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Abstract:

Analyzing the composition of hydrocarbon by using gas chromatograph in petrochemical laboratory RU III Plaju has no limit for allowed impurities. One of the contained impurities is sulfur that can demage the component inside the gas chromatograph. So we need a research to make an additional apparatus (sulfur trap) that can reduce the sulfur content in sample but does not change the composition of hydrocarbon. Zeolite is an effective adsorbent in reducing sulfur. To increase its adsorption, zeolite is activated physically and chemically. In this research, 100 grams of zoelit was heated at 300, 350, 400, 450, 500 and 550^{o}C for one hour. Then it was added with a solution of diethanolamine (DEA) with concentration of 0.5, 1, 2, 3, and 4 N. Sample flowed through the zeolite with flow rates of 100, 300, and 500 ml/min. The optimum condition was obtained at heating temperature of 450^{o}C, adding 2 N of DEA solution, and 100 ml/min of flow rate with a percentage of sulfur adsorption of 99.97. The sample was still representative because there was no change in the composition of hydrocarbon.

Keywords: *sulfur trap, gas chromatograph, zeolite, adsorbent, diethanolamine*

INTRODUCTION

In oil and gas industrial activities, the laboratory has an important role because material or feed which will be processed, being processed or has been processed in a unit must be analyzed whether it fits the specifications or not. The analyzed samples in the laboratory can be solid, liquid, and gas. Some of the equipments which are used for analysis are moisturemete, pycnometer, UV-Vis spectrophotometer, hygrometer, gas chromatograph, and so on. Analysis of gas samples for hydrocarbon and non-hydrocarbon can be done by using a gas chromatograph or better known as GC. GC has various types of configurations depending on the needs in consumer, such as in the Petrochemical Laboratory of PT Pertamina Refinery Unit III Plaju which uses GC with configuration FID (*Flame Ionization Detector*), TCD (*Thermal Conductivity Detector*), and SCD (*Sulfur Chemiluminscence Detector*). The GC which is being operated has no the limitation of allowed impurities sample for analysis activities. The impurities in sample can be sulfur compounds such as hydrogen sulfide (H_2S), carbonyl sulfide (COS), methyl mercaptan (CH_4S), and others. According to the technicians who came when the installation of the equipment, the high content of impurities should be avoided because it can cause the performance degradation or damage the equipment. It is known that sulfur compounds are corrosive so that it can cause corrosion in parts of the GC such as columns, valves even to the detector. Although it is recommended to avoid the analysis of samples with high impurities, that does not mean it should not be done at all. This is due to the samples which are sent have various sulfur content every day from low to high, depending on the type of oil feed used whether it is sweet crude, sour crude or cocktail. If samples with high sulfur are analyzed with normal GC, the effects will not be seen now but will be seen in the future.

Zeolite

Zeolite is well-known as one of the adsorbents that can adsorb sulfur and carbon dioxide. But it must be activated by physically or chemically. The name zeolite comes from the words "zein" which means boiling and "lithos" which means rock. Zeolites are natural rocks or minerals that are chemically classified as silica minerals and are declared as hydrated silicate alumina, smooth in shape, and are the result of secondary products that are stable because they originate from the processes of sedimentation, weathering, and hydrothermal activity. (Sutarti, 1994). Zeolite is an alumina silica (Si / Al) compound which has a relatively large pore and surface area, so it has high adsorption ability. Zeolites with high Si content such as clinoptilolite, mordenite, and ferrierite are classified as acidic rocks. (Ismaryata, 1999). Zeolites are cavity crystals which formed by three-dimensional tetrahedral alumina silica system and have regular structure with cavities inside which are filled with alkali or alkaline earth metal as a counterweight to their charges. The cavities are a channel system in which water molecules are filled.

