

H₂S Dissociation In Natural Gas becomes H₂ And S₈ By Zeolite And Caocomposite Synthesis Catalyst

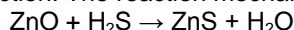
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Abstract: The petrochemical industry is predicted for the next few years to still use raw materials from fossil fuels such as natural gas. The natural gas used still contains H₂S which is corrosive and has the risk of poisoning the catalyst so that the presence of H₂S is avoided before it damages or degrades the performance of the catalyst as used in the steam reforming or steam converting process. Several studies aimed at recovering hydrogen and sulfur. One such effort is through a thermal dissociation process. To dissociate H₂S into hydrogen gas and S₂ gas, an operating temperature of 1300°C is required. This method is less economical to apply to industry because it requires large amounts of energy and does not produce solid sulfur [9]. As a result researchers used catalysts to reduce energy consumption and also sought to convert into solid sulfur. From several studies by Nguyen et al, 2015 [8], zeolite modification with metal has the potential to increase H₂S absorption in room temperature. It is hoped that the invention can be considered as an alternative ZnO catalyst. Therefore, in this study an attempt was made to make a catalyst made from natural zeolite combined with a metal compound, CaO. The catalyst preparation process is carried out by the impregnation method, in which there are 3 variations of the catalyst based on CaO : Natural Zeolite ratio that is, 1 : 5, 1 : 7.5, and 1 : 10. These three types of catalyst have been tested using SEM and XRD, where the results show success in the impregnation process. Furthermore, in this study a trial was carried out on the use of catalysts to absorb the gas that became the raw material. The mass of the catalyst in each variation of the composition used is also varied in mass, namely 40 gr, 50 gr, 60 gr, 70 gr, and 80 gr. In the process, variations in the feed flow rate of the catalyst are varied, namely 5, 10, 30, 50, and 80 Liters / minute. Therefore, it is known that the composition of CaO and Zeolite 1 : 5 is the best composition and produces the highest conversion. The lower the flow rate and the higher the value of the catalyst mass, the better dissociation of H₂S.

Index Terms: Adsorbent, H₂S, ZnO, Zeolite, CaO, Dissociation.

1. INTRODUCTION

However, the quality of Natural gas used as the raw material contains H₂S which is corrosive and highly potential to be degrading the catalyst performance within the steam reforming or steam converting process. Thus, the H₂S presence in the natural gas has to be removed before it was used as the raw material for production. The reaction mechanism is as follows:



In this process the sulfur contained in natural gas will be adsorbed on ZnO while H₂O remained along with the natural gas. ZnO adsorbent which has been binding sulfur to ZnS cannot be regenerated so that it gradually experiences saturation, as a result the adsorbent must be replaced with new adsorbent every time saturation occurs. Sulfur bound to ZnO adsorbent will form ZnS which will become a waste, while this adsorption process also produce water that potentially reduced the partial pressure. Considering the adsorbent high cost due to the high consumption, also the potential of H₂S was unable to be utilized in this process, it has led some researchers to find a more economical process. There are several studies aimed to recover hydrogen and sulfur, one of them is by a thermal dissociation process. To dissociate H₂S into hydrogen gas and S₂ gas, an operating temperature of 1300°C is required. This method is less economical to apply to industry because it requires large amounts of energy and does not produce solid sulfur [9]. As a result, some study used a catalyst in order to reduce the energy consumption while sought to convert them into solid sulfur. Zhakkarov et al (2004) [11] used cobalt sulfide catalysts to decompose H₂S into hydrogen (H₂) and solid sulfur (S₈) at room temperature. In the results of his research it was mentioned that H₂S can be dissociated to form solid sulfur through several stages of the reaction mechanism that takes place on the surface of the catalyst namely molecular adsorption, dissociative chemisorption, the release of hydrogen molecules and sulfur recombination. In this study, solid sulfur was successfully

obtained, but the resulting H₂S conversion was still quite low at 10-20%. Zhao et al. (2007) [12] dissociated H₂S in corona pulsed discharge reactors with the help of electric power of 6.9-30 kV and with the addition of gas balances Ar, He, N₂ and H₂. In his research, the results showed that the presence of gas balance affects H₂S dissociation. The presence of argon gas can increase the maximum H₂S dissociation conversion by 25%. Carried out the dissociation of H₂S at 28°C using an MgO metal oxide catalyst which took place in a fixed bed reactor [5]. In his research, the remaining undissociated H₂S <0.6 ppm. Based on the development of these studies, it turns out that the process of H₂S dissociation can take place at low temperatures if using a catalyst. Zeolite is a natural material that is very easy to find, and the price is also very affordable. Zeolites can be monetized through ion exchange with metals to increase the absorption capacity of H₂S as shown in Table 1. [8].

