C).

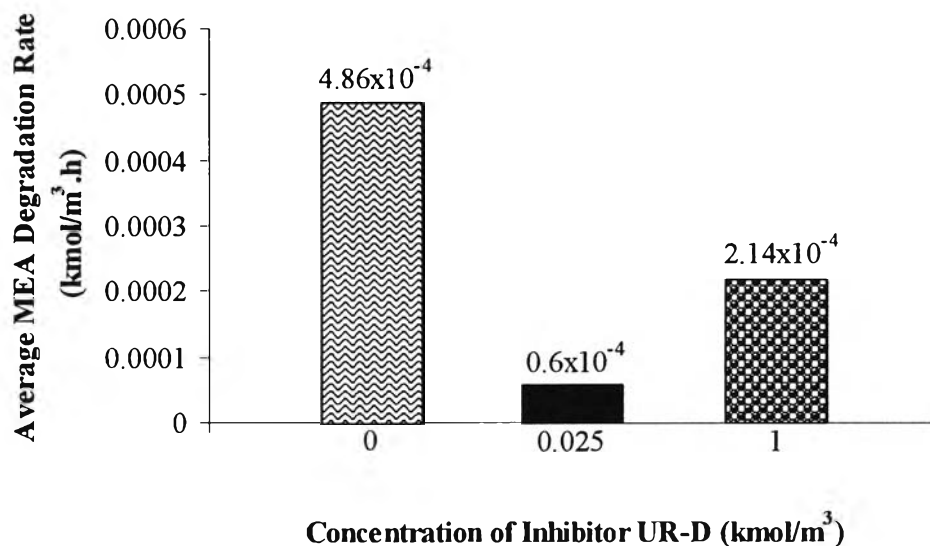


Figure 4.17 The performance of inhibitor UR-D on MEA-H₂O-O₂-SO₂ degradation system (5 kmol/m³ MEA, 6% O₂, 6 ppm SO₂, and 120°C).

The comparison of the effectiveness between inhibitor UR-A and UR-D, the optimum concentration of inhibitor UR-A is 0.05 kmol/m³ whereas the optimum concentration of inhibitor UR-D is 0.025 kmol/m³. The percentage of degradation inhibition of inhibitor UR-A and UR-D are 71 and 87, respectively. Based on these results, it can be concluded that inhibitor UR-D is more effective than inhibitor UR-A. The further experiment was conducted using a higher concentration range of inhibitor UR-D (i.e. 1 kmol/m³), at this concentration of inhibitor UR-D, it still dissolved in MEA solution.

4.7 The Performance of Blended Inhibitors; UR-A blend with UR-B and UR-A blend with UR-C

Since inhibitor UR-A, UR-B and UR-C at suitable concentrations are potential additives that effectively inhibit the MEA degradation rate in the presence of O₂ and SO₂, and each of them acted with a different mechanism, it was decided to try blending inhibitors UR-A with UR-B and UR-A with UR-C in order to take

advantage of the different mechanisms. The experiments were performed using 5 kmol/m³ MEA solution with a 6% O₂ and 196 ppm SO₂ simulated flue gas stream. All the experiments were carried out at 120°C (regenerator condition).

MEA-H₂O-O₂-SO₂-UR-A-UR-B degradation system was the first to be studied. Both of inhibitor UR-A and UR-B are potential additive so it was desired to try a blend of both inhibitor UR-A and UR-B. Inhibitor UR-A was added at a concentration of 0.05 kmol/m³, which was the optimum concentration in minimize the MEA degradation rate. Inhibitor UR-B was then added to the solution at a concentration of 0.01 kmol/m³. The results are shown in Figures 4.18 and 4.19. The average MEA degradation rate was 0.14×10⁻⁴ kmol/m³.h which was approximately 54 times lower than that of the run carried out in the absence of inhibitor (i.e. 7.6×10⁻⁴ kmol/m³.h). The percentage of degradation inhibition of 0.05 kmol/m³ UR-A blend with 0.01 kmol/m³ UR-B was found to be 98. This shows that a blend of inhibitor UR-A and UR-B is more effective in retarding the MEA degradation in the present of both O₂ and SO₂ than either UR-A or UR-B alone.