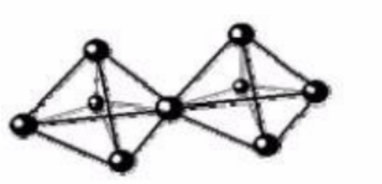

Figure 1. Tetrahedral Alumina and Silika in Zeolite Structure

The basic framework of the zeolite structure consists of tetrahedral $(AlO_4)^{5-}$and $(SiO_4)^{4-}$ unit which are connected through oxygen atoms. In this structure, Si^{4+} structure can be replaced by Al^{3+} with isomorphic substitution. The formula for zeolite cell units is Mx / n {(AlO2) x (SiO2) y}. z H2O, where M is the alkali / alkaline earth cation, n is the valence of alkali / alkaline earth metals, {} is the alumina framework, z is the number of hydrated water molecules, and x and y are the number of tetrahedrons per unit cell. Usually y / x is worth 1-5. But zeolites with high silica value of y / x are made up to 10 - 100 or even higher. (Flanigen, 1991).

Zeolite structure contains channels or cavities which contain cations and water molecules (Weller, 1994). Cations are active and generally act as ion exchanges. Water can be removed reversibly which is generally done by applying the heat.

The characteristics of zeolite structures (Sutarti, 1994) :

1. Highly porous, because the zeolite crystals are formed of tetrahedral SiO_4 and AlO_4.
2. The molecular-sized pores, because the zeolite pores are formed from piles of rings ring formed from stacks of 6, 8, 10, or 12 tetrahedrals.
3. Cation exchanger, because the difference in charge ofAl^{3+} san Si^{4+} akes Al atoms can be negatively charged crystal frameworks and need neutralizing cations. Neutral cations that are not part of this framework are easily replaced by other cations.
4. Acidic solids, because the replacement of neutralizing cations with protons makes zeolites Bronsted acid solids.
5. Easy to modify because every tetrahedral can be contacted with modifying materials.

Zeolite has several properties such as (Amelia, 2003) :

1. Dehydration
   Dehydration is a process that aims to release water molecules from the crystal lattice to form a cavity with a larger surface and is no longer protected by something that affects the adsorption process. Dehydration has the main function of releasing water molecules from the zeolite framework so as to enhance the activity of zeolites. The number of water molecules corresponds to the number of pores or empty volume that will be formed when the zeolite crystal cell unit is heated.
2. Adsorption
   In normal circumstances, a vacuum within the zeolite crystals filled by free water molecules and located around cations. When the zeolite crystals are heated at temperatures above 100°C the water will come out so that the zeolites can function as adsorbers of gases or liquids. Dehydration causes zeolites to have a very opened pore structure, and has a wide internal surface that is able to adsorb large amounts of substances beside water and is able to seperate molecular substances based on their molecular size and polarity.
3. Ion Exchanger
   The ion exchange in zeolites is the process by which the original ions present in intra-crystalline are replaced by other cations from the solution.
4. Catalyst
   Zeolite is a good catalyst because it has large pores with a large surface and also has an active side. In the presence of the intra crystalline

cavities, zeolite can be used as catalyst.

5. Filter / Separator
   Zeolite can separate based on differences in size, shape and polarity of the filtered molecules. Zeolite can separate gas molecules or substances from a particular mixture because they have an enough large cavity with various diameters.

The zeolite obtained from the preparation process can be used for various purposes. However, the power of the adsorption, ion exchange, and catalyst from the zeolite is not maximal yet. To obtain zeolite with high ability, several treatments are needed, including preparation, activation and modification (Sutarti, 1994).