TABLE 1
THE RESULTS OF THE ZEOLITE AND METAL COMBINATION FOR ABSORBING H₂S

Sample	Me ²⁺ conc. of the exchange solution (M)	Metal content by ICP (wt.%)	BET specific surface area (m ² /g)	H ₂ S adsorption capacity (mg S/g)
NaX	n.a	n.a	492	0.9
CuX	0.5	20	111	13.1
ZnX	0.5	14	427	23.5
CoX	0.5	3.9	n.a	6.9
MnX	0.5	3.7	n.a	0.9
NiX	0.5	5.4	n.a	0.8
CaX	0.5	n.a	n.a	0.4

Source: Nguyen et al. 2015[8].

From some of the studies above, zeolite modification with metal has the potential to be able to increase the absorption of H₂S in room temperature. It is hoped that the invention can be considered as an alternative ZnO catalyst. Based on the analysis of the description in the background above, the use of ZnO and MgO catalysts has been able to meet the H₂S concentration requirements at Desulfurizer outlet, but it still requires quite a high cost. Consideration from several previous studies, found the problem formulation that ZnO absorbent and MgO catalyst still has a significant cost in the desulfurization process. Therefore, the composite synthesis of Zeolite and CaO catalysts at a lower cost can be an alternative absorbent of ZnO in the H₂S separation process in natural gas at Desulfurizer.

2 MATERIAL AND METHOD

2.1 Material

In this study commercial CaO catalysts were used which varied as much as 40-90 grams. While the H₂S raw material is obtained from Natural Gas with a composition as summarized in Table 2.

2.2 Experimental Method

The research took place on a fixed bed reactor made of stainless steel with a diameter of 2 inches and a length of 23 inches.

TABLE 2
THE COMPOSITION OF NATURAL GAS OF

Composition	Inlet	Outlet
Hydrogen	0.00548%	0.00564%
C ₆ +	0.83%	0.09%
Propane	1.11%	0.90%
i-butane	0.12%	0.19%
n-butane	0.12%	0.19%
i-pentane	0.08%	0.09%
n-pentane	0.49%	0.05%
Carbon Dioxide	4.06%	4.63%
Ethane	3.78%	4.20%
Methane	89.41%	89.65%
Total	100%	100.00%

This research was conducted at the Fertilizer Factory with the description of the process as follows: Fill the fixed bed reactor with a CaO zeolite catalyst composite of 40 - 80 grams. Before the research process is carried out, first do the system purging using N₂ with the help of a vacuum pump so that there is no more oxygen in the system. N₂ from the battery limit is connected to the fixed bed reactor inlet and then sucked by a vacuum pump at the output of the solid and gas product tank so that the entire system is fed by N₂. Do the purging process for 10 minutes. After the purging process is declared complete, stop the flow of N₂ into the system by closing the inlet valve N₂ fixed bed reactor. Open the fixed bed reactor inlet valve to flow H₂S according to the desired flow rate (5000 - 80000 mL / min) for 15 minutes. During the reaction process H₂S gas will decompose into hydrogen gas (H₂) and sulfur solids (S₈). H₂ and S₈ products will flow into the product tank with a separator inside, so that solid sulfur will be retained while H₂ gas will flow into the product gas tank. Take gas products H₂ and H₂S that are not converted in natural gas and then the concentration is analyzed using gas chromatography and spectrophotometry, while the solid sulfur product is observed visually, calculated by mass balance and analyzed by spectrophotometry. The

schematic of the research process is shown in Figure 1.

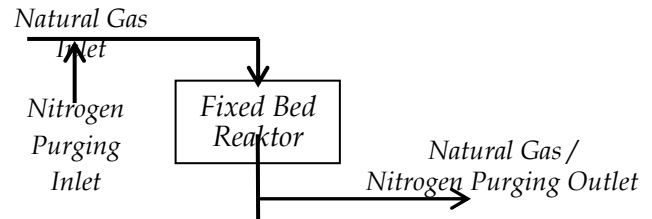


Figure 1. Schematic of the research process

H₂S conversion is obtained by calculating H₂S inlet and outlet concentration analysis data results into Equation (1).