MEA-H₂O-O₂-SO₂-UR-A-UR-C degradation system was also studied. inhibitor UR-A was added at a concentration of 0.05 kmol/m³, which was the optimum concentration determined earlier. Also, 0.0025 kmol/m³ of inhibitor UR-C (optimum concentration) was added, and the results are shown in Figures 4.18 and 4.19. The average MEA degradation rate was 4.48×10⁻⁴ kmol/m³.h which was approximately 1.7 times lower than that of the run carried out in the absence of inhibitor. The percentage of degradation inhibition of 0.05 kmol/m³ UR-A blend with 0.0025 kmol/m³ UR-C was found to be 41. Inhibitor UR-A blend with UR-C shows a higher degradation rate, 4.48×10⁻⁴ kmol/m³.h, than the systems with only one inhibitor, 0.46×10⁻⁴ kmol/m³.h for inhibitor UR-A and 0.9×10⁻⁴ kmol/m³.h for inhibitor UR-C. The blended inhibitor UR-A and UR-C are also less effective than inhibitor either UR-A or UR-C alone. Since both inhibitors UR-A and UR-C are effective in the inhibition of the oxidative degradation of MEA, the addition of both inhibitors do not improve the oxidative degradation this is because the antagonism effect. On this basis, there is no apparent benefit of using a blend of inhibitor UR-A and UR-C.

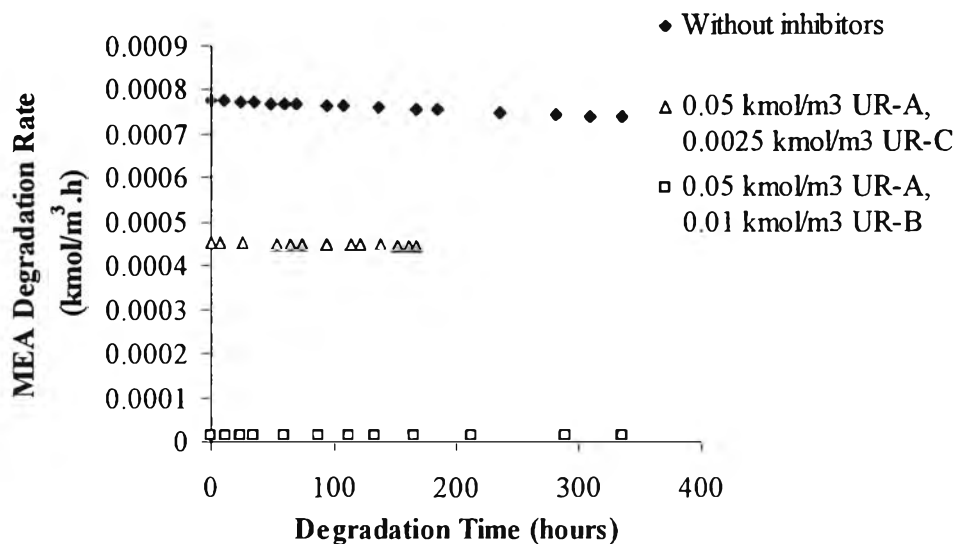


Figure 4.18 Effects of blended inhibitors on MEA-H₂O-O₂-SO₂ degradation system (5 kmol/m³ MEA, 6% O₂, 196 ppm SO₂, and 120°C).