1. Preparation
   This stage aims to obtain product sizes that are suitable for the intended use. This preparation consists of the stages of crushing until grinding.
2. Activation.
   The zeolite activation process can be done in two ways, physically and chemically. Physical activation is by heating the zeolite which aims to evaporate the trapped water in the zeolite crystal pores so that the surface area of the pores increases. Heating is carried out in an ordinary oven at a temperature of 300 to 400°C for laboratory scale or using a rotary furnace by vacuum heating for 3 hours or vacuuming for 5 to 6 hours for large scale. Chemical activation is carried out with a solution of H_2SO_4 or NaOH in order to clean the pore surface, remove impurities, and rearrange the location of the exchanged atoms. Pereaksi kimia ditambahkan pada zeolit yang telah disusun dalam tangki dan diaduk dalam jangka waktu tertentu. Zeolit kemudian dicuci dengan air sampai netral dan selanjutnya dikeringkan. Chemical reagents are added to zeolite that has been arranged in a tank and stirred for a certain time. Then zeolite is washed with water until it is neutral. Next the zeolite is dried.
3. Modification
   In the water treatment process, activated zeolites are able to adsorb heavy metal ions that form cations. In order to adsorb heavy metals containing anions, microorganisms and other organic substances, zeolites need to be modified. Modification is done by coating the zeolite with pyridine vinyl organic polymer, natural organic polymer or with manganese.

In 2017 Abdullah Saleh, Rera Oktaria, and Yuni Aviva Sarah did a study to improve the purity of CNG with zeolites. The best conditions in the process of increasing the purity of CNG occured at a gas flow rate of 1 L / min by heating at a temperature of 400ºC at 92.88 mol%. Based on research which is done by Denny Widhiyanuriyawan and Nurkholis Hamidi (2013), the best results were obtained for the duration of zeolite activation at 120 minutes. Diethanolamine or DEA, is an organic compound with the formula of $NH(CH_2CH_2OH)_2$. DEA is widely used in producing lubricants for the textile industry. In addition, DEA is used as a surface active agent in paint emulsions, shampoos and washing liquids. DEA can generally be found in the process of sweetening gas in the oil and gas industry because of its good adsorption ability of CO_2 and sulfur. According to J.I Hurtes in the Removal of H_2S and CO_2 from Biogas by Amine Adsorption, that amine compounds such as diethanolamine is one of the alternative compounds in the process of adsorption of sulfur content. In Pertamina Refinery Unit III Plaju, DEA is used in the extraction to reduce the impurities such as sulfur with an operating condition of 20% wt.

METHOD

Procedure for Determination of Sulfur Content Adsorption

1. Heat the zeolite in a furnace at 300 ºC for 60 minutes
2. Cool in desiccator for 1 hour
3. Weigh zeolite around 100 gr
4. Add 100 ml of DEA 0.5; 1; 2; 3; and 4N into zeolite
5. Stir and heat at 90oC for 2 hours
6. Cool in desiccator for 1 hour
7. Put it in a sulfur trap tube
8. Flow the hydrocarbon gas through the sulfur trap, set the gas flow rate using a flowmeter at 100, 300, and 500 ml / min
9. Take the gas that has passed through the sulfur trap with a sample balloon
10. Analyze sulfur content by using NSX 2100V

11. Repeat the experiment for different heating temperatures (350, 400, 450, 500, and 550 °C)

Composition of Hydrocarbon Analysis

1. Arrange the sulfur trap with the optimum zoelite
2. Flow the hydrocarbon gas through the sulfur trap
3. Take the gas that has passed through the sulfur trap with a sample balloon
4. Analyze the composition of hydrocarbon