H₂S Conversion (%) =

$$\frac{H_2S \text{ inlet Concentration} - H_2S \text{ outlet Concentration}}{H_2S \text{ inlet Concentration}} \times 100\% \quad (1)$$

2.3 Mathematical Modeling of H₂S Decomposition Reaction Constants

In fixed bed reactors, the rate constant of the H₂S dissociation reaction rate can be obtained from the translation of the reaction rate equation in the tubular reactor flow system [4] with reaction order 1 [7].

$$F_{(H_2S)_0} \frac{dX}{dW} = -r_{H_2S} \quad (2)$$

$$-r_{H_2S} = k C_{(H_2S)_0} (1 - X) \quad (3)$$

$$-\ln(1-X) = k C_{(H_2S)_0} \frac{W}{F_{(H_2S)_0}} \quad (4)$$

Where C (H₂S) 0 is the initial H₂S concentration (mol / cm³), F (H₂S) 0 is the mass flow rate of H₂S (mol / sec), k is the rate of the reaction rate constant (1 / second), -r_{H₂S} is the rate H₂S (mol / sec.g) reduction reactant reaction, W is the catalyst mass (g), and X is H₂S conversion. By plotting the catalyst mass (W) as abscissa and -ln (1-X) as an ordinate in a graph, the value (k C (H₂S) 0 / F (H₂S) 0) will be obtained as the slope value of the graph. So, from this equation can be calculated the value of the reaction speed constant.

3 RESULT AND DISCUSSION

3.1 Effect of Feed Flow and Catalyst Mass on H₂S Conversion.

The following graph shows the effect of catalyst mass and flow of feed on the H₂S conversion produced in each variation of the combination of CaO and Zeolite as catalysts

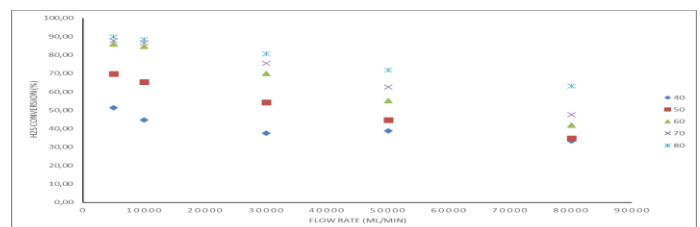


Figure 2. Effect of Feed Flow Rate and Catalyst Mass on H₂S Conversion in Comparison of Comparison of CaO and Zeolite 1 : 5.

From Figure 2. above, H₂S conversion with a constant gas flow rate of 5,000 mL / min and 1: 5 catalyst composition at 40 g, 50 g, 60 g, 70 g, and 80 g respectively is 71,736%, 82,688 %, 86.467%, 91.705%, and 91.746%. For a constant gas flow rate of 10,000 mL / min at 40 g, 50 g, 60 g, 70 g, and 80 g, respectively 69.386%, 74.982%, 78.747%, 79.386%, and 80.654%. For a constant gas flow rate of 30,000 mL / min at 40 g, 50 g, 60 g, 70 g, and 80 g, respectively 61,065%, 63,114%, 67,061%, 70,578%, and 75,272%. For a constant gas flow rate of 50,000 mL / min at 40 g, 50 g, 60 g, 70 g, and 80 g, respectively are 51,013%, 53,438%, 57,841%, 62,658%, and 65,992%. For a constant gas flow rate of 80,000 mL / min at each weight of 40 g, 50 g, 60 g, 70 g, and 80 g are 36.312%, 45.047%, 51.714%, 57.037%, and 62.516%. From these data it can be concluded that in the 1: 5 catalyst composition and in the constant flow rate of the feed gas, the higher the catalyst mass, the higher the H₂S conversion produced.