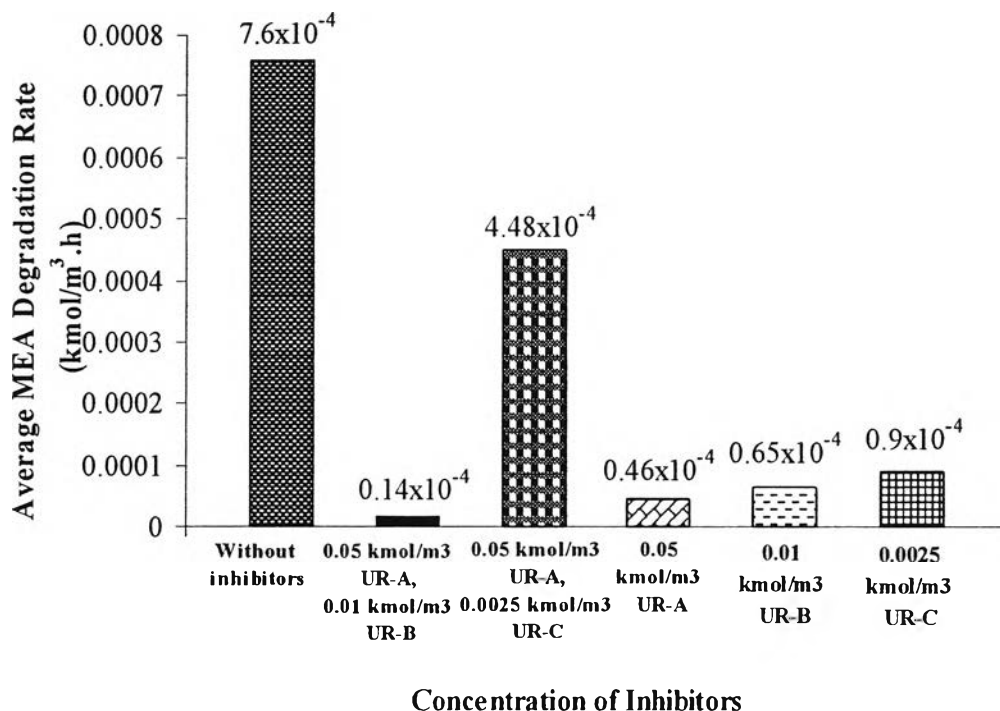


Figure 4.19 The performance of blended inhibitors on MEA-H₂O-O₂-SO₂ degradation system (5 kmol/m³ MEA, 6% O₂, 196 ppm SO₂, and 120°C).

A blend of inhibitor UR-A and UR-B yielded the lowest MEA degradation rate, whereas a blend of UR-A and UR-C was not as good as UR-A blend with UR-B or the individual UR-A or UR-C. Inhibitor UR-A blend with UR-B shows lower degradation rate, 0.14×10^{-4} kmol/m³.h, than the systems with only one inhibitor, 0.46×10^{-4} kmol/m³.h for inhibitor UR-A and 0.65×10^{-4} kmol/m³.h for inhibitor UR-B. Therefore, both of inhibitor UR-A and UR-B are still effective at significantly reducing the MEA degradation rate even in the blended inhibitors system. The functionality of each inhibitor, inhibitor UR-A is a scavenger that can react with dissolved O₂ whereas inhibitor UR-B is a stabilizing agent that can react with intermediate. The nature of both inhibitors will help together to reduce the oxidative degradation rate.

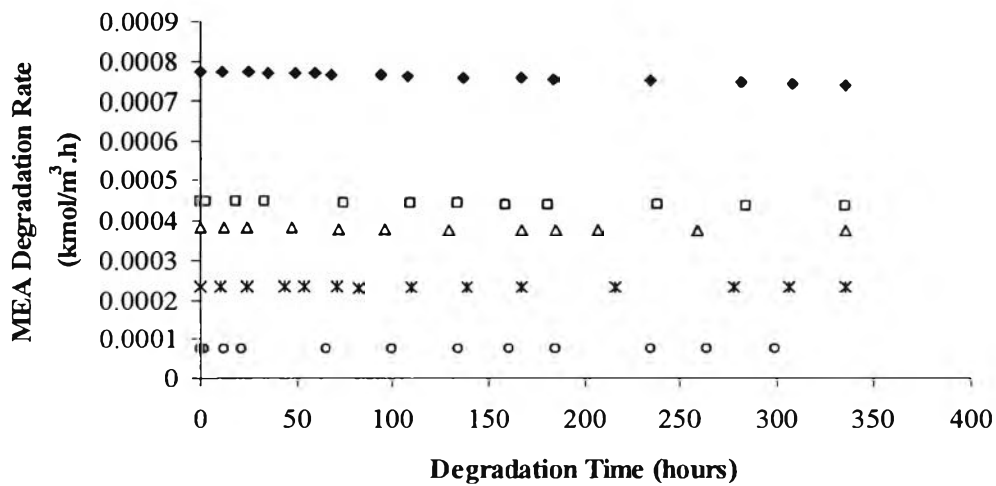
4.8 The Performance of Degradation Inhibitors in CO₂ Loading

MEA-H₂O-O₂-SO₂-CO₂ degradation system more realistically represents CO₂ absorption from coal-fired power plant flue gases, because it accounts for the presence of CO₂. The evaluation of degradation inhibitors were done using experimental runs with CO₂ loading of 0.33 mol CO₂/mol MEA and one without CO₂ loading at temperature of 120°C, O₂ concentration of 6%, SO₂ concentration of 196 ppm in 5 kmol/m³ MEA. The degradation rates were plotted against times as shown in Figure 4.20, whereas the performances of degradation inhibitors for these degradation systems are shown in Figure 4.21.