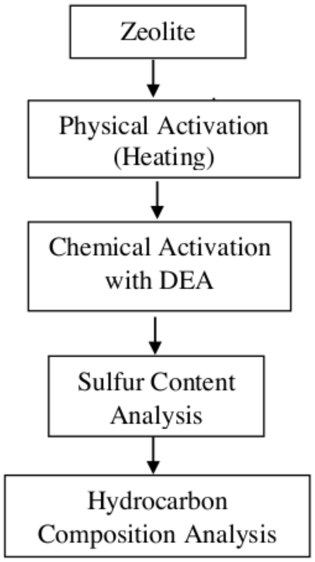

Figure 2. Scheme of Sulfur Trap

RESULT

Sulfur Adsorption at Flow Rate of 100 ml / min

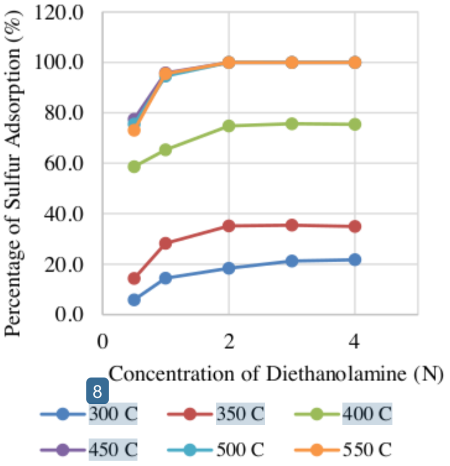

Figure 3. Percentage of Sulfur Adsorption at Flow Rate of 100 ml/min

At the heating temperature of 300 °C, the percentage of sulfur adsorption was still low, around 20. This was caused by the number of pores in the zeolite were still small. The number of pores in the zeolite could be increased by heating which aimed to release the water or other impurities trapped in the zeolite pores.

The percentage of the sulfur adsorption was increased significantly, starting from a heating temperature of 400 °C by adding 1N DEA solution could adsorb 60% until 88% for DEA 4N solution. After passing the temperature of 450 °C the adsorption of sulfur started to stagnate, not too much difference. This could be said that the physical activation process had reached its optimum point. From the concentration of DEA solution used, DEA solution with a concentration of 2N could adsorb the most sulfur and would be saturate when the concentration was increased.

The optimum point of adsorption sulfur with flow rate of 100 ml / min was obtained by heating zeolites at 450 °C and adding 2N DEA solution. Sulfur adsorption reached 99.97%.

Sulfur Adsorption at Flow Rate of 300 ml / min

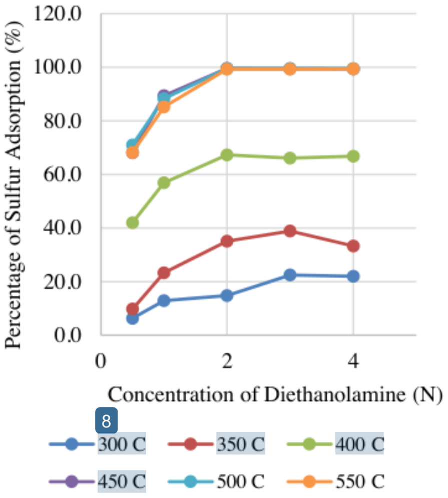

Figure 4. Percentage of Sulfur Adsorption at Flow Rate of 300 ml/min

From the figure 4, there was a difference in the form of the graph between the variable of flow rate at 100 ml / min and 300 ml / min. This indicated that the process of sulfur adsorption was started to be disrupted due to a greater flow rate of the sample passing the sulfur trap. The greater the flow rate gas, the less contact time between sulfur and zeolite.The highest adsorption process obtained by heating the zeolite at 450°C and the addition of 2N DEA solution. The percentage of sulfur adsorption was 99.53.

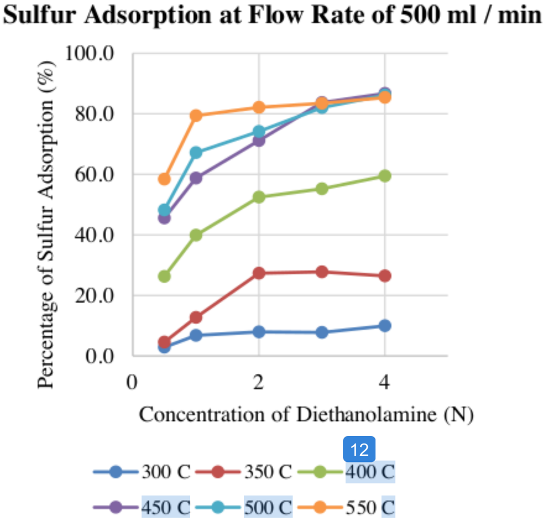

Figure 5. Percentage of Sulfur Adsorption at Flow Rate of 500 ml/min

From figure 5, there was difference in pattern with figure 3 and 4 because the adsorption of sulfur occured faster than before. This made the contact time between zeolite and sulfur become lesser so that zeolite was not optimal in adsorbing the sulfur in the hydrocarbon gas samples. The highest percentage of sulfur adsorption occurred by heating the zeolite at temperature of 450°C and adding DEA solution with a concentration of 4N. The percentage sulfur adsoprtion was 86.71.