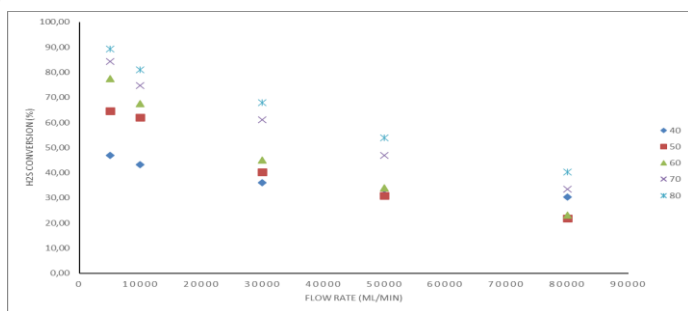


Figure 3 Effect of Feed Flow Rate and Catalyst Mass on H₂S Conversion in Comparison of CaO and Zeolite Catalysts 1: 7.5

From Figure 3 above the resulting H₂S conversion with a constant gas flow rate of 5,000 mL / min and a catalyst composition of 1: 7.5 at 40 g, 50 g, 60 g, 70 g, and 80 g, respectively, is 68.406%, 73.668%, 82.5993%, 89.536% and 89.536%. For a constant gas flow rate of 10,000 mL / min at 40 g, 50 g, 60 g, 70 g and 80 g, respectively 44.828%, 68.406%, 75.501%, 77.19%, and 79.41%. For a constant gas flow rate of 30,000 mL / min at each weight of 40 g, 50 g, 60 g, 70 g, and 80 g are 47.46%, 61.333%, 63.4877%, 71.81%, and 76.52%. For a constant gas flow rate of 50,000 mL / min at 40 g, 50 g, 60 g, 70 g, and 80 g, respectively are 35.823%, 51.484%, 55.241%, 61.97% and 66.031%. For a constant gas flow rate of 80,000 mL / min at each weight of 40 g, 50 g, 60 g, 70 g, and 80 g are 20.956%, 40.088%, 45.826%, 50.217%, and 57.295%. From these data it can be concluded that in the catalyst composition 1: 7.5 and in the constant flow rate of the feed gas, the higher the catalyst mass will also result in higher H₂S conversion.

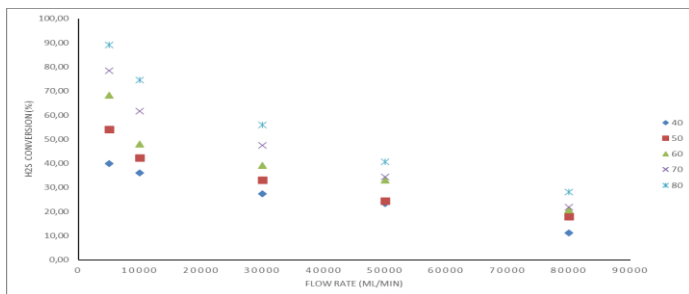


Figure 4 Effect of Feed Flow Rate and Catalyst Mass on H₂S Conversion in Comparison of CaO and Zeolite Catalysts 1: 10

From Figure 4 above the resulting H₂S conversion with a constant gas flow rate of 5,000 mL / min and a 1: 10 catalyst composition at 40 g, 50 g, 60 g, 70 g, and 80 g, respectively, is 67,001%, 80, 177%, 86.544%, 90.0372% and 90.818%. For a constant gas flow rate of 10,000 mL / min at 40 g, 50 g, 60 g, 70 g, and 80 g, respectively are 52,084%, 60,976%, 69,097%, 71,385%, and 89,185%. For a constant gas flow rate of 30,000 mL / minute at 40 g, 50 g, 60 g, 70 g and 80 g, respectively 44.467%, 56.8786%, 69.470%, 66.887%, and 69.5382% . For a constant gas flow rate of 50,000 mL / min at 40 g, 50 g, 60 g, 70 g, and 80 g, respectively 30.4998%, 47.1863%, 48.281%, 52.201%, and 59.246% . For a constant gas flow rate of 80,000 mL / min, each weighing 40 g, 50 g, 60 g, 70 g, and 80 g is 16.5743%, 31.213%, 79.097%, 45.9095%, and 49.812%. From these data it can be concluded that in the 1: 10 catalyst composition and in the constant flow rate of the feed gas, the higher the catalyst mass will also result in higher H₂S conversion. From the whole graph above it can be concluded that the increase in H₂S conversion at each increase in catalyst mass will occur in the entire catalyst composition. In addition, each graph also shows a trend that tends to decrease in the conversion of H₂S at each increase in feed gas flow lane. This is due to changes in space velocity and residence time in the reactor when the catalyst mass changes and feed gas flow rate. Space velocity is defined as the volumetric amount of reactant flow rate compared to the volume or mass of the catalyst. As the catalyst mass increases, space velocity will decrease and residence time will increase [6]. This will cause the contact time between H₂S and CaO catalyst to be longer and the resulting H₂S conversion will be higher.