The average degradation rate of run without CO₂ loading was found to be 7.6×10^{-4} kmol/m³.h. When 0.33 loading of CO₂ was added to the same degradation system, the MEA degradation rate was reduced to 4.4×10^{-4} kmol/m³.h. This accounted for 1.7 times of rate reduction. With the use of Equation (3.1), the percentage of degradation inhibition of CO₂ was calculated as 42. It can be observed that the MEA degradation rate loss was reduced with the inclusion of CO₂ loading in MEA-H₂O-O₂-SO₂-CO₂ system. It is possible that the effect of solubility and large excess of CO₂ in MEA solution could displace the effect of O₂ and SO₂, resulting in a retardation of the O₂-SO₂ induced MEA degradation. This confirms that CO₂ could

actually act as a degradation inhibitor, because CO₂ reduces the amount of O₂ and SO₂ that could enter into the MEA solution to induce degradation. Although under the same degradation conditions, the effect of CO₂ in retarding the O₂-SO₂ induced MEA degradation was not as strong as the effect obtained from inhibitor UR-A, UR-B, and UR-C as shown by their the percentage of degradation inhibition.

It was found that at 0.01 kmol/m³ of inhibitor UR-B and 0.33 CO₂ loading yielded the lowest MEA degradation rate and the average MEA degradation rate was 0.74×10^{-4} kmol/m³.h which was approximately 6 times lower than that of the run carried out in the absence of inhibitor UR-B (i.e. 4.4×10^{-4} kmol/m³.h). The percentage of degradation inhibition of inhibitor UR-B in MEA-H₂O-O₂-SO₂-CO₂ degradation system was found to be 83. Inhibitor UR-B has been shown to be an effective inhibitor of retarding the MEA degradation rate in the present of O₂, SO₂ and CO₂. This is because inhibitor UR-B is not degrading in the present of CO₂. With 0.33 CO₂ loading and 0.0025 kmol/m³ of inhibitor UR-C were added to the same degradation system, the average MEA degradation rate was 2.31×10^{-4} kmol/m³.h. This accounted for 1.9 times of rate reduction. With the use of Equation (3.1), the percentage of degradation inhibition of inhibitor UR-C in MEA-H₂O-O₂-SO₂-CO₂ degradation system was 48; this result was not as good as 0.01 kmol/m³ of inhibitor UR-B with 0.33 CO₂ loading. A further run was performed with 0.05 kmol/m³ of inhibitor UR-A and 0.33 CO₂ loading, and the average MEA degradation rate was 3.77×10^{-4} kmol/m³.h which was approximately 1.2 times lower than that of the run carried out in the absence of inhibitor UR-A. The percentage of degradation inhibition of inhibitor UR-A in MEA-H₂O-O₂-SO₂-CO₂ degradation system was found to be 14; this result was not as good as 0.01 kmol/m³ of inhibitor UR-B and 0.33 CO₂ loading. This makes inhibitor UR-B the best additive for industrial applications.



- ◆ 0 CO₂ loading, 196 ppm SO₂
- 0.33 CO₂ loading, 196 ppm SO₂
- △ 0.33 CO₂ loading, 196 ppm SO₂, 0.05 kmol/m³ UR-A
- × 0.33 CO₂ loading, 196 ppm SO₂, 0.0025 kmol/m³ UR-C
- 0.33 CO₂ loading, 196 ppm SO₂, 0.01 kmol/m³ UR-B

Figure 4.20 Effects of CO₂ loading and degradation inhibitors on MEA-H₂O-O₂-SO₂ degradation system (5 kmol/m³ MEA, 6% O₂, 196 ppm SO₂, and 120°C).