Composition of Hydrocarbon Analysis

The next step was to analyze the composition of the hydrocarbon gas to check if there was a difference between before passing the sulfur trap (inlet) and after passing the sulfur trap (outlet). After obtaining the optimum point of physical activation at 450°C and chemical activation by using 2N diethanolamine solution, a hydrocarbon composition analysis was performed. As shown in table 1 there was no significant difference in the composition of hydrocarbon both in the inlet and outlet of the sulfur trap. The sulfur trap in GC could be applied and the sample was still representative.

Table 1. Concentration of Hydrocarbon in Sample

Component	Concentration (%mol)	
	Inlet	**Outlet**
Ethane	0,00	0,00
Propylene	80,80	80,55
Propane	15,59	15,86
n-Butane	2,74	2,74
i-Butane	0,13	0,13
iso-Butylene	0,57	0,56
trans-Butylene	0,14	0,13
cis-Butylene	0,03	0,03
Total	**100,00**	**100,00**

CONCLUSION

Based on the research that has been done, it can be concluded that the optimum point of the making sulfur trap can be done by heating zeolite at 450°C for one hour. Furthermore, zeolite is chemically activated by adding DEA 2N solution. The percentage of sulfur adsorption is 99.97 with flow rate of 100 mL / min. This sulfur trap make the sample still representative because there is no change in the hydrocarbon composition.

REFERENCES

1. Amelia, R. 2003. *Pengaruh Konsentrasi Molekul Pengarah Terhadap Kristalinitas dan Komposisi Mineral Zeolit pada Modifikasi Zeolit Alam Wonosari*. Semarang : UNDIP.
2. Flanigen, E.M. dan Khatami. 1971. *Infrared Structural Studies of Zeolite Frameworks*. New York Union Carbide Corporation.
3. Ismaryata. 1999. *The Study of Acidic Washing Temperature and Calcination Effect on Modification Process of Natural Zeolite as an Anion Exchanger*. Semarang : Universitas Dipenegoro.

4. J.I Hurtes, N. Giraldo and S.Izquierdo. *Removal of H_2S and CO_2 from Biogas by Amine adsorption*. Meksiko.
5. Pertamina. 2018. *"Material Safety Data Sheet"*. Plaju : Pertamina RU III.
6. _____. 2018. *TKI Pengenceran Caustic Dan DEA pada Unit Purifikasi.* Plaju : Pertamina RU III
7. Saleh, Abdullah., Rera Oktariya, dan Yuni Aviva Sarah. 2017. *Pengaruh Massa Zeolit dan Laju Alir Compressed Natural Gas Terhadap Peningkatan Metana Melalui Proses Pemurnian*. Unsri Jurnal Teknik Kimia Vol. 23, No. 2.
8. Sigot, Lea., Gaelle Ducom, Patrick Germain. 2015. *Adsorption of Hydrogen Sulfide (H_2S) on Zeolite (Z) : Retention Mechanism*. Prancis : Universite de Lyon.
9. Sutarti, M dan Rachmawati. 1994. *Zeolit Tinjauan Literatur*. Jakarta : Pusat Dokumentasi dan Informasi Ilmiah LIPI.
10. Weller, M. T. 1994. *Inorganic Materials Chemistry*. Oxford : : Oxford University Press.
11. Widhiyanuriyawan, Denny dan Nurkholis Hamidi. 2013. *Variasi Temperatur Pemanasn Zeolit Alam NaOH Untuk Pemurnian Biogas*. Malang : Jurnal Energi Dan Manufaktur Vol. 6, No. 1.

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