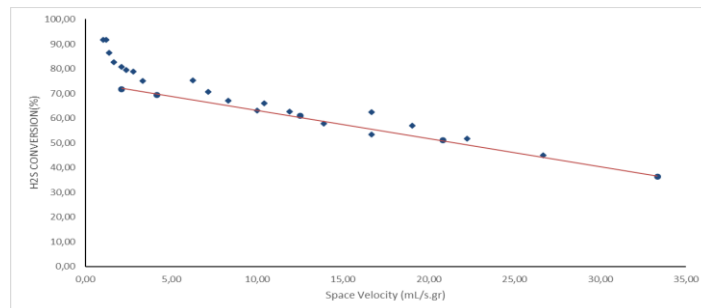


Figure 5. Effect of Space Velocity on H₂S Conversion in 1: 5 Compositions

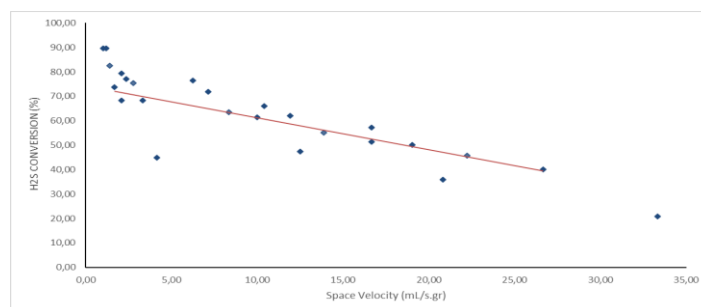


Figure 6. Effect of Space Velocity on H₂S Conversion in 1: 7,5 Compositions

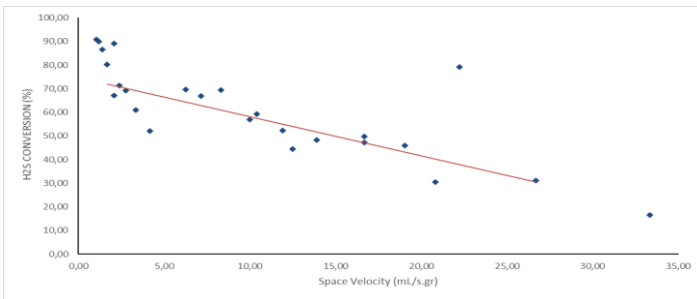


Figure 7. Effect of Space Velocity on H₂S Conversion in 1: 10 Compositions.

Figure 5, Figure 6, and Figure 7 show that the higher the velocity value of space velocity, the higher the value of H₂S conversion. The value of space velocity will depend on the ratio of feed flow rate with catalyst mass, so that the lowest feed flow rate and heaviest catalyst mass will produce the lowest space velocity, which is at feed flow rate of 5,000 mL / min and catalyst mass of 70-90g. In addition, the factor that can influence this is the porosity of the catalyst bed (Φ). The porosity of the catalyst bed can be defined as the fraction of the volume of empty space to the total volume of catalyst bed.

$$\Phi = \frac{\text{Volume Bed} - \text{Volume Katalis}}{\text{Volume Bed}} \dots\dots (5)$$

$$\Phi = 1 - \frac{\text{Volume Katalis}}{\text{Volume Bed}} \dots\dots (6)$$

$$\Phi = 1 - \frac{\text{Massa Katalis}}{\rho_{partikel}} \times \frac{1}{\text{Volume Bed}} \dots\dots (7)$$

$$\Phi = 1 - \frac{\rho_{bulk}}{\rho_{partikel}} \dots\dots (8)$$

This study uses a Fixed Bed Reactor with bed volume and particle density is constant at 101.29 cm³ and 3.35 g / cm³, so the higher the catalyst mass, the porosity of the bed decreases. Reduced porosity of the bed causes a reduction in contact between the catalyst and H₂S, causing a decrease in conversion. As shown in Figure 8.