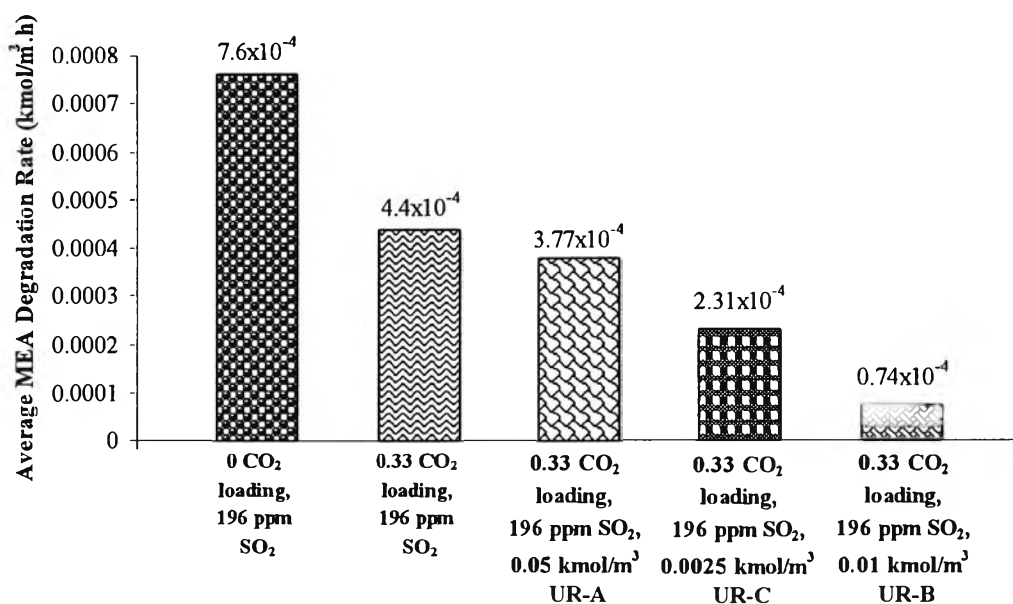


Figure 4.21 The performance of degradation inhibitors on MEA-H₂O-O₂-CO₂-SO₂ degradation system (5 kmol/m³ MEA, 6% O₂, 196 ppm SO₂, and 120°C).

Table 4.2 Summary of the performance of degradation inhibitors.

Degradation Systems	Average Degradation Rate (kmol/m ³ .h)x10 ⁻⁴		%Degradation Inhibition
	Without Inhibitor	With Inhibitor	
MEA-H ₂ O-O ₂ -0ppm SO ₂ -50 mkmol/m ³ UR-A	4.48	1.19	73
MEA-H ₂ O-O ₂ -6ppm SO ₂ -50 mkmol/m ³ UR-A	4.86	1.43	71
MEA-H ₂ O-O ₂ -196ppm SO ₂ -50 mkmol/m ³ UR-A	7.6	0.46	94
MEA-H ₂ O-O ₂ -0ppm SO ₂ -10 mkmol/m ³ UR-B	4.48	0.31	93
MEA-H ₂ O-O ₂ -6ppm SO ₂ -10 mkmol/m ³ UR-B	4.86	0.05	99
MEA-H ₂ O-O ₂ -196ppm SO ₂ -10 mkmol/m ³ UR-B	7.6	0.65	91
MEA-H ₂ O-O ₂ -0ppm SO ₂ -2.5 mkmol/m ³ UR-C	4.48	0.84	81

Degradation Systems	Average Degradation Rate ($\text{kmol}/\text{m}^3 \cdot \text{h}) \times 10^{-4}$		%Degradation Inhibition
	Without Inhibitor	With Inhibitor	
MEA-H ₂ O-O ₂ -6ppm SO ₂ -2.5 mkmol/m^3 UR-C	4.86	1.09	78
MEA-H ₂ O-O ₂ -196ppm SO ₂ -2.5 mkmol/m^3 UR-C	7.6	0.9	88
MEA-H ₂ O-O ₂ -6ppm SO ₂ -25 mkmol/m^3 UR-D	4.86	0.6	88
MEA - H ₂ O - O ₂ - 196ppm SO ₂ - 50 mkmol/m^3 UR-A - 10 mkmol/m^3 UR-B	7.6	0.14	98
MEA - H ₂ O - O ₂ - 196ppm SO ₂ - 50 mkmol/m^3 UR-A - 2.5 mkmol/m^3 UR-C	7.6	4.48	41
MEA - H ₂ O - O ₂ - 196ppm SO ₂ - 0.33 CO ₂ loading 50 mkmol/m^3 UR-A	4.4	3.77	14
MEA - H ₂ O - O ₂ - 196ppm SO ₂ - 0.33 CO ₂ loading 10 mkmol/m^3 UR-B	4.4	0.74	83
MEA - H ₂ O - O ₂ - 196ppm SO ₂ - 0.33 CO ₂ loading 2.5 mkmol/m^3 UR-C	4.4	2.31	48