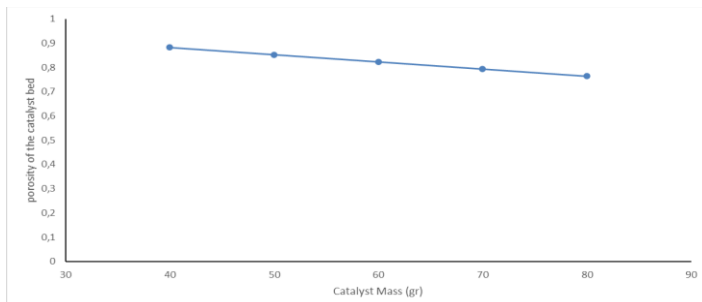


Figure 8. Effect of catalyst mass on bed porosity

3.2 Effect of Feed Flow Rate on Reaction Speed Constants.

The type of reactor used in this study is a Fixed Bed Reactor where the rate of H₂S dissociation reaction rate can be defined as a function of the mass flow rate, conversion and catalyst mass.

$$F_{(H_2S)_0} \frac{dX}{dW} = -r_{H_2S}$$

(9)

The type of reactor used in research It is known that the H₂S dissociation reaction is first order [7], then the reaction rate is proportional to the reaction rate constant and the reduction in reactant concentration. of mass flow rate, conversion and catalyst mass.

$$-r_{H_2S} = k C_{(H_2S)_0} (1 - X) \dots\dots (10)$$

So that by combining and integrating the equation above the equation is obtained:

$$\frac{-r_{H_2S}}{\ln(1-X)} = \frac{k C_{(H_2S)_0} W (1-X)}{F_{(H_2S)_0}} \dots\dots (11)$$

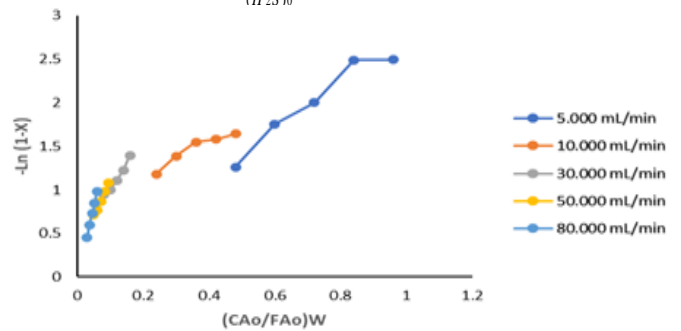


Figure 9. Effect of Feed Flow Rate on Reaction Speed Constants at Composition 1: 5

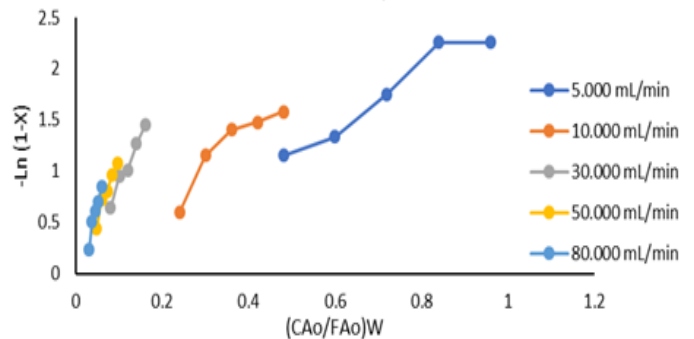


Figure 10. Effect of Feed Flow Rate on Reaction Speed Constants at Composition 1: 7,5

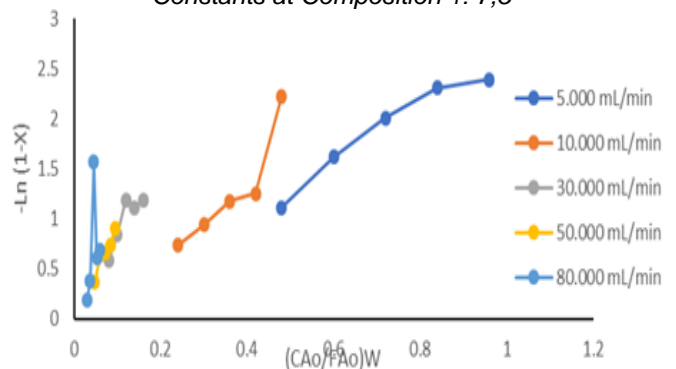


Figure 11. Effect of Feed Flow Rate on Reaction Speed Constants at Composition 1: 10

Based on Figure 9, Figure 10, and Figure 11 shows the rate reaction constant is the slope of the graph of the function and the value is getting bigger with increasing feed flow rate. Seen in all three graphs have the same pattern in each flow. The greater the feed flow rate and the heavier the catalyst mass,

the greater the rate of reaction constant. This is in line with the concept of space velocity which when the catalyst mass increases, it will require a longer residence time so as to inhibit the reaction rate. At a greater feed flow rate, H₂S conversion results in a decrease so that the partial pressure of the H₂S reactants will be higher ($P_{H_2S} = P_{H_2} \text{ Sinlet} \times (1 - X_{H_2S})$). Increasing the pressure of H₂S reactants can reduce the volume of space so that H₂S molecules will more easily collide so that the reaction rate will be higher [6]

3.3 Effect of catalyst composition and mass on H₂S conversion.

The following is a graph showing the effect of catalyst composition and mass on H₂S conversion at 5,000 mL / min feedstream.

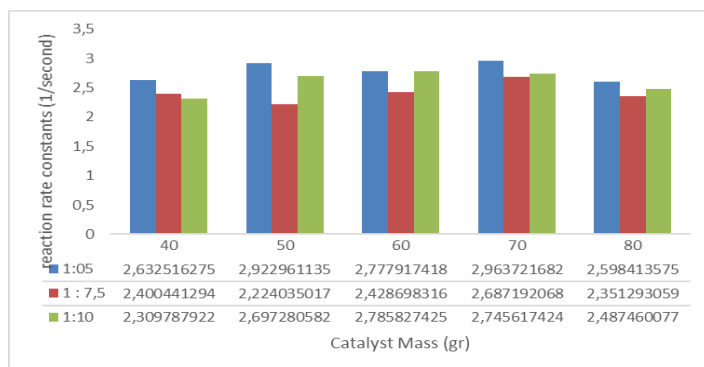


Figure 12 Effect of Composition and Mass of Catalysts on Reaction Rate Constants at Feed Flow Rate of 5,000 mL / min

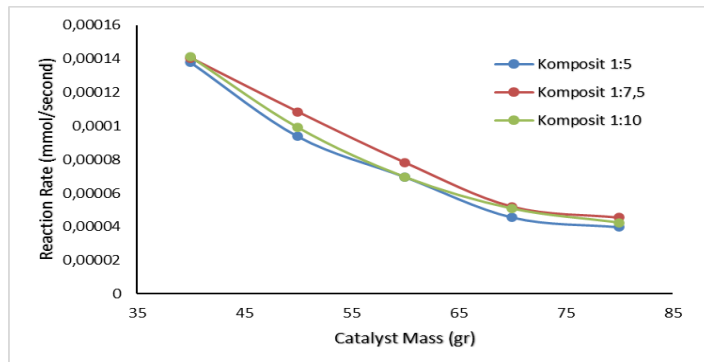


Figure 13. Effect of Composition and Mass of Catalysts on Reaction Rate at Feed Flow Rate of 5,000 mL / min

The chart above is intended to see the best catalyst composition of this study. Comparisons were made on H₂S conversion data at 5,000 mL/min gas feed flow rate. This is because that the results of this study at a gas feed flow rate of 5,000 mL/min produced the highest conversion value in each catalyst composition and the lowest reaction rate constant. From this graph it can be concluded that the change in catalyst composition and catalyst mass will affect the reaction rate constants. From the research results obtained the highest H₂S conversion in the catalyst composition 1: 5 with a catalyst mass of 80 grams at a gas feed flow rate of 5,000 mL/min. For the lowest flow rate constant, the catalyst composition is 1: 7.5 with a catalyst mass of 50 gr at the gas feed lane 5,000 mL/min.

4 CONCLUSION

The variation of the combination of Zeolite composites: CaO and catalyst mass gives an effect on the value of H₂S dissociation conversion produced at each variation of feed flow rate. The less zeolite content in the composite combination and the greater the mass of the catalyst, the higher the value of H₂S dissociation conversion produced. The variation of feed flow rate and combination of Zeolite: CaO composites has an influence on the value of H₂S dissociation conversion and the reaction rate constant. Where the lower the feed flow rate and the less zeolite content in the catalyst composite combination, the higher the value of H₂S dissociation conversion. While for the reaction rate constants will be higher when there is an increase in the flow rate and the use of catalysts with lower Zeolite content.

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